Contents

PROPOSED SYLLABUS

B.Sc. (Part II) Chemistry
PHYSICAL CHEMISTRY (SC-118)

UNIT-I : GASEOUS STATE

Postulates of kinetic theory of gases, derivation of kinetic equation, deviation from ideal behaviour, vander Waals equation of state.

Critical phenomena : PV isotherms of real gases, continuity of states, the isotherms of vander Waals equation, relationship between critical constants and Vander Waals constants, the law of corresponding states, reduced equation of state.

Elementary idea of root man square, average and most probable velocities, qualitative discussion of Maxwell's distribution of molecular velocities, collision number, mean free path and collision diameter.

UNIT-II : CHEMICAL KINETICS

Chemical Kinetics : Chemical kinetics and its scope, rate of a reaction, factors influencing the rate of a reaction concentration, temperature pressure, solvent, light, catalyst. Concentration dependence of rates, mathematical characteristics of simple chemical reactions zero order, first order, second Order. Pseudo order, half life. Determination of the order of reaction by differential method, method of integration, method of half life period and isolation method.

Theories of chemical kinetics : Effect of temperature on rate of reaction, Arrhenius equation, concept of activation energy. Simple collision theory of unimolecular reactions, transition state theory (mathematical treatment).

UNIT-III : CATALYSIS

Catalysis, characteristics of catalysed reactions, classification of catalysis, enzyme catalysis including its kinetics, industrial applications of catalysis.

UNIT-IV : COLLOIDAL STATE

Definition of colloids, classification of colloids. Solids in liquids (sols) : Properties kinetic, optical and electrical. Stability of colloids, protective action, Hardy-Schulze law, gold number. Elementary idea of liquids in liquids (emulsions), types of emulsions, preparation, Emulsifers. General applications of colloids.

UNIT-V : LIQUID STATE

Elementary idea of intermolecular forces, structural differences between solids, liquids and gases, liquid crystals, classification and structure, differences between liquid crystal, solid and liquid.

UNIT-VI : SOLID STATE

Crystalline and amorphous solids main differences, Laws of crystallography, space lattice, unit cell, Miller indices, Bragg's equation (only derivation).

UNIT-VII : THERMODYNAMICS-I

Definition of thermodynamic terms : system, surroundings etc., types of systems, intensive and extensive properties. state and path functions, thermodynamic process. Concept of heat and work.

First law of thermodynamics : Statement and mathematical formulation, definition of internal energy and enthalpy. Elementary idea of heat capacity, Joule-Thomson coefficient and inversion temperature.

(a) Second law of thermodynamic : Need for the second law, Different statements of the law, Carnot cycle and its efficiency

(b) Entropy : Concept, entropy as a state function, entropy as a function of V and 'T', entropy as a function of P and T, entropy as a criteria of spontaneity and equilibrium.,

(c) Concept of free energy and work function : Derivation of Gibbs-Helmholtz equation and Clausius-Clapeyron equation and applications.

(d) Third law of thermodynamics : Statements of third law of thermodynamics and Nernst heat theorem.

UNIT-VIII : THERMOCHEMISTRY

Enthalpy of reaction and formation, Hess' law of heat summation and its applications, Enthalpy of reaction at constant pressure and constant volume. Enthalpy of neutralization. Temperature dependence of enthalpy, Kirchoffs equation.

UNIT-IX : PHASE EQUILIBRIUM

Statement and meaning of the terms used in phase rule, application of phase rule to water system and lead-silver systems. Henry's law, Nernest distribution law, derivation of law distribution in case of association, application of distribution law to solvent extraction.

UNIT-X : ELECTROCHEMISTRY-I

Specific conductance and equivalent conductance, Measurement of equivalent conductance, Variation of equivalent and specific conductance with dilution.

Migration of ions and Kohhausch's law, important applications of the law. Transport number, its definition. Applications of conductivity measurements : Determination of degree of dissociation, determination of solubility product of a sparingly soluble salt.

UNIT-XI: EIECTROCHEMISTRY-II

Types of reversible electrodes gas-metal ion, metal-metal ion, metal-insoluble salt-anion and redox electrodes, electrode reactions, Nernst equation, Concept of single electrode potential, standard hydrogen electrode, reference electrode, standard electrode potential, Sign conventions. Electrolytic and galvanic cells-reversible and irreversible cells.Concentration cell with and without transport (derivation not required), Applications of concentration cells. Definition of pH and determination of pH using hydrogen electrode. Buffers, mechanism of buffer action, Henderson-Hessel equation. Hydrolysis of salts.

UNIT-XII : SPECTROSCOPY

Introduction, electromagnetic radiations, regions of the spectrum, Elementary idea of infrared, rotational and vibrational spectrum, Raman Spectrum.

UNIT-XIII : PHOTOCHEMISTRY

Interaction of radiation with matter; difference between thermal and photochemical processes. Laws of photochemistry : Beer's law and Stark-Einstein law. Quantum yield and reasons for low and high quantum yields of photochemical reactions. Definitions of fluorescence, phosphorescence and photosensitization.

UNIT-XIV : DILUTE SOLUTIONS AND COLLIGATIVE PROPERTIES

Colligative properties, Raoult's law of relative lowering of vapour pressure, molecular weight determination, Elevation of boiling point and depression of freezing point, relation between molecular weight and elevation in boiling point and depression in freezing point. Experimental methods for determining molecular weights from elevation of boiling point and depression in freezing point. vant' Hoff factor.

UNIT-XV: PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

Polar and non polar molecules, dipole moment, its determination and applications, magnetic properties of substances

UNIT

1

GASEOUS STATE

LEARNING OBJECTIVES

- Kinetic Equation of Gases
- Molecular Velocities
- Ideal or Perfect Gas
- Limitations of the Equation PV = RT or Deviation from Ideal Behaviour
- Critical Phenomenon
- Various Equations of State
- Law of Corresponding States or Reduced Equation of State
- Collision Diameter
- Mean Free Path
- Collision Number
  - ☐ Summary
  - ☐ Student Activity
  - ☐ Test Yourself

• 1.1. KINETIC EQUATION OF GASES

[I] Postulates of Kinetic Theory of Gases

Kinetic theory of gases was given by Krönig, Clausius, Maxwell etc. to explain the behaviour of gases theoretically. This theory is applicable only to a perfect or an ideal gas. The ***main postulates or assumptions*** of the kinetic theory are :

(1) A gas consists of a large number of small particles, called ***molecules.*** *The molecules are so small that their actual volume can be neglected in comparison to the total volume of the gas.*

(2) The molecules are in a state of constant rapid motion in all possible directions, colliding with each other and with the walls of the containing vessel.

(3) The molecules are perfectly elastic. Thus, there is no loss of kinetic energy when they collide with each other or with the walls of the containing vessel.

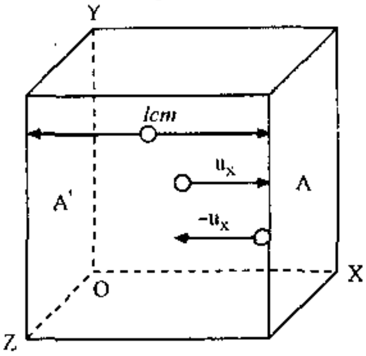


Fig. 1. Kinetic picture of gas molecules

(4) The molecules do not exert any appreciable mutual force of attraction.

(5) The pressure of a gas is due to the bombardment of the moving molecules on the walls of the containing vessel.

(6) The kinetic energy of the molecules is directly proportional to the absolute temperature of the gas.

(7) There is no effect of gravity on the gas molecules.

[II] Derivation of Kinetic Equation of Gases

From the above postulates, the kinetic equation of gases can be derived easily as follows:

Consider a gas enclosed in a cubical vessel of volume V, each side of the cube being l cm. Let the number of gas molecules be n, mass of each molecule be m and the velocity be u cm/sec. The velocity can be resolved into three components u_x, u_y and u_z along the three axes X, Y and Z, mutually at right angles to one another. These components will be related to the velocity (u) by the expression,

$$u^2 = u_x^2 + u_y^2 + u_z^2 \qquad \ldots(1)$$

For the sake of simplicity, consider one molecule moving with a velocity u_x along the X-axis striking the faces, A and A′. On striking the wall A, it will rebound in opposite direction with the same velocity. Therefore,

Momentum of the molecule before collision = mu_x

Momentum of the molecule after collision $= m(-u_x) = -mu_x$

∴ Change in momentum per collision $= (mu_x) - (-mu_x) = 2mu_x$.

After striking the wall A, the molecule will have to travel a distance of l cm before striking the wall A′ the molecule will strike the wall A in l/u_x sec. In other words, the number of collisions suffered by the molecule per second will be u_x/l on the walls A and A′.

∴ Change in momentum per molecule per second along X-axis

$$= 2mu_x \times \frac{u_x}{l} = \frac{2mu_x^2}{l}$$

Similarly, we can derive expressions along Y- and Z-axes.

∴ Change in momentum per molecule per second along Y-axis

$$= \frac{2mu_y^2}{l}$$

Change in momentum per molecule per second along Z-axis

$$= \frac{2mu_z^2}{l}$$

∴ Total change in momentum per molecule per second

$$= \frac{2mu_x^2}{l} + \frac{2mu_y^2}{l} + \frac{2mu_z^2}{l} = \frac{2m}{l}(u_x^2 + u_y^2 + u_z^2) = \frac{2mu^2}{l}$$

Total change in momentum per second for all the molecules

$$= \frac{2mu^2}{l} \times n = \frac{2mnu^2}{l} \qquad \ldots(2)$$

According to Newton's second law of motion, the rate of change of momentum (*i.e.*, change of momentum per second) is the applied force. So, we have,

$$\text{Force} = \frac{2mnu^2}{l}$$

The gas pressure, by definition, is the force per unit area. Thus,

$$\text{Pressure, } P = \frac{\text{Force}}{\text{Area}} = \frac{2mnu^2/l}{6l^2} = \frac{1}{3} \cdot \frac{mnu^2}{l^3}$$

$$\therefore \quad P = \frac{1}{3}\frac{mnu^2}{V} \quad \text{(As volume of cube, } V = l^3\text{)} \qquad \ldots(3)$$

or

$$PV = \frac{1}{3} mnu^2 \qquad \ldots(4)$$

This equation is known as *kinetic equation of gases*. Equation (3) gives the pressure exerted by an ideal gas.

For 1 mole of a gas, equation (4) can be written as,

$$PV = \frac{1}{3} mNu^2$$

where N = Avogadro's number.

[III] Applications of Kinetic Equation of Gases

(1) Derivation of Equation PV = RT : According to the postulates of kinetic theory of gases, the kinetic energy $\left(\frac{1}{2}mnu^2\right)$ of the molecules and absolute temperature (T) of the gas are directly proportional to each other.

Thus, $\frac{1}{2} mnu^2 \propto T$ or $\frac{1}{2} mnu^2 = kT$ (where, k = constant).

or $\frac{3}{2} \times \frac{1}{3} mnu^2 = kT$ or $\frac{1}{3} mnu^2 = \frac{2}{3} kT$

According to kinetic equation of gases, $PV = \frac{1}{3} mnu^2$

$$PV = \frac{2}{3} kT \qquad \ldots(1)$$

or
$$\frac{PV}{T} = \frac{2}{3} k = \text{constant}$$

For 1 g mole of a gas, the value of constant is equal to R, *i.e.*, gas constant. Therefore,

$$\frac{PV}{T} = R \quad \text{or} \quad PV = RT.$$

(2) Consistency of Various Gas Laws

(i) Boyle's law : According to it, *'at constant temperature, the volume of a given mass of a gas is inversely proportional to pressure', i.e.,*

$$V \propto \frac{1}{P}, \text{ at constant } T$$

or
$$PV = \text{constant, at constant } T.$$

From kinetic equation, we have,

$$PV = \frac{1}{3} mnu^2 = \frac{2}{3} \times \frac{1}{2} mnu^2$$

The kinetic energy of the gas, $E = \frac{1}{2} mnu^2$

$$\therefore \quad PV = \frac{2}{3} \cdot E \qquad \ldots(2)$$

At constant temperature, kinetic energy (E) of the gas is constant.

$$\therefore \quad PV = \text{constant.}$$

This is Boyle's law.

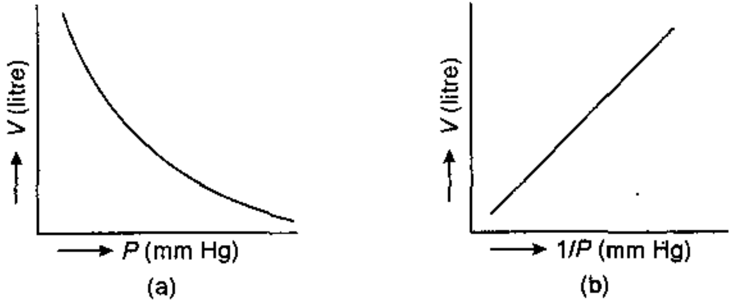


Fig. 2. Graphical representation of Boyle's law (a) a plot of *V* versus *P* for a gas sample is hyperbola (b) a plot of *V* versus 1/*P* is a straight line.

(ii) Charles' law : According to it, *'at constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature,' i.e.,*

$$V \propto T, \text{ at constant } P$$

As already derived, from equation (2), we have

$$PV = \frac{2}{3} \cdot E \quad \text{or} \quad V = \frac{2}{3} \cdot \frac{E}{P}$$

At constant pressure,

$$V = \text{constant} \times E \quad \text{or} \quad V \propto E$$

But we know that $E \propto T$, where T is absolute temperature.

$$\therefore \quad V \propto T$$

This is Charles' law.

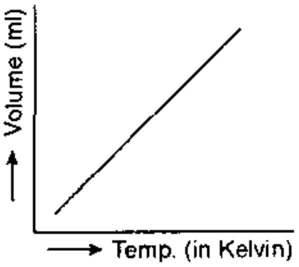


Fig. 3. Graph showing that at constant pressure volume of a given mass of gas is directly proportional to kelvin temperature which is a straight line.

(iii) Avogadro's hypothesis : According to it, *'equal volumes of all gases under same conditions of temperature and pressure contain equal number of molecules'*. If the molar amount is doubled the volume is doubled.

For any two gases, the kinetic equation can be written as,

$$P_1V_1 = \frac{1}{3} m_1n_1u_1^2 = \frac{2}{3} \times \frac{1}{2} m_1n_1u_1^2$$

$$P_2V_2 = \frac{1}{3} m_2n_2u_2^2 = \frac{2}{3} \times \frac{1}{2} m_2n_2u_2^2$$

When pressures and volumes of the gases are the same, *i.e.*, $P_1 = P_2$ and $V_1 = V_2$, it follows that,

$$\frac{1}{2} m_1n_1u_1^2 = \frac{1}{2} m_2n_2u_2^2 \qquad ...(3)$$

When the gases are also at the same temperature, their mean kinetic energy will also be the same, *i.e.*,

$$\frac{1}{2} m_1u_1^2 = \frac{1}{2} m_2u_2^2 \qquad ...(4)$$

Dividing equation (3) by (4), we get,

$$n_1 = n_2$$

This is Avogadro's hypothesis.

Molar gas volume : It follows as a corollary of Avogadro's hypothesis that one mole of any gas at a given temperature (T) and pressure (P) has the same fixed volume. This volume is called the **molar gas volume** or **molar volume.** In order to compare the molar volumes of gases, chemists use a fixed reference temperature and pressure. This is called standard temperature and pressure (abbreviated STP). The standard temperature used is 0°C (or 273 K) and the standard pressure is 760 mm Hg (or 1 atm). At STP, we find experimentally that one mole of any gas occupies a volume of 22.4 litres. In the form of an equation, we can write, 1 mole of a gas at STP = 22.4 litres.

(iv) Graham's law of diffusion : According to it, *'the rate of diffusion (r) of a gas is inversely proportional to the square root of the density (d) of the gas, at constant pressure'*, *i.e.*,

$$r \propto \frac{1}{\sqrt{d}}, \text{ at constant pressure}$$

From kinetic equation, we have

$$PV = \frac{1}{3} \quad u^2 \quad \text{or} \quad u = \sqrt{\left(\frac{3PV}{mn}\right)} = \sqrt{\left(\frac{3P}{d}\right)}$$

$$\left(\text{As } \frac{mn}{V} = \frac{\text{Total mass of the gas}}{\text{Volume}} = \text{density of the gas, } d\right)$$

Therefore, at constant pressure, $u \quad \frac{\;}{\sqrt{d}}$

The rate of diffusion (r) of the gas is directly proportional to the mean velocity (u) of the molecules, *i.e.*, $u \propto r$.

$$\therefore \qquad r \propto \frac{1}{\sqrt{d}}.$$

This is Graham's law of diffusion.

Ex. 1. ***If a gas diffuses at a rate of one half as fast as*** O_2***, find the molecular mass of the gas.***

Solution. Applying Graham's law of diffusion,

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

or

$$\frac{1/2}{1} = \sqrt{\frac{32}{M_1}}$$

Squaring both sides of the equation,

$$\left(\frac{1}{2}\right)^2 = \frac{32}{M_1}$$

or

$$\frac{1}{4} = \frac{32}{M_1}$$

or

$$M_1 = 128$$

So molecular mass of the unknown gas = **128**.

(v) Dalton's law of partial pressures : According to Dalton's law of partial pressures, *the total pressure of a mixture of gases is equal to the sum of the partial pressures of all the gases present.*

Suppose n_1 molecules each of mass m_1 of a gas A are contained in a vessel of volume V. Then, according to the kinetic theory, the pressure, p_A of the gas A will be given by,

$$p_A = \frac{1}{3}\frac{m_1 n_1 u_1^2}{V}$$

Now, suppose n_2 molecules, each of mass m_2 of another gas B are contained in the same vessel at the same temperature and there is no other gas present at that time. The pressure, p_B of the gas B is then given by,

$$p_B = \frac{1}{3}\frac{m_2 n_2 u_2^2}{V}$$

If both gases are present in the same vessel at the same time, the total pressure, P is given by,

$$P = \frac{1}{3}\frac{m_1 n_1 u_1^2}{V} + \frac{1}{3}\frac{m_2 n_2 u_2^2}{V} = p_A + p_B$$

Similarly, if three, four or more gases, *e.g.*, A, B, C, D, *etc* are present in the same vessel, the total pressure is given by,

$$P = p_A + p_B + p_C + p_D + \dots$$

This is Dalton's law of partial pressures.

Ex. 1. ***What pressure is exerted by a mixture of 2.00 g of H_2 amd 8-00 g of N_2 at 273 K in a 10 litre vessel ?***

Solution : Applying the ideal gas equation

$$P = n\frac{RT}{V},$$

we can find the partial pressure of H_2 and N_2

$$\text{Moles of } H_2 = \frac{2.00}{2.02} = 0.990$$

$$\text{Moles of } N_2 = \frac{8.00}{28}\ 0.286$$

$$\therefore \quad P_{H_2} = \frac{(0.990 \text{ mole}) \times (0.0821 \text{ lit atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})}{10.0 \text{ litre}}$$

$$= 2.20 \text{ atm.}$$

$$P_{N_2} = \frac{(0.286 \text{ mole}) \times (0.0821 \text{ lit atm K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})}{10.0 \text{ litre}}$$

$$= 0.64 \text{ atm.}$$

$$\therefore \quad P_{\text{total}} = P_{H_2} + P_{N_2}$$

$$= 2.20 \text{ atm} + 0.64 \text{ atm}$$

$$= \mathbf{2.84 \text{ atm.}}$$

(3) Kinetic Energy of One Mole of a Gas : According to kinetic equation of gases, for one mole of a gas,

$$PV = \frac{1}{3} mNu^2 \qquad \text{(where } N = \text{Avogadro's number)}$$

or

$$PV = \frac{2}{3} \times \frac{1}{2} mNu^2 \qquad \dots(5)$$

The kinetic energy (E) of one mole of a gas is given by,

$$E = \frac{1}{2} mNu^2$$

Thus, from equation (5),

$$PV = \frac{2}{3} . E = RT$$

or

$$\boldsymbol{E = \frac{3}{2} RT}$$

For n mole of an ideal gas, the kinetic energy will be given by (3/2) nRT.

Ex. 1 : ***Calculate the kinetic energy of two moles of CO_2 at 300 K, assuming it to be an ideal gas.***

Solution : (a) The kinetic energy (E) of 2 moles of an ideal gas is given by :

$$E = \frac{3}{2} nRT$$

$$E = \frac{3}{2} \times 2 \times 8.314 \times 300 = \mathbf{7482.6\ J.}$$

Ex. 2 : ***Calculate in ergs the kinetic energy of a mono-atomic gas (molecular weight 20.2) molecule, moving with a velocity of 5×10^4 cm/s.***

(b) The kinetic energy $= \frac{1}{2} mu^2 = \frac{1}{2} \times \frac{20.2}{6.023 \times 10^{23}} \times (5 \times 10^4)^2$

$$= \mathbf{41.92 \times 10^{-5}\ erg\ molecule^{-1}}$$

• 1.2. MOLECULAR VELOCITIES

The gas molecules travel with different velocities. These are of three types :

[I] Average Velocity (v or <u>)

It is defined as, *'the average of the velocities of all molecules at any time'.*

If $u_1, u_2, u_3, \dots u_n$ are the velocities of individual molecules in a gas and n is the total number of molecules contained in a gas, then the ***average velocity*** is given by,

$$\langle u \rangle \text{ or } v = \frac{u_1 + u_2 + u_3 + \dots + u_n}{n}$$

[II] Root Mean Square Velocity or R.M.S. Velocity (u*)

It is defined as, *'the square root of the mean of squares of all velocities of the molecules'.*

$$\therefore \qquad \text{R.M.S. velocity} = \sqrt{\left(\frac{u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2}{n}\right)}$$

Mean square velocity u^2 is given by $\left(\frac{u_1^2 + u_2^2 + u_3^2 + \dots + u_4^2}{n}\right)$

[III] Most Probable Velocity (α or $\overline{u}$)

It is defined as, *'the velocity possessed by the maximum number of molecules of the gas'.*

The relationship of most probable velocity to the average velocity and root mean square velocity can be developed from the following expressions :

$$\text{Average velocity, } v = \sqrt{\left(\frac{8RT}{\pi M}\right)}$$

$$\text{Root mean square velocity, } u = \sqrt{\left(\frac{3RT}{M}\right)}$$

$$\text{Most probable velocity, } \alpha = \sqrt{\left(\frac{2RT}{M}\right)}$$

Thus, Average velocity, $v = 0.9213 \times$ R.M.S. velocity, u

Most probable velocity, $\alpha = 0.8164 \times$ R.M.S. velocity, u

From the above equations, it can be seen that the ratio of the three velocities are given by :

$$\alpha : v : u = 1 : 1.128 : 1.224$$

[IV] Calculation of RMS Velocity From Kinetic Equation of Gases

From kinetic gas equation, we can calculate the root mean square velocity of gas molecules under different conditions of temperature, pressure, etc., as shown below.

(1) When only temperature is given : For 1 mole of a gas, we have from kinetic equation

$$PV = \frac{1}{3} mNu^2 = RT \qquad (\because PV = RT)$$

or

$$u = \sqrt{\left(\frac{3RT}{mN}\right)} = \sqrt{\left(\frac{3RT}{M}\right)}$$

where, $mN = M$ = molecular weight

$$\therefore \qquad u = \sqrt{\left(\frac{3 \times 8.314 \times 10^7 \times T}{M}\right)}$$

or $$u = 1.58 \times 10^4 \times \sqrt{\left(\frac{T}{M}\right)}$$

Knowing the value of T, we can calculate u.

(2) When both pressure and temperature are given : From kinetic equation, we have for 1 mole of a gas,

$$PV = \frac{1}{3} mNu^2 = \frac{1}{3} Mu^2 \qquad (M = \text{molecular weight})$$

or $$u = \sqrt{\left(\frac{3PV}{M}\right)} \qquad \ldots(1)$$

The value of V can be determined from N.T.P. considerations, *i.e.*,

$$\frac{PV}{T} = \frac{P_0V_0}{T_0}$$

(where, P_0, V_0 and T_0 correspond to N.T.P. *values)*

or $$V = \frac{P_0V_0}{T_0} \times \frac{T}{P}$$

Thus, the value of V can be calculated and substituted in equation (1).

(3) When both pressure and density are given : For 1 mole of a gas, the kinetic equation is written as,

$$PV = \frac{1}{3} mNu^2 = \frac{1}{3} Mu^2 \text{ or } u = \sqrt{\left(\frac{3PV}{M}\right)} = \sqrt{\left(\frac{3P}{D}\right)}$$

[As $d = M/V$ = density]

Knowing the values of P and d, we can calculate u.

Ex. 1 : ***Calculate the velocity of a molecule of oxygen at N.T.P. and 500°C.***

Solution : The velocity of a molecule is given by ***(When only temperature is given)* :**

$$u = 1.58 \times 10^4 \sqrt{\left(\frac{T}{M}\right)}$$

where, M = Molecular weight of $O_2 = 32$.

(a) At N.T.P., $T = 0°C = 0 + 273 = 273$ K.

$$\because \qquad u = 1.58 \times 10^4 \times \sqrt{\left(\frac{273}{32}\right)}$$

$$= \mathbf{46{,}149.4 \text{ cm per sec.}}$$

(b) At 500°C, $T = 500 + 273 = 773$ K

$$\therefore \qquad u = 1.58 \times 10^4 \times \sqrt{\left(\frac{773}{32}\right)} = \mathbf{77{,}655.4 \text{ cm per sec.}}$$

Ex. 2 : ***The density of hydrogen at 0°C and 760 mm pressure is 0.00009 g/cm³. Find the RMS velocity and the average velocity of hydrogen molecules (density of Hg = 13.6 g/cm³).***

Solution : In this case, the values of density and pressure are given. Therefore, the RMS velocity (u) is given by

$$u = \sqrt{\left(\frac{3P}{d}\right)}$$

$P = 760$ mm $= 76$ cm $= 76 \times 13.6 \times 981$ dynes/sq cm and $D = 0.00009$ g/cm^3.

$$u = \sqrt{\left\{\frac{3 \times 76 \times 13.6 \times 981}{0.00009}\right\}} = \mathbf{183{,}844.2 \text{ cm/s}}$$

The average velocity (v) is given by :

$$v = 0.9213u = 0.9213 \times 183{,}844.2 = \mathbf{169{,}375.6 \text{ cm/s.}}$$

Ex. 3 : ***Calculate the RMS velocity of hydrogen gas at 27°C.***

(b) $$u = 1.58 \times 10^4 \times \sqrt{\left(\frac{T}{M}\right)} = 1.58 \times 10^4 \times \sqrt{\left(\frac{300}{2}\right)}$$

$$= \mathbf{19.35 \times 10^4\ cm\ s^{-1}}$$

Ex. 4 : ***Calculate the RMS velocity of oxygen molecules at a temperature of 27°C and 740 mm pressure.***

Solution : (a) The RMS velocity is given by :

$$u = \sqrt{\left(\frac{3PV}{M}\right)} \qquad \ldots(1)$$

$$P = 74 \times 13.6 \times 981 \text{ dyne cm}^{-2}; \qquad M = 32$$

The value of V can be calculated from NTP concept, *i.e.*,

$$\therefore \qquad u = \sqrt{\frac{3 \times 78 \times 13.6 \times 981 \times 22785}{44}} = \mathbf{40145.22\ cm/s}$$

$$\frac{PV}{T} = \frac{P_0V_0}{T_0}$$

$P = 74$ cm, $T = 273 + 27 = 300$ K, $V = ?$; $P_0 = 76$ cm, $V_0 = 22400$ c.c., $T_0 = 273$ K.

$$\therefore \qquad \frac{74 \times V}{300} = \frac{76 \times 22400}{273}$$

$$\therefore \qquad V = \frac{76 \times 22400 \times 300}{74 \times 273} = 25{,}280.6 \text{ c.c.}$$

Thus from equation (1), $u = \sqrt{\left(\frac{3 \times 74 \times 13.6 \times 981 \times 25280.6}{32}\right)} = \mathbf{48372.6\ cm/s.}$

Ex. 5 : ***Calculate the temperature at which root mean square velocity of SO_2 molecules is the same as that of O_2 molecules at 27°C.***

Solution : The RMS velocity (u_1) of O_2 molecules at 27°C.

$$= 1.58 \times 10^4 \sqrt{\left(\frac{300}{32}\right)}$$

The RMS velocity (u_2) of SO_2 molecules at T K

$$= 1.58 \times 10^4 \sqrt{\left(\frac{T}{64}\right)}$$

$$\because \qquad u_1 = u_2$$

$$\therefore \quad 1.58 \times 10^4 \sqrt{\left(\frac{T}{64}\right)} = 1.58 \times 10^4 \sqrt{\left(\frac{300}{32}\right)}$$

$$\text{or} \qquad \frac{T}{64} = \frac{300}{32} \qquad \text{or} \qquad T = \frac{300 \times 64}{32} = \mathbf{600\ K = 327°C}$$

• 1.3. IDEAL OR PERFECT GAS

A gas which strictly obeys Boyle's and Charles' laws at all temperatures and pressures is known as an *ideal* or *perfect gas*. The characteristics of an ideal gas are as follows :

(i) The compressibility (Z) of an ideal gas is unity, *i.e.*,

$$Z = \frac{PV}{nRT} = 1$$

(ii) The product of pressure and volume of an ideal gas at constant temperature is constant.

(iii) If an ideal gas is cooled at constant pressure, its volume decreases continuously, till at –273°C its volume becomes zero.

(iv) If it is allowed to expand without doing any external work, it shows no thermal effect.

(v) There is no force of attraction between molecules of an ideal gas.

Differences Between an Ideal and Real Gas

(i) A real gas does not obey various gas laws particularly at low temperatures and high pressures. Only at high temperatures and low pressures, real gas tends towards ideal behaviour.

(ii) The volume of a real gas does not become zero at –273°C. In fact, when cooled sufficiently, a real gas is suddenly converted into liquid state.

(iii) There are no attractive forces btween molecules in an ideal gas, while these forces exist in a real gas.

(iv) Molecular collisions in an ideal gas are perfectly elastic, while it is not so in a real gas.

• 1.4. LIMITATIONS OF THE EQUATION PV = RT OR DEVIATIONS FROM IDEAL BEHAVIOUR

The general gas equation, $PV = RT$ derived from the postulates of the kinetic theory is valid for an ideal gas only. Real gases obey this equation only approximately and that too at high temperature and low pressure. The higher the pressure and lower the temperature, the greater are the deviations from the ideal behaviour. In general, the more easily liquefiable and highly soluble gases exhibit larger deviations. Thus, gases like CO_2, SO_2 etc. show much larger deviations than N_2, H_2, O_2 etc.

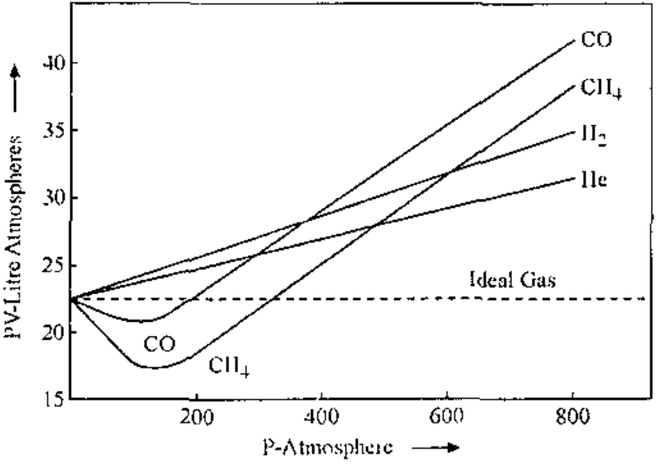


Fig. 4. P–PV curve for differnt gases.

Regnault and Amagat studied the effect of pressure on volumes of gases like H_2, He and CO_2 etc. at constant temperature and the curves are as shown in figure (4). According to them, if Boyle's law is obeyed, the values of PV for a given mass of a gas should be constant at all pressures and the graph should be a straight line parallel to the pressure axis, as shown by dotted line. But, it is only an ideal behaviour which no real gas will exhibit. Hydrogen and helium ***at all pressures are less compressible*** than Boyle's law requires, *i.e.*, PV increases with increase in pressure at constant temperature right from the very beginning. On the other hand, CO_2 and other gases ***at low pressures are more compressible*** than Boyle's law requires, *i.e.*, PV decreases with increase in pressure at constant temperature. This continues with an increase in pressure till PV passes through a minimum at a certain stage. With further increase in pressure, the compressibility is less than expected, *i.e.*, PV increases with increase in pressure and this continues thereafter.

At low temperatures, the deviations are much more pronounced than at high temperatures.

[I] Improvements by vander Waals

In order to explain the deviations of real gases from ideal behaviour vander Waals suggested that it is necessary to modify the kinetic theory of gases. The following two postulates of the kinetic theory, according to him, do not appear to hold good under all conditions.

(i) The volume occupied by the gaseous molecules is negligibly small as compared to the total volume of the gas.

This postulate can be justified only under ordinary conditions of temperature and pressure. At low pressure or high temperature, the volume of the gas is comparably large and so the small volume occupied by the gas molecules can be neglected without producing any appreciable error. However, at high pressure or low temperature, the volume of the gas becomes small and now even the small volume occupied by the molecules cannot be neglected, as the molecules are incompressible. Hence, *under conditions of high pressure and low temperature, the above postulate is not valid.*

(ii) The mutual force of attraction between gaseous molecules is negligible.

This postulate also holds good at low pressure or high temperature, because under these conditions, the volume of the gas is large and the molecules lie far apart from one another. But at high pressure or at low temperature, the volume of the gas is small and the molecules lie closer to one another. Thus, the *intermolecular forces of attraction cannot be neglected. So, at high pressure and low temperature, the above postulate is also not valid.*

So, it is necessary to apply suitable corrections to the ideal gas equation to make it applicable to real gases. vander Waals introduced two correction terms in the ideal gas equation to account for the errors introduced as a result of neglecting the volume of the molecules and intermolecular forces of attraction.

(i) Volume correction : For an ideal gas, $PV = RT$, where V is the total volume occupied by 1 g mole of the gas. As the molecules are incompressible, the volume occupied by them remains the same irrespective of pressure. vander Waals suggested that a factor b should be subtracted from V, the total volume in order to get the ideal volume, which is compressible. Thus, the volume which is compressible is not V but $(V - b)$. So, Ideal volume $= V - b$.

The factor b is constant and is characteristic of each gas. It is known as *co-volume, effective volume or excluded volume.* It has been shown that the co-volume is nearly $4\sqrt{2}$ times the actual volume occupied by all the molecules contained in the gas.

(ii) Pressure correction : Consider a molecule lying somewhere in the middle of the vessel as shown in figure (5). It is attracted uniformly on all sides by other molecules. These forces neutralise each other and hence there is no resultant force of attraction on the molecule. However, as the molecule approaches the wall of the containing vessel, it experiences force of attraction which tends to drag it backwards. Hence, it will strike the wall with a lower velocity and will exert a lower pressure than it would have done if there were no forces of attraction at all [Fig. (6)]. Thus, it is necessary to add a certain quantity to the pressure P of the gas in order to get the ideal pressure. So,

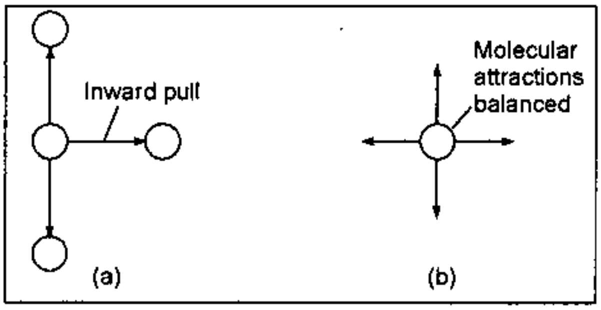


Fig. 5. (a) A molecule about to strike the wall has a net inward pull. (b) A molecule in the interior of gas has balanced attractions.

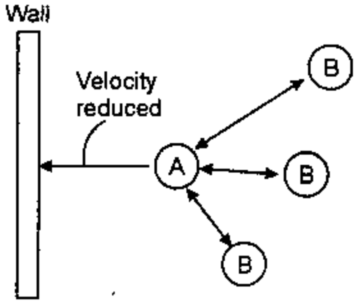


Fig. 6. The striking molecule A is pulled inward by molecules B which reduces the velocity of A and causes the decrease of pressure.

$$\text{Ideal pressure} = P + p'$$

where, p' is the pressure due to intermolecular forces of attraction. The value of p' depends upon (i) the number of molecules per unit volume in the bulk of the gas, *i.e.*, directly on the density of the gas and (ii) the number of molecules striking the wall at any given time which in turn also depends upon the density of the gas. Thus, correction factor p' is proportional to the square of the density (d) of the gas or is inversely proportional to the square of volume (V) [As, density $\propto$ 1/Volume]. So,

$$p' \propto d^2 \propto \frac{1}{V^2} \qquad \text{or} \qquad p' = \frac{a}{V^2}$$

where, a is a constant depending upon the nature of the gas and is known as *coefficient of attraction.* Thus,

$$\text{Ideal pressure} = P + \frac{a}{V^2}$$

Introducing the above two corrections in the gas equation $PV = RT$, we get the following equation :

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \text{...(1)}$$

This is known as ***vander Waals equation.*** The constants a and b are also known as ***vander Waals constants.***

For n moles of a gas, the vander Waals equation becomes :

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$\left(\because\ p \propto n^2 d^2 \propto \frac{n^2}{V^2} = \frac{n^2 a}{V^2}\right)$$

[II] Discussion of vander Waals Equation or Drawbacks of vander Waals Equation

We can now explain the departure of real gases from ideal behaviour at different pressures and temperatures as shown in figure (4) on the basis of vander Waals equation.

(i) At low pressures : When the pressure is low, the volume will be sufficiently large and b can thus be easily neglected in its comparison. Thus, the vander Waals equation (1) becomes,

$$\left(P+\frac{a}{V^2}\right)V=RT \qquad \text{or} \qquad PV+\frac{a}{V}=RT$$

$$PV=RT-\frac{a}{V}=(PV)_{\text{ideal}}-\frac{a}{V}$$

The product PV is less than the ideal value by an amount equal to a/V. As P increases, V decreases or a/V increases and so PV becomes smaller and smaller. This explains the dip in the curve of CO_2 etc. at low pressures.

(ii) At high pressures : When the pressure is very high, the volume V is quite small. It is now not possible to neglect b. But as P is large, the factor a/V^2 can be neglected in comparison to the high value of P. Thus, equation (1) becomes,

$$P(V-b)=RT \qquad \text{or} \qquad PV-P\,.\,b=RT$$

or $$PV=RT+P.b=(PV)_{\text{ideal}}+P\,.\,b$$

Thus, PV is greater than the ideal value of PV by an amount equal to $P.b$. As P increases, the product $P.b$ increases and so PV increases. This explains why the value of PV after reaching a minimum increases with further increase of pressure.

(iii) At high temperatures : If at a given pressure, the temperature is very high, the volume of the gas will be sufficiently large to make the value of a/V^2 negligibly small. Under this condition, the value of b *can also be neglected in comparison to V. So, vander Waals equation approaches* ideal gas equation. This explains why the deviations are less at high temperatures.

(iv) Exceptional behaviour of hydrogen and helium : As both H_2 and He have comparatively small masses, the attractive forces of attraction between the molecules become too small. So, the correction term a/V^2, due to attraction factor is negligible even at ordinary temperature or low pressure. Therefore, equation (1) becomes,

$$P(V-b)=RT \quad \text{or} \quad PV=RT+P.b=(PV)_{\text{ideal}}+P.b$$

This explains the rise in the curves of H_2 and He with an increase of pressure right from the very beginning even at ordinary temperatures or low pressures.

[III] Units of vander Waals' Constants

From equation (3), the constant a is expressed by PV^2/n^2, *i.e.*, pressure × (volume)^2/mol^2. If pressure is expressed in atmospheres and volume in cm^3 the value of a will be atm cm^6 mol^{-2}. If volume is expressed in litre (or dm^3), the value of a will be **atm L^2 mol^{-2}** or **atm dm^6 mol^{-2}**. In SI system, the unit of a will be

$$\frac{(\text{Nm}^{-2})\,(\text{m}^3)^2}{(\text{mol})^2} \text{ or Nm}^4\text{ mol}^{-2}.$$

The constant b is incompressible volume per mole of a gas so, it will have the same units as volume per mole, *e.g.*, **cm^3 mol^{-1}, L mol^{-1}** or **dm^3 mol^{-1}**. In SI units, the unit of b will be **m^3 mol^{-1}**.

[IV] Effective Volume of Gas Molecules

vander Waals suggested that a correction term nb should be subtracted from the total volume V in order to get the ideal volume which is compressible. In order to understand the meaning of the term nb we consider two gas molecules as unpenetrable and incompressible spheres each of which has a diameter, r, as shown in figure (7). It is clear that the centres of the two spheres cannot approach each other more closely than the distance r. For this pair of molecules, therefore, a sphere of radius r and of volume $\frac{4}{3}\pi r^3$ constitutes what is known as *excluded volume or co-volume.* The excluded volume per molecule is thus half the above volume, *viz.*, $\frac{2}{3}\pi r^3$. The actual volume of one gas molecule of radius r' is $\frac{4}{3}\pi r'^3$. So,

$$\frac{4}{3}\pi r'^3=\frac{4}{3}\pi\left(\frac{r}{2}\right)^3=\frac{1}{6}\pi r^3$$

∴ Excluded volume per molecule

$$=\frac{2}{3}\pi r^3=4\times\frac{1}{6}\pi r^3$$

$= 4 \times$ Actual volume of the gas molecules.

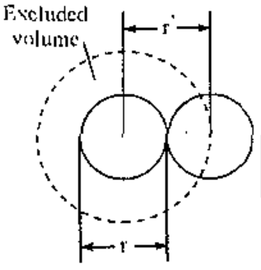


Fig. 7

• 1.5. CRITICAL PHENOMENON

The curves which are obtained by plotting pressure against volume at various constant temperatures are known as ***isotherms*** (*isos* = equal; *therm* = heat). Andrews obtained isotherms of carbon dioxide at different temperatures which are shown in figure (8).

First consider the isotherm ABCD at 12.1°C. The point A represents CO_2 in the gaseous state occupying a certain volume under certain pressure. On increasing the pressure, the volume of the gas decreases along AB in accordance with Boyle's law until at a certain pressure (at B) liquefaction occurs. Further, decrease of volume is not accompanied by any change of pressure, as shown by horizontal portion BC, until the vapour has been condensed completely at C. The liquid is only slightly compressible, so further increase of pressure produces only a very small decrease in volume. This is shown by a steep line CD which is almost vertical. Thus, along the curve AB, CO_2 exist as a gas. Along BC, it exists partly as gas and partly as liquid. Along CD, it exists completely as liquid.

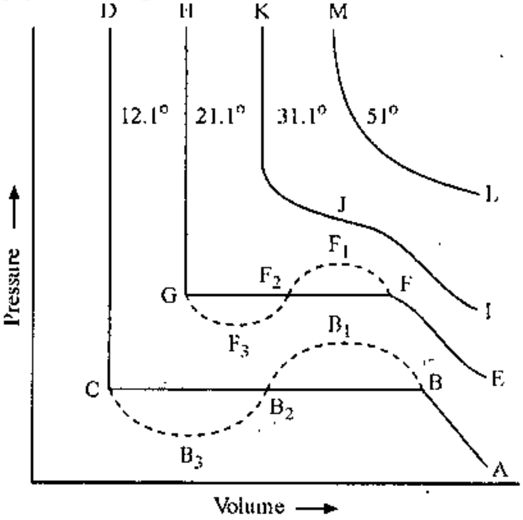


Fig. 8. Isotherms of CO_2

At higher temperature (21.1°C), a similar isotherm EFGH is obtained. It differs from the first isotherm ABCD in two respects, *viz*., (i) liquefaction starts at a higher pressure and (ii) length of the horizontal portion of the curve becomes shorter. With further rise in temperature, the horizonal portion gradually decreases until it is reduced to a point J and the isotherm becomes continuous as seen in the isotherm IJK at 31.1°C. So, there is no horizontal portion of the curve and no sudden change from the gaseous to the liquid state. At this temperature (31.1° C), the gas passes into the liquid state without any visible separation of one phase from the other. This is called ***continuous transition of state.*** The idea of continuity from the gaseous to liquid state can be explained from the isotherm IJK. The change at J shows no sharp discontinuity but a continuous transition occurs during the conversion. Above 31.1°C, the isotherms are continuous and there is no evidence of liquefaction at all.

Andrews observed that if the temperature of CO_2 was above 31.1°C it cannot be liquefied, whatever the pressure may be. Other gases also behave similarly. *So, for every gas there is a limit of temperature beyond which it cannot be liquefied, whatever high pressure may be. This limit of temperature is known as* ***critical temperature*** *(T_c) of the gas. The pressure required to liquefy a gas at critical temperature is called* ***critical pressure*** *(P_c). The volume occupied by one mole of a gas at critical temperature and critical pressure is known as* ***critical volume*** *(V_c).* The point of inflexion (*J*) is called the ***critical point.*** The isotherm passing through *J*, is called the ***critical isotherm.*** This phenomenon is called ***critical phenomenon.***

vander Waals' Equation and Critical State or Calculation of Critical Constants

For one mole of a gas, vander Waals equation,

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

may be simplified as,

$$PV-Pb+\frac{a}{V}-\frac{ab}{V^2}-RT=0$$

Multiplying throughout by V^2 and dividing by P, we get

$$V^3-bV^2+\frac{aV}{P}-\frac{ab}{P}-\frac{RTV^2}{P}=0$$

Arranging in descending powers of V, we get

$$V^3-\left(b+\frac{RT}{P}\right)V^2+\frac{aV}{P}-\frac{ab}{P}=0 \qquad ...(1)$$

This equation is cubic in V and as such there may be three real roots or one real and two imaginary roots of V for each value of P and T. In other words, for given values of P and T, there will be either three real values or one real and two imaginary values of V. This behaviour is not shown by isotherms of CO_2 in figure (8).

At 51° and 31.1°, there is only one volume for each pressure. At 12.1°, there are two different values of V corresponding to points B and C for the same pressure. However, the third volume predicted by equation (1) is missing.

By substituting the experimental values of a and b in equation (1), Thomson (1871) calculated the values of V for different values of P and T. He plotted these calculated values of V against P and the isotherms obtained by him are shown by dotted curves in figure (8). The isotherms for temperature 31.1° and above are exactly of the same form as obtained by Andrews. However, the theoretical isotherms below the critical temperature differ from experimental isotherms (of Andrews). They have no sharp breaks and the horizontal portions of the curves are replaced by wave like portions. For example, the experimental isotherms ABCD and EFGH are replaced by theoretical isotherms $ABB_1B_2B_3CD$ and $EFF_1F_2F_3GH$, respectively. In these, there are obviously three volumes represented by B, B_2 and C (and F, F_2 and G), corresponding to one pressure as predicted by equation (1). As the temperature rises, the wave portion of the curve becomes smaller and smaller and the three values of volume get closer and closer until they merge into one point J at 31.1° (critical temperature). At J, the three roots of V (say x, y and z) of equation (1) are identical. Since the temperature is critical, the value of V represents the critical volume of the gas, *i.e.*, $V = V_c$. The three values of V can be represented as,

$$(V-x)(V-y)(V-z)=0,$$

At critical point, $x = y = z = V_c$.

$$\therefore \quad (V-V_c)^3 = 0$$

Expanding and writing in decreasing powers of V, we get

$$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \qquad \ldots(2)$$

This equation must be identical with vander Waals' equation (1) at critical temperature and pressure, which may be written as

$$V^3 - \left(b + \frac{RT_c}{P_c}\right)V^2 + \frac{aV}{P_c} - \frac{ab}{P_c} = 0 \qquad \ldots(3)$$

Since equations (2) and (3) are identical, the coefficients of equal powers of V in the two equations must be equal to one another. Therefore,

$$3V_c = b + \frac{RT_c}{P_c} \qquad \ldots(4)$$

$$3V_c^2 = \frac{a}{P_c} \qquad \ldots(5)$$

$$V_c^3 = \frac{ab}{P_c} \qquad \ldots(6)$$

Dividing equation (6) by (5), we get

$$V_c = 3b \qquad \ldots(7)$$

Substituting the values of V_c in equation (5), we get

$$P_c = \frac{a}{3V_c^2} = \frac{a}{3 \times (3b)^2} = \frac{a}{27b^2} \qquad \ldots(8)$$

Substituting the values of P_c and V_c in equation (4), we get

$$T_c = \frac{8}{3} \cdot \frac{P_cV_c}{R} = \frac{8}{3} \cdot \frac{(a/27b^2) \times 3b}{R}$$

or

$$T_c = \frac{8a}{27bR} \qquad \ldots(9)$$

Determination of Critical Constants

(a) Critical temperature and critical pressure : These values can be determined by a simple method which is based on the principle that at the critical temperature, the surface of separation, *i.e.*, meniscus between the liquid and the vapour phase disappears. It is generally used when the substance is in liquid state at ordinary temperatures.

The experimental liquid is taken in a vessel V enclosed in a glass jacket J [Fig. (9)]. The temperature of J can be varied gradually by circulating a suitable liquid from a thermostat. The vessel V is connected to a mercury manometer M containing air. The temperature is first lowered so that the vessel is cooled and the surface of separation between the liquid and its vapour becomes sharp. The temperature of the jacket is raised slowly. This rise is continued till the meniscus between the liquid and its vapour just disappears. This temperature say t_1^0 is noted. The jacket is then cooled slowly till cloudiness due to the condensation of vapours appears again. This temperature t_2^0 is again noted. The ***critical temperature*** will thus be $\left(\frac{t_1 + t_2}{2}\right)$.

The mean of the pressures read from the manometer M, corresponding to temperatures t_1^0 and t_2^0 ; gives the value of ***critical pressure.***

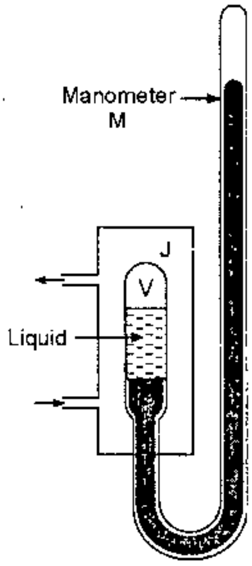


Fig. 9. Apparatus for determining T_c and P_c

(b) Critical volume : The determination of V_c takes the advantage of the observations made by Calliatet and Mathias that when mean values of the densities of liquid and saturated vapour of a substance are plotted against the corresponding temperatures, a straight line is obtained.

In figure (10), the curves VC and LC show the plots of the densities of saturated vapours and those of liquid against the corresponding temperatures. The point C, where the two curves meet gives the *critical temperature.* This point is not sharp as the curve in this range is rather flat. Therefore, the mean densities are then plotted against different temperatures when a straight line MC is obtained. The point C where this line cuts the curve VCL gives the critical temperature as the density of the liquid now becomes identical with that of vapour. The point C gives the critical density of the substance. The ***critical volume*** is obtained by dividing the molecular weight of the substance by the critical density.

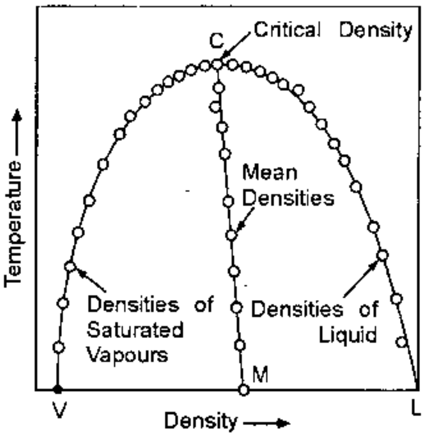


Fig. 10. Determination of V_c

Values of vander Waals Constants and Gas Constant in Terms of Critical Constants

We had already derived the following three equations :

$$3V_c = \frac{RT_c}{P_c} + b \qquad \text{...(10)}$$

$$3V_c^2 = \frac{a}{P_c} \qquad \text{...(11)}$$

$$V_c^3 = \frac{ab}{P_c} \qquad \text{...(12)}$$

Dividing equation (12) by (11), we get

$$V_c = 3b \quad \text{or} \quad b = \frac{V_c}{3} \qquad \text{...(13)}$$

From equation (11), we get $a = 3P_cV_c^2$ ...(14)

Substituting the values of a and b in equation (10), we get,

$$3V_c = \frac{RT_c}{P_c} + \frac{V_c}{3}$$

or $$\frac{RT_c}{P_c} = 3V_c - \frac{V_c}{3} = \frac{8}{3}V_c$$

or $$R = \frac{8}{3} \cdot \frac{P_cV_c}{T_c} \qquad \text{...(15)}$$

(c) From equation (15),

$$\frac{8}{3}V_c = \frac{RT_c}{P_c}$$

Squaring both the sides, we het

$$\frac{64}{9}V_c^2 = \frac{R^2T_c^2}{P_c^2} \quad \text{or} \quad V_c^2 = \frac{9R^2T_c^2}{64P_c^2}$$

Substituting the value of V_c^2 from equation (11), in the above equation, we get

$$\frac{a}{3P_c} = \frac{9R^2T_c^2}{64P_c^2} \quad \text{or} \quad a = \frac{27R^2T_c^2}{64P_c} \qquad \text{...(16)}$$

Substituting the value of V from equation (13) in equation (10), we get,

$$3 \times 3b = \frac{RT_c}{P_c} + b$$

or $$8b = \frac{RT_c}{P_c} \quad \text{or} \quad b = \frac{RT_c}{8P_c} \qquad \text{...(17)}$$

From equations (13) and (17),

$$\frac{V_c}{3} = \frac{RT_c}{8P_c}$$

or $$P_c = \frac{3RT_c}{8V_c}$$

Substituting the value of P_c in equation (16), we get

$$a = \frac{27 \times 8R^2T_c^2V_c}{64 \times 3RT_c}$$

or $$a = \frac{9}{8}RT_cV_c$$

and $$b = \frac{1}{8} \cdot \frac{RT_c}{P_c} \qquad \text{[From eq. (17)]}$$

Ex. 1 : ***Calculate the constants a and b, if $T_c = 31°C$, $P_c = 72.8$ atm and $R = 0.082$ lit atm/deg.***

The values of T_c and P_c are given by

$$P_c = \frac{a}{27b^2} \qquad \text{...(1)}$$

$$T_c = \frac{8a}{27bR} \qquad \text{...(2)}$$

Dividing (2) by (1), we get

$$\frac{T_c}{P_c} = \frac{8b}{R} \quad \text{or} \quad \frac{304}{72.8} = \frac{8b}{0.082}$$

$\therefore$ $$\mathbf{b = 0.0428 \text{ lit mole}^{-1}}$$

Substituting the value of b in equation (1), we get,

$$72.8 = \frac{a}{27 \times (0.0428)^2}$$

or $$\mathbf{a = 3.6 \text{ lit}^2 \text{ atm mole}^{-2}}$$

Ex. 2 : ***The vander Waals constants in lit atm/mole of CO_2 are : $a = 3.6$, $b = 4.28 \times 10^{-2}$. Calculate T_c and V_c for the gas.***

The values of V_c and T_c are given by,

$$V_c = 3b \qquad \text{...(1)}$$

$$T_c = \frac{8a}{27bR} \qquad \text{...(2)}$$

From equation (1), $V_c = 3 \times 4.28 \times 10^{-2} = 3 \times 0.0428 = \mathbf{0.1284 \text{ lit}}$

From equation (2), $T_c = \dfrac{8 \times 3.6}{27 \times 0.0428 \times 0.082} = 303.9 \text{ K} = \mathbf{30.9°C}$

Ex. 3 : ***One mole of NH_3 is enclosed in a five litre flask at 27°C. Calculate the pressure of NH_3 using vander Waals equation. For NH_3, $a = 4.17$ atm lit^2 mole^{-2} and $b = 0.0371$ lit mole^{-1}.***

Solution : vander Waals' equation is given by,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Substituting the values, we get

$$\left(P + \frac{4.17}{5^2}\right)(5 - 0.0371) = 0.0821 \times 300$$

or $$\left(\frac{25P + 4.17}{25}\right)(4.9629) = 0.0821 \times 300$$

or $$P = \frac{1}{25}\left[\frac{0.0821 \times 300 \times 25}{0.9629} - 4.17\right] = \mathbf{4.71 \text{ atmosphere}}$$

Ex. 4 : ***From vander Waals equation, show that***

$$P_cV_c = \frac{3}{8}RT_c$$

Solution : vander Waals equation under critical conditions is written as:

$$\left(P_c + \frac{a}{V^2}\right)(V - b) = RT_c$$

or $$V^3 - \left(b + \frac{RT_c}{P_c}\right)V_2 + \frac{a}{P_c}V - \frac{ab}{P_c} = 0 \qquad \ldots(1)$$

At critical point, the three values of volume are identical and equal to V_c. Thus,

$$(V - V_c)^3 = 0$$

or $$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \qquad \ldots(2)$$

As (1) and (2) are identical, therefore,

$$3V_c = b + \frac{RT}{P_c} \qquad \ldots(3)$$

$$3V_c^2 = \frac{a}{P_c} \qquad \ldots(4)$$

$$V_c^3 = \frac{ab}{P_c} \qquad \ldots(5)$$

Dividing (5) by (4), we get

$$V_c = 3b$$

or $$b = \frac{V_c}{3} \qquad \ldots(6)$$

Substituting the value of b in equation (3), we get

$$3V_c = \frac{V_c}{3} + \frac{RT_c}{P_c} \quad \text{or} \quad 3V_c - \frac{V_c}{3} = \frac{RT_c}{P_c}$$

or $$\frac{9V_c - V_c}{3} = \frac{RT_c}{P_c} \quad \text{or} \quad \frac{8}{3}V_c = \frac{RT_c}{P_c}$$

or $$\mathbf{P_cV_c = \frac{3}{8}RT_c}$$

Ex. 5 : ***2 moles of CO_2 at 27°C is filled in a five litre flask. Calculate its pressure using the following :***

(i) Gas equation, (ii) vander Waals equation.

For CO_2 : $a = 3.6$ atm lit^2 mole^{-2}; $R = 0.082$ lit atm, $b = 4.28 \times 10^{-2}$ lit mole^{-1}.

Solution : (i) *Pressure from gas equation :*

$$PV = nRT \quad \text{or} \quad P = \frac{nRT}{V}$$

$$\therefore \qquad P = \frac{2 \times 0.082 \times 300}{5} = \mathbf{9.84 \text{ atmospheres.}}$$

(ii) *Pressure from vander Waals' equation* :

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT \quad (\text{where } n = \text{No. of moles} = 2)$$

$$\therefore \qquad \left(P + \frac{4 \times 3.6}{5^2}\right)(5 - 0.0428 \times 2) = 0.082 \times 300 \times 2$$

$$\text{or} \qquad (25P + 14.4) = \frac{0.082 \times 300 \times 25 \times 2}{4.9144}$$

$$\text{or} \qquad 25P = \frac{0.082 \times 300 \times 25 \times 2}{4.9144} - 14.4$$

$$\text{or} \qquad P = \frac{235.8}{25} = 9.43$$

$$\therefore \qquad \text{Pressure} = \mathbf{9.43 \text{ atmospheres.}}$$

1.6. VARIOUS EQUATIONS OF STATE

vander Waals equation has been found to be accurate over a wide range of pressure and temperature. Near the critical point, it does not gives satisfactory results. Several other equations have been proposed to express P–V–T relationship in accordance with the experimental observations. These equations of state are :

[I] Clausius equation : This is vander Waals equation modified by Clausius to account for the variation of vander Waals constant a with temperature. It is given by,

$$\left[P + \frac{a}{T(V+c)^2}\right](V - b) = RT$$

where, c is a new constant. This equation is fairly satisfactory but does not hold good for all gases.

[II] Dieterici equation : Dieterici introduced an exponential factor to account for the effect of molecular attraction on the pressure. His equation is given by,

$$P\,(V - b) = RT\,.\,e^{-a/RTV}$$

where, e is the base of natural logarithm. This equation gives more satisfactory results at high pressures than the vander Waals equation.

[III] Berthelot's equation : Berthelot proposed the following empirical equation to explain the behaviour of real gases.

$$\left(P + \frac{a}{TV^2}\right)(V - b) = RT$$

[IV] Kammerling Onnes' equation or virial equation : Kammerling Onnes gave an empirical equation which gives the product PV as power series of the pressure at any given temperature. The equation is represented as :

$$PV = A + BP + CP^2 + DP^3 + \ldots$$

The factors A, B, C and D etc. are known as first, second, third, fourth etc. ***virial coefficients*** (Greek : *virial* = force).

At low pressures, the coefficient A (which is equal to RT) is important and others cancel out. At increasing pressures, other coefficients become significant.

[V] Beattie-Bridgemann equation : This empirical equation is given by :

$$PV = RT + \frac{\beta}{V} + \frac{\gamma}{V^2} + \frac{\delta}{V^3} + \ldots$$

where, β, γ, δ are also called virial coefficients.

• 1.7. LAW OF CORRESPONDING STATES OR REDUCED EQUATION OF STATE

vander Waals showed that if P, V and T of a gas are expressed in terms of critical pressure, critical volume and critical temperature of a gas, we obtain another important generalisation, known as ***law of corresponding states.***

Let, $$\frac{P}{P_c} = \pi, \quad \frac{V}{V_c} = \phi$$

and $$\frac{T}{T_c} = \theta$$

where π, ϕ and θ are known as reduced pressure, reduced volume and reduced temperature, respectively. Therefore,

$$P = \pi P_c;\ V = \phi V_c \text{ and } T = \theta T_c.$$

Substituting the values of P, V and T in vander Waals equation, we get,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

we get, $$\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right)(\phi V_c - b) = R\theta T_c$$

Substituting the values of P_c, V_c and T_c in the above equation, we get,

$$\left[\pi \cdot \frac{a}{27b^2} + \frac{a}{\phi^2 (3b)^2}\right](\phi \,.\, 3b - b) = R\,\theta \cdot \frac{8a}{27bR}$$

or $$\frac{ab}{27b^2}\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = R\theta \cdot \frac{8a}{27bR}$$

or $$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta \qquad \ldots(1)$$

The above equation known as ***vander Waals reduced equation of state*** does not involve vander Waals' constants as well as gas constant, hence it is a general equation applicable to all substances.

From equation (1), *if two substances have the same reduced temperature (θ) and the same reduced pressure (π), they will have the same reduced volume (ϕ).* This statement is known as ***law of corresponding states.*** In other words, two or more substances having the same reduced temperature and same reduced pressure and thus having the same reduced volume, are said to be in *corresponding states.*

Importance : While studying the relationship between physical properties and chemical constitution of various liquids, their properties should be studied at the same reduced temperature as pressure has practically no effect on liquids. It is seen that the boiling point of a liquid on absolute scale is nearly two-thirds of its critical temperature. Various liquids at their boiling points are thus very nearly in corresponding states and to study their physical properties at the same reduced temperature, these should be studied at their boiling points.

• 1.8. COLLISION DIAMETER

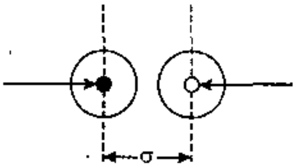


Fig. 11

When two molecules of a gas approach each other, they continue moving till a point is reached at which the mutual repulsion is so great that they have to retrace their path. ***The distance between the two centres of two such molecules at the point of closest approach, i.e., when they are about to retrace their path, is called collision diameter.*** It is represented by the Greaek symbol sigma (σ). Inspite of the fact that the molecules are infinitesimally small, they have an effective collision diameter. At 298 K and 1 atmospheric pressure, the collision diameters of H_2, He, N_2 and O_2 are 273 pm, 218 pm, 374 pm and 357 pm, respectively.

• 1.9. MEAN FREE PATH

At a given temperature, a molecule travels in a straight line before its collisions with other molecules. The distance travelled by the molecule before collision is called *free path*. The free path for a molecule changes from time to time. ***The mean distance travelled by a molecule between two successive collisions is known as mean free path.*** It is represented by λ. If l_1, l_2, l_3 are the free paths for a molecule of a gas, then the mean free path is given by

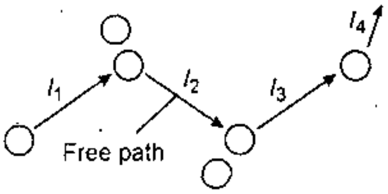


Fig. 12. Illustration of mean free path

$$\lambda = \frac{l_1 + l_2 + l_3 + \ldots\ldots\ldots + l_n}{n}$$

where n is the number of molecules with which the molecule collides. The number of molecular collisions will be less at a lower pressure or lower density and longer will be the mean free path. The mean free path is also related with the viscosity of the gas.

The mean free path, λ is given by the equation

$$\lambda = \eta \sqrt{\frac{3}{Pd}}$$

where P = pressure of the gas, d = density of the gas, η = coefficient of viscosity of the gas.

From the determination of viscosity of the gas, the mean free path can be easily calculated. The mean free paths for hydrogen and oxygen are 1.78×10^{-5} cm and 1.0×10^{-5} cm, respectively.

Effect of Temperature and Pressure on Mean Free Path

(1) Temperature : For n moles of a gas, the ideal gas equation is

$$PV = nRT \qquad \ldots (1)$$

We know that $$n = \frac{\text{Number of molecules}}{\text{Avogadro's number}} = \frac{N_0}{N}$$

Substituting the value of n in equation (1), we get

$$PV = \frac{N_0}{N} RT$$

or $$\frac{N_0}{V} = \frac{PN}{RT} \qquad \ldots (2)$$

The mean free path is given by

$$\lambda = \frac{\text{Distance travelled by the molecule per second}}{\text{Number of collisions per c.c.}}$$

$$= \frac{\langle u \rangle}{\sqrt{2}\,.\,\pi\sigma^2 \langle u \rangle \overline{N}} = \frac{1}{\sqrt{2}\,\pi\,\sigma^2\,\overline{N}} \qquad \ldots (3)$$

where σ = molecular diameter and $\overline{N}$ is the number of molecules per c.c.

From equations (2) and (3), we get, $\lambda \propto T$.

Therefore, ***the mean free path is directly proportional to the absolute temperature.***

(2) Pressure : We know that at a definite temperature, the pressure of a gas is directly proportional to the number of molecules per c.c., *i.e.*, $P \propto \overline{N}$

The mean free path is given by

$$\lambda = \frac{1}{\sqrt{2}\,.\,\pi\,\sigma^2\,\overline{N}}$$

Combining the above two equations, we get

$$\lambda \propto \frac{1}{P}$$

So, ***the mean free path at constant temperature is inversely proportional to the pressure of the gas.***

Ex. 1. ***At 0°C and 1 atmospheric pressure, the molecular diameter of a gas is 4Å. Calculate the mean free path of its molecule.***

Solution : The mean free path is given by

$$\lambda = \frac{1}{\sqrt{2}\,.\,\pi\,\sigma^2\,\overline{N}}$$

where $\overline{N}$ is the number of molecules per c.c. and σ is the molecular diameter.

It is given that, $\sigma = 4\text{Å} = 4 \times 10^{-8}$ cm.

We know that 22400 ml of gas at 0°C and 1 atmospheric pressure contains 6.02×10^{23} molecules

$\therefore$ Number of molecules per c.c., *i.e.*,

$$\overline{N} = \frac{6.02 \times 10^{23}}{22400}$$

$$= 2.689 \times 10^{19} \text{ molecules}$$

$$\therefore \qquad \lambda = \frac{1}{1.414 \times 3.14 \times (4 \times 10^{-8})^2 \times (2.689 \times 10^{19})}$$

$$= \frac{1}{1.414 \times 3.14 \times 16 \times 2.689 \times 10^{3}} = \mathbf{0.524 \times 10^{-8}\ cm.}$$

• 1.10. COLLISION NUMBER

Let us assume that the molecules are hard, impenetrable spheres of diameter σ moving with an average velocity $\langle u \rangle$. Consider the movement of the molecule A. through a cylinder of diameter 2σ [Fig. (13)]. Since the radius of each molecule is $\sigma/2$, the molecule A will collide with any other molecule B within a distance σ.

In one second the molecule travels a distance $\langle u \rangle$. This means that it sweeps out a cross-section area of $\pi\sigma^2$ colliding with all the molecules within the cylinder of diameter 2σ or volume $\pi\sigma^2 \langle u \rangle$. The zig-zag movement of the molecules does not matter as the volume swept out remains unchanged. The number of molecules present per m^3 of the gas is its density. Let $\overline{N}$ be the number of molecules per unit volume present in the gas container. The number of molecules in the cylinder swept out by the molecule A in one second is $\pi\sigma^2\overline{N} \langle u \rangle$. In other words, the number of collisions made by one molecule per second (Z_1) should be equal to $\pi\sigma^2\overline{N} \langle u \rangle$.

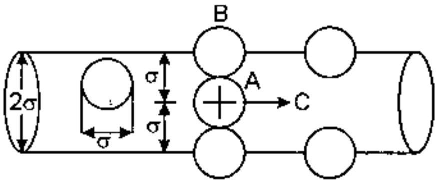


Fig. 13. Collision cylinder swept out by a molecule moving through a gas

However, the molecule is deflected more or less by each collision and the molecules with which it collides are not stationary but moving at random, resulting in all types of collisions. Some molecules may have head-on collisions, while others may have just grazing collisions. When two molecules with an average velocity $\langle u \rangle$ have head-on collision in the same direction their relative velocity will be $2 \langle u \rangle$. However when they have a grazing collision, their relative velocity will be zero. To get the average of thse two extreme cases, the midway would be to take collisions of molecules at right angle to each other giving rise to a relative velocity of $\sqrt{2} . \langle u \rangle$.

If we take into account the motion of the molecules relative to one another, more detailed calculations show that the relative average velocity is $\sqrt{2} \langle u \rangle$ instead of $\langle u \rangle$ incorporating the actual number of collisions made by a single molecule with this, the number of molecules per m^3 per second,

$$Z = \sqrt{2}\, \pi\, \sigma^2\, \overline{N} \langle u \rangle$$

where Z is known as collision number. Collision number is defined as the ***average number of collisions suffered by a single molecule per unit time per unit volume of the gas.***

Ex. 1. ***The root mean square velocity of hydrogen at STP is*** $\mathbf{1.831 \times 10^5}$ ***cm sec***$^{-1}$ ***and its mean free path is*** $\mathbf{1.78 \times 10^{-5}}$ ***cm. Calculate the collision number at STP.***

Solution : Root mean square velocity,

$$u = 1.831 \times 10^5 \text{ cm sec}^{-1}$$

Average velocity, $\langle u \rangle = 0.9213 \times 3$

$$= 0.9213 \times 1.831 \times 10^5 \text{ cm sec}^{-1} = 1.6869 \times 10^5 \text{ cm sec}^{-1}$$

We know that

$$\text{Mean free path} = \frac{\text{Average velocity}}{\text{Collision number}}$$

or $$\text{Collision number} = \frac{\text{Average velocity}}{\text{Mean free path}}$$

$$= \frac{1.6869 \times 10^{5}\ \text{cm sec}^{-1}}{1.78 \times 10^{5}\ \text{cm}} = \mathbf{9.4769 \times 10^{9}\ sec^{-1}}.$$

• SUMMARY

- Kinetic equation of gases is $PV = \frac{1}{3} mNu^2 = \frac{1}{3} Mu^2$, when N = Avogadro's number and M = Molecular weight of the gas.
- Kinetic energy of n moles of a gas, $E = \frac{3}{2} nRT$.
- **Average velocity** $\langle u \rangle$ is defined as the average of the velocities of all molecules at any time.
- **RMS velocity** (u) is defined as the square root of the mean of squares of all velocities of the molecules.
- **Most probable velocity** ($\bar{u}$) is the velocity possessed by the maximum number of gas molecules.
- Average velocity = 0.9213 × RMS velocity.
- RMS velocity is also given by the relation, $u = 1.58 \times 10^4 \times \sqrt{\frac{T}{M}}$
- An ideal gas has a compressibility of unity.
- An ideal gas has no mutual force of attraction between gas molecules.
- vander Waals improved the ideal gas equation and gave a modified equation known as vander Waals equation. For n moles of a gas, it is given by $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT.$
- Units of vander Waals constants a and b are atm. dm^6 mol^{-2} (Nm^4 mol^{-2}) and litre mol^{-1} (m^3 mol^{-1}), respectively. The units within brackets are in SI unit.
- **Critical temperature (T_c) :** The maximum limit of temperature beyond which a gas can not be liquefied whatever the pressure may be is called its critical temperature.
- **Critical pressure (P_c) :** The pressure required by a gas to liquefy a gas at critical temperature is called critical pressure.
- **Critical volume (V_c) :** The volume occupied by one mole of a gas at critical temperature and critical pressure is called critical volume.
- $P_c = \frac{a}{27b^2}, \quad V_c = 3b, \quad T_c = \frac{8a}{27Rb}$
- **Law of corresponding states :** If two gases have the same reduced temperature and same reduced pressure, they will have the same reduced volume.

- Reduced equation of state is given by
  $$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta$$
  where π, ϕ and θ are reduced pressure, reduced volume and reduced temperature, respectively.
- The average distance travelled by a molecule between two successive collisions is known as its mean free path.
- Mean free path is directly proportional to absolute temperature and inversely proportional to the pressure of the gas.
- The distance between the two centres of two molecules at the point of closest approach, *i.e.*, when they are about to retrace their path is called collision diameter (σ).
- The average number of collisions suffered by a single molecule per unit time per unit volume of the gas is known as collision number (Z).

• STUDENT ACTIVITY

1. Describe the postulates of kinetic theory of gases and also derive kinetic equation of gases.

2. Define critical constants.

3. Define law of corresponding states.

• TEST YOURSELF

Answer the following questions :

1. Discuss the postulates of kinetic theory of gases.
2. Derive kinetic equation of gases.
3. Derive different gas laws from kinetic equation of the gas.
4. Calculate the kinetic energy of an ideal gas.
5. Describe an ideal gas. What are the differences between an ideal gas and a real gas.
6. Describe the limitations of the equation $PV = RT$.
7. What improvements were made by vander Waals in the equation $PV = nRT$? Derive vander Waals equation.
8. Write the units of vander Waals constants.
9. Explain critical phenomenon. Define the critical constants.
10. Calculate the values of critical constants in terms of vander Waals constants.
11. How are critical constants determined experimentally ?
12. Define average, root mean square and most probable velocity.
13. How will you calculate RMS velocity under different conditions ?
14. Write short notes on the following :
    (i) Law of corresponding states (ii) Mean free path
    (iii) Collision diameter (iv) Collision number
15. The critical temperature of hydrogen gas is 33.2°C and the critical pressure is 12.4 atmosphere. Find out the values of 'a' and 'b' for the gas.
16. Calculate the RMS velocity of oxygen molecules at 27°C.
17. Derive the reduced equation of state for a gas.
18. What is the law of corresponding states ?

19. Explain the principle of continuity of state.

20. A gas cannot be liquefied if for a gas the temperature is greater than :
(a) Critical temperature (b) Critical pressure (c) Critical volume (d) Critical density

21. The first virial coefficient of Kammerling Onnes equation at low pressure is :
(a) PV (b) RT (c) $\frac{1}{V}$ (d) $\frac{1}{RT}$

22. The unit of vander Waals constant 'a' is :
(a) mole atm^{-1} (b) atm mole^{-1}
(c) lit^2 atm mole^{-2} (d) atm lit^{-2} mole^2

23. If the rms velocity of a gas is 100 cm s^{-1}, its average velocity is :
(a) 100 cm s^{-1} (b) 0.01 cm s^{-1}
(c) 92.13 cm s^{-1} (d) 81.64 cm s^{-1}

24. The conpressibility factor of an ideal gas is :
(a) Zero (b) Infinite (c) 2.0 (d) 1.0

25. The temperature at which the second virial coefficient of a real gas is zero, is known as :
(a) Critical temperature (b) Boiling point
(c) Boyle temperature (d) Freezing point

26. The virial state equation for a real gas is :
(a) $PV = RT + \frac{B'}{V} + \frac{C'}{V^2} + \dots$ (b) $PV = RT + CP^2 + DP^3 + \dots$
(c) $PV = RT + RT^2 + RT^3 + \dots$ (d) $PV = RT + \frac{B'}{V} + \frac{C'}{V} + \dots$

27. At 27°C the kinetic energy of 2 moles of an ideal gas is :
(a) 1800 cal (b) 900 cal (c) 600 cal (d) 3600 cal

28. Fill in the Blanks

(i) The average energy of translational motion of gas molecules is proportional only to the ....

(ii) Real gases behave ideally at .... temperatures and .... pressures.

(iii) At 273 K, rms velocity of methane molecules would be .... ms^{-1}.

(iv) vander Waals replaced the volume term, V in the ideal gas equation by ....

(v) The intermolecular forces which exist between the neutral molecules are known as ....

(vi) The temperature at which the average velocity of O_2 molecules would be twice that at 20°C is .... K.

(vii) Average kinetic energy of gas molecules is .... to absolute temperature.

(viii) The unit of vander Waals constant a is .... and b is ....

(ix) The pressure of real gases is less than that of ideal gases because of ....

(x) The reduced equation of state is given by ....

ANSWERS

15. $a = 21.439$ atm L^2 mol^{-2}, $b = 0.253$ lit mol^{-1} **16.** 4.835×10^4 cm sec^{-1}

20. (a) **21.** (b) **22.** (c) **23.** (c) **24.** (d) **25.** (c) **26.** (a) **27.** (a)

28. **(i)** absolute temperature **(ii)** high, low **(iii)** 652 **(iv)** $(V - b)$ **(v)** vander Waals forcess **(vi)** 586 K **(vii)** directly proportional **(viii)** lit^2 atm mole^{-2}, lit mole^{-1} **(ix)** mutual attractions **(x)** $\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta$.

* * *

UNIT

2

CHEMICAL KINETICS

LEARNING OBJECTIVES

- Rate of Chemical Reaction
- Velocity Coefficient
- Molecularity of Reaction
- Order of Reaction
- Factors Affecting the Rate of Reaction
- Zero Order Reaction
- First Order Reaction
- Pseudo-Unimolecular Reactions
- Second Order Reaction
- Determination of Order of Reaction
- Activation Energy
- Collision Theory for Unimolecular Reactions
- Transition State Theory
    - ☐ Summary
    - ☐ Student Activity
    - ☐ Test Yourself

• 2.1. RATE OF CHEMICAL REACTION

Rate of chemical reaction is defined as, *'**the rate at which the concentration of a reactant changes with time**'*, *i.e.*,

$$\text{Reaction rate} = \frac{\text{Change in concentration}}{\text{Time interval}}$$

The rate at which a reaction proceeds can be followed by measuring the concentration of either the reactant or product. If dx represents the amount of the reactant changed during a small interval of time dt, then the reaction rate is represented by dx/dt. If, on the other hand, dc represents the concentration of the reactant left behind after a short interval of time dt, then the reaction rate is also represented by $-dc/dt$. The negative sign implies that the concentration of the reactant decreases with time or rate of reaction decreases with time. The unit of reaction rate is mol L^{-1} s^{-1}.

For a reaction, $A + B \longrightarrow C + D$, the reaction rate can be expressed as

$$-\frac{d[A]}{dt} \quad \text{or} \quad -\frac{d[B]}{dt} \quad \text{or} \quad +\frac{d[C]}{dt} \quad \text{or} \quad +-\frac{d[D]}{dt}$$

Consider the reaction, $2N_2O_5\,(g) \longrightarrow 4NO_2\,(g) + O_2\,(g)$. The rates of reaction can be expressed as,

$$-\frac{d[N_2O_5]}{dt} \quad \text{or} \quad +\frac{d[NO_2]}{dt} \quad \text{or} \quad +\frac{d[O_2]}{dt}$$

All the rates can be equated as,

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = +\frac{d[O_2]}{dt}$$

• 2.2. VELOCITY COEFFICIENT

Consider the following reaction :

$$A + B \longrightarrow \text{Products}$$

If a and b are the initial concentrations of the reactants A and B and if x be the number of moles of each reactant undergoing reaction after time t, then the concentrations A and B after time t will be

$(a-x)$ and $(b-x)$ respectively. According to the law of mass action, the reaction rate (dx/dt) is given by

$$\frac{dx}{dt} \propto (a-x)(b-x) \quad \text{or} \quad \frac{dx}{dt} = k\,(a-x)(b-x)$$

where, k is a constant known as *velocity constant, rate constant, velocity coefficient or specific reaction rate.* It is characteristic of the reaction.

If $(a-x) = 1$ and $(b-x) = 1$, then

$$k = \frac{dx}{dt} = \text{Rate of reaction}$$

So, velocity coefficient is defined as, ***the rate of reaction under conditions when the molecular concentration of each reactant is unity.***

• 2.3. MOLECULARITY OF REACTION

It is defined as, ***the total number of molecules of all the reactants taking part in a chemical reaction as represented by a simple equation.***

Examples. (i) Inversion of cane sugar (Molecularity = 2)

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+ \text{ ions}} C_6H_{12}O_6 + C_6H_{12}O_6$$

(ii) Dissociation of ammonia (Molecularity = 2)

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

(iii) In general, for a reaction, $n_1A + n_2B \longrightarrow n_3C + m_2D$ the molecularity will be $n_1 + n_2$.

So, reactions having molecularity 1, 2, 3 etc., are known as *unimolecular, bimolecular, trimolecular* reactions, respectively.

• 2.4. ORDER OF REACTION

Reactions are generally classified on the basis of their order of reaction. It is defined as,

'The total number of reacting molecules whose concentration changes during the chemical reaction.'

In other words, it is also defined as,

'The total number of reacting molecules whose concentration determines the rate of reaction'.

(a) If A $\longrightarrow$ Products and $(dx/dt) = k\,[A]$, then

Order of reaction = 1

(b) If A + B $\longrightarrow$ Products and $(dx/dt) = k\,[A][B]$, then

Order of reaction = 2

(c) If $n_1A + n_2B + n_3C + \ldots \longrightarrow$ Products, and

$$\frac{dx}{dt} = k\,[A]^{n_1}\,[B]^{n_2}\,[C]^{n_3} \ldots, \text{ then}$$

Order of reaction $= n_1 + n_2 + n_3 + \ldots$

(a) If A + 2B $\longrightarrow$ Products, and $\dfrac{dx}{dt} = k$, then

Order of reaction = 0

In general, order of reaction is also defined as, ***the sum of the powers to which the concentration (or pressure) terms of the reactants are raised in order to determine the rate of a reacton.***

Relation between Molecularity and Order of Reaction

Till recently, the molecularity and order of reaction were regarded as synonymous. But, it has now been found that in certain cases the two are not identical. For example, during the inversion of cane sugar into glucose and fructose or the hydrolysis of ethyl acetate in presence of acid catalyst, apparently two molecules take part, making the reactions bimolecular. But actually, the concentration of only one of reactants changes, *i.e.*, concentration of water does not appreciably change. Hence, the reactions though bimolecular are of the first order.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+ \text{ ions}} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+ \text{ ions}} CH_3OOH + C_2H_5OH$$

Thus, often molecularity of a reaction coincides with its order, but the two need not be always identical. The molecularity must be an integral value, but the order of reaction may be zero, whole number or even fractional. Whereas molecularity can be given on the basis of some proposed theoretical mechanism so as to satisfy the experimental findings, the order of reaction can be obtained from experimental results.

For complex reactions, occurring in steps, the molecularity of each step will be different, while the order of reaction will be determined by the slowest step.

Table-1. Difference between order of reaction and molecularity

Molecularity	Order of reaction
1. It is equal to the number of molecules of reactants which take part in a single step chemical reaction.	1. It is equal to the sum of the powers of the molar concentrations of the reactants in the rate expression.
2. It is a theoretical concept which depends on the rate determining step in the reaction mechanism.	2. It is an expermientally determined quantity which is obtained from the rate for the overall reaction.
3. It is always a whole number.	3. It may be whole number, zero or fractional value.
4. It is obtained from a single balanced chemical equation.	4. It cannot be obtained from a balanced chemical equation.
5. It reveals some basic facts about reaction mechanism.	5. It does not reveal anything about reaction mechanism.

Most of the reactions are of the first and second orders. According to kinetic theory of gases, the reaction occurs due to collisions of molecules. For a second order reaction, two molecules have to collide which is reasonably possible. But the chances of three, four or even more molecules colliding simultaneously are very remote and so reactions of higher orders are very rare. There are a number of complex reactions involving a number of molecules. But in such cases, the reactions occur in several stages and slowest stage is the rate determining step and it gives the order of reaction.

The following reaction, though involving ten molecules is of the second order.

$$KClO_3 + 3H_2SO_4 + 6FeSO_4 \longrightarrow 3Fe_2(SO_4)_3 + KCl + 3H_2O$$

• 2.5. FACTORS AFFECTING THE RATE OF REACTION

The following factors influence the rate of reactions.

(i) ***Effect of concentration*** **:** We know that the rate of a reaction falls with time, so it is clear that the rate of reaction is directly proportional to the concentration of reactants.

(ii) ***Effect of temperature*** **:** The rate of reaction increases with rise in temperature. In most cases, a rise of 10°C in temperature doubles and in some cases even trebles the rate of a reaction. The ratio of the velocity constants of a reaction at two temperatures differing by 10°C is called *temperature coefficient* of the reaction.

$$\text{Temperature coefficient} = \frac{\text{Rate constant at } 35°\text{C}}{\text{Rate constant at } 25°\text{C}} = \frac{k_{35}}{k_{25}}$$

(iii) ***Effect of nature of reactants*** **:** Rates of reactions are effected considerably by the nature of reactants. For example, consider the two well known oxidation reactions taking place in aqueous solution. One is the oxidation of ferrous ion, Fe^{2+} and the other of oxalate ion, $C_2O_4^{2-}$, by permanganate ion in acid medium.

(a) $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O$

(b) $5C_2O_4^{2-}(aq) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O$

The first reaction is much faster than the second. As MnO_4^- ion is common in both the reactions, the difference clearly lies in the nature of ferrous and oxalate ions. Fe^{2+} ion is a simple ion, whereas $C_2O_4^{2-}$ ion is a polyatomic ion and contains a number of covalent bonds which have to be broken in the oxidation reaction.

(iv) ***Effect of catalyst*** **:** A catalyst generally increases the rate of a reaction at a given temperature. A catalyst is generally specific in its action, *i.e.*, it may affect the rate of one particular process only. In very few cases, a catalyst may decrease the rate of a reaction.

(v) ***Effect of surface area of reactants*** **:** In heterogeneous reactions, particle size decreases and so the surfac area for the same mass increases. The smaller particles, therefore, react more rapidly than the larger particles.

(vi) ***Effect of radiation*** **:** We know that the energy associated with each photon of radiation is given by $h\nu$, where h is Planck's constant and ν is the frequency of the radiation concerned. The rate of certain reactions may be speeded up by the absorption of photons of certain radiations. Such reactions are called ***photochemical reactions.***

• 2.6. ZERO ORDER REACTION

A reaction in which the concentration of the reactants does not change with time and the reaction rate remains constant throughout is said to be a zero order reaction.

[I] Rate Expression for Zero Order Reaction

Consider the following zero order reaction, A $\longrightarrow$ Products

$\therefore$ Reaction rate, $\frac{dx}{dt} = k$ (k = velocity constant)

or $dx = k\,dt$

On integration, we get $\int dx = \int k\,dt$

or $x = kt + I$ where, I = integration constant ...(1)

When $t = 0$, then $x = 0$.

$\therefore$ $I = 0$

$\therefore$ From equation (1), $x = kt$ or $k = \frac{x}{t}$ ...(2)

Equation (2) is known as ***zero order rate expression.***

[II] Characteristic

(i) The dimension of velocity constant is concentration × time^{-1} or mole lit^{-1} time^{-1} or mole lit^{-1} s^{-1}, if time is expressed in second.

[III] Example

(i) Several photochemical reactions and heterogeneous reactions (enzymic) are of zero order, *e.g.*, the photochemical combination of H_2 and Cl_2 in presence of sunlight to give HCl is of zero order.

$$H_2\,(g) + Cl_2\,(g) \xrightarrow{\text{Sunlight}} 2HCl\,(g)$$

• 2.7. FIRST ORDER REACTION

A reaction in which the reaction rate depends only on one concentration term is said to be a first order reaction.

For example, if A $\longrightarrow$ Products

then, reaction rate $= \frac{dx}{dt} = k\,[A]$

[I] Rate Expression For First Order Reaction

Consider the following simplest first order reaction.

$$A \longrightarrow \text{Products}$$

Let a mole/litre be the initial concentration of the reactant A. Suppose x mole/litre of A decomposes in time t, leaving behind $(a - x)$ mole/litre of it. For a first order reaction, the reaction rate at any time t is given by :

$$\frac{dx}{dt} = k\,[A] = k\,(a - x)$$

where, k is the velocity constant or rate constant.

or $\frac{dx}{a - x} = k\,dt$ ...(1)

In order to get the value of k, we integrate equation (1). So,

$$-\log_e (a - x) = kt + I \quad \text{...(2)}$$

where, I is the integration constant.

When $t = 0$, $x = 0$, therefore, from equation (2),

$$I = -\log_e a$$

Substituting the value of I in equation (2),

$$-\log_e (a - x) = kt - \log_e a$$

or $$k = \frac{1}{t}\log_e \frac{a}{a-x} \qquad \ldots(3)$$

$$k = \frac{2.303}{t}\log_{10} \frac{a}{a-x} \qquad \ldots(4)$$

(As $\log_e x = 2.303 \log_{10} x$)

Equations (3) and (4) are known as ***first order rate expressions.*** The constant k is called the ***first order rate constant.***

[II] Characteristics of First Order Reaction

(i) ***The value of velocity constant is independent of the units in which concentration of the reactant is expressed.*** If unit of concentration is changed to say n times its original value, then equation (4) becomes

$$k = \frac{2.303}{t}\log_{10}\frac{n.a}{n.a - n.x} = \frac{2.303}{t}\log_{10}\frac{na}{n(a-x)}$$

$$= \frac{2.303}{t}\log_{10}\frac{a}{a-x}$$

This is the same as equation (4).

(ii) ***The dimension of first order rate constant is reciprocal of time i.e., t^{-1}.*** From equation (4), we have

$$k = \frac{1}{\text{time}} \cdot \frac{\text{concentration}}{\text{concentration}} = \frac{1}{\text{time}}$$

If time is expressed in second or minute, k is expressed in ***second^{-1}*** or ***minute^{-1}***, respectively.

(iii) ***The time taken to complete a certain fraction of a reaction is independent of the initial concentration of the reactant.*** Suppose $t_{1/2}$ is the time taken to reduce the concentration of reactant A to half, *i.e.*, from a to $a/2$, then $x = a/2$. From equation (4), we get

$$k = \frac{2.303}{t_{1/2}}\log_{10}\frac{a}{a-(a/2)} = \frac{2.303}{t_{1/2}}\log_{10} 2$$

or $$t_{1/2} = \frac{2.303}{k}\log_{10} 2 = \frac{2.303}{k} \times 0.3010 = \frac{0.693}{k} \qquad \ldots(5)$$

Equation (5) is thus independent of a, *i.e.*, the initial concentration of the reactant.

[III] Examples of First Order Reaction

(i) Decomposition of hydrogen peroxide in aqueous solution.

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$$

(ii) Hydrolysis of methyl acetate in presence of acid.

$$CH_3COOCH_3 + H_2O \xrightarrow{\text{Acid}} CH_3COOH + CH_3OH$$

(iii) Hydrolysis of cane sugar in presence of acid.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Acid}} C_6H_{12}O_6 + C_6H_{12}O_6$$

Ex. 1 : ***The decomposition of hydrogen peroxide was studied by titrating it at different intervals of time with potassium permanganate. Calculate the velocity constant for it from the following data, if the reaction is of the first order.***

t (sec)	*0*	*600*	*1200*
$KMnO_4$ (ml)	*22.8*	*13.8*	*8.2*

Sol. The first order rate expression is : $k = \frac{2.303}{t}\log\frac{a}{a-x}$

The amount of $KMnO_4$ is proportional to the amount of H_2O_2 present, so the volume of $KMnO_4$ used at zero time corresponds to initial concentration (a) and the volume used after time t, corresponds to $(a-x)$ at that time. Inserting these values in the above equation, we get

$$k_{600} = \frac{2.303}{600}\log\frac{22.8}{13.8} = 0.000837\ s^{-1}$$

$$k_{1200} = \frac{2.303}{1200} \log \frac{22.8}{8.2} = 0.000852\ \text{s}^{-1}$$

The average value of velocity constant,

$$k = \frac{0.000837 + 0.000852}{2} = \mathbf{0.000844\ sec^{-1}}$$

Ex. 2 : ***The optical rotation of sucrose in presence of dil. HCl at various intervals is given in the following table:***

t (min.)	*0*	**10**	**20**	*40*	*100*	∞
Rotation (degree)	***32.4***	***28.8***	***25.5***	***19.6***	***6.7***	***– 14.1***

Show that reaction is of the first order.

Sol. The inversion of sucrose will be a first order reaction if the above data conforms to the equation,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x} = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

where r_0, r_1 and r_∞ are the optical rotations at the start of the reaction, after time t and at the completion of reaction, respectively. Inserting the values in the above equation, we get

$$k_{10} = \frac{2.303}{10} \log \frac{32.4 - (-14.1)}{28.8 - (-14.1)} = \frac{2.303}{10} \log \frac{46.5}{42.9} = 0.008060\ \text{min}^{-1}$$

$$k_{20} = \frac{2.303}{20} \log \frac{32.4 - (-14.1)}{25.5 - (-14.1)} = \frac{2.303}{20} \log \frac{46.5}{39.6} = 0.008037\ \text{min}^{-1}$$

$$k_{40} = \frac{2.303}{40} \log \frac{32.4 - (-14.1)}{19.6 - (-14.1)} = \frac{2.303}{40} \log \frac{46.5}{33.7} = 0.008054\ \text{min}^{-1}$$

$$k_{100} = \frac{2.303}{100} \log \frac{32.4 - (-14.1)}{6.7 - (-14.1)} = \frac{2.303}{100} \log \frac{46.5}{20.8} = 0.008040\ \text{min}^{-1}$$

The constancy in the value of k shows that the reaction is of the first order.

Ex. 3 : ***A first order reaction is 15% complete in 20 minutes. How long will it take to be 60% complete?***

Sol. For a first order reaction, we have

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

or $$\frac{2.303}{t_1} \log_{10} \frac{a_1}{a_1 - x_1} = \frac{2.303}{t_2} \log_{10} \frac{a_2}{a_2 - x_2} \qquad \ldots\text{(i)}$$

Here, $x_1 = \frac{15}{100} a_1 = 0.15 a_1\ t_1 = 20$

$x_2 = \frac{60}{100} a_2 = 0.6 a_1\ t_2 = ?$

Inserting these values in equation (i), we get

$$\frac{2.303}{20} \log_{10} \frac{a_1}{a_1 - 0.15 a_1} = \frac{2.303}{t_2} \log_{10} \frac{a_2}{a_2 - 0.6 a_2}$$

or $$\frac{1}{20} \log_{10} \frac{a_1}{0.85 a_1} = \frac{1}{t_2} \cdot \log_{10} \frac{a_2}{0.4 a_2}$$

or $$t_2 = 20 \times \frac{\log(1/0.4)}{\log(1/0.15)} = 20 \times \frac{\log(100/40)}{\log(100/85)}$$

$\therefore$ $$\mathbf{t_2 = 112.76\ minutes.}$$

Ex. 4 : ***Show that the case of unimolecular reaction, the time required for 99.9% of the reaction to take place is ten times that required for half of the reaction.***

Sol. For unimolecular reaction, the rate expression may be written as

$$k = \frac{2.303}{t_1} \log_{10} \frac{a}{a-x}$$

For half the reaction, let the time taken be t_1, then $x = 0.5a$.

$$\therefore \qquad k = \frac{2.303}{t_1} \log_{10} \frac{a}{a - 0.5a}$$

$$\text{or} \qquad t_1 = \frac{0.693}{k} \qquad \ldots\text{(i)}$$

Suppose the time taken for 99.9% of the reaction is t_2, then $x = 0.999a$.

$$k = \frac{2.303}{t_2} \log_{10} \frac{a}{a - 0.999a} \qquad \ldots\text{(ii)}$$

$$\text{or} \qquad k = \frac{2.303}{t} \log 10^3 \quad \text{or} \quad t_2 = \frac{2.303 \times 3}{k} = \frac{6.909}{k}$$

Dividing (ii) by (i), we get

$$\frac{t_2}{t_1} = \frac{6.909}{k} \div \frac{6.693}{k} = 10 \text{ or } \boldsymbol{t_2 = 10\, t_1}.$$

Ex. 5 : ***1 ml of methyl acetate was added to 20 ml of N/20 HCl at 25°C. 2 ml of the reaction mixture was withdrawn at different times and titrated with a standard alkali.***

Time (minutes)	0	75	119	183	∞
ml of alkali used	19.24	24.20	26.60	29.32	42.03

Show that the hydrolysis of methyl acetate is a pseudo unimolecular reaction.

Sol. The reaction will be of the first order or pseudo unimolecular reaction if the data conforms to the first order rate expression

$$k = \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

where V_0, V_t and V_∞ are the volumes of alkali used at the start of the reaction, after time t and at the end of the reaction, respectively. Thus,

$$k_{75} = \frac{2.303}{75} \log \frac{42.03 - 19.24}{42.03 - 24.20} = \frac{2.303}{75} \log \frac{22.79}{17.83} = 0.00327 \text{ min}^{-1}$$

$$k_{119} = \frac{2.303}{119} \log \frac{42.03 - 19.24}{42.03 - 26.60} = \frac{2.303}{119} \log \frac{22.79}{15.43} = 0.00327 \text{ min}^{-1}$$

$$k_{183} = \frac{2.303}{183} \log \frac{42.03 - 19.24}{42.03 - 29.32} = \frac{2.303}{183} \log \frac{22.79}{12.71} = 0.00319 \text{ min}^{-1}$$

As the values of k are nearly constant, the reaction is pseudo unimolecular.

Ex. 6 : ***Dinitropentaoxide decomposes as follows :***

$$-d\,[N_2O_5]/dt = k_1\,[N_2O_5]$$

$$d\,[NO_2]/dt = k_2\,[N_2O_5]$$

$$d\,[O_2]/dt = k_3\,[N_2O_5]$$

What is the relation between k_1, k_2 and k_3?

Sol. The decomposition of dinitropentaoxide is a first order reaction, so

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2} O_2$$

According to stoichiometry, the rate of the above reaction can be expressed by the following relations :

$$-\frac{d\,[N_2O_5]}{dt} = \frac{1}{2} \frac{d\,[NO_2]}{dt} = \frac{1}{\frac{1}{2}} \frac{d\,[O_2]}{dt}$$

$$\text{or} \qquad k_1\,[N_2O_5] = \frac{1}{2} k_2\,[N_2O_5] = 2k_3\,[N_2O_5]$$

$$\text{or} \qquad k_1 = \frac{k_2}{2} = 2k_3 \qquad \ldots\text{(i)}$$

$$\text{or} \qquad 2k_1 = k_2 = 4k_3 \qquad \ldots\text{(ii)}$$

So, relation between k_1, k_2 and k_3 can be expressed by either equation (i) or (ii).

• 2.8. PSEUDO-UNIMOLECULAR REACTIONS

Reactions which are not unimolecular, but obey the first order rate expression are known as *pseudo-unimolecular reactions*. For example, hydrolysis of methyl acetate, inversion of cane sugar etc. are pseudo-unimolecular reactions. In general, when the order of reaction is generally less than the molecularity of a reaction, it is said to be a ***pseudo order reaction***.

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

The reaction is bimolecular but the rate of reaction is given by,

$$\frac{dx}{dt} = k\,[CH_3COOCH_3]$$

The concentration of water does not change during the course of the reaction, as it is taken in excess.

Similarly, for the reaction,

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6,$$

the rate of reaction is given by

$$\frac{dx}{dt} = k\,[C_{12}H_{22}O_{11}]$$

because the value of $[H_2O]$ remains constant as it is taken in excess.

• 2.9. SECOND ORDER REACTION

A reaction is said to be of the second order if its reaction rate depends on two concentration terms of reactants.

For example,

$$2A \longrightarrow \text{Products.}$$

The rate of reaction at any given time is given by

$$\frac{dx}{dt} = k\,[A]^2$$

[I] Rate Expression for Second Order Reactions

(a) When there is only one reactant or both reactants have equal concentrations : Consider the following reactions :

$$2A \longrightarrow \text{Products.}$$

or $$A + B \longrightarrow \text{Products.}$$

Let a be the initial concentration of each of the two reactants and $(a - x)$ be their concentration after any time t. Then, according to the law of mass action, the reaction rate is given by

$$\frac{dx}{dt} = k\,(a-x)\,(a-x) = k\,(a-x)^2 \qquad \text{or} \qquad \frac{dx}{(a-x)^2} = k\,dt$$

where k is the velocity constant.

In order to get the value of k, we integrate the above expression, *i.e.*,

$$\int \frac{dx}{(a-x)^2} = \int k\,dt$$

or $$\frac{1}{(a-x)} = kt + I \qquad (I = \text{integration constant}) \ldots(1)$$

When $t = 0, x = 0$, therefore, from equation (1),

$$I = \frac{1}{a}$$

Substituting the value of I in equation (1), we get

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

---

* It is assumed that the concentration of the substance which is taken in excess does not appreciably change during the course of the reaction.

$$\text{or} \qquad \frac{1}{a-x} - \frac{1}{a} = kt$$

$$\text{or} \qquad k = \frac{1}{t}\left[\frac{1}{a-x} - \frac{1}{a}\right]$$

$$\text{or} \qquad k = \frac{1}{t} \cdot \frac{x}{a\,(a-x)} \qquad \ldots(2)$$

Equation (2) is known as *second order rate expression.*

(b) When the initial concentrations of both reactants are not equal : Let a and b be the initial concentrations of reactants A and B and let $(a-x)$ and $(b-x)$ be their respective concentrations after any time t. The reaction rate will thus be given by

$$\frac{dx}{dt} = k\,(a-x)\,(b-x) \qquad \text{or} \qquad \frac{dx}{(a-x)(b-x)} = k\,dt$$

$$\text{or} \qquad \frac{1}{(a-b)}\left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right] dx = k\,dt \qquad \ldots(3)$$

In order to get the value of k, we integrate equation (3), *i.e.*,

$$\frac{1}{(a-b)} \int \left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right] dx = \int k\,dt$$

$$\text{or} \qquad \frac{1}{(a-b)}\left[\int \frac{dx}{(b-x)} - \int \frac{dx}{(a-x)}\right] = \int k\,dt$$

$$\text{or} \qquad \frac{1}{(a-b)}\left[-\log_e (b-x) + \log_e (a-x)\right] = kt + I \qquad \ldots(4)$$

(I = Integration constant)

When $t = 0, x = 0$, therefore, from (4),

$$\frac{1}{(a-b)}\left[-\log_e b + \log_e a\right] = I \qquad \text{or} \qquad I = \frac{1}{(a-b)} \log_e \frac{a}{b}$$

Substituting the value of I in equation (4), we get

$$\frac{1}{(a-b)} \log_e \frac{(a-x)}{(b-x)} = kt + \frac{1}{(a-b)} \log_e \frac{a}{b}$$

$$\text{or} \qquad k = \frac{1}{t\,(a-b)} \log_e \frac{b\,(a-x)}{a\,(b-x)} \qquad \ldots(5)$$

Equation (5) is known as *second order rate expression.*

[II] Characteristics of Second Order Reactions

(i) ***The rate constant is not independent of the unit in which the concentration is expressed.***

Let the new unit be n times the first value. So, from equation (2),

$$k' = \frac{1}{t} \times \frac{nx}{na \times n\,(a-x)} = \frac{1}{t}\,\frac{x}{a\,(a-x)} \cdot \frac{1}{n}$$

The new value of k, *i.e.*, k' is $1/n$ times the original value.

(ii) ***Unit of rate constant.***

From equation (2), the rate constant will be expressed in terms of (1/time) × (conc/conc^2) or (conc)$^{-1}$ (time)$^{-1}$. If concentration is expressed in mole L^{-1} and time in second, then k will be expressed in (mol L^{-1})$^{-1}$ (s)$^{-1}$ or mol^{-1} L s^{-1}.

(iii) ***The time taken to complete a certain fraction of the reaction is inversely proportional to the initial concentration of the reactant.***

Let $t_{1/2}$ be the time required for the completion of half the reaction, *i.e.*, $x = 0.5a$. Substituting this value in equation (2), we get

$$k = \frac{1}{t_{1/2}} \cdot \frac{0.5a}{a\,(a-0.5a)} = \frac{1}{t_{1/2}} \cdot \frac{0.5a}{a \times 0.5a} = \frac{1}{a\,t_{1/2}}$$

or $$t_{1/2} = \frac{1}{k.a} \quad \text{or} \quad t_{1/2} \propto \frac{1}{a}$$

(iv) ***If one of the reactants is present in excess, the second order reaction becomes of the first order.***

For different initial concentrations of the reactants, we have from equation (5),

$$k = \frac{1}{t\,(a-b)} \log_e \frac{b\,(a-x)}{a\,(b-x)}$$

When one of the reactants, say A is present in very large excess, we can neglect x and b in comparison to a. The above equation then reduces to :

$$k = \frac{1}{t\,a} \log_e \frac{b\,a}{a\,(b-x)} = \frac{1}{t\,a} \log_e \frac{b}{b-x}$$

Since a remains constant throughout the change, we have

$$k\,.\,a = \frac{1}{t} \log_e \frac{b}{b-x}$$

$$K' = \frac{1}{t} \cdot \log_e \frac{b}{b-x}$$

This equation is identical with first order rate expression.

[III] Examples of Second Order Reactions

(i) *Hydrolysis of an ester by an alkali.*

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

(ii) *Decomposition of ozone into oxygen.*

$$2O_3 \longrightarrow 3O_2$$

Ex. 1 : ***A second order reaction where a = b is 20% completed in 500 seconds. How long will it take for the reaction to go to 60% completion?***

Sol. For a second order reaction, where $a = b$,

$$\therefore \qquad k = \frac{1}{t} \cdot \frac{x}{a\,(a-x)}$$

When the reaction is 20% complete, $x = 0.2a$

$$\therefore \qquad k = \frac{1}{500} \cdot \frac{0.2\,a}{a\,(a-0.2\,a)} = \frac{1}{500} \cdot \frac{0.2\,a}{a \times 0.8a} = \frac{1}{2000\,a}$$

Suppose it takes t_1 seonds for the reaction to go to 60% completion.

Now, $$k = \frac{1}{t_1} \cdot \frac{0.6a}{a\,(a-0.6a)} = \frac{1}{t_2} \cdot \frac{0.6a}{a \times 0.4a} = \frac{1}{t_1} \cdot \frac{3}{2a}$$

or $$\frac{1}{t_1} \cdot \frac{3}{2a} = \frac{1}{2000a}$$

$$\mathbf{t_1 = 3000\ sec.}$$

Ex. 2 : ***A second order reaction with two reactants is started with 0.1M concentrations of each reactant. It is 20% completed in 500 seconds. How long will it take the reaction to go to 70% completion?***

For a second order reaction when the concentrations are equal, we have

$$k = \frac{1}{t} \cdot \frac{x}{a\,(a-x)}$$

For 20% completion : $a = 0.1, x = 0.2 \times 0.1 = 0.02; t = 500$

$$\therefore \qquad k = \frac{1}{500} \times \frac{0.02}{0.1\,(0.1-0.02)} = \frac{1}{500} \times \frac{0.02}{0.1 \times 0.01} = \frac{1}{200}$$

For 60% completion : $a = 1; x = 0.6 \times 0.1 = 0.06; t = ?$

$$\therefore \qquad k = \frac{1}{t} \times \frac{0.06}{0.1\,(0.1-0.06)}$$

or $$\frac{1}{200} = \frac{1}{t} \times \frac{0.06}{0.1-0.04}$$

or $$t = \frac{200 \times 0.06}{0.1 \times 0.04} = 3000 \text{ seconds.}$$

• 2.10. DETERMINATION OF ORDER OF REACTION

[I] Integration Method (Hit and Trial Method)

In this method, the initial concentrations of all reactants are determined. The concentration of the reacting substances is then determined by analysing the reaction mixture at different intervals of time. The different values of a and x are then substituted in rate expressions of the first, second and third order reactions. The order of reaction is given by that equation which gives a nearly constant value of k. This method, therefore, involves the trial of one equation after another till the correct one is found. This method is extensively used for simpler reactions.

[II] Fractional Change Method or Half-change Method (Method of equi-fractional parts)

We know that the time required to complete a certain fraction (say one half) of the reaction, is independent of initial concentration for a first order reaction, is inversely proportional to the initial concentration for second order reaction, is inversely proportional to the square of the initial concentration for a third order reaction. In general, the time required for the completion of the same fraction of the reaction is inversely proportional to the initial concentration raised to the power which is one less than the order of reaction, *i.e.*,

$$t \propto \frac{1}{a^{n-1}}$$

where, n is the order of reaction.

If t_1 and t_2 be the times for the completion of the same fraction of reaction with different initial concentrations a_1 and a_2 and if n is the order of reaction, then

$$t_1 \propto \frac{1}{a_1^{n-1}} \quad \text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}}$$

or $$\frac{t_1}{t_2} = \frac{a_2^{n-1}}{a_1^{n-1}} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

or $$\log \frac{t_1}{t_2} = (n-1) \log \frac{a_2}{a_1}$$

or $$n = 1 + \frac{\log (t_1/t_2)}{\log (a_2/a_1)}$$

For gaseous systems, if p_1 and p_2 be the pressures at times t_1 and t_2, then

$$n = 1 + \frac{\log (t_1/t_2)}{\log (p_2/p_1)}$$

So, in this method, we start with two different concentrations of the reactants and note the time for the completion of any fraction, say, half change in each case. By substituting these values in the last equation, we can calculate the order of reaction, n.

[III] Ostwald's Isolation Method

This method is applicable particularly for those reactions where two or more reactants are involved. The experiments are carried out by taking all reactants except one in excess. The reactant which is not taken in excess is said to be ***isolated****. The order of reaction is then determined with respect to the isolated reactant. The order of the whole reaction will then be the sum of these individual orders of reaction.

Consider a general reaction

$$n_1\text{A} + n_2\text{B} + n_3\text{C} \longrightarrow \text{Products}$$

Let the order of reaction be n_1 when A is isolated, *i.e.*, B and C are taken in excess, n_2 when B is isolated, *i.e.*, A and C are taken in excess and n_3 when C is isolated, *i.e.*, A and B are taken in excess. The total order of the reaction will thus be given by $n_1 + n_2 + n_3$.

---

* It is assumed that the concentration of the substance which is taken in excess does not appreciably change during the course of the reaction.

[IV] Graphical Method

In this method, the values of x (amount decomposed) are plotted against t (time). The value of dx/dt at any time is determined from the graph (Fig. 1) by measuring the angle θ, since $dx/dt = \tan\theta$.

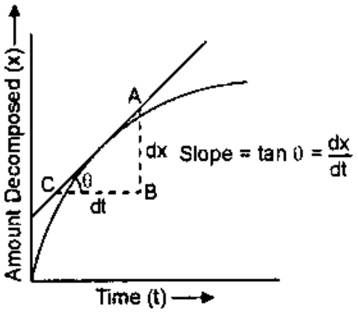


Fig. 1

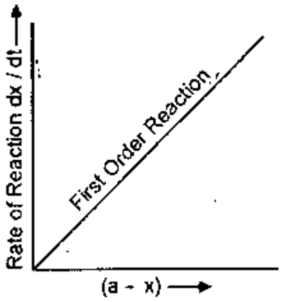


Fig. 2

The various values of dx/dt (Y-axis) are plotted against the corresponding concentrations $(a - x)$ on X-axis as shown in figure (2). If we get a straight line, the reaction is of the first order. In case, a straight line is obtained by plotting dx/dt and $(a - x)^2$ or $(a - x)^3$, the reaction is of second or third order, respectively.

Ex. 1 : ***The half life periods for the thermal decomposition of phosphine at three different pressures are given below :***

Initial pressure (mm)	*707*	*79*	*37.5*
Half life (sec)	*84*	*84*	*84*

Calculate the order of reaction. ***(Meerut 2000)***

Sol. 1st Method : Since the half life periods are the same, irrespective of the initial concentrations or pressures, the reaction is of the first order.

2nd Method : We know that :

$$n = 1 + \frac{\log (t_1/t_2)}{\log (a_2/a_1)}$$

or

$$n = 1 + \frac{\log (t_1/t_2)}{\log (p_2/p_1)} \qquad (\because\ a \propto p)$$

For first set :

$$\therefore \qquad n = 1 + \frac{\log (84/84)}{\log (79/707)} = 1 + 0 \quad \text{or} \quad n = 1$$

For second set :

$$n = 1 + \frac{\log (84/84)}{\log (07.5/79)} = 1 + 0 = 1 \quad \text{or} \quad n = 1$$

∴ Order of reaction = **1.**

Ex. 2 : ***Time for half change (t) of a gas undergoing thermal decomposition for various initial pressures was found as :***

Pressure (mm)	*750*	*500*	*250*
Time (minutes)	*105*	*235*	*950*

Find the order of the reaction.

Sol. The order of reaction is given by

$$n = 1 + \frac{\log (t_1/t_2)}{\log (p_2/p_1)}$$

For first set :

$$\therefore \qquad n = 1 + \frac{\log (105/235)}{\log (500/750)} = 1 + \frac{0.3498}{0.1760}$$

$$= 1 + 1.98 = 2.98 \approx 3 \qquad \rightleftharpoons$$

For second set :

$$n = 1 + \frac{\log(235/950)}{\log(250/500)} = 1 + \frac{0.6066}{0.3010}$$

$$= 1 + 2.01 = 3.01 \approx 3$$

$\therefore$ Order of reaction = **3.**

Ex.34 : ***The following data were obtained for a gaseous reaction :***

Initial pressure (mm)	*200*	*300*	*400*
Half period (min)	*150*	*99.8*	*75.3*

Calculate the order of reaction.

Sol. $$n = 1 + \frac{\log(t_1/t_2)}{\log(p_2/p_1)}$$

$\therefore$ $$n = 1 + \frac{\log(150/99.8)}{\log(300/200)} = 1 + \frac{0.1769}{0.1761} = 1 + 1 = 2$$

Similarly, $$n = 1 + \frac{\log(150/75.3)}{\log(400/200)} = 1 + \frac{0.2992}{0.3010} = 1 + 1 = 2$$

Order of reaction = **2.**

• 2.11. ACTIVATION ENERGY

Arrhenius (1889) put forward the hypothesis that all the molecules of a reactant do not take part in the chemical reaction. It is only a certain number of molecules known as *active molecules* that may take part in the reaction. The molecules not capable of taking part in the reaction are known as *passive molecules.*

On raising the temperature, the equilibrium between active and passive molecules is supposed to shift over rapidly, so that not only we have an increased collision frequency, but still more, we have a largely increased number of active molecules ready to take part in the reaction. The equilibrium is represented as

$$M_{\text{passive}} \rightleftharpoons M_{\text{active}}$$

$$K_a = \frac{[M_{\text{active}}]}{[M_{\text{passive}}]}$$

$$\text{Rate of the reaction} \propto [M_{\text{active}}] = K_a\,[M_{\text{passive}}]$$

According to this concept, passive or non-reactive molecules can be activated by absorption of energy. An expression connecting the temperature with the equilibrium constant (K) of a reversible reaction was given by van't Hoff on thermodynamical grounds. The relation is given by

$$\frac{d\log_e K}{dt} = \frac{\Delta E}{RT^2} \qquad \text{...(1)}$$

where, ΔE is the heat of reaction or energy change.

For a reversible reaction :

$$A + B \rightleftharpoons C + D$$

we have, $$K_c = \frac{k_1}{k_2} = \frac{[C][D]}{[A][B]}$$

where k_1 and k_2 are the velocity constants for forward and backward reactions, respectively.

$\therefore$ $$\log_e K_c = \log_e k_1 - \log_e k_2$$

From van't Hoff isochore, we have

$$\frac{d\log_e K_c}{dT} = \frac{\Delta E}{RT^2} \quad \text{or} \quad \frac{d\log_e (k_1/k_2)}{dT} = \frac{\Delta E}{RT^2}$$

It follows that $$\frac{d\log_e k_1}{dT} = \frac{E_1}{RT^2} + B \qquad \text{...(2)}$$

and $$\frac{d\log_e k_2}{dT} = \frac{E_2}{RT^2} + B \qquad \text{...(3)}$$

where $E_1 - E_2 = \Delta E$ and B is a constant.

It has been found that B is independent of temperature and is equal to zero, so that

$$\frac{d \log_e k_1}{dT} = \frac{E_1}{RT^2}$$

and

$$\frac{d \log_e k_2}{dT} = \frac{E_2}{RT^2}$$

In general,

$$\frac{d \log_e k}{dT} = \frac{E_1}{RT^2} \quad \text{or} \quad d \log_e k = \frac{E}{RT^2} \cdot dT \qquad \ldots(4)$$

On integration, we get

$$\log_e k = -\frac{E}{RT} + \text{constant} \qquad \ldots(5)$$

or more general,

$$k = Ae^{-E/RT} \qquad \ldots(6)$$

where $A =$ constant, known as ***frequency or Arrhenius factor*** of the reaction or ***collision number.*** It is also known as ***pre-exponential factor.*** E is a term which has the dimensions of energy. If R is measured in calories, then E is measured in calories per mole. Equation (6) is the famous Arrhenius equation for the rate constant.

On taking logarithms, equation (6) can be written as follows :

$$\log_e k = \log_e A - \frac{E}{RT}$$

Differentiating it with respect to temperature, we get

$$d \log_e k = \frac{E}{RT^2} dT \qquad \ldots(7)$$

Integrating equation (7) between proper limits, we have

$$\int_{k_1}^{k_2} d \log_e k = \int_{T_1}^{T_2} \frac{E}{RT^2} dT$$

or

$$\log_{10} \frac{k_2}{k_1} = \frac{E}{2.303\, R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad \ldots(8)$$

[III] Determination of Activation Energy

If we measure the velocity constants of a reaction at two different temperatures, it is possible to calculate the value of activation energy (E) from equation (8). The value of E can also be evaluated graphically.

If $\log_{10} k$ is plotted against $1/T$, we get a straight line, the slope of which is equal to $-E/2.303$ R or $-E/4.576$. Knowing the slope, E can be easily evaluated. The intercept on $\log_{10} k$ axis gives the value of $\log A$.

The Arrhenius equation holds equally good for homogeneous and heterogeneous reactions. Heterogeneous and catalytic reactions also give straight lines over a very wide range of temperatures.

If there is a marked deviation from a straight line on plotting $\log k$ and $1/T$, then it gives an indication that the observed reaction is a composite one made up of two or more concurrent reactions influenced by one of the reactions and it may predominate, so that the slope of the curve corresponds to the value of E proper to this reaction.

For many reactions taking place at ordinary temperatures, the energy of activation is of the order of 20,000 cal/mole and under such circumstances the temperature coefficient (t_c) is found to satisfy van't Hoff rule, *e.g.*, at 300K, the value of t_c is given by

$$\log_e t_c = \log_e \frac{k_{T+10}}{k_T} = \frac{d \log_e k}{dt} \times 10 = \frac{E}{RT^2} \times 10$$

$$\therefore \quad \log_e \frac{k_{T+10}}{k_T} = \frac{20{,}000}{2 \times (300)^2} \times 10 \approx 1$$

$$\therefore \quad \frac{k_{T+10}}{k_T} \approx e \approx 2.7$$

Ex. 1 : ***For a first order reaction, the rate constant is found to be 7.0×10^{-7} at $7^\circ C$ and 9×10^{-4} at $57^\circ C$. Calculate the energy of activation and its specific reaction rate at $127^\circ C$.***

Sol. We know that, $\log \dfrac{k_2}{k_1} = \dfrac{E}{2.303\,R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$

where, E = activation energy, $T_1 = 273 + 7 = 280$ K, $k_1 = 7 \times 10^{-7}$,
$T_2 = 273 + 57 = 330$ K, $k_2 = 9 \times 10^{-4}$.

So, from equation (8), we get

$$\log (9 \times 10^{-4}) - \log (7 \times 10^{-7}) = \frac{E}{2.303 \times 1.987}\left[\frac{1}{280} - \frac{1}{330}\right]$$

$$= \frac{E}{2.303 \times 1.987}\left[\frac{330 - 280}{280 \times 330}\right]$$

or $$\log (9 \times 10^{-4}) - \log (7 \times 10^{-7}) = \frac{E \times 50}{2.303 \times 1.987 \times 280 \times 330}$$

or $$\bar{4}.9542 - \bar{7}.8451 = \frac{E \times 50}{2.303 \times 1.987 \times 280 \times 330}$$

or $$E = \frac{2.303 \times 1.987 \times 330 \times 3.1091}{50} = \mathbf{26.29 \times 10^3\ cal/mole.}$$

Specific reaction rate at 127°C, *i.e.*, 400 K is given by

$$\log k_{400} - \log k_{280} = \frac{26290}{2.303 \times 1.987}\left[\frac{1}{280} - \frac{1}{400}\right]$$

$$= \frac{26290}{2.303 \times 1.987}\left[\frac{400 - 280}{400 \times 280}\right]$$

or $$\log k_{400} - \log (7 \times 10^{-7}) = \frac{26290 \times 120}{2.303 \times 1.987 \times 400 \times 280} = 6.153.$$

or $$\log k_{400} = \log (7 \times 10^{-7}) + 6.153$$

$$= -7.8451 \times 6.153 = -1.6921$$

or $$k_{400} = \mathbf{0.02032\ min^{-1}}.$$

• 2.12. COLLISION THEORY FOR UNIMOLECULAR REACTIONS

It seems to be difficult as to how the collision theory could possibly be used to explain the mechanism of unimolecular reactions. In unimolecular processes only one molecule takes part in the reaction, then a question arises :

How do molecules in unimolecular reactions attain their energy of activation? Lindemann (1922) suggested its answer by pointing out that the behaviour of unimolecular reactions can be explained on the basis of bimolecular collisions provided we postulate that a time lag exists between activation and reaction during which activated molecules may either react or be deactivated to ordinary molecules. Thus, the rate of reaction will not be proportional to all the molecules activated, but only to those which remain active. Lindemann suggested that the above reaction takes place as follows :

First stage : $\mathrm{A + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + A}$

Second stage : $\mathrm{A^* \xrightarrow{k_3}}$ Products

The first stage involves collision of reacting molecules forming a few activated molecules represented by A^*, with a velocity constant k_1, after which time-lag occurs. During this time-lag the activated molecules lose their excess energy and revert to the original state, with a velocity constant k_2.

Alternatively, the activated molecules may decompose into products, with a velocity constant k_3.

Rate of activation $= k_1\,[A]^2$

Rate of deactivation $= k_2\,[A^*]\,[A]$

Rate of decomposition $= k_3\,[A^*]$

According to the **stationary or steady state principle**, whenever a short-lived reaction intermediate occurs in a system, its rate of formation can be taken as equal to its rate of disappearance. Applying this principle, we have

$$k_1\,[A]^2 = k_2\,[A^*]\,[A] + k_3\,[A^*]$$

or

$$= [A^*]\,\{k_2\,[A] + k_3\}$$

$$[A^*] = \frac{k_1\,[A]^2}{k_2\,[A] + k_3}$$

Since the rate of reaction is proportional to the concentration of activated molecules, we can, therefore, write that,

$$\text{Rate of reaction} = -\frac{d\,[A]}{dt} = k_3\,[A^*]$$

or

$$-\frac{d\,[A]}{dt} = \frac{k_1 k_3\,[A]^2}{k_2\,[A] + k_3} \qquad \ldots(1$$

(i) At high pressure : At sufficiently high pressure, the term $k_2\,[A]$ is far greater than k_3, which can thus be neglected. Equation (1) then reduces to

$$-\frac{d\,[A]}{dt} = \frac{k_1 k_3}{k_2}\,[A] = k'[A]$$

Hence, the reaction is of the **first order**, as the rate of reaction is proportional to the concentration of only one molecule of the reactant. Thus, if concentration of A is high, the reaction should be of the first order.

(ii) At low pressure : At low pressure, $k_3 >> k_2\,[A]$, therefore, $k_2\,[A]$ can be neglected in comparison to k_3. Therefore, equation (1) reduces to

$$-\frac{d\,[A]}{dt} = \frac{k_1 k_3}{k_3}\,[A]^2 = k_1\,[A]^2 \qquad \ldots(2)$$

Hence, the reaction is of the second order. Thus, if the concentration of A is low, the reaction becomes of the second order.

• 2.13. TRANSITION STATE THEORY

According to transition state theory, the rate of a reaction is the number of activated complexes passing per second over the top of potential energy barrier. This rate is equal to the concentration of activated complex times the average velocity with which a complex moves across to the product side. The activated complex is not in a state of stable equilibrium, since it lies at a maximum potential energy.

Postulates of Transition State Theory

(i) As the reacting molecules approach each other there is a continuous series of changes in bond distances. These changes are accompanied by energy changes.

(ii) The reactant molecules are changed into an energy rich intermediate *called activated complex or transition state* (fig. 3).

(iii) The activated complex may be formed by some loose association or bonding of reactant molecules with necessary rearrangement of valence bonds and energy. If it is a unimolecular reaction, the reactant molecule may produce the activated complex by rearrangement of atoms and redistribution of energy.

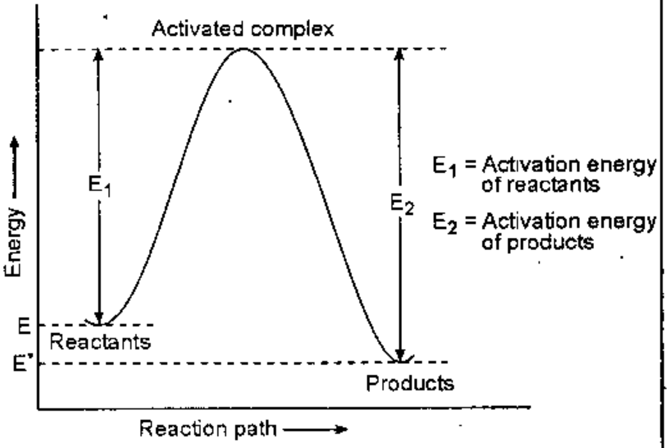


Fig. 3

(iv) The activated complex, though unstable, has a transient existence. It is treated formally as a definite molecule with an independent entity. The activated complex remains in equilibrium with the reactants and its potential energy is maximum. Finally, the activated complex decomposes into products.

(v) The activation energy of reaction in the light of this theory, is the additional energy which the reacting molecules must acquire to form the activated complex.

Thermodynamic or Mathematical Treatment of Transition State Theory

Consider a bimolecular reaction between reactants A and B. According to transition state theory,

$$\underset{\text{Reactants}}{A + B} \rightleftharpoons \underset{\substack{\text{Activated}\\\text{complex}}}{X^*} \longrightarrow \text{Products}$$

The equilibrium constant (K^*) for the formation of activated complex is,

$$K^* = \frac{[X^*]}{[A]\,[B]} \quad \text{or} \quad [X^*] = K^*\,[A]\,[B] \qquad \ldots(1)$$

According to transition state theory, the rate of reaction is the number of activated complexes which pass over the potential energy barrier per unit time. This, in turn, is equal to the concentration of activated complex multiplied by the frequency at which the complex would decompose into products. Mathematically,

$$\frac{dx}{dt} = [X^*] \times \text{Rate (or frequency) of dissociation of activated complex} \qquad \ldots(2)$$

From equations (1) and (2), we get

$$\frac{dx}{dt} = K^*\,[A]\,[B] \times \text{Rate (or frequency) of dissociation of activated complex.}$$

The activated complex would decompose only if enough vibrational energy is supplied to the system, so that the atoms vibrate with certain critical frequency, leading to bond breaking. Therefore,

Frequency of dissociation of activated complex = E_{vib}/h ...(3)

where, E_{vib} = average vibrational energy at temperature T and h = Planck's constant.

$$\text{But,} \quad E_{vib} = kT = \frac{RT}{N} \qquad (\because\ k = R/N) \ldots(4)$$

From equations (3) and (4) frequency of dissociation of activated complex = RT/Nh

$$\therefore \quad \frac{dx}{dt} = K^*\,[A]\,[B] . \frac{RT}{Nh} \qquad \ldots(5)$$

For conversion of reactants into products,

$$\frac{dx}{dt} = k\,[A]\,[B] \qquad (k = \text{rate constant}) \ldots(6)$$

From equations (5) and (6),

$$k\,[A]\,[B] = K^*\,[A]\,[B] . RT/Nh$$

$$k = K^* . RT/Nh \qquad \ldots(7)$$

Equation (7) is the **mathematical statement of transition state theory.**

According to thermodynamics, K^* can be correlated with ΔG^* through the following relation,

$$\Delta G^* = -RT \ln K^*$$

where ΔG^* = (Free energy of activated complex) – (Free energy of reactants). ΔG^* is known as standard free energy change

$$\therefore \quad \Delta G^* = \Delta H^* - T\Delta S^*$$

$$\therefore \quad -RT \ln K^* = \Delta H^* - T\Delta S^*$$

$$\text{or} \quad \ln K^* = \frac{-(\Delta H^* - T\Delta S^*)}{RT}$$

$$\text{or} \quad K^* = e^{-(\Delta H^* - T\Delta S^*)/RT} \qquad \ldots(8)$$

From equations (7) and (8) we get,

$$k = \frac{RT}{Nh} \cdot e^{-(\Delta H^* - T\Delta S^*)/RT}$$

$$k = \frac{RT}{Nh} \cdot e^{-\Delta H^*/RT} \,.\, e^{\Delta S^*/R} \qquad \ldots (9)$$

…(9

where, ΔH^* = standard enthalpy change, *i.e.*, standard heat of activation,

ΔS^* = *standard entropy change, i.e., standard entropy of activation.*

Equation (9) can be applied not only to bimolecular, but also to unimolecular and trimolecular processes. Morever, it can be applied to reactions in solution also.

Comparison of Transition State Theory With Collision Theory.

(i) From transition state theory, *i.e.*, according to equation (9)

$$k = \frac{RT}{Nh} \cdot e^{-\Delta H^*/RT} \,.\, e^{\Delta S^*/R}$$

From collision theory, $k = PZe^{-E/RT}$

where P = probability factor or steric factor

Z = collision number or collision frequency. Comparing both equations, we have

$$PZe^{-E/RT} = \frac{RT}{Nh} \cdot e^{-\Delta H^*/RT} \,.\, e^{\Delta S^*/R}$$

or

$$PZe^{-\Delta H^*/RT} = \frac{RT}{Nh} \cdot e^{-\Delta H^*/RT} \,.\, e^{\Delta S^*/R} \qquad (\because\ E = \Delta H^*)$$

or

$$PZ = \frac{RT}{Nh} \,.\, e^{\Delta S^*/R}$$

or

$$P = \frac{RT}{ZNh} \cdot e^{\Delta S^*/R}$$

The steric factor P is thus related to entropy of activation.

(ii) In collision theory, no account is taken of the internal motions of the reactant molecules, whereas in transition state theory, account is taken of the internal degrees of freedom of reactant molecules and the changes these undergo on reaction.

(iii) The concept of entropy of activation in transition state theory is very useful for qualitative purposes. Thus, for bimolecular processes, this is an advantage over the collision theory.

• SUMMARY

- The rate at which the concentration of a reactant changes with time is known as rate of chemical reaction, *i.e.*, $\frac{dx}{dt}$ or $\left(-\frac{dc}{dt}\right)$.
- **Molecularity :** It is the total number of molecules of all the reactants taking part in a chemical reaction as represented by a simple equation.
- **Order of reaction :** It is the sum of the powers to which the concentration (or pressure) terms of the reactants are raised to determine the rate of a reaction.
- Molecularity is always a whole number, while order of reaction can be zero, whole number or fractional number.
- The rate of reaction is directly proportional to concentration of reactants, temperature, surface area of reactants.
- A zero order reaction is a reacttion in which the concentrations of the reactants do not change with time, *e.g.*,

$$H_2\,(g) + Cl_2\,(g) \xrightarrow{\text{Sunlight}} 2HCl\,(g)$$

- A first order reaction is a reaction in which the reaction rate depends only on one concentration term of the reactants, *e.g.*,

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Acid}} C_6H_{12}O_8 + C_6H_{12}O_6$$

- A second order reaction is a reaction in which the reaction rate depends on two concentration terms of the reactants, *e.g.*,

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa\ \ C_2H_5OH$$

- **Activation energy :** The excess energy that the reactant molecules having energy, less than the threshold energy must acquire in order of react and give the final products is known as activation energy.
- Unit of reaction rate = mol L^{-1} s^{-1}
- **Units of rate constant**

  (i) Zero order reaction $= \frac{\text{conc}}{\text{time}} = (\text{conc})\,(\text{time})^{-1} = \text{mol L}^{-1}\,\text{s}^{-1}$

  (If concentration is expressed in mol L^{-1} and time in second)

  (ii) First order reaction $= \frac{1}{\text{time}} = (\text{time})^{-1} = \text{s}^{-1}$

  (iii) Second order reaction $= \frac{1}{(\text{conc})^2} \cdot \frac{1}{\text{time}} = (\text{conc})^{-2}\,(\text{time})^{-1}$

  $= (\text{mol L}^{-1})^{-2}\,(\text{s})^{-1} = \text{mol}^{-2}\,\text{L}^2\text{s}^{-1}$
- **Rate expressions**

  (i) Zero order reaction : $k = \frac{x}{t}$

  (ii) First order reaction : $k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$

  where, a = initial concentration of reactant, x = concentration of reactant undergoing reaction in time t.

  (iii) Second order reaction

  (i) $k = \frac{1}{t} \cdot \frac{x}{a\,(a-x)}$ [When $a = b$]

  (ii) $k = \frac{2.303}{t\,(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$ [When $a \neq b$]
- Order of reaction (n) can be calculated by half change method by the following formula :

$$n = 1 + \frac{\log t_1 - \log t_2}{\log p_2 - \log p_1}$$

  where, p_1 = pressure of the system at time t_1, p_2 = pressure of the system at time t_2.
- The activation energy (E) can be calculated from the following formula :

$$\log_{10} \frac{k_2}{k_1} = \frac{E}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

  where, k_1 and k_2 are the rate constants at absolute temperatures T_1 and T_2.
- For a reaction, $n_1\text{A} + n_2\text{B} \qquad n_3\text{C} + n_4\text{D}$, we can equate the reaction rates as :

$$\text{Reaction rate} = -\frac{1}{n_1}\frac{d\,[\text{A}]}{dt} = -\frac{1}{n_2}\frac{d\,[\text{B}]}{dt} = +\frac{1}{n_3}\frac{d\,[\text{C}]}{dt} = +\frac{1}{n_4}\frac{d\,[\text{D}]}{dt}$$

• STUDENT ACTIVITY

1. Define order of reaction.

2. Mention the factors on which the rate of chemical reaction depends.

3. What is a first order reaction ? Give one important characteristic of it.

4. Describe any one method to determine the order of reaction.

• TEST YOURSELF

Answer the following questions :

1. Explain the rate of chemical reaction. Discuss the factors affecting the reaction rate.
2. *Define molecularity and order of reaction.*
3. Describe the main differences between molecularity and order of reaction.
4. Why reactions of higher orders are rare ?
5. What is a zero order reaction ? Derive the rate expression for it and mention its characteristics.
6. What is a first order reaction ? Derive the rate equation for a first order reaction. Discuss its characteristics.
7. What is a second order reaction ? Derive the rate equation for it when :
   (i) The concentrations of both reactants are equal.
   (ii) The concentrations of both reactants are different.
8. Discuss the characteristics of a second order reaction.
9. Define pseudo order reaction with examples.
10. Describe the methods used to determine he order of reaction.
11. Explain activation energy. How it is determined ?
12. *Discuss the collision theory for unimolecular reactions.*
13. Discuss the transition state theory.
14. The dimension of first order rate constant is :
    (a) time^{-1} (b) time (c) time × conc (d) $\text{time}^{-1} \times \text{conc}^{-1}$
15. The dimension of second order rate constant is :
    (a) times × conc (b) $\text{time}^{-1} \times \text{conc}^{-1}$
    (c) $\text{time} \times \text{conc}^{-1}$ (d) $\text{time}^{-1} \times \text{conc}^{-2}$
16. The hydrolysis of methyl acetate by acid is of :
    (a) Zero (b) First order (c) Second order (d) Third order
17. The hydrolysis of ethyl acetate by NaOH is of :
    (a) Zero (b) First order (c) Second order (d) Third order
18. The half life period of a first order reaction is 20 min. The time required for the concentration of the reactant to change from 0.4 M to 0.1 M is :
    (a) 20 min (b) 40 min (c) 60 min (d) 80 min
19. The ratio of the time required for 75% of a first order reaction to complete to that required for 50% of the reaction is :
    (a) 4 : 3 (b) 1 : 2 (c) 2 : 1 (d) 3 : 2

20. The time required to decompose half of the reaction for a n^{th} order reaction is also doubled. The order of reaction is :

(a) 0 (b) 1 (c) 2 (d) 3

21. A first order reaction is 75% completed in 32 minutes. For 50% completion, it will take : :

(a) 4 min (b) 8 min (c) 16 min (d) 32 min

22. The elementary step of the reaction $2Na + Cl_2 \longrightarrow 2NaCl$ is found to follow third order reaction kinetics. The molecularity of the reaction is :

(a) 0 (b) 1 (c) 2 (d) 3

23. Fill in the blanks

(i) A first order reaction is 15% complete in 20 min. It will take .... min to be 60% complete.

(ii) The rate of reaction is nearly doubled on increasing the temperature by ....

(iii) The order of reaction of decomposition of H_2O_2 is ....

(iv) If the rate constant, $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$, the order of reaction is ....

(v) If the rate constant has the unit sec^{-1}, the order of reaction is ....

(vi) The hydrolysis of ethyl acette in acidic medium is .... order reaction.

ANSWERS

14. (a) **15.** (b) **16.** (b) **17.** (c) **18.** (b) **19.** (c) **20.** (a) **21.** (c) **22.** (d)

23. **(i)** 112.8 min **(ii)** 10°C **(iii)** one **(iv)** 1/2 **(v)** one

(vi) First

❑❑❑

CHAPTER

3

CATALYSIS

LEARNING OBJECTIVES

- Catalyst and Catalysis
- Catalytic Promoters
- Catalytic Poisons
- Theories of Catalysis
- Biochemical or Enzyme Catalysis
- Industrial Applications of Catalysis

❑ Summary
❑ Student Activity
❑ Test Yourself

• 3.1. CATALYST AND CATALYSIS

Berzelius (1835) found that the speed of a number of reactions is increased due to the presence of a small quantity of a foreign substance. He also found that these substances remain chemically unchanged at the end of the reaction. He termed these substances as **catalysts** and the phenomenon itself is known as **catalysis**. A familiar example is that of the decomposition of $KClO_3$. The decomposition of $KClO_3$ is very slow even at high temperature, but a small quantity of MnO_2 increases the rate of decomposition to a very great extent and MnO_2 remains chemically unchanged at the end of the reaction.

$$2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2 + [MnO_2]$$

But later on it was observed that there are certain substances which can retard the rate of a chemical reaction. Hence, Ostwald defined that,

"A catalyst is a substance which influences the speed of a chemical reaction without itself undergoing any chemical change at the end of the reaction."

Catalysis is mainly divided into two types, *viz.*, homogeneous catalysis and heterogeneous catalysis.

[I] Homogeneous Catalysis

When the catalyst is present in the same phase as that of the reactants, the phenomenon is known as homogeneous catalysis.

(a) Examples of homogeneous catalysis in gas phase

(i) Oxidation of sulphur dioxide (SO_2) to sulphur trioxide (SO_3) with nitric oxide (NO) as catalyst,

$$\underset{\text{Gas}}{2SO_2} + \underset{\text{Gas}}{O_2} + \underset{\text{Gas}}{[NO]} \longrightarrow \underset{\text{Gas}}{2SO_3} + [NO]$$

(ii) Decomposition of acetaldehyde (CH_3CHO) with iodine (I_2) as catalyst,

$$\underset{\text{Vapour}}{CH_3CHO} + \underset{\text{Vapour}}{[I_2]} \longrightarrow \underset{\text{Gas}}{CH_4} + \underset{\text{Gas}}{CO} + [I_2]$$

(b) Examples of homogeneous catalysis in solution phase

Many reactions in solutions are catalysed by acids (H^+) and bases (OH^-).

(i) Decomposition of hydrogen peroxide (H_2O_2) in the presence of iodide ion (I^-) as catalyst,

$$2H_2O_2 \xrightarrow{I^-} 2H_2O + O_2$$

(ii) Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst,

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H_2SO_4} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(iii) Hydrolysis of an ester in the presence of acid or alkali.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+/OH^-} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

[II] Heterogeneous Catalysis

When the catalyst is in a different phase than that of reactants, the phenomenon is known as heterogeneous catalysis.

Some examples of heterogeneous catalysis with reactants in the gas, liquid or the solid phase are given below.

(a) Heterogeneous catalysis with gaseous reactants (contact catalysis)

(i) Oxidation of ammonia to nitric oxide (NO) in the presence of a platinum gauze (a stage in the manufacture of nitric acid).

$$\underset{\text{Gas}}{4NH_3} + \underset{\text{Gas}}{5O_2} + \underset{\text{Solid}}{[Pt]} \longrightarrow 4NO + 6H_2O + [Pt]$$

(ii) Combination of sulphur dioxide (SO_2) and oxygen in the presence of finely divided platinum or vanadium pentoxide, V_2O_5, *(contact process for sulphuric acid).*

$$\underset{\text{Gas}}{2SO_2} + \underset{\text{Gas}}{O_2} + \underset{\text{Solid}}{[Pt]} \longrightarrow 2SO_3 + [Pt]$$

(iii) Hydrogenation reactions of unsaturated organic compounds are catalysed by finely divided nickel.

$$\underset{\text{Ethene (gas)}}{H_2C{=}CH_2} + \underset{\text{Gas}}{H_2} + \underset{\text{Solid}}{[Ni]} \longrightarrow \underset{\text{Ethane}}{H_3C{-}CH_3} + [Ni]$$

Vegetable oils are tri-esters of glycerol with higher unsaturated acid (oleic acid). When hydrogen is passed through the *vegetable oils* in presence of nickel, the carbon-carbon double bonds of the acid portions are hydrogenated to yield *solid fats (vanaspati ghee).*

(iv) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron. *(Haber's process for ammonia).*

$$\underset{\text{Gas}}{N_2} + \underset{\text{Gas}}{3H_2} + \underset{\text{Solid}}{[Fe]} \longrightarrow 2NH_3 + [Fe]$$

(b) Heterogeneous catalysis with liquid reactants

(i) The decomposition of aqueous solutions of hydrogen peroxide (H_2O_2) is catalysed by manganese dioxide (MnO_2) or platinum in colloidal form.

$$\underset{\text{Liquid}}{2H_2O_2} + \underset{\text{Solid}}{[Pt]} \longrightarrow 2H_2O + O_2 + [Pt]$$

(ii) Benzene and ethanoyl chloride (CH_3COCl) react in the presence of anhydrous aluminium chloride to form phenyl methyl ketone ($C_6H_5COCH_3$).

$$\underset{\text{Liquid}}{C_6H_6} + \underset{\text{Liquid}}{CH_3COCl} + \underset{\text{Solid}}{[AlCl_3]} \longrightarrow C_6H_5COCH_3 + HCl + [AlCl_3]$$

(c) Heterogeneous catalysis with solid reactants

The decomposition of potassium chlorate ($KClO_3$) is catalysed by manganese dioxide (MnO_2).

$$\underset{\text{Solid}}{2KClO_3} + \underset{\text{Solid}}{[MnO_2]} \longrightarrow 2KCl + 3O_2 + [MnO_2]$$

The above reaction is heterogeneous, though both reactants are in the same phase (solid), because the solid forms a new phase.

[III] Classification of Catalysis

Catalytic reactions are of the following four types :

(a) *Positive catalysis*
(b) *Negative catalysis*
(c) *Auto-catalysis*
(d) *Induced catalysis*

(a) Positive catalysis : ***When the catalyst used accelerates the speed of a chemical reaction, it is known as a positive catalyst and the phenomenon is known as positive catalysis.*** For example, the rate of decomposition of hydrogen peroxide increases in the presence of colloidal platinum as catalyst.

$$\text{(i)}\quad 2H_2O_2 \xrightarrow[\text{Catalyst}]{Pt} 2H_2O + O_2$$

Other reactions are :

(ii) $2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$

(iii) $N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$

(iv) $2SO_2 + O_2 \xrightarrow{\text{Pt or NO}} 2SO_3$

(b) Negative catalysis : ***When the foreign substance retards the speed of a chemical reaction, it is known as a negative catalyst and the phenomenon is known as negative catalysis.*** The following are examples of this type.

(i) Decomposition of hydrogen peroxide

$$2H_2O_2 \xrightarrow{H_3PO_4} 2H_2O + O_2$$

(ii) Oxidation of chloroform

$$4CHCl_3 + 3O_2 \xrightarrow{C_2H_5OH} 4COCl_2 + 2Cl_2 + 2H_2O$$

(iii) Tetraethyl lead as antiknock

When tetraethyl lead, $Pb(C_2H_5)_4$ is added to petrol, it retards the too rapid or explosive combustion of the fuel which is responsible for the working of the engine.

Explanation of negative catalysis : The mechanism of negative catalysis could be different for different reactions, *e.g.*,

(1) By poisoning a catalyst. A negative catalyst may work by poisoning a catalyst which already happens to be present in the reaction mixture. For example, the traces of alkali dissolved from the glass of the container, catalyse the decomposition of hydrogen peroxide (H_2O_2). However, the addition of an acid would destroy the alkali catalyst and thus prevents decomposition.

(2) By breaking a chain reaction. In some cases, negative catalysts are believed to operate by breaking the chain of reactions. For example, the combination of H_2 and Cl_2, which is a chain reaction, is negatively catalysed by nitrogen trichloride (NCl_3).

$$Cl_2 \longrightarrow \underset{\text{Free radicals}}{Cl\cdot + Cl\cdot}$$

$$H_2 + Cl\cdot \longrightarrow HCl + H\cdot$$

$$H\cdot + Cl_2 \longrightarrow HCl + Cl\cdot$$

NCl_3 breaks the chain of reactions by absorbing the propagating species ($Cl\cdot$) and the reaction stops.

$$NCl_3 + Cl\cdot \longrightarrow \frac{1}{2}N_2 + 2Cl_2$$

(c) Auto-catalysis : ***When one of the products formed in the reaction itself acts as a catalyst, the substance is known as an auto-catalyst and the phenomenon is known as auto-catalysis.***

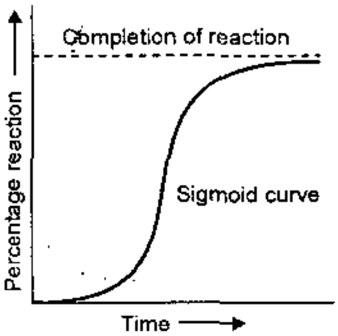


Fig. 1. Curve showing the rise of rate of reaction with time.

In auto-catalysis the initial rate of the reaction rises as the catalytic product is formed, instead of decreasing steadily (See fig. 4). The curve plotted between reaction rate and time shows a maximum when the reaction is complete.

(i) For example, hydrolysis of ethyl acetate by water is an auto-catalytic reaction, since acetic acid liberated in this reaction acts as a catalyst.

$$CH_3COOC_2H_5 + H_2O \longrightarrow \underset{\text{Auto-catalyst}}{CH_3COOH} + C_2H_5OH$$

(ii) The oxidation of oxalic acid by acidic $KMnO_4$ is catalysed by the presence of Mn^{2+} ions formed in the solution. In the beginning, the colour of $KMnO_4$ disappears slowly, but as Mn^{2+} is formed in the solution, the colour discharges rapidly. So, Mn^{2+} ions acts as auto-catalyst.

$$\underset{\text{Violet}}{2MnO_4^-} + 5C_2O_4^{2-} + 16H^+ \longrightarrow \underset{\text{Colourless}}{2Mn^{2+}} + 10CO_2 + 8H_2O$$

(iii) The free arsenic produced by the decomposition of arsine (AsH_3) auto-catalyses the reaction.

$$2AsH_3 \xrightarrow[\text{Catalyst}]{} 2As + 3H_2$$

(d) Induced catalysis : ***When one reaction influences the speed of other, which is not possible under ordinary conditions, the phenomenon is known as induced catalysis.***

For example, sodium sulphite solution is readily oxidised in air but sodium arsenite solution is not oxidised by passing a current of air through it. However, if air is passed through a mixture of sodium sulphite and sodium arsenite solution, the oxidation of both take place. Here the oxidation of sodium sulphite acts as a catalyst for the oxidation of sodium arsenite solution.

[IV] Characteristics of Catalytic Reactions

Although there are different types of catalytic reactions, the following features or characteristics are common to most of them. These features are often referred to as the **criteria of catalysis.**

(1) A catalyst remains unchanged in mass and chemical composition at the end of the reaction.

Qualitative and quantitative analysis show that a catalyst undergoes no change in mass or chemical composition. However, it may undergo a physical change. Thus, granular manganese dioxide (MnO_2) used as a catalyst in the thermal decomposition of potassium chlorate is left as a fine powder at the end of the reaction.

(2) A small quantity of catalyst is generally needed to produce almost unlimited reaction.

Sometimes, a trace of a metal catalyst is required to affect very large amounts of reactants. For example, one ten-millionth of its mass of finely divided platinum is, however, needed to catalyse the decomposition of hydrogen peroxide.

On the other hand, there are catalysts which need to be present in relatively large amount to be effective. Thus, in Friedel-Craft's reaction,

$$C_6H_6 + C_2H_5Cl \xrightarrow{\text{Anhy. } AlCl_3} C_6H_5C_2H_5 + HCl$$

Anhydrous aluminium chloride functions as a catalyst effectively when present to the extent of 30 percent of the mass of benzene.

(3) A catalyst cannot, in general, initiate a reaction.

In most cases, a catalyst speeds up a reaction already in progress and does not initiate (or start) the reaction. But there are certain reactions where the reactants do not combine for very long period (perhaps years). For example, a mixture of hydrogen and oxygen, which remains unchanged almost indefinitely at room temperature, can be brought to reaction by the catalyst *platinum black* in a few seconds.

$$H_2 + O_2 \xrightarrow{\text{Room temp.}} \text{No reaction}$$

$$2H_2 + O_2 \xrightarrow{\text{Pt black}} 2H_2O$$

It is thus now considered that the catalyst can initiate a reaction. According to this view, the reacting molecules (in the absence of catalyst) do not posses minimum kinetic energy for successful collisions. The molecules rebound from collisions without reacting at all.

(4) A catalyst is more effective when finely divided.

In heterogeneous catalysis, the solid catalyst is more effective when in a state of fine sub-division than when used in bulk. So, a lump of platinum will have much less catalytic activity than colloidal or platinised asbestos. Finely divided nickel is a better catalyst than lumps of solid nickel, because former occupies greater surface area than the latter.

(5) A catalyst is specific in its action.

While a particular catalyst works for one reaction, it will not necessarily work for another reaction. Different catalysts, moreover, can bring about completely different reactions for the same substance. For example, formic acid gives carbon dioxide and hydrogen when passed over hot copper.

$$HCOOH \xrightarrow{Cu} CO_2 + H_2,$$

However, with hot aluminium oxide, formic acid gives carbon monoxide and water.

$$HCOOH \xrightarrow{Al_2O_3} CO + H_2O$$

(6) Change of temperature changes the rate of a catalytic reaction as it would do for the same reaction without a catalyst.

We have already studied the effect of temperature change on reversible reactions under Le-Chatelier's principle. Some catalysts are, however, physically altered by a rise in temperature and hence their catalytic activity may be decreased. This is particularly true with colloidal solutions like that of platinum, since a rise in temperature may cause their coagulation. In such a case, the rate of reaction increases up to a certain point and then gradually decreases. ***The rate of reaction is maximum at a particular temperature which is known as the optimum temperature.***

(7) A catalyst does not alter the final position of equilibrium, although it decreases the time required to establish it.

It means that in a reversible reaction the catalyst accelerates the forward and the reverse reactions equally. Thus, the ratio of the rates of two opposing reactions, *i.e.*, *the equilibrium constant*, remains unchanged.

The effect of a catalyst on the time required for equilibrium to be established for the reaction

$$A + B \rightleftharpoons C + D$$

is shown in fig. (2). In the beginning, the concentrations of A and B are maximum and so the rate of forward reaction is maximum. As the time passes, the rate of the reaction decreases till the equilibrium is established. For the reverse reaction, the initial concentrations of C and D are zero and the rate of reaction is lowest. As the time passes, the rate of reaction increases till the equilibrium is established. Similar curves of the rates of reactions with the catalyst show that the rates of the forward reaction and the reverse reaction are changed equally but the equilibrium is established in a much shorter time.

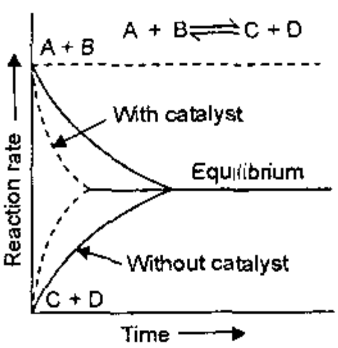


Fig. 2. The effect of a catalyst onthe tim required for the equilibrium to be established.

For example, in the Haber's process for ammonia,

$$N_2 + 3H_2 \overset{Fe}{\rightleftharpoons} 2NH_3$$

the reaction is very slow. In the presence of the catalyst, the equilibrium is reached much earlier but the percentage yield remains unchanged. The iron catalyst decreases the time to attain equilibrium but cannot change the percentage yield.

Energy considerations also show that the final state of equilibrium cannot be changed by the catalyst. Suppose the catalyst accelerates the forward reaction more than the reverse reaction. This will shift the equilibrium point, which cannot happen without the supply of energy to the system. But a catalyst unchanged in mass and composition at the end of the reaction, cannot supply the required energy.

• 3.2. CATALYTIC PROMOTERS

The activity of a catalyst can often be increased by the addition of a small quantity of a second material. This second substance is either not a catalyst itself for the reaction or it may be a feeble catalyst.

A substance which, though itself not a catalyst, promotes the activity of a catalyst is *called a promoter or an activator.*

[I] Examples of Promoters

(i) In some reactions, mixtures of catalysts are used to obtain the maximum catalytic efficiency. For example, in the synthesis of methanol (CH_3OH) from carbon monoxide and hydrogen, a mixture of zinc oxide and chromium oxide is used as a catalyst.

$$CO + 2H_2 \xrightarrow[Cr_2O_3]{ZnO} CH_3OH$$

(ii) Molybdenum (Mo) or aluminium oxide (Al_2O_3) promotes the activity of iron catalyst in the Haber's synthesis for the manufacture of ammonia.

$$N_2 + 3H_2 \underset{+Mo}{\overset{Fe}{\rightleftharpoons}} 2NH_3$$

[II] Explanation of Promoter's Action

The theory of promotion of a catalyst is not clearly understood. It may probably be due to :

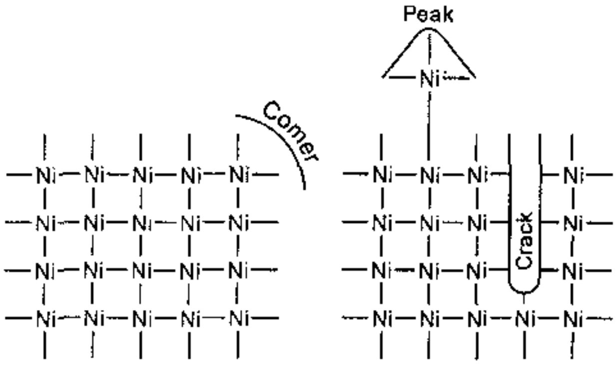


Fig. 4. Peaks, corners and cracks.

(1) ***Increase of peaks and cracks.*** The presence of the promoter increases the peaks and cracks on the catalyst surface. This increases the concentration of the reactant molecules and hence the rate of reaction (Fig. 3).

(2) ***Change of lattice spacing.*** The lattice spacing of the catalyst is changed thus enhancing the spaces between the catalyst particles. The adsorbed molecules of the reactant (say H_2) are further weakened and cleaved. This makes the reaction go faster. The phenomenon of promotion is a common feature of heterogeneous catalysis (Fig. 4).

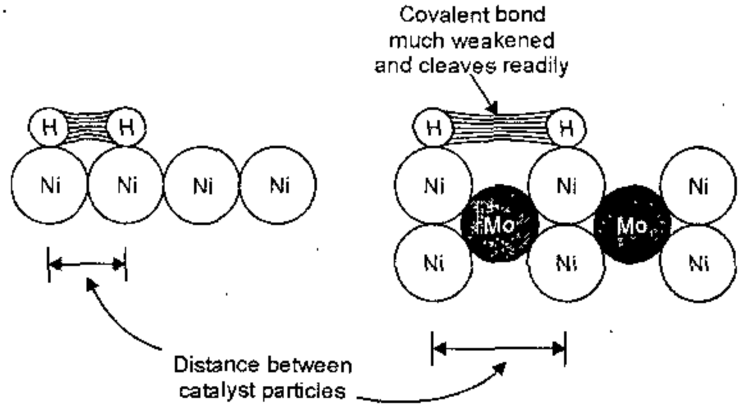


Fig. 4. How the change of crystal lattice spacing of catalyst makes the reaction go faster ?

• 3.3. CATALYTIC POISONS

Very often a heterogeneous catalyst is rendered ineffective by the presence of small amounts of impurities in the reactants.

A substance which destroys the activity of the catalyst to accelerate a reaction, is called a catalytic poison and the process is called catalytic poisoning.

(a) Examples of Catalytic Poisoning

(1) The platinum catalyst used in the oxidation of hydrogen is poisoned by carbon monoxide.

$$2H_2 + O_2 \xrightarrow[\text{Poisoned by CO}]{\text{Pt}} 2H_2O$$

(2) The platinum catalyst used in the oxidation of sulphur dioxide (contact process) is poisoned by arsenic oxide (As_2O_3).

$$2SO_2 + O_2 \xrightarrow[\text{Poisoned by } As_2O_3]{\text{Pt}} 2SO_3$$

(3) The iron catalyst used in the synthesis of ammonia (Haber's process) is poisoned by H_2S.

$$N_2 + 3H_2 \xrightarrow[\text{Poisoned by } H_2S]{\text{Fe}} 2NH_3$$

(b) Explanation of Catalytic Poisoning

(1) ***The poison is adsorbed on the catalyst surface in preference to the reactants*** : Even a monomolecular layer makes the surface unavailable for further adsorption of the reactants. The poisoning of iron catalyst by H_2S comes in this class.

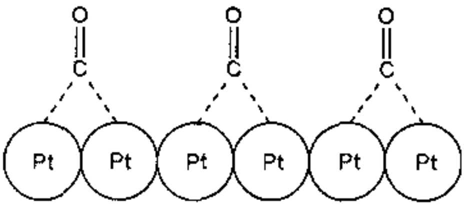


Fig. 5. Poisoning of platinum catalyst by carbon monoxide.

(2) ***The catalyst may combine chemically with the impurity*** : The poisoning of iron catalyst by H_2S

comes in this class.

$$Fe + H_2S \longrightarrow FeS + H_2$$

3.4. THEORIES OF CATALYSIS

Many theories have been put forward to explain the catalytic activity of catalyst. A few important theories are given below :

(1) Intermediate Compound Formation Theory

According to this theory, a catalyst first combines with one of the reactants to form an intermediate compound of activity greater than that of the reactants. This intermediate compound then reacts with another reactant to form the product and so gives back the catalyst. If A and B are two reactants and C is a catalyst, then according to this theory.

$$\begin{aligned} A + C &\longrightarrow AC \\ AC + B &\longrightarrow AB + C \\ \hline A + B + [C] &\longrightarrow AB + [C] \end{aligned}$$

This theory can be fully explained by the following examples :

(1) In the oxidation of SO_2 by air, NO which acts as a catalyst, first combines with oxygen to form NO_2 (intermediate compound) which oxidises SO_2 and gives back nitric oxide.

$$\begin{aligned} 2NO + O_2 &\longrightarrow 2NO_2 \\ [SO_2 + NO_2 &\longrightarrow SO_3 + NO] \times 2 \\ \hline 2SO_2 + O_2 + [2NO] &\longrightarrow 2SO_3 + [2NO] \end{aligned}$$

(2) In the formation of ether from alcohol, *H_2SO_4 which is used as catalyst first forms an* intermediate compound $C_2H_5HSO_4$.

$$\begin{aligned} C_2H_5OH + H_2SO_4 &\longrightarrow C_2H_5HSO_4 + H_2O \\ C_2H_5HSO_4 + C_2H_5OH &\longrightarrow C_2H_5OC_2H_5 + H_2SO_4 \\ \hline C_2H_5OH + C_2H_5OH + [H_2SO_4] &\longrightarrow C_2H_5OC_2H_5 + H_2O + [H_2SO_4] \end{aligned}$$

(3) Formation of methylbenzene, $C_6H_5CH_3$ by reaction between benzene (C_6H_6) and methyl chloride (CH_3Cl) using anhydrous aluminium chloride, $AlCl_3$, as catalyst (Friedel-Craft's reaction).

$$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl$$

Mechanism :

$$CH_3Cl + AlCl_3 \longrightarrow \underset{\text{Intermediate compound}}{[CH_3]^+ [AlCl_4]^-}$$

$$C_6H_6 + [CH_3]^+ [AlCl_4]^- \longrightarrow C_6H_5CH_3 + AlCl_3 + HCl$$

(4) Thermal decomposition of potassium chlorate ($KClO_3$) *in the presence of manganese* dioxide (MnO_2).

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

Mechanism :

$$2KClO_3 + 6MnO_2 \longrightarrow \underset{\text{Intermediate compound}}{6MnO_3} + 2KCl$$

$$6MnO_3 \longrightarrow 6MnO_2 + 3O_2$$

It may be noted that the actual isolation of intermediate compounds which would prove their existence is very difficult. As already stated, by their very nature they are unstable. In general, the intermediate compounds suggested as being formed are usually possible rather than proved.

(2) Adsorption Theory or Modern Theory of Heterogeneous Catalysis

Adsorption theory explains the mechanism of a reaction between two gases catalysed by a solid *(heterogeneous or contact catalysis)*. According to this theory, the catalyst acts by adsorption *of the reacting molecules on its surface. Generally speaking, four steps can be put forward for* heterogeneous catalysis. For example, for the following reaction,

$$A(g) + B(g) \xrightarrow{\text{Catalyst}} C(g) + D(g)$$

the steps are as follows :

Step 1. Adsorption of reactant molecules. The reactant molecules A and B strike the catalyst surface. They are held up at the surface by weak vander Waals forces (physical adsorption) or by partial chemical bonds *(chemisorption)* [Fig. (6)–1].

Step 2. Formation of activated complex. The particles of the reactants adjacent to one another join to form an *intermediate complex* (A – B). The activated complex is unstable. It has only a fleeting existence [Fig. (6)–2].

Step 3. Decomposition of activated complex. The activated complex breaks to form the products C and D. The separated particles of the products are held to the catalyst surface by partial chemical bonds [Fig. (6)–3].

Step 4. Desorption of products. The particles of the products are *desorbed* or released from the surface. They are stable and can lead to an independent existence [Fig. (6)–4].

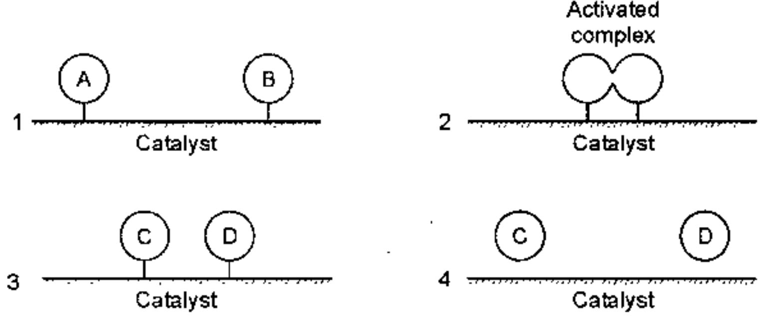
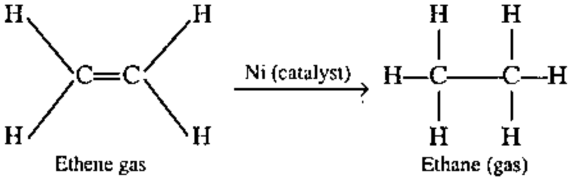


Fig. 6. Mechanism of contact catalyst.

The mechanism of contact catalysis may vary in details, depending on the nature of the reactants. Consider the example of hydrogenation of ethene in presence of nickel [Fig. (7)]. In this casse, ethene adds hydrogen in the presence of nickel as a catalyst to yield ethane.



The catalyst functions according to the following steps.

Step 1. Adsorption of hydrogen molecules. Hydrogen molecules are adsorbed on the nickel surface due to the residual valence bonds of the nickel atoms.

Step 2. H—H bonds are broken. The H—H bond is smaller (0.74 Å) than Ni—Ni bond. Therefore, the H—H bond of the adsorbed hydrogen molecule is stretched and weakened. The weakened bond breaks, separating the hydrogen atoms. The separated hydrogen atoms are held to the nickel surface by chemical bonds.

Step 3. Formation of the activated complex. The chemisorbed hydrogen atoms then attach to ethene molecule by partial chemical bonds. Therefore, unstable activated complex is formed.

Step 4. Decomposition of the activated complex and desorption of ethane molecule. The unstable activated complex decomposes to form ethane molecule. The freed catalyst surface is again available for further action.

The adsorption theory explains the catalytic activity as follows :

(1) Metals in a state of fine sub-division or colloidal form are rich in free valence bonds and hence they are more efficient catalysts than the metal in lumps.

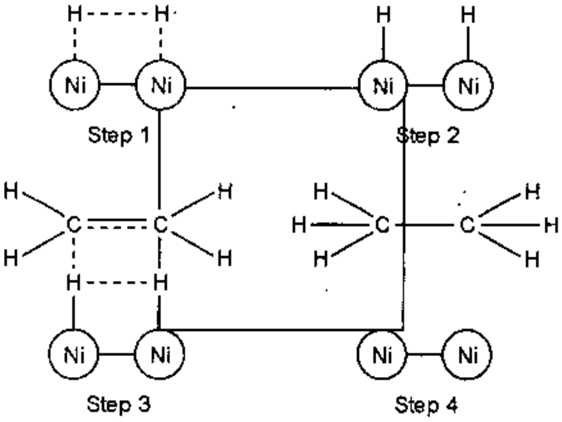


Fig. 7. Mechanism of the hydrogenation of ethene on nickel surface.

(2) A promoter increases the valence bonds on the catalyst surface by changing the crystal lattice and thereby increasing the active centres.

(3) Catalytic poisoning occurs because the so-called poison blocks the free valence bonds on its surface by preferential adsorption or by chemical combination.

• 3.5. BIOCHEMICAL OR ENZYME CATALYSIS

Enzymes are complex nitrogeneous organic compounds. They are produced in the living cells of plants and animals. On dissolving in water they form the colloidal solution, hence they behave as very active catalysts in certain biochemical reactions and are known as **biochemical catalysts** and the phenomenon itself is known as **biochemical catalysis.**

[I] Characteristics of Enzyme Catalysts

(1) Enzymes form a colloidal solution in water and hence they are very active catalysts.

(2) Like inorganic catalysts they cannot disturb the final state of equilibrium of a reversible reaction.

(3) They are highly specific in nature, *i.e.*, one catalyst cannot catalyse more than one reaction.

(4) They are highly specific to temperature. The optimum temperature of their activity is 35°C to 40°C. They are deactivated at 70°C.

(5) Their activity is increased in the presence of certain substances, known as co-enzymes.

(6) A small quantity of enzyme catalyst is sufficient for a large change.

(7) They are destroyed by U.V. rays.

(8) Their efficiency is decreased in presence of electrolytes.

[II] Examples of Enzyme Catalysis

The following are some examples of biochemical or enzyme catalysis.

(1) Manufacture of ethyl alcohol from cane sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

(2) Manufacture of acetic acid from ethyl alcohol

$$C_2H_5OH + O_2 \xrightarrow{\text{Mycoderma aceti}} CH_3COOH + H_2O$$

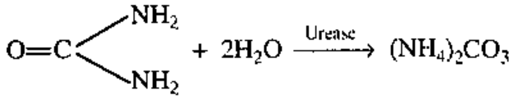
(3) Conversion of starch into maltose

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

(4) In the estimation of urea

Urease enzyme completely converts urea into ammonium carbonate.



$$O{=}C(NH_2)_2 + 2H_2O \xrightarrow{\text{Urease}} (NH_4)_2CO_3$$

(5) In digestive tract

(a) In stomach, pepsin enzyme converts proteins into peptides, whereas in intestines, pancreas *trypsin converts proteins into amino acids by hydrolysis. These amino acids are absorbed by blood* and are used in the building of tissues.

(b) The enzyme ptyalin present in human saliva converts starch into glucose.

$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Ptyalin}} \underset{\text{Glucose}}{nC_6H_{12}O_6}$$

[III] Kinetics of Enzyme Catalysis or Michaelis-Menten Equation

A reactant in an enzyme catalysed reaction is known as *substrate*. According to the mechanism of enzyme catalysis, the enzyme combines with the substrate to form a complex, as suggested by Henri (1903). He also suggested that this complex remains in equilibrium with the enzyme and the substrate. Later on in 1925, Briggs and Haldane showed that a steady state treatment could be easily applied to the kinetics of enzymes. Some photochemical reactions and some enzymic reactions are reactions of the zero order.

With S representing substrate, E the enzyme, ES an enzyme-substrate complex and P the products, the mechanism of the enzyme catalysed reaction is presumed to be adequately represented by

$$E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_3} E + P$$

where k_1, k_2, k_3 are the rate constants for the respective reactions.

The rate of formation of the complex ES is evidently given by the following equation,

$$\frac{d[ES]}{dt} = 0 = k_1 [E][S] - k_2 [ES] - k_3 [ES]$$

$$= k_1 [E][S] - (k_2 + k_3) [ES] \qquad \ldots(1)$$

where [E], [S] and [ES] represent molar concentrations of the free enzyme, substrate and the complex, *i.e.*, bound or reacted enzyme, respectively.

Now [E] cannot be experimentally measured. The equilibruim between the free and bound enzyme is given by the enzyme conservation equation, *i.e.*,

$$[E]_0 = [E] + [ES]$$

where $[E]_0$ refers to the total enzyme concentration. So,

$$[E] = [E]_0 - [ES]$$

On substituting the value of [E] in equation (1), we get

$$\frac{d[ES]}{dt} = k_1 \{[E]_0 - [ES]\} [S] - (k_2 + k_3) [ES] = 0 \qquad \ldots(2)$$

As the reaction proceeds, the intermediate complex formed in accordance with the suggested mechanism, decomposes instantaneously according to the same mechanism. On applying the steady state principle, we have

$$\frac{d[ES]}{dt} = 0$$

At the stationary state, equation (2) may be written as,

$$k_1 \{[E]_0 - [ES]\} [S] = (k_2 + k_3) [ES]$$

or $$k_1 [E]_0 [S] = \{(k_2 + k_3) + k_1 [S]\} [ES]$$

$$[ES] = \frac{k_1 [E]_0 [S]}{(k_2 + k_3) + k_1 [S]} = \frac{[E]_0 [S]}{\frac{k_2 + k_3}{k_1} + [S]}$$

The rate of formation of the product, P, *i.e.*, r is represented by the equation,

$$r = \frac{d[P]}{dt} = k_3 [ES] \qquad \ldots(3)$$

Substituting the value of [ES] in equation (3), we get

$$r = \frac{d[P]}{dt} = \frac{k_3 [E]_0 [S]}{\frac{k_2 + k_3}{k_1} + [S]}$$

The quantity $\frac{(k_2 + k_3)}{k_1}$ is known as *Michaelis constant* and may be denoted by K_m. Therefore,

$$\frac{d[P]}{dt} = \frac{k_3 [E]_0 [S]}{K_m + [S]} \qquad \ldots(4)$$

Equation (4) is known as *Michaelis-Menten* equation.

Further simplification of equation (4) can be made. If it is assumed that all the enzyme has reacted with the substrate at high concentrations the reaction will be going on at maximum rate. No free enzyme will remain so that $[E]_0 = [ES]$. So, from equation (3), we get

$$r_{max} = V_{max} = k_3 [E]_0$$

where V_{max} refers to maximum rate, using the notation of enzymology. So, Michaelis-Menten equation can also be written as,

$$r = \frac{V_{max} [S]}{K_m + [S]}$$

If $r = V_{max}/2$, *i.e.*, if the rate of formation of product is equal to half of the maximum rate at which the reaction proceeds at high concentration of substrate, then

$$K_m = [S]$$

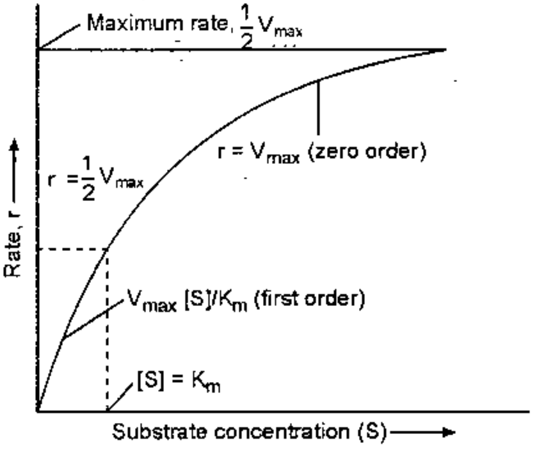


Fig. 8

Thus, ***Michaelis constant is equal to that concentration of substrate, S at which the rate of formation of the product is half the maximum rate obtained at a high concentration of substrate.***

From equation (4), we can draw the following conclusions :

(i) If [S] is very small as compared to K_m, the factor $K_m/[S]$ will be very large as compared to unity and so the rate of formation of P, *i.e.*, $d[P]/dt$ will be directly proportional to [S]. In other words, the reaction will be of *the first order with respect to S* [Fig. (8)].

(ii) If [S] is very large as compared to K_m, the factor $K_m/[S]$ will be negligibly small as compared to unity and so the rate of formation of P, *i.e.*, $d[P]/dt$ will be independent of the concentration [S]. In other words, *the reaction will be of zero order with respect to S* (Fig. 8).

(iii) If [S] is very small or very large, the reaction remains of the first order with respect to the total concentration, $[E]_0$ of the enzyme.

• 3.6. INDUSTRIAL APPLICATIONS OF CATALYSTS

The presence of a catalyst is very useful in many industrially important reactions, which are either very slow or take place at a very high temperature. Hence, to decrease the cost of production it is essential to make use of a suitable catalyst. A few important examples of heterogeneous catalytic reaction of industrial applications are given as follows :

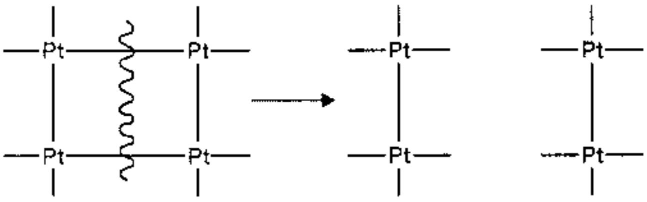


Fig. 9. Sub-division of a catalyst maks it more efficient due to the incrrease of free valence bonds.

	Reaction	Catalyst and other favourable conditions
1.	**Haber's process** for the manufacture of ammonia $N_2 + 3H_2 \longrightarrow 2NH_3$	Finely divided Fe + molybdenum (as promoter) 200 atm. pressure and temperature, 400°—450°C.
2.	The manufacture of chlorine by **Deacon's process** $4HCl + O_2 \longrightarrow 2H_2O + 2Cl_2$	Cupric chloride + excess of air at a temperature of 500°C.
3.	**Ostwald's process** for the manufacture of HNO_3 $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$ $2NO + O_2 \longrightarrow 2NO_2$ $4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$	Platinised asbestos + excess of air (as promoter) and temp. 300°C.
4.	Manufacture of hydrogen by **Bosch's process** $\underbrace{(CO + H_2)}_{\text{Water gas}} + H_2O \longrightarrow CO_2 + H_2O$	Ferric oxide + Cr_2O_3 (as a promoter) at a temp. of 400°—600°C.
5.	Manufacture of methyl alcohol from water gas $\underbrace{CO + H_2}_{\text{Water gas}} + H_2 \longrightarrow CH_3OH$	$ZnO + Cr_2O_3$ (as a promoter), 200 atms. pressure and temp of 450°C.
6.	**Chamber process** for the manufacture of H_2SO_4 $2SO_2 + O_2 + [NO] \longrightarrow 2SO_3 + [NO]$ $SO_3 + H_2O \longrightarrow H_2SO_4$	Nitric oxide
7.	Acetic acid from acetaldehyde $2CH_3CHO + O_2 \longrightarrow 2CH_3COOH$	V_2O_5

• SUMMARY

- A catalyst is a substance which changes the speed of a chemical reaction without itself undergoing any chemical change at the end of the reaction.
- When the catalyst is present in the same phase as that of the reactants, the phenomenon is known as homogeneous catalysis.
- When the catalyst is in a different phase than that of the reactants, the phenomenon is known as heterogeneous catalysis.
- When the catalyst used increases the speed of a chemical reaction, it is called a positive catalyst.
- When the catalyst used decreases the speed of a chemical reaction, it is called a negative catalyst.
- A substance which though itself is not a catalyst increases the activity of a catalyst is known as promotor or activator.
- A substance which destroys the activity of a catalyst is known as poison.
- Characteristics of a catalyst :
  - **(i)** A catalyst remains unchanged in mass and chemical composition at the end of the reaction.
  - **(ii)** A small quantity of a catalyst is generally needed to produce the reaction.
  - **(iii)** A catalyst can not, in general start a reaction.
  - **(iv)** A catalyst is more effective, when it is finely divided.
  - **(v)** A catalyst is specific in its action.
  - **(vi)** Change of temperature changes the rate of a catalytic reaction as it would do for the same reaction without a catalyst.
  - **(vii)** A catalyst does not change the final state of equilibrium, although it decreases the time required to establish it.
  - **(viii)** The efficiency of a catalyst is maximum at a certain temperature, known as optimum temperature.
- When enzymes act as catalysts, the reaction is known as enzyme catalysis.
- Characteristics of enzyme catalysis :
  - **(i)** Enzymes form a colloidal solution in water, so they are very active catalysts.
  - **(ii)** Like inorganic catalysts they cannot disturb the final state of equilibrium of a reversible reaction.
  - **(iii)** They are highly specific in nature, *i.e.*, one catalyst cannot catalyse more than one reaction.
  - **(iv)** They are highly specific to temperature. The optimum temperature of the activity of enzymes is 35°C to 40°C. They are deactivated at –7°C.
  - **(v)** Their activity is increased in the presence of certain substances, known as co-enzymes.
  - **(vi)** A small quantity of enzyme catalyst is sufficient for a large change.
  - **(vii)** They are destroyed by U.V. rays.
  - **(viii)** Their efficiency is decreased in presence of electrolytes.

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• STUDENT ACTIVITY

1. Discuss the characteristics of catalyst.

2. What is enzyme catalysis ? Mention the kinetics of enzyme catalysis.

3. *Describe three industrial applications of catalysis.*

4. Define catalytic promoters and catalytic poisons.

• TEST YOURSELF

Answer the following questions :

1. Mention the characteristics of a catalyst.
2. Write short notes on the following :
   (i) Homogeneous catalysis (ii) Heterogeneous catalysis
   (iii) Positive catalysis *(iv) Negative catalysis*
   (v) Auto-catalysis (vi) Induced catalysis
3. What are catalytic promoters and catalytic poisons ?
4. Discuss the theories of catalysis.
5. Describe the industrial applications of catalysts.
6. What is enzyme catalysis ? Describe the charactristics of enzyme catalysis.
7. Discuss the kinetics of enzyme catalysis.
8. Derive Michaels-Menten equation.
9. Define Michaels constant.
10. In the hydrogenation of oils the catalyst used is :
    (a) Iron (b) Platinum (c) Nickel (d) Molybdenum
11. The effect of a catalyst in a chemical reaction is to change the :
    (a) Activation energy (b) Equilibrium concentration
    (c) Heat of reaction (d) Final product
12. Which of the following statements is universally correct?
    (a) A catalyst remains unchanged at the end of the reaction
    (b) A catalyst physically changes at the end of the reaction
    (c) A catalyst takes part in the chemical reaction
    (d) A catalyst can induce chemical reaction
13. A substance that retards the rate of chemical reaction in the presence of a catalyst is called :
    (a) An inhibitor (b) A positive catalyst
    (c) An auto-catalyst (d) A promoter
14. A catalyst poison is essentially :
    (a) A homogeneous catalyst (b) A heterogeneous catalyst
    (c) An inhibitor (d) An auto-catalyst
15. Catalyst poisons (temporary poisoning) act by :
    (a) Chemically combining with the catalyst
    (b) Getting adsorbed on the active centres on the catalyst surface
    (v) Chemical combination with any one of the reactants
    (d) Coagulating the catalyst
16. Which of the following types of the metal make the most efficient catalyst?
    (a) Transition metals (b) Alkali metals

(c) Alkaline earth metals (d) Coloured metals

17. Enzymes are :

(a) Micro-organisms (b) Proteins.

(c) Inorganic compounds (d) Moulds

18. The enzyme pyralin used for digestion of food is present in :

(a) Saliva (b) Blood (c) Intestine (d) Adrenal gland

19. Glucose or fructose is converted into C_2H_5OH in the presence of :

(a) Invertase (b) Maltase (c) Zymase (d) Diastase

20. A catalyst increases the rate of a chemical reaction by :

(a) Increasing the activation energy (b) Decreasing the activation energy

(c) Reacting with reactants (d) Reacting with products

21. Which of the following statement is correct?

(a) Enzymes are in colloidal state (b) Enzymes are catalysts

(c) Enzymes catalyse any reaction (d) Urease in an enzyme

22. Which of the following statement is correct for a catalyst?

(a) It supplies energy to the system (b) It alters the rate of the reaction

(c) It alters the equilibrium constant (d) It is used up in the reaction

23. Which statement is incorrect for heterogeneous catalysis?

(a) Catalyst is absorbed on the surface

(b) Active centres are found on the surface of catalyst

(c) Catalyst increases the energy of activation

(d) None of these

24. Fill in the blanks

(i) The substance which retards the reaction rate is known as .... catalyst.

(ii) The .... of a catalyst increases when it is finely divided.

(iii) In the conversion of urea into ammonium carbonate .... acts as a catalyst.

(iv) The presence of a catalyst .... the activation energy of the reaction.

ANSWERS

10. (c) **11.** (a) **12.** (a) **13.** (a) **14.** (c) **15.** (b) **16.** (a) **17.** (b) **18.** (a) **19.** (c)
20. (b) **21.** (c) **22.** (b) **23.** (c)

24. **(i)** negative **(ii)** efficiency **(iii)** Urease **(iv)** decreases.

❑❑❑

UNIT

4

COLLOIDAL STATE

STRUCTURES

• 4.1. INTRODUCTION

Thomas Graham (1861) divided soluble substances into two classes *viz.*,

(i) Crystalloids, *i.e.*, salt, urea, sugar and other crystalline substances which could rapidly diffuse through vegetable and animal membranes. Such solutions are called ***true solutions*** in which the diameter of the dispersed particles ranges from 1 Å to 10 Å.

(ii) Colloids, *i.e.*, starch, gelatin, gum, proteins and other amorphous substances which could not diffuse through vegetable and animal membranes (Greek; kola = glue and eiodos = like).

In a **suspension**, as sand stirred into water, the dispersed particles are aggregates of millions of molecules. The diameter of these particles is of the order of 2000 Å or more.

A **colloidal solution** *is regarded as an intermediate between a true solution and coarse suspension.*

When the diameter of the particles of a substance dispersed in a solvent ranges from about 10 Å to 2000 Å, the system is called ***colloidal solution, colloidal dispersion*** or simply a ***colloid.*** The material with particle size in the colloidal range is said to be in the ***colloidal state***.

Colloidal solution is a heterogeneous system consisting of two phases.

(a) Dispersed phase : The substance whose particles are distributed in a medium is called the dispersed phase.

(b) Dispersion medium : The medium in which the particles of the dispersed phase are distributed is called the dispersion medium.

• 4.2. DIFFERENCES BETWEEN SUSPENSION, COLLOIDAL SOLUTION AND TRUE SOLUTION

The differences between a true solution, colloidal solution and suspension are given in the following table.

S.N.	Characteristic property	Suspension	Colloidal solution	True solution
1.	Nature	Heterogeneous	Heterogeneous	Homogeneous
2.	Size range	Particles are greater than 10^{-5} cms (or 0.1 μ or 100 $m\mu$) in diameter.	Particles are between 10^{-5} and 10^{-7} cms (or 0.1 μ to 1 $m\mu$) in diameter.	Particles are less than 10^{-7} cms (or 1 $m\mu$) in diameter.
3.	Visibility	Particles are visible under a microscope or even with a naked eye.	Particles are generally visible under ultramicroscope.	Particles are not visible even under ultramicroscope.
4.	Diffusibility	Do not diffuse	Diffuse slowly	Diffuse rapidly
5.	Filtrability	Can be filtered even by an ordinary filter paper.	Can be filtered through an animal membrane, through which the colloidal particles do not pass.	Cannot be filtered.
6.	Molecular weight	Low	High	Low
7.	Osmotic pressure $\left(\text{O.P.} \propto \frac{1}{\text{M.W.}}\right)$	High	Low	High
8.	Colour	—	Depends upon the shape and size of the particle	Depends upon the nature of the ion.
9.	Tyndall effect	Do not exhibit	Exhibit	Do not exhibit
10.	Brownian movement	Do not exhibit	Exhibit	Exhibit
11.	Electrophoresis	Do not exhibit	Exhibit	Exhibit
12.	Coagulation	—	Can be coagulated by adding electrolytes.	Can be precipitated by adding suitable electrolytes.
13.	Presence of electric charge	—	Particles carry either positive or negative charge.	Particles do not carry any charge.

• 4.3. PREPARATION OF COLLOIDAL SOLUTIONS

Colloidal solutions *(also known as sols)* can be prepared by different methods depending on the nature of the substances. Many substances., *e.g.*, gelatin, starch etc. form colloidal solutions by merely dissolving them in water. Metals and inorganic substances are brought into the colloidal state by special methods. Two types of methods, viz., dispersion methods and condensation methods are mainly used:

[I] Dispersion Methods

Dispersion methods are those in which the particles of bigger size are broken into smaller colloidal particles. The different ways are :

(i) Mechanical dispersion : The substance to be dispersed is suspended in dispersion medium to form a coarse suspension. This suspension is passed through a *colloid mill* which consists of two metal discs rotating in opposite directions at a speed of about 7000 revolutions per minute.

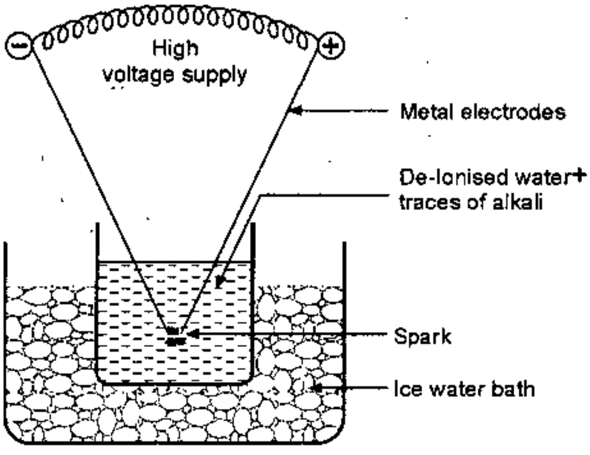

Fig. 1. Bredig's arc method.

(ii) Electro-dispersion (Bredig's arc method) : This method is generally employed in preparing hydrosols of metals, *i.e.*, Ag, Au, Cu, Pt etc. Two rods of metal to be dispersed are kept immersed in cold water containing some KOH and a direct electric arc is struck between them [Fig. (1)]. The vapours of the metal condense to form colloidal particles. The traces of alkali act as stabilising agent.

(iii) Peptisation : If a freshly prepared $Fe(OH)_3$ precipitate is treated with a small quantity of $FeCl_3$ solution, it immediately forms a dark reddish brown colloidal solution of $Fe(OH)_3$. Similarly, a colloidal solution of $Al(OH)_3$ is obtained when freshly precipitated $Al(OH)_3$ is treated with a small quantity of dil. HCl, the amount of acid added being insufficient to convert the hydroxide completely into chloride.

The process of transferring back a fresh precipitate into colloidal form is known as peptisation.

Peptisation is the converse of coagulation or in other words, it is the re-dispersion of a coagulated sol. Substances like $FeCl_3$ and HCl which bring about peptisation are known as ***peptising agents.***

Cause of peptisation : The peptising action is due to the preferential adsorption of one of the ions of the electrolyte, which then gives to the colloidal particle a positive or negative charge, according to the charge on the adsorbed ion. For example, $Fe(OH)_3$ adsorbs Fe^{3+} ions from $FeCl_3$ (peptising agent) and thereby gets a positive charge on the surface. Similarly, charged particles get separated yielding smaller sized colloidal particles of the type $[Fe(OH)_3] Fe^{3+}$.

Similarly, As_2S_3 precipitate obtained by pasing H_2S through arsenious oxide solution peptises on treatment with excess of H_2S and yields a negatively charged sol of $[As_2S_3] S^{2-}$.

[II] Condensation Methods

Condensation methods are those in which the substances forming a true solution are converted into colloidal form. These are as follows :

(i) By chemical reaction : The methods are :

(a) Double decomposition : It is used in the preparation of sols of sulphides, *e.g.*, sols of As_2S_3 and HgS are obtained by passing H_2S through their salt solutions.

A solution of 1.0 g As_2O_3 in 500 ml of boiling water is obtained. It is cooled and H_2S gas is allowed to pass slowly. When the intensity of yellow colour of the sol does not increase further, the passing of H_2S is stopped.

$$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$$

The excess of H_2S is removed either by boiling the colloidal solution or by bubbling H_2 through it, when a yellow sol of As_2S_3 is obtained.

(b) Hydrolysis : A colloidal solution of ferric hydroxide is obtained by adding a freshly prepared saturated solution of ferric chloride (2 or 3 c.c.) drop by drop to 500 ml of boiling distilled water. Ferric chloride hydrolyses to give a brown sol of ferric hydroxide.

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$

The hydrochloric acid formed and unhydrolysed ferric chloride are separated by dialysis to get pure Fe $(CH)_3$ sol.

(c) Reduction : A colloidal solution of gold (or purple of Cassius) is obtained by reduction of auric chloride with stannous chloride or by HCHO.

$$2AuCl_3 + 3SnCl_2 \rightarrow 2Au + 3SnCl_4$$

$$2AuCl_3 + 3HCHO + 3H_2O \rightarrow 2Au + 3HCOOH + 6HCl$$

A trace of K_2CO_3 is added to neutralise the acid formed whose presence renders the sol unstable.

(d) Oxidation : A colloidal solution of sulphur is obtained by the oxidation of H_2S with dil. HNO_3 or sulphurous acid.

$$3H_2S + 2HNO_3 \rightarrow 2NO + 4H_2O + 3S$$

$$2H_2S + H_2SO_3 \rightarrow 3H_2O + 3S$$

The colloidal solution of sulphur so formed is treated with saturated salt solution when sulphur is precipitated. It is filtered, washed with water to remove salt and then washed further when the precipitate of sulphur peptises and forms a colloidal solution.

(ii) By exchange of solvent, *i.e.*, by lowering of solubility : Colloidal solution of a substance can be prepared by dissolving it in one solvent and pouring this solution in another solvent in which it is less soluble, *e.g.*, a sulphur or phosphorus sol can be prepared by adding their saturated alcoholic solution in water.

(iii) Passing vapours of an element into a liquid : When the vapours of a boiling element are passed through a liquid, condensation takes place sometimes with the formation of a soluble sol, *e.g.*, mercury sol can be prepared by passing a stream of vapours from the boiling element into cold water containing a suitable stabilising agent.

• 4.4. PURIFICATION OF COLLOIDAL SOLUTIONS

The colloidal solutions prepared by the above methods contain impurities. These impurities must be removed in order to make the sol stable. This is done by either of the following methods.

(1) Dialysis : The purification of colloidal solution by this method is based on the inability of the sol particles to pass through an animal membrane or a parchment paper which allows only the molecules or the ions to pass through. The vessel in which dialysis is carried out is known as ***dialyser*** [Fig. (2)]. A dialyser consists of a special type of vessel open at both the ends. To the lower end a membrane is stretched. This membrane allows only the solvent and other molecules to pass through it, but it is impermeable to the colloidal particles. The dialyser is then suspended in a larger vessel containing pure distilled water. The distilled water is periodically renewed by allowing water to flow into the outer larger vessel and removing it by means of a syphon. Dialysis is continued till no further contamination of the washing liquid occurs.

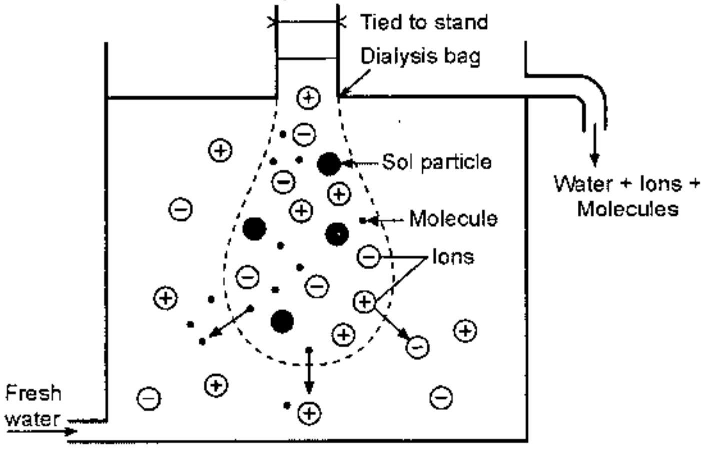

Fig. 2. Dialysis method.

(2) Electrodialysis : In this process, dialysis is carried out under the influence of electric field [Fig. (3)] Potential is applied between the metal screens supporting the membranes. This speeds up the migration of ions to the opposite electrodes. So, dialysis is greatly accelerated.

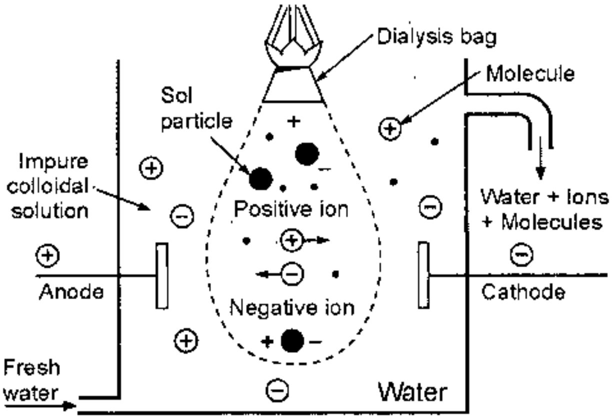

Fig. 3. Electrodialysis method.

Electrodialysis is not meant for the removal of non-electrolytic impurities like sugar, urea etc.

(3) Hot dialysis : In hot dialysis, a temperature of 65–90°C increases the rate of dialysis by about three times. Heating is done by placing an electrical heating unit in the dialyser. All hydrophobic sols cannot withstand the high temperature and the membranes may give off undrained colloidal impurities.

(4) Ultrafiltration : Sols pass through an ordinary filter paper. Its pores are too large to retain the colloidal particles. However, if the filter paper is impregnated with collodion and then dipped in HCHO or glacial acetic acid, the pore size is much reduced. Such a modified filter paper is called an ***ultra-filter****.

The separation of the sol particles from the liquid medium and electrolytes by filtration through an ultrafilter is called ***ultrafiltration.*** It is a slow process. Gas pressure or suction is applied

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Preparation of ultrafilters : The preparation involves the impregnation of special filter paper with collodion (5% solution of nitrocellulose in a mixture of alcohol and ether) and subsequently hardening by dipping it in a solution of HCHO and finally drying. The size of pores of ultrafilter may be altered by varying the concentration of collodion solution. The pore size of ultrafilters can be determined by the rate of penetration of water or by forcing air through the wetted membrane. During ultrafiltration, the sol particles are left behind on the ultrafilter, which can be redispersed in the pure dispersion medium.

to speed it up. The colloidal particles are left on the *ultrafilter* in the form of slime. The slime is then stirred into fresh dispersion medium to get the pure sol. By using graded ultrafilters, the technique of ultrafiltration can be used to separate sol particles of different sizes.

• 4.5. TYPES OF COLLOIDAL SYSTEMS

A colloidal system is a biphasic system consisting of ***(i) dispersed phase*** and ***(ii) dispersion medium.*** Therefore, the **two** phases can either be solid, liquid or gas. Thus, different types of colloidal system depending upon the nature of the dispersed phase and dispersion phase are possible, which can be summarised in the following table with examples.

S.N.	Dispersed phase	Dispersion medium	Name of the colloidal system	Examples
1.	Solid	Solid	Solid sol.	Gems, precious stones etc., alloys.
2.	Liquid	Solid	Gels or jellies	Jelly, butter, cheese.
3.	Gas	Solid	Solid foam	Pumice stone, cork, foam rubber.
4.	Solid	Liquid	Colloidal solution, sol	Sols of metals, sulphur etc., paint, ink.
5.	Liquid	Liquid	Emulsion	Milk.
6.	Gas	Liquid	Foam	Soap lather, shaving cream, whipped cream.
7.	Solid	Gas	Aerosol	Smoke, dust.
8.	Liquid	Gas	Liquid aerosol	Fog, cloud, mist.

A gas dispersed in a gas forms a homogeneous mixture and so do not form a colloidal solution.

• 4.6. LYOPHILIC AND LYOPHOBIC COLLOIDS

A substance which passes into the colloidal state, simply by bringing it in contact with water is known as ***hydrophilic colloid*** (*hydro* = water, *philic* = loving). But if any solvent like organic liquid is used instead of water, then the more general term *lyophilic colloid* (*lyo* = solvent; *philic* = loving) is used. Gum, starch, soap are ***lyophilic colloids.*** These colloids when once precipitated can again be brought back directly into the colloidal state. Hence, they are also known as ***reversible colloids.*** (Colloidal state   precipitate). Reversible colloids are also termed ***as resoluble*** or ***non-electrocratic*** colloids.

Substances like metals, metal sulphides cannot be brought into the colloidal state simply by bringing them in contact with water and, therefore, special methods are devised for the purpose. Hence, they are known as ***hydrophobic colloids*** (*hydro* = water; *phobic* = hating). In case of solvent other than water, the general term ***lyophobic*** is used. Further, if these colloids are precipitated, then it is not very easy to reconvert the precipitate directly into the colloidal state. Hence, they are termed as ***irreversible colloids*** (colloidal state → precipitate), ***irresoluble or electrocratic*** colloids.

Differences between lyophilic and lyophobic sols

S.N.	Lyophilic sols	Lyophobic sols
1.	Prepared by direct mixing with dispersion medium.	Not prepared by direct mixing with the medium.
2.	Viscosity higher than dispersion medium, set to a gel.	Viscosity almost the same as of medium, do not set to a gel.
3.	Little or no charge on particles.	Particles carry positive or negative charge.
4.	Do not show Tyndall effect.	Show Tyndall effect.
5.	Particles migrate to anode or cathode or not at all.	Particles migrate to either anode or cathode.
6.	Particles are generally solvated.	No solvation of particles.
7.	Precipitated by higher concentration of electrolytes.	Precipitated by low concentration of electrolytes.
8	Reversible.	Irreversible.

• 4.7. ULTRAMICROSCOPE

Zsigmondy and Siedentopf (1903) devised ultramicroscope [Fig. (4)] to study Tyndall effect. It consists of an ordinary microscope with a special arrangement for focussing a beam of light. The light from an arc lamp S is allowed to pass through a projection lens L_1 and objective lens L_2 and focussed into a vessel containing a colloidal solution C. The light scattered-from colloidal particles now enters the microscope M placed at right angle to the path of light. The colloidal particles look as pin points of light. We do not see the colloidal particles in this ultramicroscope but see the light scattered by them.

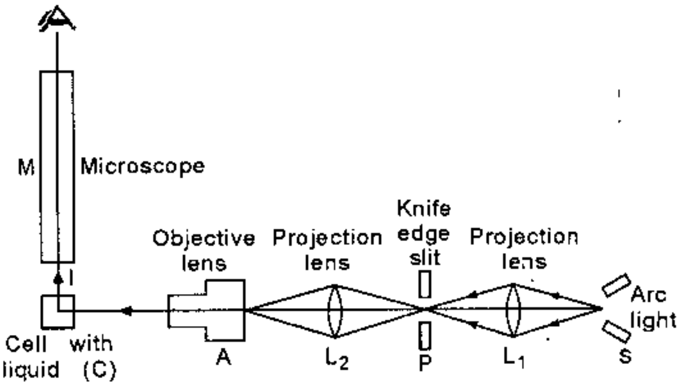


Fig. 4. Ultramicroscope.

As each particle can be detected as *'spot'* of light, therefore, slit ultramicroscope helps to determine the number of particles in a definite volume. The great value of the slit consists in the ability by its use to suction off a portion of the fluid which is being examined. Zsigmondy (1912) devised an immersion ultramicroscope, which was used with strongly coloured liquids. In it, illumination objective and microscope objective are brought as close as possible, and the liquid to be investigated can be used as a drop between the two lenses.

The ultramicroscope does not give any information regarding the shape and size of colloidal particles.

• 4.8. TYNDALL EFFECT

When a strong beam of light is passed through a true solution, it cannot be seen unless the eye is kept directly in the path of light, but when the same beam of light is passed through a sol and viewed at right angles, the path of the light becomes illuminated. This is due to the fact that sol particles absorb light energy and then emit it in all directions in space. This scattering of light illuminates the path of the beam in the colloidal solution. ***The phenomenon of the scattering of light by the colloid particles is called Tyndall effect.*** The illuminated beam or cone formed (figure 5) by the scattering of light by the sol particles is often referred to as ***Tyndall beam*** or ***Tyndall cone.***

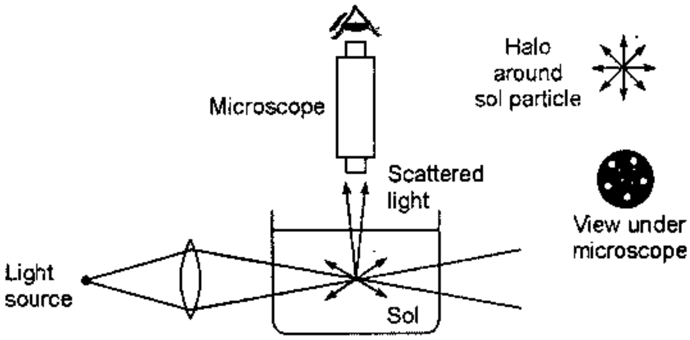


Fig. 5. Tyndall effect.

If the sol particles are large enough, the sol may even appear turbid in ordinary light as a result of Tyndall scattering. As ions or solute molecules are too small to scatter light, the beam of light passing through a true solution is not visible when viewed from the side. So, Tyndall effect can be used to distinguish a colloidal solution from a true solution.

The blue colour of sky, hazy illumination of the light beam from the film projector in a smoke filled theatre or light beams from the head-lights of a car on a dusty road are common examples of Tyndall effect.

• 4.9. BROWNIAN MOTION

R. Brown (1827) observed that when a sol is examined with an ultramicroscope, the suspended particles are seen as shining specks of light. By following an individual particle, it is observed that the particle is undergoing a constant rapid motion in straight lines in all possible directions [Fig. (6)].

The continuous rapid zig-zag movement executed by the colloidal particles in a dispersion medium is known as ***Brownian movement.***

Suspensions and true solutions do not exhibit Brownian motion. It was seen that Brownian motion was independent of the nature of the colloidal particles but was more rapid when the particles are smaller and the solution is less viscous.

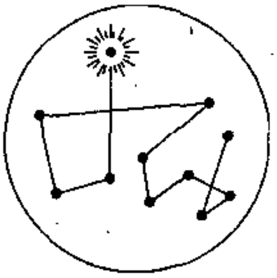


Fig. 6. An illustration of Brownian motion.

Explanation : It was proved that the motion of the particles is due to the unequal bombardment of the suspended particles by the molecules of the dispersion medium in which they are dispersed [Fig. (7)]. On this basis, Einstein suggested that colloidal particles must behave like dissolved molecules and gas laws should apply to these systems, just as they were applied to true solutions.

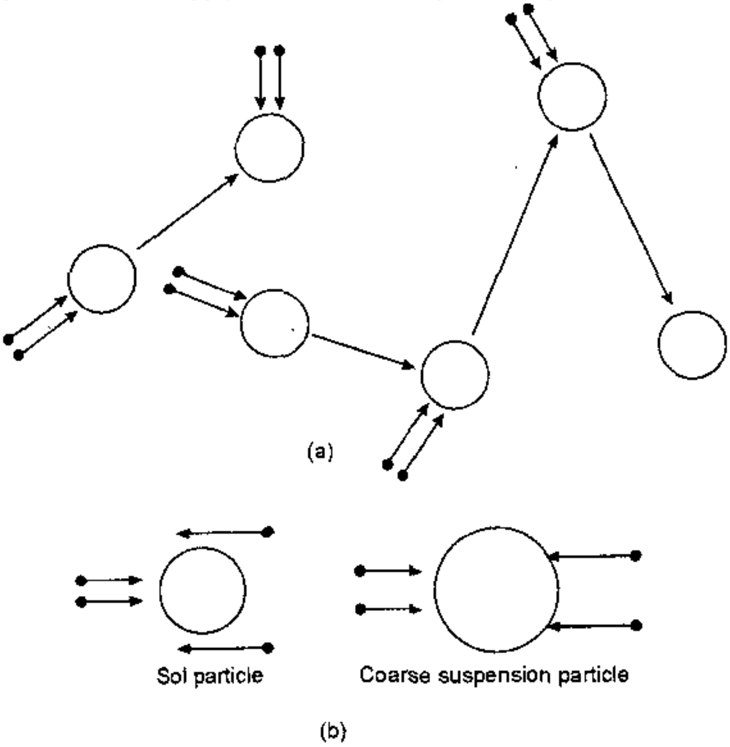


Fig. 7. (a) The bombardment on the sides of the colloidal particles by molecules of dispersion medium causes the *random motion of the particle. (b) Illustration showing how Beownian motion vanishes in course suspension.*

As the particles increase in size, the probability of unequal bombardment diminishes and eventually the collisions on different sides equalise each other. As the size is reduced, the probability of unequal bombardment rapidly increases, whereby the Brownian movement becomes more and more violent.

Applications and Importance

(i) Confirmation of kinetic theory : It is a direct demonstration of ceaseless motion of molecules as pictured by kinetic theory of motion.

(ii) Determination of Avogadro's number : With the help of ultramicroscope, the number of particles in a given mass of the gas can be counted and the Avogradro's number, *i.e.*, the number of molecules in one mole of gas can be calculated.

(iii) In stabilising colloidal solution : The zig-zag motion prevents the setting of colloidal particles by gravity and thus helps in stabilising the colloidal solutions to some extent.

• 4.10. ELECTROPHORESIS

The sol particles carry a charge either positive or negative. It was first observed by Linder and Picton (1892) and is used to indicate the migration of colloidal particles in an electric field. When the particles move towards the cathode, the phenomenon of migration of particles is known as *cataphoresis* and migration towards the anode is known as *anaphoresis*. But in practice, a more general term *electrophoresis* is used. So, ***electrophoresis is defined as the movement of colloidal particles towards oppositely charged electrode under the influence of electric field.***

Electrophoresis can be studied by the simple apparatus [Fig. (8)] which consists of a U-tube fitted with a funnel shaped reservoir and a stop cock. A small amount of water is placed in the U-tube and then some quantity of the sol is taken, so as to form a layer under the pure dispersion medium. An electric current is then applied, by connecting the two electrodes dipped in the solution. It will be seen that the particles begin to migrate towards the oppositely charged electrode. If the sol is coloured, then the movement of the particles can be observed directly by naked eyes. But if the sol is not coloured, then the electrophoretic migration can be observed by microscope or ultramicroscope. When the colloidal particles reach the electrode they lose their charge and generally coagulate into coarse particles.

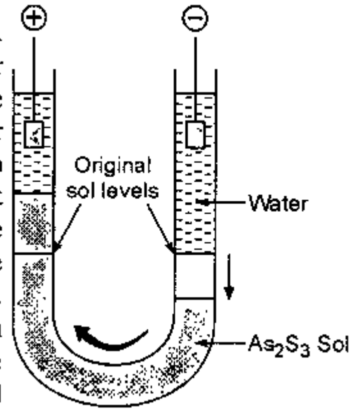


Fig. 8. Electrophoresis.

Applications of Electrophoresis

(i) **In determining the charge :** The nature of the charge on a colloidal particle can be ascertained by its migration in an electric field.

(ii) **In electro-deposition of rubber :** The latex obtained from the sap of certain trees is an emulsion of negatively charged rubber particles dispersed in water. This can be deposited on any substance which is made the anode during electrolysis.

(iii) **In the removal of colloidal smoke from outgoing gases :** The removal of negatively charged carbon particles from smoke can be done by passing the smoke between positively charged metal electrodes. The principle has been utilised in the construction of ***Cottrell precipitator.***

(iv) Electrophoresis has proved to be of great importance in medicine, industry etc. *e.g.*, in characterising proteins causing diseases as well as in the isolation of enzymes. Flavin enzyme was similarly isolated from yeast by Theorell (1932).

(v) **Lyophobic sols show electrophoresis** : This is because the colloidal particles are electrically charged, which move under the influence of electric field.

• 4.11. ELECTRO-OSMOSIS

A sol is electrically neutral. So, the dispersion medium carries an equal but opposite charge to that of the dispersed particles. Thus, the medium will move in opposite direction to the dispersed phase under the influence of applied potential. When the dispersed phase is kept stationary, the medium is actually found to move to the electrode of sign opposite than its own.

The movement of the dispersion medium under the influence of applied potential is known as electro-osmosis.

Electro-osmosis is a direct consequence of the existence of zeta potential between the sol particles and the medium. When the applied potential exceeds the zeta potential, the diffused layer moves and causes electro-osmosis.

The phenomenon of electro-osmosis can be studied by using a U-tube [fig. (9)] in which a plug of moist clay (a negative sol) is fixed. The two limbs of the tube are filled with water to the same level. The platinum electrodes are dipped in water and potential applied. It is observed that water level rises on the cathode side, while it falls on the anode side. This motion of the medium towards the negative electrode, shows that the charge on the medium is positive. Similarly, for a positively charged sol, electro-osmosis will occur in the reverse direction.

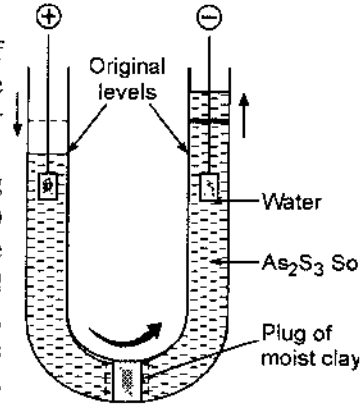


Fig. 9. Electro-osmosis.

Applications of Electro-osmosis

(i) In the preparation of pure colloids. The case in point is the preparation of colloidal silicic acid of low molecular weight, *i.e.*, in a state of fine sub-division.

(ii) In the tanning of hides and impregnation of similar materials.

(iii) In the manufacture of gelatin for photographic emulsions. The object is to get a gelatin free from fat, minerals and reducing constituents. This phenomenon is also applied in the manufacture of high grade glue.

(iv) In the dying of peat, a process due to von Schwerin (1903).

• 4.12. COAGULATION

It has been known for some time that on the addition of a very small amount of suitable electrolytes to a sol, the corresponding substances are thrown out of the solution and form a precipitate. If a suitable quantity of sodium chloride is added to a ferric hydroxide sol, the sol becomes turbid and ultimately precipitates. The electrolyte thus causes the colloid particles to coalesce. So, ***the process by means of which the particles of the dispersed phase in a sol are precipitated is known as coagulation or flocculation.***

It has been observed that :

(i) An ion having a charge opposite to that of the sol is responsible for coagulation. This ion is known as ***active ion****, e.g., in the coagulation of negatively charged sols the cations are the active ions and anions are the active ions in the coagulation of positively charged sols.*

(ii) The coagulating or flocculating power of the active ion increases with increase in the valency of the active ion.

Hardy-Schulze Law

Hardy and Schulze gave a law, after observing the regularities concerning the sign and valence of the active ion. This law is known as ***Hardy-Schulze law.*** It can be defined as.

'Greater the valency of the active ion, greater is the coagulating power of the active ion.'

Thus, in the case of a positively charged sol the coagulating power of anions is in the order of $PO_4^{3-} > SO_4^{2-} > Cl^-$, whereas the coagulating power is in the order of $Al^{3+} > Ba^{2+} > Na^+$ in the case of negatively charged sols. The precipitate after being coagulated is known as ***'coagulum'.***

The amount of electrolyte required to produce coagulation depends upon the total surface exposed by the colloidal particles. Hence, more concentrated sols require more electrolyte for coagulation. *The minimum concentration of an electrolyte required to bring about coagulation or flocculation of a sol is known as* ***coagulation or flocculation value.*** It is evident, therefore that polyvalent ions are the most effective active ions in causing coagulation.

The coagulation of one sol may be effected by mixing an oppositely charged second sol. Thus, when a positive sol of $Fe(OH)_3$ is mixed with an equivalent amount of a negative sol of As_2S_3, both get coagulated and separate out. This process is known as ***mutual coagulation of sols.***

• 4.13. PROTECTION

Lyophilic sols are more stable towards electrolytes. It is due to the fact that these particles are highly solvated and the electrolyte does not penetrate easily to coagulate lyophilic sols. On the other hand, lyophilic sols are readily precipitated by small amounts of electrolytes. However, these sols are often stabilised by the addition of lyophilic sols. ***So, the property of lyophilic sol to prevent the coagulation of a lyophobic sol is called protection.*** The lyophilic substance which is used to protect a lyophobic sol from coagulation is called a ***protective colloid.*** This protection is due to the fact that the particles of the lyophobic sol adsorb the particles of the lyophilic sol. Thus, the lyophilic colloid forms a coating around the lyophobic sol particles The lyophobic colloid thus behaves as a lyophilic sol and is precipitated less easily by electrolytes [Fig. (10)].

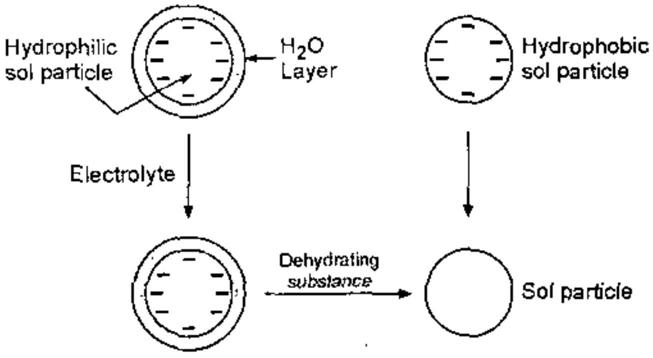


Fig. 10. Phenomenon of protection.

Thus, if a little gelatin (protective colloid) is added to a gold sol the latter is protected. The protected gold sol is no longer precipitated on the addition of an electrolyte, say NaCl.

Gold Number

Different protective colloids have different protective powers. Zsigmondy showed that protective power of a protective colloid can be measured in terms of its ***gold number.*** Gold number may be defined as *'the number of milligrams of a protective colloid which will just stop the coagulation of* 10 ml *of a given gold sol on adding* 1 ml of 10% *sodium chloride solution'.*

If no protective colloid is present in the gold sol, it will turn from red to blue. The smaller the gold number of a protective colloid, the greater is its protective power.

Gold Number

Colloid	Gold number
Casein	0.1
Gelatin	0.005–0.01
Dextrin	6.20
Starch (potato)	25.0
Colloidal SiO_2	∞
Gum arabic	0.15–0.25

Thus, starch has a high gold number, which shows that it is an ineffective protective colloid, while gelatin has a small gold number and is thus an effective protective colloid.

Problem : Gold number of starch is 25. Calculate its amount to be added into 100 ml of gold sol so that it is not coagulated in presence of 10 ml of 10% NaCl solution.

Solution : Gold number of starch is 25 means 25 mg of starch is added to prevent coagulation of 10 ml of gold sol by 1 ml of 10% NaCl solution. For 100 ml of gold sol, 250 mg of starch is needed to prevent coagulation by 1 ml of 10% NaCl solution. But for 10 ml of 10% NaCl solution, only $\frac{25 \times 1}{10}$ mg or 25 mg of starch is required.

• 4.14. STABILITY OF LYOPHOBIC COLLOIDS

Preventing coagulation of a colloidal solution by any means is known as *stabilising the colloid.* Bancroft (1915) gave the position with regard to stability. He said that *'any substance may be brought into a colloidal state, provided the particles of the dispersed phase are so small that the Brownian movement keeps the particles suspended and provided the coagulation of the particles is prevented by a suitable surface film'.*

It was observed that lyophobic sols are stable due to their electric charge. As most of the lyophobic sols are prepared by preferential adsorption of ions, the mutual repulsion of particles is responsible for their stability. The sols become unstable, as soon as they are robbed off their charge. However, in case of lyophilic sols, the stability is due to electric charges as well as solvation—a phenomenon in which the colloid particle is surrounded by a thin film of the solvent. The layer of the solvent forms an envelope around each colloidal particle and thus pre-forms an envelope around each colloidal particle and thus prevents the particles from coming together. Groups like –COOH and $-NH_2$ in proteins and –OH in hydroxides and polysaccharides can bind water molecules. Lyophilic sols are coagulated when first the solvent layer and then the charge of the ion are removed.

Factors Affecting Stability : There are numerous factors which affect the stability of a colloidal system.

(i) Brownian movement : As a result of this movement, the particles are in constant rapid motion, whereby aggregation of particles is prevented. So, the sol remains stable. But as soon as Brownian motion ceases, the sol becomes unstable. It is, therefore, expected that a sol will be more stable, the higher the dispersity and greater the charge on the particles.

(ii) Addition of electrolytes : As described before, a sol becomes unstable by the addition of suitable quantity of electrolytes. It is now established that the presence of electrolytes has a powerful effect on the potential difference between the particles of the dispersed phase and the dispersion medium and that this potential difference is closely connected with the stability of sols.

(iii) Effect of concentration of the sol : Ghosh and Dhar (1927) showed that a number of positively charged sols follow the rule that, greater the concentration of the sol greater the amount of electrolyte required to coagulate the sol. In other words, the greater the concentration of the sol, greater is its stability.

(iv) Effect of dilution : Chaudhury (1928) showed that the dilution of a sol also affects the stability, which is decreased. The reason is that the decrease of the charge and total surface of sol particles with dilution decrease the stability of the sol. Mukherjee (1930) attempted to find out a relation between dilution and stability of a sol by measuring the migration velocity of the particles, but found the relation to be complicated.

(v) Rate of addition of electrolyte : Dhar (1925) showed that the amount of electrolyte required to confer stability on a sol depends upon the rate at which it is added. This phenomenon is known as *'acclimatization of sols'*. There are two types of acclimatizations : in some cases, less electrolyte is required, when it is added slowly or in small quantities at a time, and in other cases, the amount required is more. The former and latter are known as positive and negative acclimatizations, respectively. This phenomenon is probably due to charge occurring in the stabilisation by electrolytes.

(vi) Temperature : It is seen that decrease of temperature confers more stability on the sols. Reid and Burton (1928) showed that heat alone is sufficient to cause coagulation.

(vii) Mechanical agitation : It has been seen that mechanical agitation decreases the stability of sols. Freundlich and Loebmann (1922) showed that the sol of CuO was found to be coagulated by mechanical agitation. The rate of coagulation is proportional to the square of the rate of stirring.

(viii) Ultra-violet light and X-ray radiations : Many lyophobic sols are coagulated by U–V light and *X*-rays or rays even from radiations of radium. It is seen that the coagulation effect of the rays is independent of the sign of the colloid. Lal and Ganguly (1930) studied the coagulating influence of U–V light on sols of AgI, Au, Ag, V_2O_5, $Th(OH)_2$, As_2S_3 etc.

• 4.15. ISOELECTRIC POINT

Isoelectric point is that point at which the concentration of the positive ions in solution becomes equal to that of the negative ions. Similarly, in case of colloidal solutions, a sol may be positively charged in presence of an acid, due to the preferential adsorption of H^+ ions. On the contrary, a sol may be negatively charged in presence of an alkali, due to the preferential adsorption of OH^- ions. However, there must be an intermediate H^+ ion concentration at which the colloidal particles are neither positively nor negatively charged. Hence, the isoelectric point in case of colloidal solution, *is that point at which the colloidal solutions have no charge at all.*

Isoelectric point plays an important part in the stabilization of a sol. The stability of a sol is due to the presence of zeta potential (see subsequent pages) which is zero at the isoelectric point. At this point, the colloidal particles will not move towards any electrode under the influence of electric field. Hardy said that at isoelectric point, the colloidal particles are electrophoretically inert. Isoelectric point also occurs in protein sols. A protein solution is amphoteric. In acidic medium, a protein sol is positively charged, while in an alkaline medium, it is negatively charged. At a certain point or at a certain pH, the particles will have equal positive and negative charges. Different protein sols have different isoelectric points, *e.g.*, isoelectric point for a gelatin sol occurs at pH = 4.7. Below pH 4.7, the colloidal particles of gelatin move towards the cathode, while at pH greater than 4.7 the particles move towards the anode.

• 4.16. EMULSIONS

Emulsions are liquid-liquid colloidal systems. In other words, an emulsion may be defined ***as a dispersion of finely divided liquid droplets in another liquid.***

Generally, one of the two liquids is *water* and the other, which is immiscible is designated as *oil*. Either liquid can constitute the dispersed phase.

(1) Types of Emulsions : There are two kinds of emulsions :

(i) Water in oil type : In it water is the dispersed phase and oil acts as dispersion medium, *e.g.*, butter etc. It is designated by W/O or *w*-in-*o*.

(ii) Oil in water type : In it oil particles form the dispersed phase and water is the dispersion medium, *e.g.*, milk, vanishing creams etc. It is designated by O/W or *o*-in-*w*.

Tests for Types of Emulsion : The two types of emulsions can be experimentally identified in a number of ways, which are as follows :

(i) *Conductivity method :* If the conductivity of the emulsion is large, the emulsion is of O/W type, as these emulsions are more conducting. But if the conductivity is low, it is of W/O type, as they are less conducting.

(ii) *Filter paper method :* In this method, a drop of emulsion is kept on a piece of filter paper. If the liquid spreads easily and readily, leaving a spot at the centre, then the emulsion is of O/W type. In case the emulsion does not spread, the emulsion is of W/O type.

(2) Preparation of Emulsions : Emulsions can be prepared by shaking or stirring the two phases with the addition of a suitable emulsifier. The type of emulsion formed, depends on the angles of contact of the two liquids with the solid emulsifier.

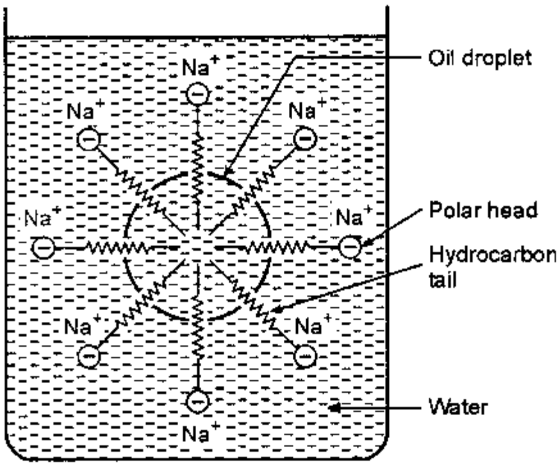


Fig. 11. Role of emulsifier.

The liquid to be dispersed is added in small quantities to the dispersion medium, where it is spread into a thin, unstable film which spontaneously breaks up into droplets under the influence of surface tension. Many emulsifying machines are used, such as homogenizers, in reducing the size of globules.

A condensation method is used to prepare concentrated O/W emulsions. It consists in allowing vapours of oil to pass through an aqueous solution containing an emulsifying agent.

(3) Emulsifiers or Emulsifying Agents: The two types of emulsions *i.e.*, W/O or O/W type, do not remain stable and after sometime, the two layers separate. It means that an emulsion formed by merely shaking two liquids is unstable. But in order to get stable emulsions it is necessary to add a third substance known as *emulsifier* or *emulsifying agent* in suitable small quantity. By adding an emulsifier, a stable emulsion of high concentration can be obtained.

The emulsifiers are generally long chain compounds with polar groups, such as soaps of various kinds, long chain sulphonic acids and alkyl sulphates. The function of an emulsifier is to lower the interfacial tension between the dispersed phase and the dispersion medium so as to facilitate the mixing of the two liquids.

In compounds like soap, the aliphatic portion is soluble in oil, while the end group (sulphonic acid etc.) called a polar group (because its unsymmetrical grouping contributes a dipole moment to the compound) is soluble in water. The soap molecules get concentrated at the interface between water and oil in such a way that their polar end (–COONa) and hydrocarbon chain (R-) dip in water and oil, respectively as shown in figure 11. This allows the two liquids to come in close contact with each other.

Soluble substances like iodine also act as emulsifiers, in the case of ether/water emulsions. Some mixed stabilising agents also act as emulsifiers, *e.g.*, ethyl alcohol and lycopodium powder, acetic acid and lamp black, clay and sodium oleate etc.

(4) Properties of Emulsions : Since an emulsion is a colloidal system of liquid dispersed in liquid, therefore, its properties are common to those of colloidal solutions.

(a) Concentration and size of the particle : In an emulsion, the amount of solid substance dissolved is very small as compared to that of the dispersion medium. An emulsion contains droplets of diameter 0.008–0.05 mm.

(b) Electrical conductivity : It has been found that emulsions of O/W type are characterised by higher electrical conductivity, while emulsions of W/O type have a lower or no electrical conductivity.

(c) Electrophoresis : Like colloidal particles, the droplets of emulsion are also electrically charged. Hence, they migrate towards the oppositely charged electrode under the influence of electric current.

(d) Dilution : On increasing the amount of dispersion medium, a separate layer is formed.

(e) Brownian motion : Just like colloidal particles, droplets of emulsion are also in a state of constant rapid zig-zag motion.

(f) Optical properties : Droplets of emulsion scatter light to different extent, depending upon their size.

(5) Reversal of Phase : The change of an emulsion of O/W type to W/O type or vice-versa is known as *'reversal of phase'*. An O/W emulsion, *e.g.*, olive oil in water, containing a sodium or potassium soap as emulsifying agent, may be converted into W/O type by the addition of salts of bivalent or trivalent cations.

(6) Breaking of Emulsions : Emulsions can be broken or demulsified to get the constituent liquids by heating, freezing, centrifuging or by addition of appreciable amounts of electrolytes. They are also broken by destroying the emulsifier. For example, an oil-water emulsion stabilised by soap is broken by the addition of a strong acid. The acid converts soap into insoluble free fatty acids.

(7) Uses of Emulsions : Emulsions find numerous applications in daily life, medicine, industry and cosmetics. They may be described as follows :

Daily articles of life : Milk is an emulsion of fat dispersed in water stabilised by casein and as all know is practically a complete food. Ice cream. is an emulsion, in which ice particles are dispersed in cream, stabilised by gelatin. Artificial beverages, coffee, fruit jellies are all emulsions in nature. The cleansing action of ordinary soap is due to a large extent on the production of O/W emulsion.

A number of medicines and pharmaceutical preparations are emulsions in nature. It is assumed that in this form, they are more effective. Cod-liver oil, castor oil, petroleum oil are used as medicines which are all emulsions. Asphalt emulsified in water is used for building roads, without the necessity of melting the asphalt. Most of the cosmetics used are emulsions as they permit uniform spreading and promoting the penetration into the skin. Vanishing cream is an O/W type emulsion. Hair creams, cold creams are W/O type emulsions.

A variety of emulsions of oils and fats are used in leather industry to make leather soft and pliable and also to make it waterproof. Emulsions are also used in oil and fat industry, paints and varnishes, plastic industry, adhesives, cellulose and paper industry etc.

• 4.17. ELECTRICAL DOUBLE LAYER OR ZETA POTENTIAL

In order to explain the origin of charge on a colloidal particle, von Helmholtz postulated the existence of an electrical double layer of opposite charge at the surface of separation between a solid and liquid, *i.e.*, at solid liquid interface.

According to modern views, when a solid is in contact with a liquid, a double layer appears at the surface of separation. One part of the double layer is fixed on the surface of the solid. It is known as ***fixed part*** of the double layer and it consists of either negative or positive ions. The second part of the double layer consists of a ***mobile*** or ***diffuse*** layer of ions which extends into the liquid phase. This layer consists of ions of both the charges but the net charge is equal and opposite to that on the fixed part of the double layer. This arrangement is shown in figure (12). In figure (a), the fixed part of the double layer comprises of positive charges, while in figure (b), the fixed part of the double layer consists of negative charges.

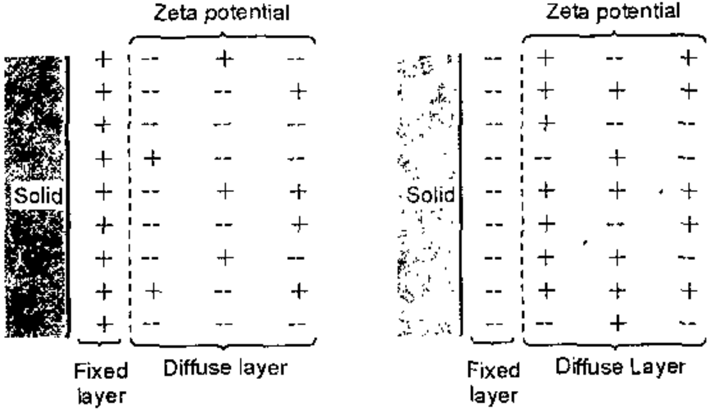


Fig. 12. Electrical double layer.

The presence of charges of opposite signs on the fixed and diffuse parts of the double layer produces a potential between the two layers. This potential is known as **electrokinetic potential** or **zeta potential.** It is represented by ζ(zeta). It is therefore the electromotive force which is developed between the fixed layer and the dispersion medium.

The ions which are preferentially adsorbed by the sol particles, are held in the fixed part of the double layer. It is these ions which give the characteristic charge to the sol particles.

It is supposed that ***the charge on a colloidal particle is due to the preferential adsorption of either positive or negative ions on the particle surface.*** If the particles have a preference to adsorb negative ions they acquire negative charge or vice-versa. The negative charge on As_2S_3 sol is due to the preferential adsorption of sulphide ions on the particle surface. The sulphide ions are given by the ionisation of hydrogen sulphide, which is present in traces. Similarly, the negative charge on metal sol particles obtained by Bredig's method is due to the preferential adsorption of hydroxyl ions given by the traces of alkali present. The positive charge on sol of $Fe(OH)_3$ prepared by the hydrolysis of ferric chloride is due to the preferential adsorption of ferric ions on the surface of the particles. The ferric ions are obtained by the dissociation of ferric chloride present in traces in the sol.

From the above, it is clear that the ion which is more nearly related chemically to the colloidal particle is preferentially adsorbed by it. So, in As_2S_3 sol, sulphide and not hydrogen ion is preferred and in $Fe(OH)_3$ sol, ferric and not chloride ion is preferred as shown below :

$$[As_2S_3]S^{2-} \mid 2H^+ \text{ and } [Fe(OH)_3]Fe^{3+} \mid 3Cl^-$$

Now consider stannic oxide sol. If a freshly prepared precipitate of stannic oxide is peptised by a small amount of HCl, the colloidal solution carries a positive charge. If the precipitate is peptised by a small amount of NaOH, the colloidal solution carries a negative charge. In the first type of sol, a small amount of stannic chloride $SnCl_4$ is formed and Sn^{4+} ion is preferred over Cl^- ion. So, the sol gets ***positively charged.*** In the second type of sol, a small amount of sodium stannate Na_2SnO_3 is formed and now the SnO_3^{2-} ion is preferred over Na^+ ions. So, the sol gets ***negatively charged.*** The structure of the sol particles in the two cases can be represented as :

Positive sol : $[SnO_2]\, Sn^{4+} \mid 4Cl^-$

Negative sol : $[SnO_2]\, SnO_3^{2-} \mid 2Na^+$

The chloride and sodium ions form the diffuse part of the electrical double layer.

Another case is the formation of positively and negatively charged sols of silver iodide. If a dilute solution of $AgNO_3$ is added to a slight excess of KI solution, a negative sol of AgI is obtained, due to the adsorption of iodide ions. The structure of the particles is represented as $[AgI]\, I^- / K^+$. If a dilute solution of KI is added to a slight excess of $AgNO_3$ solution, a positive sol of AgI is obtained, due to the adsorption of silver ions. The structure of the particle is shown as $[AgI]Ag^+ / NO_3^-$. If on the contrary, equivalent amounts of $AgNO_3$ and KI are mixed, there is complete precipitation of silver iodide and no sol is formed.

• 4.18. ORIGIN OF CHARGE

All the dispersed particles of a sol carry a positive or negative charge. In order to explain the origin of charge on a colloidal particle, following views have been given.

(i) ***Charge is ionic in nature :*** It has been shown that colloids, ***e.g.***, sodium palmitate and soap dissociate and produce ions. So, the charge is produced as a result of the formation of ions. But this view does not hold good for non-electrolytic colloids such as clay, smoke etc. as they also carry a charge.

(ii) Charge is frictional in nature : In earlier days, it was regarded that the source of the charge on colloid particles is essentially physical and it was suggested that the charge resembled the frictional electricity brought about by the contact of such substances as glass and silk in this case, substance with higher dielectric constant will render the sol negatively charged.

(iii) Association of electrolytes : It has been observed that small quantities of electrolytes are associated with colloidal systems and that if they are removed by persistent dialysis or by other methods, the sols become unstable and the particles grow in size and are finally precipitated. It is probable that in many cases, traces of ions present in the sol are responsible for the charge and the stability of colloidal particles. It is seen that stable sols of gold, silver etc. can be obtained by Bredig's arc method by passing an electric current between electrodes of the metals under water. Water contains a little KOH or any other alkali. One ion is retained by the colloidal particles, giving the same charge to the colloidal particles and the other ion is retained by the dispersion medium.

(iv) Formation of electrical double layer : See proceding article.

Significance of charge : The charge on a colloidal particle is of great importance as shown below.

(i) In industrial applications of colloids : A number of processes like electro-deposition of rubber, removal of smoke, purification of water, tanning of leather depend upon the presence of charge on a colloidal particle.

(ii) In stability of sols : As all colloidal particles have the same charge, they are kept apart due to mutual repulsions and so they do not coalesce with one another to form bigger particles. If the charge is removed, they come closer together and get coagulated.

• 4.19. APPLICATIONS OF COLLOIDS

The applications of colloids can broadly be divided into three types :

(i) *Natural applications,*
(ii) *Technical applications,*
(iii) *Analytical applications.*

[A] Natural Applications :

(i) ***Rain :*** Cloud is a colloidal system in which water particles are distributed in air. When air which has become saturated with water vapours, reaches the cooler parts of the atmosphere, cloud is formed as a result of condensation. Further cooling and condensation form bigger drops of water which fall due to gravity in the form of rain.

(ii) ***Blood :*** Blood is a colloidal system, having albuminoid substance as the dispersed phase carrying a negative charge. The stoppage of bleeding by the application of alum or ferric chloride can be explained on the basis of coagulation, as in this case Al^{3+} acts as active ion for the coagulation of negatively charged albuminoid particles.

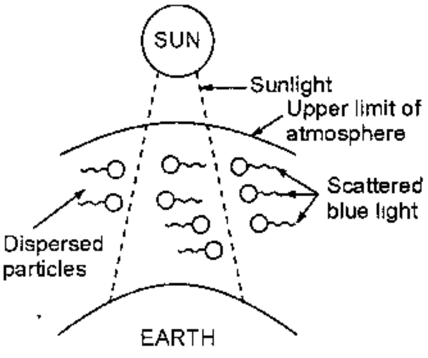


Fig. 13. Blue colour of the sky.

(iii) ***Blue colour of the sky :*** This is an application of Tyndall effect. The upper atmosphere contains colloidal dust or ice particles dispersed in air. As the sun rays enter the atmosphere [Fig. (13)], these strike the colloidal particles. They absorb sunlight and scatter light of blue colour (4600–5100 Å). The light that is incident at earth's surface is considerably reddened due to the removal of most of the blue light in the upper atmosphere (figure 13).

(iv) ***Articles of daily use :*** Milk which is a complete food is an emulsion of oil in water (O/W) type stabilised by casein. Butter is an emulsion of water dispersed in fat (O/W) type. Fruit juice is a colloidal system having juice dispersed in the solid tissue of the fruit. Ice cream is ice particles dispersed in cream.

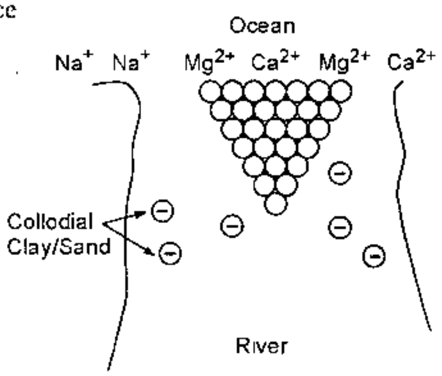


Fig. 14. Formation of delta.

(v) ***Formation of deltas :*** The river water contains colloidal particles of sand and clay which carry negative charge. The sea water on the other hand, contains positive ions such as Na^+, Mg^{2+}, Ca^{2+}. As the river water meets sea water, these ions coagulate the sand or clay particles which are precipitated as ***delta*** [Fig. (14)].

[B] Technical Applications : These are numerous technical applications of colloids, but we shall explain only the important ones.

(i) ***Rubber industry :*** Rubber is obtained from the sap of certain trees. The sap—also known as latex—is a colloidal system of colloidal particles dispersed in water, stabilised by protein contents. On coagulating the latex by various methods, colloidal gel, known as rubber is obtained.

The rubber particles carry a negative charge. When rubber is to be deposited on any material, then two electrodes are made. The anode is made of that substance on which rubber has to be deposited. On passing an electric current, rubber thus deposits on the substance.

(ii) ***Tanning of leather :*** Both hide and leather are colloidal substances and possess gel structures. When hide is soaked in any tanning agent which consists of tannin (a sol containing negatively charged particles), mutual coagulation of the two takes place due to oppostie charges. This process is known as *tanning* and the hide becomes more and more leather like, imparting hardness to it.

(iii) ***Soils and clays :*** The value of a **soil**, *i.e.*, its ability to retain moisture is dependent on the colloidal properties of ***humus***—an important constituent of the soil. When soil is completely saturated with H^+ ions, it is known as *'clayic acid'* and the salts derived from this acid are known as *'clayates'*. There are colloids, *e.g.*, $Fe(OH)_3$, $Al(OH)_3$, amorphous silicates and bacteria which are present in soils.

(iv) ***Purification of sewage and water :*** Sewage consists of impure particles dispersed in water and is thus colloidal in nature, carrying a negative charge. The dirt particles carrying a negative charge are coagulated on the oppositely charged positive electrode and are thus removed. The deposit is then used as manure. The method for sewage purification is known as *'activated sludge process'*.

(v) ***Photography :*** Photographic plates are thin glass plates coated with a fine suspension of silver bromide and gelatin. Silver bromide dispersed in gelatin gel forms photographic emulsion. The AgBr sol may be produced by mixing gelatin solution containing dilute solution of $AgNO_3$ with dilute alkali bromide, whereby insoluble AgBr is formed in a fine suspension, stabilised by gelatin which is then painted on thin glass plates.

(vi) Metallurgy of alloys : The technical property of an alloy depends upon the size of the subdivided particles in it. Thus, alloys which are brittle and non-elastic have a coarse structure. As the degree of dispersion is increased, the hardness of the alloy is also increased.

(vii) Colours of various materials : The colour of various materials is due to colloid metal and colloid metallic compound. The red colour of ruby glass is due to colloidal gold. Yellow glass owes its colour to colloidal silver. Colloidal chromium imparts colour to artificial rubies.

(viii) Dyeing : Cotton, silk and wool are all colloidal in nature having a gel structure. The dyestuffs include a number of substances having different properties; their degree of dispersion is colloidal.

(ix) Smoke and fumes precipitation : Smoke is a system in which carbon particles are dispersed in air carrying a negative charge. In large industrial cities smoke comes out from the chimney and the carbon particles present in it are very injurious to human health. So, to remove carbon particles, use is made of *'Cottrell electrical precipitator'* [Fig. (15)] in which the smoke is made to pass through a positively charged anode in the chimney, when carbon particles settle down. According to a modern method, the smoke is led to a chamber fitted with a metallic knob charged to a very high *positive potential (50,000 volts). The gases free from smoke,* pass from the top of the chimney.

(x) Medicines : Most of the medicines which are used, are colloidal and are effective due to their easy assimilation and absorption by the human system. *Colloidal antimony* is effective in curing kalazar. *Colloidal sulphur* is effective in curing skin diseases and in killing germs. *Colloidal calcium* and *gold* are used as intramuscular injections to increase the vitality of human system in serious diseases. *Colloidal silver or argyrol* is used for curing granulations. *Milk of magnesia*, an emulsion, is used for stomach troubles.

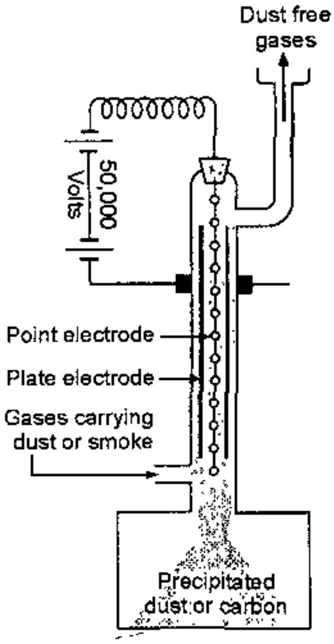


Fig. 15. Cottrell precipitator.

[C] Analytical Applications :

(i) Qualitative and quantitative analysis : A knowledge of the behaviour of colloids and their mode of formation play an important role in analytical problems.

In volumetric analysis, hydrophilic colloids alter the end point, *e.g.*, in a titration of HCl and NaOH, the amount of deviation in the end point is increased with increasing amounts of colloids. In the volumetric estimation of silver by Mohr's method, the phenomenon of adsorption comes into being.

In gravimetric analysis, definite crystalline precipitates are desired and the procedure thus adopted aims to get sufficiently bigger particles, because extremely small particles may pass through the filter paper. To prevent adsorption of the undesirable molecules with the desired precipitate, it is necessary to precipitate the solution at the boiling point and fairly dilute solution should be used.

(ii) Detection of natural from artificial honey : Ley's test for detecting the natural honey from artificial honey consists in treating few drops of the honey with an ammoniacal silver salt solution. If the honey is natural or pure, then the metallic silver produced assumes a reddish yellow colour due to the traces of albumin or ethereal oils, which act as protective colloids and maintain the colloidal silver in a high degree of dispersion. A dark yellow or greenish precipitate is formed with artificial honey.

(iii) Identification of traces of noble metals : Noble metals when present in the colloidal form produce very bright and intense colours. Cassius purple test indicates the presence of colloidal gold.

• SUMMARY

- The process of converting a fresh precipitate into colloidal state by means of an electrolyte is called peptisation.
- Dialysis is a procss of purification of colloidal solutions from crystalloids by means of a parchment paper or an animal membrane.
- A colloidal solution is a system in which the dispersed phase is solid and dispersion medium is liquid.

- A substance which passes into colloidal state simply by bringing it in contact with water is called a hydrophilic colloid, *e.g.*, gum.
- A substance which cannot pass into colloidal state by bringing it in contact with water is called a hydrophobic colloid, *e.g.*, colloidal solution of gold.
- **Tyndall effect :** When a beam of light is passed through a colloidal solution, the path of the *light becomes illuminated. This phenomenon is known as Tyndall effect.*
- **Brownian motion :** The continuous rapid zig-zag motion executed by the colloidal particles in a dispersion medium is known as Brownian motion.
- **Electrophoresis :** The movement of colloidal particles towards the oppositely charged electrodes under the influence of electric field is known as electrophoresis.
- **Electro-osmosis :** The movement of the dispersion medium under he influence of applied potential is known as electro-osmosis.
- **Coagulation :** *The process by means of which the particle of the dispersed phase in a sol is* precipitated by an electrolyte is known as coagulation.
- **Hardy-Schulze law :** Greater the valency of the active ion, greater is the coagulating power of the active ion.
- **Protection :** The property of lyophilic colloidal solution to prevent the coagulation of a lyophobic colloidal solution is called protection.
- **Gold number :** It is the number of milligrams of a protective colloid which just stops the coagulation of 10 ml of a given gold colloidal solution on adding 1 ml of 10% sodium chloride solution.
- **Emulsion :** A dispersion of finely divided liquid droplets in another liquid is known as an emulsion. It is of two types, *viz.*, oil-in-water type and water-in-oil type emulsions.
- The third substance added to an emulsion to stabilise it. is known as an emulsifier.

• STUDENT ACTIVITY

1. Write a short note on peptisation.

2. Describe one method for the purification of colloidal solutions.

3. What is an emulsion ? Mention the role of an emulsifier.

4. Write a note on gold number.

5. State and explain Hardy-Schulze law.

6. Write a short note on Tyndall effect.

• TEST YOURSELF

Answer the following questions :

1. Explain the terms colloidal state and colloidal solution.
2. Define dispersed phase and dispersion medium.
3. Describe the methods for the preparation of colloidal solutions.
4. Write a short note on peptisation.
5. Mention the methods for the purification of colloidal solutions.
6. Give five differences between a true solution and colloidal solution.
7. Explain the types of colloidal systems with examples.
8. How will you prepare the colloidal solutions of the following ?
(i) Arsenious sulphide (ii) Gold (iii) Ferric hydroxide (iv) Sulphur
9. Write a note on lyophilic and lyophobic colloids.
10. Write short notes on the following :
(i) Tyandall effect (ii) Brownian motion (iii) Electrophoresis
(iv) Electro-osmosis (v) Dialysis (vi) Ultramicroscope
11. State and explain coagulation.
12. State and explain Hardy-Schulze law.
13. Define isoelectric point.
14. What is an emulsion ? Describe the types of emulsions.
15. Give the methods of preparing emulsions. Discuss the properties of emulsions.
16. Write a note on electrical double layer.
17. Describe the applications of colloids.
18. Discuss the origin of charge on the colloidal particle. Explain its significance also.
19. Classify the following sols according to their charge :
(i) Gold (ii) Ferric hydroxide (iii) Gelatin (iv) Blood
(v) Sulphur (vi) As_2S_3
20. What will be the charge on the following ?
(i) AgI in $AgNO_3$ (ii) AgI in KI
(iii) As_2S_3 in H_2S (iv) $Fe(OH)_3$ in $FeCl_3$
21. Explain the following facts :
(a) A sulphur sol is coagulated by adding a little electrolyte, whereas a gelatin sol is apparently unaffected.
(b) What happens when a colloidal solution of gold is brought under the influence of electric field?
(c) What happens when an electrolyte is added to colloidal v\solution of gold ?
(d) What happens when a beam of light is passed throught a colloidal solution of gold ?
(e) A colloidal solution is stabilised by addition of gelatin.
(f) Presence of H_2S is essential in As_2S_3 sol though H_2S ionises and should precipitate the sol.
(g) Why ferric chloride or alum is used for stoppage of bleeding ?
22. The following will have the maximum coagulating power :
(a) Na^+ (b) Sn^{4+} (c) Ba^{2+} (d) Al^{3+}.

23. Milk is :
(a) Gel (b) Sol (c) Aerosol (d) Emulsion

24. The size of colloid particles is :
(a) $> 0.1\ \mu$ (b) $1\ m\mu - 0.1\ \mu$ (c) $> 1\ m\mu$ (d) $> 5000\ m\mu$

25. A freshly prepared precipitate of SnO_2 peptised by HCl will carry the following charge :
(a) Neutral (b) Positive (c) Negative (d) Amphoteric

26. Every colloid system is :
(a) Homogeneous (b) Heterogeneous
(c) Contains one phase (d) Homogeneous and heterogeneous both.

27. The following is a hydrophobic colloid :
(a) Gelatin (b) Gum (c) Starch (d) Sulphur

28. Gold sol prepared by different methods will have different colours. It is due to :
(a) Difference in size of colloid particles (b) Gold shows variable valency
(c) Different concentrations of gold (d) Presence of impurities.

29. Following is an emulsifier :
(a) Oil (b) Water (c) NaCl (d) Soap

30. The sky appears blue. It is due to :
(a) Reflection (b) Absorption (c) Scattering (d) Refraction

31. Which of the following reaction will give colloidal solution :
(a) $Cu + HgCl_2 \rightarrow Hg + CuCl_2$ (b) $Cu + CuCl_2 \rightarrow Cu_2Cl_2$
(c) $2Mg + CO_2 \rightarrow 2MgO + C$ (d) $2HNO_3 + 3H_2S \rightarrow 3S + 4H_2O + 2NO$

32. Fat is :
(a) Emulsion (b) Gel (c) Colloidal solution (d) Solid sol

33. Colloidal solutions cannot be purified by :
(a) Dialysis (b) Electrodialysis
(c) Ultrafiltration (d) Electrophoresis

34. The charge on As_2S_3 sol is due to the adsorption of :
(a) H^+ (b) OH^- (c) S^{2-} (d) O_2^-

35. Surface tension of lyophilic sols is :
(a) Lower than water (b) More than water (c) Equal to water
(d) Sometimes lower and sometimes more than water

36. On addition of 1.0 ml of 10% NaCl to 10 ml gold sol in the presence of 0.0250 gm of starch, the coagulation is just stopped. The gold number of starch is :
(a) 0.025 (b) 2.5 (c) 2.5 (d) 25.0

37. Which of the following is a lyophilic colloid?
(a) Milk (b) Fog (c) Blood (d) Gelatin

38. Fill in the blanks
(i) True solutions are .... systems.
(ii) In a colloidal system .... phases are present.
(iii) In aerosol .... is the dispersed phase and .... is the dispersion medium.
(iv) Hair cream is an example of .... system.
(v) The process of converting a fresh precipitate into a colloidal solution is known as ....
(vi) Tyndall effect is due to the .... of light.
(vii) The precipitating effect of an ion in dispersed phase of opposite charge .... with the valence of the ion
(viii) Breaking of emulsions is also known as ....
(ix) The emulsifier in milk is ....
(x) Formation of deltas is an example of ....

ANSWERS

21. (a) A sulphur sol consists of negatively charged particles dispersed in water. When an electrolyte is added to it, the sol being lyophobic in nature is easily coagulated.

On the other hand, gelatin sol is lyophilic in nature and gelatin particles are heavily hydrated and so water envelopes around them and prevents their coming in contact with the electrolyte. Hence, it is not easily coagulated on addition of electrolyte.

(b) When colloidal gold solution is brought under electric field, the gold particles move towards anode and lose their charge and get coagulated. This shows that gold particles carry a negative charge (*electrophoresis*).

(c) When an electrolyte is added to gold sol, the cation of the electrolyte neutralises the negative charge on the colloidal particles and the sol gets coagulated.

(d) When a beam of light is passed through a colloidal solution, the path of the light becomes visible when viewed through an ultramicroscope, due to scattering of light by colloidal particles (**Tyndall effect**).

(e) A colloidal solution is stabilised by the addition of gelatin. This is due to the fact that gelatin being a lyophilic colloid forms a protective layer around the colloidal particles. Thus protective layer prevents the precipitating ions from reaching the sol particles and in this way they are prevented from being precipitated.

(f) According to modern view, at the surface of separation of solid and liquid, an electrical double layer is formed. One of the layer is called fixed layer which points towards the particle and the other layer called the mobile layer points towards the dispersion medium. The fixed layer contains the ions of one charge, either positive or negative and those ions are preferentially adsorbed which are chemically alike. So, to stabilise As_2S_3 sol, S^{2-} ions given by H_2S form the fixed layer, thus giving negative charge to As_2S_3 particle, *i.e.*, $[As_2S_3]S^{2-}| 2H^+$. Thus, because of the same charge, As_2S_3 particles do not come closer to get coagulated. So, unlike other electrolytes. H_2S stabilises As_2S_3 sol.

(g) Blood is a negatively charged sol in which albuminoid substance is dispersed in water. When $FeCl_3$ or alum is added, the trivalent ions, Fe^{3+} or Al^{3+} coagulate the blood. Thus, bleeding is stopped.

22 (b), **23.** (d), **24** (b), **25** (b), **26** (b), **27** (d), **28** (a), **29.** (d),
30. (c), **31.** (d) **32.** (a) **33.** (d) **34.** (c), **35.** (a), **36.** (d), **37.** (d),

40. **(i)** homogeneous **(ii)** two **(iii)** liquid, solid
(iv) emulsion **(v)** peptisation **(vi)** scattering
(vii) increases **(viii)** demulsification **(ix)** casein **(x)** coagulation

UNIT

5

LIQUID STATE

LEARNING OBJECTIVES

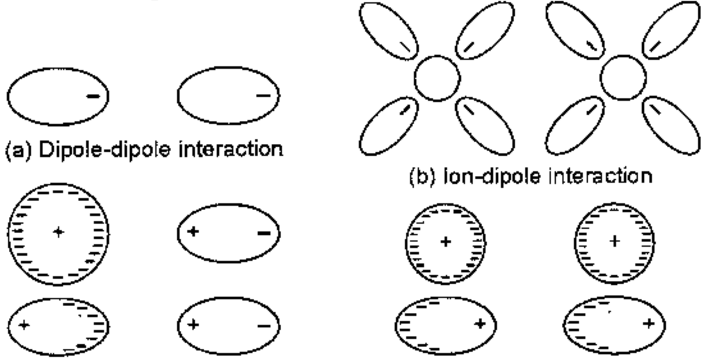
- Intermolecular Forces in Liquids
- Structure of Liquids
- Structural Differences Between Solids, Liquids and Gases
- Liquid Crystals
- Differences Between Liquid, Liquid Crystal and Solid
- Thermography
  - ☐ Summary
  - ☐ Student Activity
  - ☐ Test Yourself

• 5.1. INTERMOLECULAR FORCES IN LIQUID

The forces of attraction between molecules are known as inter-molecular forces or vander Waals forces. These are short range forces and are weak in comparison to chemical bonds. They are responsible for several important attractions between electrically neutral molecules. These forces are responsible for holding the molecules of the liquid in a given space. In liquids, the following main inter-molecular forces work :

(1) Dipole-dipole forces : Polar molecules align themselves so that the positive end of one molecule attracts the negative end of another molecule and so on. Such interactions are known as dipole-dipole interactions and the forces causing these interactions are known as **dipole-dipole forces**. If these forces are considerable, the liquid has a high boiling point and in case of a solid, it has a high melting point.

(2) Ion-dipole forces : We know that ions have great tendency to attract polar molecules. The positive ion attracts the negative pole and the negative ion attracts the positive pole of the polar molecule. Such an interaction is known as ion-dipole interaction and the forces causing these interactions are known as **ion-dipole forces**.



(a) Dipole-dipole interaction

(b) Ion-dipole interaction

(c) Dipole-induced dipole interaction

(d) Instantaneous dipole-induced dipole interaction

Fig. 1. Principal intermolecular forces.

(3) Dipole-induced dipole forces : When permanent polar molecules approach neutral molecules their positive poles attract the electron cloud of the neutral molecules causing distortion. The neutral molecules become polarised and are said to have induced dipoles. The forces causing these interactions are known as **dipole-induced dipole forces**.

(4) London forces : The electrons are in constant motion and so the charge distribution of a neutral molecule fluctuates. At any given time, a molecule may act as an instantaneous dipole, inducing a dipole effect in a nearby molecule. This generates an attraction between the instantaneous dipole and the induced dipole. These attractions are known as ***London forces*** (given by Fritz London, 1930). They occur in all atoms and molecules, both polar and non-polar. London forces are weaker than dipole-dipole forces and their strength increases as the number of electrons in the atom or molecule increases.

London forces are short-range forces as the attraction energy, known as London energy varies inversely as the sixth power of distance between the molecules. (The intermolecular energy of attraction involved in continuous generation of dipoles and their subsequent decay is known as London energy).

$$\text{London energy} = -\frac{d}{r^6}$$

where r = distance between the molecules and d = constant.

(5) Hydrogen bonding : When a hydrogen atom is covalently bonded to a small strongly electronegative atom, a highly polar molecule is formed. A sufficient positive charge is acquired by the hydrogen end of such a molecule to attract and form a hydrogen bond with a nearby electronegative atom. The hydrogen atom may not be involved in such bonding, there may be any other atom capable of attracting bonded electrons towards itself to produce dipole. The strongest bonds are formed between H and F, N or O. Intermolecular hydrogen bonding occurs between two different molecules, whereas intramolecular hydrogen bonding occurs between atoms or groups within the same molecule. Hydrogen bonding is stronger than dipole-dipole forces and contributes mainly to the inter-molecular forces in liquids. It is the characteristic property of several liquids.

• 5.2. STRUCTURE OF LIQUIDS

On cooling a gas sufficiently, it condenses into liquid state, which when further cooled turns into solid state. The volume occupied by a liquid is much less (upto nearly 0·001) than that in the gaseous state. So, liquids and solids are regarded as condensed states of matter.

A liquid state lies between the gaseous and the solid states, because there is neither the complete disorder and free random motion as in gases nor the rigid and well-ordered arrangement and total absence of free translational motion of molecules as in solids.

In liquids, the average inter-molecular distance is much smaller than in case of gases, so that the inter-molecular force of attraction is upto 10^6 times as strong as in gases. The inter-molecular forces between liquid molecules are strong enough to prevent free random motion but not strong enough to prevent the displacement within the boundaries of the liquid surface, *i.e.*, the position of molecules in liquids are not rigidly fixed.

The molecules of liquid are in a state of constant random motion, but the motion is much smaller as compared to gaseous molecules. Much of the space in a liquid is occupied by molecules with only a small fraction of space being available for free motion. This leads to higher density, little compressibility and slower rate of diffusion than that of gases.

The average kinetic energy of liquid molecules is proportional to absolute temperature. An increase of temperature increases the kinetic energy and the distance between the molecules. This lowers the inter-molecular forces of attraction. When the kinetic energy of molecules, due to rise in temperature is sufficient enough to overcome the attractive forces completely, the liquid structure breaks down to free the molecules which assumes the gaseous form. This temperature is known as ***boiling point of the liquid.***

A crystal expands only about 10% in volume on melting, which means only about 3% increase in inter-molecular spacing. So, the ordered arrangement of crystal is not completely destroyed on melting. The increased kinetic energy only introduces a disorder all over the crystal making free motion possible to some extent. Therefore, the liquid may be considered to have a semi-crystalline structure extending over short ranges and disorder over long ranges. The *X*-ray diffraction study of liquids conform the short range crystalline structure. If liquids were completely disordered, the scattering pattern of *X*-rays would have been continuous without any maxima or minima. However, the pattern shows a few maxima and minima which shows the presence of regular patterns of orderly arrangement in liquids also.

• 5.3. STRUCTURAL DIFFERENCES BETWEEN SOLIDS, LIQUIDS AND GASES

Of the three states of matter, the solid state in crystalline form shows a complete ordered arrangement of molecules, atoms or ions as the case may be and the gaseous state at high temperature and low pressure shows complete randomness or disorder. The liquid state lies in between these two extremes of order and disorder. Fig. (2) shows a two dimensional picture of the three states of matter.

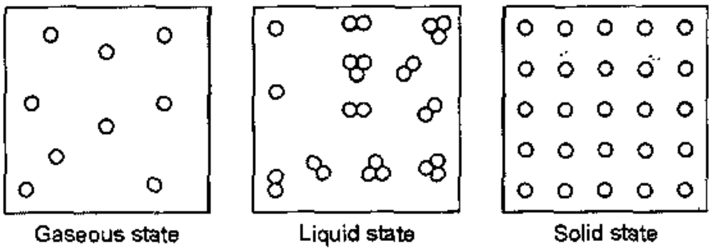


Fig. 2. Two dimensional arrangement of molecules in gases, liquids and crysalline solids.

In solids, there is a close packing of molecules, atoms or ions. This arrangement exists to some extent in the liquid state. In gases, there is no such arrangement of close packing of molecules or atoms which are taken to be like spheres.

The definite and ordered arrangement *of the constituents of a solid extends over a large* distance. This is known as **long range order**. The liquids show only a **short range order,** while gases show no order at all.

A liquid may be taken to be a condensed gas or a molten solid. In solids, the molecules are rigidly fixed and so it has a definite shape and a definite volume. In a gas, the molecules have random motion and so it has neither a definite shape nor a definite volume. *In a liquid, the molecules* are not as rigidly fixed as in solids. The molecules in liquid state have some freedom of motion which, however, is much more restricted than that in gases. Therefore, a liquid has a definite volume but indefinite shape. It is much less compressible and far denser than a gas.

The molecules in a liquid are not far apart from one another, so the inter-molecular forces are fairly strong. The characteristic properties of liquids arise from the nature and magnitude of these intermolecular forces.

• 5.4. LIQUID CRYSTALS

Most liquids are *isotropic, i.e.,* their optical, mechanical, electrical and magnetic properties have the same value in every direction in the liquid. Crystalline solids, except those belonging to the cubic system of crystals, are *anisotropic, i.e.,* the above physical properties or some of them vary in magnitude according to the direction of the crystal. The most common observed sign of anisotropy is double refraction, which is found in six out of seven crystal systems. Only cubic *crystals have the same refractive index in every direction.*

Reinitzer (1888) observed that cholesteryl benzoate ($C_6H_5COOC_{27}H_{45}$) and some other substances melt first to a milky liquid, which suddenly becomes clear at a definite temperature above the melting point. They first fuse sharply yielding turbid liquids and then equally sharply at a higher temperature giving clear liquids. These changes are exactly reversed on cooling at the same temperature. *Cholesteryl benzoate fuses sharply at 145°C to give a turbid liquid* which on further heating changes suddenly into a clear state at 178°C. The above changes are reversed on cooling. The clear liquid when cooled first changes into turbid state at 178°C and then into solid state at 145°C. Lehmann found that these milky liquids are double refracting. Now a number of organic compounds are known which melt first to a doubly refracting liquid, often called a ***crystalline liquid*** or ***liquid crystal.*** *The liquid crystal changes sharply to a clear isotropic liquid at higher* temperature. Some substances show 2, 3 or even 4 different liquid crystalline forms, with definite transition temperatures between them.

The first temperature at which solid changes into turbid liquid is known as ***transition point*** and the second temperature at which turbid liquid changes into clear liquid is known as ***melting point.*** *The changes are generally represented as :*

$$p\text{-Cholesteryl benzoate} \overset{145°\text{C}}{\rightleftharpoons} \underset{\text{(Liquid state; Mesomorphic state)}}{p\text{-Chloresteryl benzoate}}$$

$$\overset{178°\text{C}}{\rightleftharpoons} \underset{\text{(Liquid)}}{p\text{-Cholesteryl benzoate}}$$

The substances showing liquid crystal character are highly stable and do not decompose on heating.

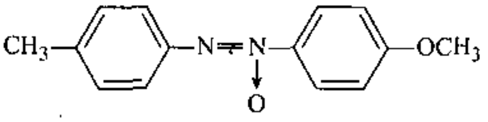
[I] Types and Structures of Liquid Crystals

Friedel introduced the terms *mesomorphic state, mesoform* or *mesophase* to show that liquid crystals are intermediate between solid crystals and isotropic liquids. He showed that they fall into three categories : (i) *Nematic* (ii) *Smectic* (iii) *Cholesteric.*

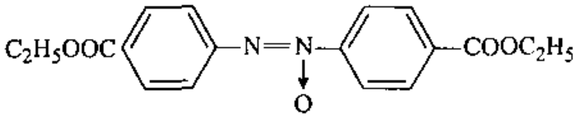
(i) Nematic liquid crystals : Nematic or thread like liquids were given the name because mobile threads are often visible in them. *X*-ray diffraction shows diffuse halos very similar to those found in the isotropic liquids and in the same positions but somewhat sharper, indicating that the ordered regions are larger, or better ordered or both. There is no sign of a layer like structure, but it is assumed that the molecules are aggregated into swarms with the long axes of the molecules parallel or nearly so, as shown in figure 3 (b). The anisotropy involves a pronounced tendency for the molecules to be parallel in group swarms. The application of quite small electric or magnetic fields orients the swarms in the same direction. The electric dipole moment of a nematic swarm is about 10^5 times that of a single molecule, indicating that the number of molecules in the swarm is of the order of 10^5. The nematic liquids lose their turbidity, becoming clear, when the swarms are oriented in an electric or magnetic field. Near the solid surface, the swarms tend to orient themselves at the same angle to the surface, producing an oriented layer of molecules in the liquid.

Fig. 3

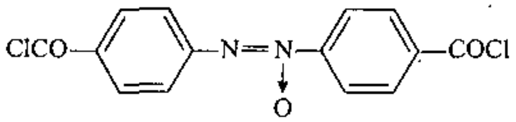
The anomalous viscosity is found in nematic liquids, the flow of nematic liquids is very similar to that of isotropic liquids. The examples of nematic liquid crystals are a number of rather elongated aromatic molecules, especially those containing the azoxy group, *e.g.*, *p*-azoxyanisole, is not a liquid crystal, showing that quite fine details of arrangement of attractive groups are important in deciding whether the liquid is isotropic or doubly refracting.



and ethyl *p*-azoxybenzoate,



are isotropic, but the corresponding acid chloride is not.



(ii) Smectic liquid crystals : Smetic state is shown by common soaps at high temperatures (≈ 200°C) or in presence of water and so the name given to this phase. *i.e.*, smectic means soap like.

Smectic liquid crystals do not flow as normal liquids but they flow in layers. The layers can slide over one another, because of weak forces of attraction. The smetic state is more ordered than the nematic type, because it has an additional one-dimensional translational order. In compounds where both states exist, smectic state occurs at a lower temperature.

Certain cases are known in which the crystalline solid passes through one smetic phase before being changed into the liquid. The temperature of transition from one phase to another is also fixed. For example, cholesteryl myristate has two mesomorphic phases, before it is changed into the liquid.

$$\text{Crystal} \xrightleftharpoons{78°\text{C}} \text{Mesophase I} \xrightleftharpoons{78°\text{C}} \text{Mesophase II} \xrightleftharpoons{83°\text{C}} \text{Liquid}$$

On cooling, the above changes are exactly reversed.

(iii) Cholesteryl liquid crystals : Some liquid crystals, such as chloresteryl esters show in addition to nematic behaviour, some colour effect under polarised light. So, a special name *cholesteryl* phase is given.

Because of optically active molecules, the cholesteric state has a spontaneous twist about an axis normal to the director. The helical arrangement is left or right handed. This state has an appreciable optical rotatory power. The plane of polarised light is rotated by a few thousand degree per mm which is thousand times greater than the rotatory power of a solid crystal, *e.g.*, quartz. The pitch of the helix decreases with rise of temperature and wavelength of reflection falls out.

Only a few types of chemical constitution favour the formation of liquid crystals. It is desirable that the molecules should be long and that some strongly attractive groups should be present to promote adhesion between adjacent molecules. Several esters and esters of cholesteryl form smectic liquid crystals, also a few soaps including thallous soaps and ammonium oleate. (Most of the soaps do not form liquid crystals).

[II] Uses of Liquid Crystals

(i) They are used in electronic display instruments because of their electrical and optical properties. For example, they are used in gas-liquid chromatography and in digital displays like digital wrist watches, pocket calculators.

(ii) They are used for detecting tumours in the body by using a method called *thermography*.

(iii) They are used as solvents for studying the structure of anisotropic molecules spectroscopically.

(iv) They are used as commercial lubricants.

(v) They are most suited to biological functions. As the colour of liquid crystals depend sensitively on temperature, these are, therefore, used in measuring skin temperature. The proteins and fats, which are important constitutents of food, also exist or get changed into liquid crystal state before digestion and are, therefore, easily assimilated in the body. The state also plays an important role in nutritional and other processes.

• 5.5. DIFFERENCES BETWEEN LIQUID, LIQUID CRYSTAL AND SOLID

(1) The liquid crystals possess a structure between that of a liquid and a crystalline solid.

(2) In a liquid the molecules have disordered arrangement and they are able to move relative to each other. In a solid crystal, the molecules have fixed ordered arrangement in fixed positions. In liquid crystals, the molecules have an ordered internal arrangement, *i.e.*, are arranged parallel to each other but can flow together like a liquid. Therefore, the liquid crystals have fluidity of liquids and a laterally ordered arrangement of crystals.

(3) True liquids in pure state, except mercury and other molten metals are generally transparent, but *liquid crystals show turbidity, i.e., are translucent.*

(4) True liquids and crystals having a symmetrical arrangement in all directions are *isotropic*, *i.e.*, they possess same physical properties in all directions, but liquid crystals are *anisotropic*, *i.e.*, they exhibit different physical properties in different directions.

(5) The anisotropicity of liquid crystals is seen particularly in their optical behaviour, *e.g.*, they show double refraction (*i.e.*, splitting unpolarised light into two beams of polarised light having polarisation perpendicular to one another) and give interference patterns in polarised light.

• 5.6. THERMOGRAPHY

The cholestric type of liquid crystals are used for detecting tumours in the body by a process known as **thermography**. Cholesteric type of liquid crystals consist of molecules possessing structure of helical type, the pitch of which changes with change in temperature. As such the wavelength of the rays reflected from them are different at different temperatures. This is specially marked by changing colour of the reflected ray. Since the local temperature of the tumour affected part of the body is different from the unaffected part, the rays of light reflected through a liquid crystal from the two parts have different wavelengths.

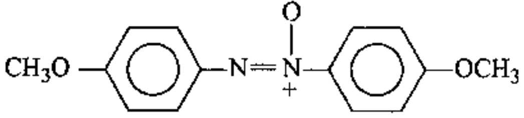
(ii) Seven segment cell : The substances used for liquid crystal displays in pocket calculators and wrist watches are nematic type liquid crystals. Their optical characteristics are affected by an electric field. A thin film of liquid crystal is put between transparent electrodes that are arranged on glass in special patterns. When a particular electrode segment is energised, the orientations of the molecules in the liquid crystal vary and so the substance becomes opaque. By activating appropriate segments in this fashion, different letters or numbers can be formed. An important advantage of these displays is that they cousume very little energy and so the battery lasts longer.

• SUMMARY

- **Dipole-dipole forces :** When polar moleculs align themselves so that the positive end of one molecule attracts the negative end of another molecule, then we get dipole-dipole forces.
- **Ion-dipole forces :** The forces which cause the positive ion to attract the negative pole and the negative ion to attract the positive pole of the polar molecule are called ion-dipole forces.
- **Dipole-induced dipole forces :** When permanent polar molecules approach neutral molecules their positive poles attract the electron cloud of the neutral molecules causing distortion. The neutral molecule becomes polarised and have induced dipoles. The forces causing these interactions are called dipole-induced dipole forces.
- **London forces :** The attractions between the instantaneous dipole and induced dipole are called London forces.

  $$\text{London energy} = -\frac{d}{r^6}$$

  where r is the distance between the molecules and d = constant.
- Solids show long range order, liquids show short range order, while gases show no order at all.
- **Liquid crystals :** Some organic solids having rod-like molecules do not melt to give the liquid substances directly. They, instead, pass through an intermediate state called the liquid crystal state, often referred to as the liquid crystal.
- *p*-Ozoxyanisole having the following structure is liquid crystal.



- Liquid crystals have the fluidity of a liquid and optical properties of solid crystals.
- Liquid crystals are of three types :

  (i) Nematic liquid crystals : They have molecules parallel to each other like soda straws but they are free to slide or roll individually.

  (ii) Smectic liquid crystals : The molecules in this type of crystal are also parallel but these are arranged in layers. The layers can slide past each other.

  (iii) Chloroesteric liquid crystals : As in nematic crystals a chloroe of crystal, the molecules are parallel but arranged in layers. The molecules in successive layers are slightly rotated with respect to the layers above and below so as to form a spiral structure.

• STUDENT ACTIVITY

1. Name the intermolecular forces present in liquids.

2. What are liquid crystals ? Describe their classification and structure.

3. What are the differences between liquid, liquid crystal and solid ?

• TEST YOURSELF

Answer the following questions :

1. Explain the intermolecular forces present in liquids. How these forces originate ?
2. Mention the qualitative description of structure of liquids.
3. Write a note on structural differences between solids, liquids and gases.
4. What are liquid crystals ? How are they classified ?
5. Discuss the structures of nematic, smectic and chloresteric liquid crystals.
6. Mention the uses of liquid crystals.
7. Mention the differencs between liquid crystal, solid and liquid.
8. Write a short note on thermography.
9. A liquid crystal is used :
   (a) To detect tumours in the body (b) In electronic display instruments.
   (c) As commercial lubricants (d) All of the above.
10. A liquid crystal is :
    (a) A mesomorphic state of a substance.
    (b) *A para-crystalline state.*
    (c) An intermediate state between solid and liquid.
    (d) All of the above.
11. The structural difference between a liquid and its vapour is that the layer disappears at the :
    (a) Critical temperature (b) Boiling point
    (c) Boyle's temperature (d) Freezing point.
12. The nature of force which binds together the molecules of a liquid is :
    (a) Gravitational (b) Electro-magnetic
    (c) Nuclear (d) None of the above.
13. Soaps show smectic state at :
    (a) Ordinary temperature (b) High temperature
    (c) Very low temperature (d) All temperatures.
14. A liquid possesses :
    (a) Short range order (b) Short range disorder
    (c) Intermediate state (d) None of the above.
15. The intermolecular force between two molecules in a liquid is proportional to the *n*th power of the intermolecular distance, the value of *n* is :
    (a) 2 (b) -2 (c) 7 (d) -7
16. **Fill in the blanks**

(i) The liquid crystals have the fluidity of a .... and optical properties of a ....

(ii) p-Ozoxyanisole is an example of ....

(iii) *In .... liquid crystals, the molecules are parallel to each other like* soda straws but are free to slide or roll individually.

(iv) Liquids show .... range order.

(v) London energy is given by ....

ANSWERS

9. (d), **10.** (d), **11.** (a), **12.** (b), **13.** (b), **14.** (c), **15.** (d).

16. **(i)** liquid, solid **(ii)** liquid crystal **(iii)** nematic **(iv)** short **(v)** $-d/r^6$.

❑❑❑

UNIT

6

SOLID STATE

LEARNING OBJECTIVES

- Crystallography, Crystalline and Amorphous Solids
- Differences Between Crystalline and Amorphous Solids
- Law of Constancy of Interfacial Angles
- Laws of Symmetry in Crystal Systems
- Space Lattice
- Unit Cell
- Bravais Space Lattices
- Crystal Systems
- Law of Rationality of Indices (Miller Indices)
- Bragg's Equation
- Structure of Sodium Chloride (NaCl) Crystal
    - ❑ Summary
    - ❑ Student Activity
    - ❑ Test Yourself

• 6.1. CRYSTALLOGRAPHY, CRYSTALLINE AND AMORPHOUS SOLIDS

Crystallography is that branch of science which deals with the geometry, properties and structure of crystals and crystalline substance.

Solids are substances having incompressibility, rigidity and mechanical strength. In solids, the molecules, atoms or ions are closely packed and are held together by strong cohesive forces, *i.e.*, in solids there is a well ordered molecular arrangement. *If the solid has a definite geometrical shape, it is called a* ***crystalline solid****, e.g.*, NaCl, KCl etc. *and if it does not have a definite geometrical shape it is called an* ***amorphous solid****, e.g.*, glass, plastic, rubber etc.

• 6.2. DIFFERENCES BETWEEN CRYSTALLINE AND AMORPHOUS SOLIDS

(1) Characteristic geometry : In crystalline solids, the molecules or atoms are arranged in a definite and ordered manner in three dimensional space. Thus, they have a definite and regular geometry. In amorphous solids, the molecules or atoms do not have any pattern of arrangement and, therefore, they do not have a definite geometry. Moreover, in crystalline solids, the definite and ordered arrangement of molecules, atoms or ions extends over a large distance, termed ***as long range order.*** It is seen that in a few amorphous solids, there is an ordered arrangement of molecules or ions, but it does not have a long range order.

(2) Isotropy and anisotropy : Crystalline solids are ***anisotropic***, *i.e.*, their physical properties like electrical conductivity, thermal conductivity, refractive index, viscosity, mechanical strength etc. are different in different directions. If a ray of light enters a crystal, it splits up into two components, each following a different path and moving with different velocity, and we have a phenomenon known as **double refraction**. In figure 1, a two dimensional arrangement of only two different kinds of atoms is shown. If the properties are measured along the direction AB, they will be different from those measured along the direction CD, as shown. *Anisotropy is an evidence for the existence of an ordered molecular arrangement.*

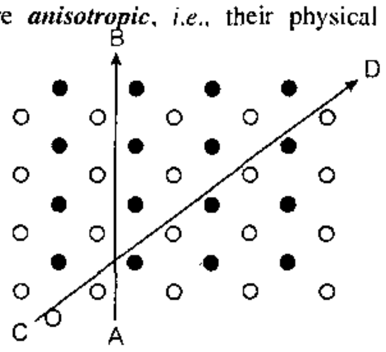


Fig. 1. Isotropy and anisotropy

Amorphous solids are ***isotropic***, *i.e.*, their physical properties are the same in all directions. It is because in amorphous solids, the atoms or molecules are arranged at random and in a disordered manner. So, all directions are identical and all properties will be the same in different directions.

(3) Melting point : A crystalline solid has a sharp melting point, *i.e.*, it changes immediately into liquid state. Amorphous solid does not have a sharp melting point, *e.g.*, glass when heated slowly, softens and starts flowing without a definite and abrupt change into liquid state.

(4) Regular and irregular cut : A crystalline solid on being cut with a sharp edged knife gives a clean cleavage, while an amorphous solid breaks irregularly as shown in figure (2).

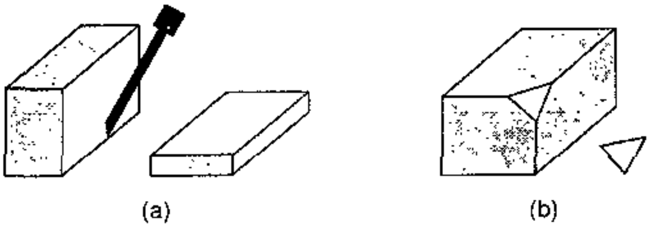

(a) (b)

Fig. 2. Cutting of solids.

Microcrystalline solids : Some solid materials occur as powders or agglomerates of fine particles and appear to be amorphous. On examining an individual particle under a microscope, it is seen to possess a definite crystalline shape. *Therefore, those solids in which the crystals are so small that they can be seen only under a powerful microscope are known as* ***microcrystalline*** *solids.*

• 6.3. LAW OF CONSTANCY OF INTERFACIAL ANGLES

Crystals are bound by plane faces. *The angle between any two faces is called the interfacial angle.* The shapes of the crystals as well as the size of the faces may change widely of one and the same substance because of the conditions of formation of crystals. But the interfacial angles between any two faces remain the same in every case as shown in figure 3. According to the law of constancy of interfacial angles, *"The angle between the corresponding faces or planes forming the external surface of a crystal remains constant for a given substance, no matter how the face is developed."* For example, the interfacial angles in all NaCl crystals are found to be 90°, irrespective of the size and shape of the faces. So, interfacial angle determination plays an important part in the study of crystals.

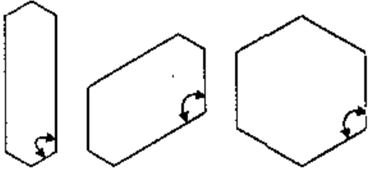


Fig. 3. Interfacial angles

• 6.4. LAWS OF SYMMETRY IN CRYSTAL SYSTEMS

There are various types of symmetries known as elements of symmetry in a crystal, the common types being :

(a) Centre of symmetry, *(b) Axis of symmetry,* *(c) Plane of symmetry.*

(a) Centre of symmetry : *Centre of symmetry of a crystal is such a point that any line drawn through this point intersects the surface of the crystal at equal disances in both directions.*

(b) Axis of symmetry : *An axis of symmetry is an imaginary line, about which the crystal may be rotated such that it presents the same appearance more than once during one complete revolution.*

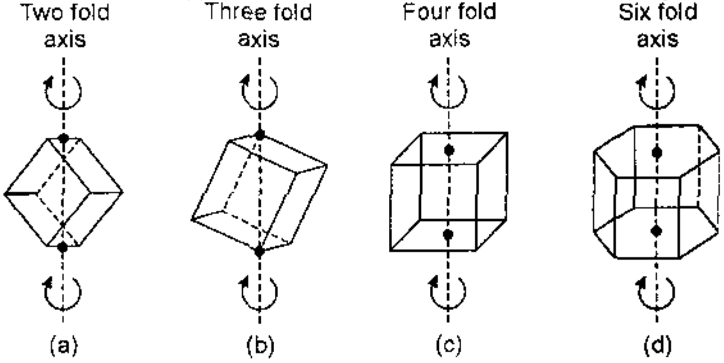


Fig. 4. Axes of symmetry

If the crystal presents the same appearance n times in one complete revolution the axis is said to be one of ***n*-fold axis**. The only values of n can be 2, 3, 4 and 6, when the axis is known as **two-fold** (or **diad-axis**), **three-fold** (or **triad-axis**), **four-fold** (or **tetrad-axis**) and **six-fold** (or **hexad-axis**), respectively (fig. 4). The angles between pairs of axes of symmetry are 30°, 45°, 60° and 90°. The axis of symmetry is always perpendicular to possible crystal face and parallel to a possible interfacial crystal edge.

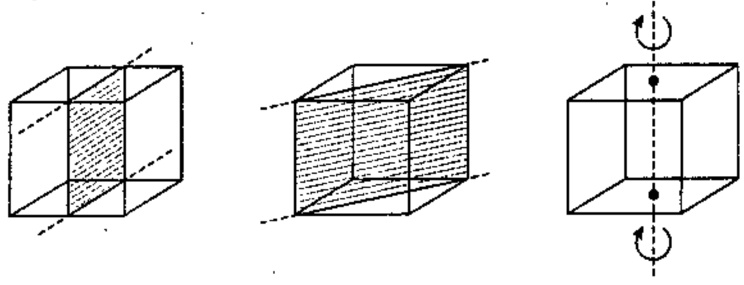
(c) Plane of symmetry : *If a crystal can be divided by an imaginary plane passing through its centre into two equal portions each of which is a mirror image of the other, the crystal is said to possess a plane of symmetry.*

It must be noted that plane and axis of symmetry constitute the elements of symmetry, while the centre of symmetry is not an element of symmetry. Furthermore, a crystal may have one or more than one plane or axis of symmetry, but it cannot have more than one centre of symmetry.

Elements of Symmetry

As mentioned above, there are three different types of symmetries in a crystal. But a crystal may have different numbers of each type of symmetry. The total number of centre, planes and axes of symmetries possessed by a crystal is known as ***elements of symmetry*** of the crystal. For example, a cubic crystal like NaCl has a total of 23 elements of symmetry as explained below :

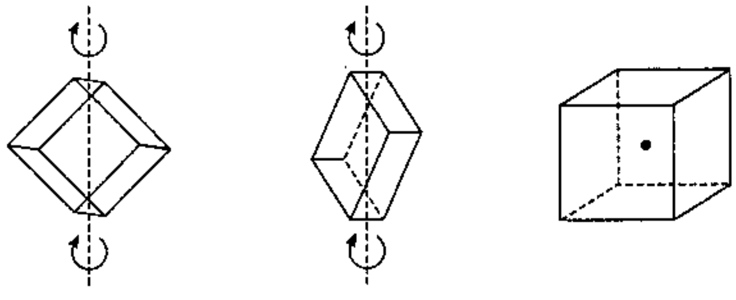
(a) Rectangular planes of symmetry : One such symmetry is shown in figure 5(a). There will be two more such planes, each of which will be perpendicular to the plane shown. Thus, there are 3 rectangular planes of symmetry.



(a) Rectangular plane of symmetry

(b) Diagonal plane of symmetry

(c) Axis of four-fold symmetry



(d) Axis of three fold symmetry

(e) Axis of two fold symmetry

(f) Centre of symmetry

Fig. 5. Elements of symmetry

(b) Diagonal planes of symmetry : One plane passing diagonally through the cube is shown in figure 5(b). There can be 6 such planes.

(c) Axes of four fold symmetry : One such symmetry is shown in figure 5(c). There will be 3 such four fold axes at right angles to each other.

(d) Axes of three fold symmetry : One such axis passing through appropriate corners of the cube is shown in figure 5(d). There will be 4 such axes.

(e) Axes of two fold symmetry : One such axis coming from opposite edges in shown in figure 5(e). There will be 6 such axes.

(f) Centre of symmetry : There will be one centre of symmetry as shown in figure 5(f).

Total numbers of symmetry of elements of all types in a cubic crystal are :

Plane of symmetry = 3 + 6 = 9 elements

Axes of symmetry = 3 + 4 + 6 = 13 elements

Centre of symmetry = 1.

$\therefore$ Total number of symmetry elements = **23.**

• 6.5. SPACE LATTICE

The position of atoms, molecules or ions in a crystal, relative to one other in space, are usually designated by points. Such a representation is called a ***space lattice***. A space lattice is thus defined as an *array of points in three dimensional space.*

An example of array of points in a three-dimensional space lattice is shown in figure (6). Each point represents an identical atom or group of atoms.

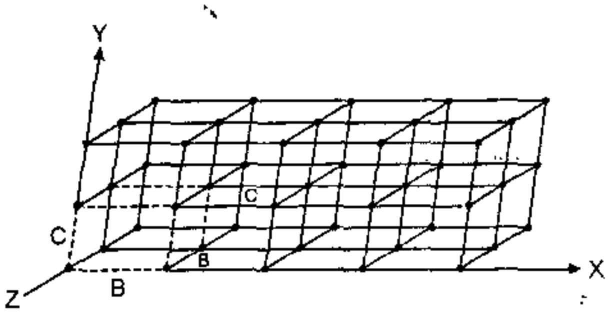


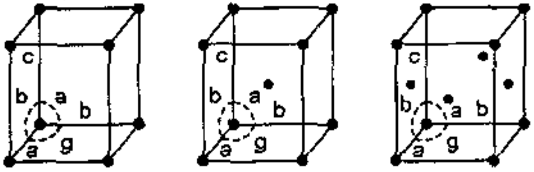
Fig. 6. Space lattice.

• 6.6. UNIT CELL

The lattice point can be broken up into a number of unit cells. It can be done by joining the points by a regular network of lines as shown in fig. 9. *A unit cell is thus the smallest repeating unit in space lattice which when repeated over and over again results in a crystal of the given substance.* Each unit cell, in turn, must be constituted of atoms, molecules or ions, as the case may be, and arranged to give the particular geometrical configuration of the crystal.

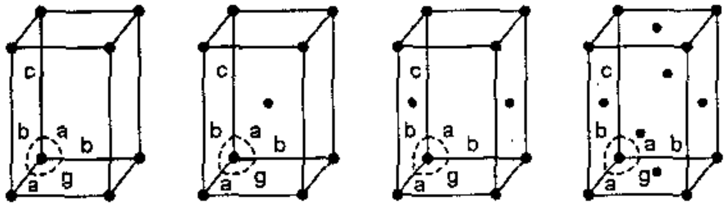
• 6.7. BRAVAIS SPACE LATTICES

Bravais (1848) established that there are 14 unique and basic ways in which points can be arranged in three-dimensional point lattices. These 14 basic arrangements, known as *Bravais* or



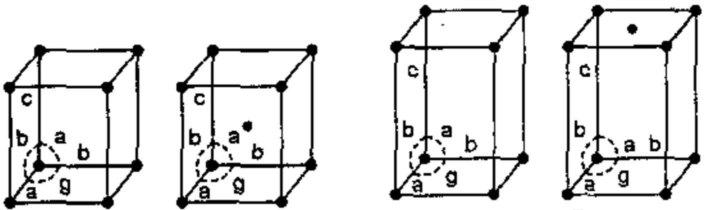
Simple or primitive Body centred Face centred

(a) Cubic



Simple or primitive Body centred End centred Face centred

(b) Orthorhombic



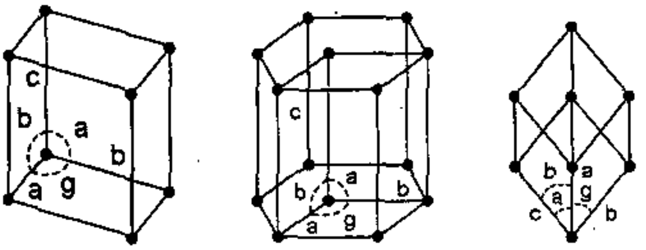
Simple Body centred

Tetragonal

Simple End centred

Monoclinic

(c)



Tridinic Hexagonal Rhombohedral

(d)

Fig. 8. Crystal systems.

space lattices are shown in fig. (7), where the black circles indicate the location and number of lattice points involved. The Bravais space lattice associated with different crystal systems are shown in fig. (7). The parameters of unit cell, *i.e.*, interfacial angle α, β and γ and the intercepts *a*, *b* and *c* are shown in each case.

The crystal belonging to cubic systems have 3 types of Bravais lattices depending on the shapes of the unit cells (fig. 8). These are :

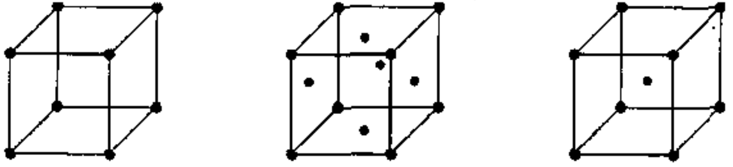

(a) (b) (c)

Fig. 8. Cubic space lattices

(a) Simple or primitive cubic lattice : In it, points are situated at all the 8 corners of each unit [fig 7(a)].

(b) Face centred cubic lattice : In it, the points are situated at all the 8 corners as well as at the centre of each of the six faces of the cube [fig. 8(b)].

(c) Body centred cubic lattice : In it, the points are situated at all the 8 corners of each unit and one point is situated at the centre of the cube [fig. 8(c)].

Ex. 1. ***Calculate the number of atoms (n) is a (i) simple cubic unit cell (ii) Body cuenterd cubic unit cell (iii) face centred cubic unit cell and (iv) diamond unit cell.***

Solution : (i) In simple cubic unit cell, one atom is situated at each corner. So each atom is shared by 8 unit cells, *i.e.*, its one-eight part belongs to each cube. Thus, number of atoms, $n = 1/8 \times 8 = 1$ atom.

(ii) In body centred cubic unit cell, 8 atoms are situated at 8 corners and 1 atom at the centre of the cube. As each corner atom is shared by 8 unit cells, so sharing of 8 corners = $8 \times 1/8 = 1$ atom. One atom is placed at the centre and so, $n = 1 + 1 = 2$ atoms.

(iii) In face centred cubic unit cell, 8 atoms are situated at 8 corners, so, their share = $8 \times 1/8 = 1$ atom. One atom is situated at the centre of each of the 6 faces which is shared by 2 unit cells. So, the share of 6 faces = $6 \times 1/2 = 3$ atoms. So, $n = 1 + 3 = 4$ atoms.

(iv) In diamond unit cell, 8 atoms are situated at 8 corners of the cube and each atom is shared by 8 unit cells, 6 atoms are present in 6 faces and each atom is shared by 2 unit clls. 4 atoms are also present inside the unit cell.

$$\therefore \qquad n = 8 \times \frac{1}{8} + 6 \times \frac{1}{2} + 4 = 1 + 3 + 4 = 8 \text{ atoms.}$$

• 6.8. CRYSTAL SYSTEMS

The crystallographers divided 32 point groups and 14 space lattices into seven crystal systems. There are as shown in the following table.

Crystal Systems and Their Characteristics

System	Axial characteristics	Minimum symmetry	Examples
1. Cubic	$\alpha = \beta = \gamma = 90°$ $a = b = c$	Four three-fold axes	NaCl, KCl Diamond, CaF_2 (fluorspar)
2. Tetragonal	$\alpha = \beta = \gamma = 90°$ $a = b \neq c$	One four-fold axis	SnO_2 (cassiterite) TiO_2 (rutile)
3. Monoclinic	$\alpha = \gamma = 90°$ $\beta \neq 90°$ $a \neq b \neq c$	One two-fold axis	$Na_2SO_4.10H_2O$ $Na_2B_4O_7.10H_2O$ S (monoclinic)
4. Triclinic	$\alpha \neq \beta \neq \gamma \neq 90°$ $a \neq b \neq c$	None	$K_2Cr_2O_7.H_3BO_3$ $CuSO_4.5H_2O$
5. Hexagonal	$\alpha = \beta = 90°$ $\gamma = 120°$ $a = b \neq c$	One six-fold axis	PbI_2 Mg, Beryl, ZnO (zincite)
6. Rhombohedral (Trigonal)	$\alpha = \gamma = 90°$ $\beta \neq 90°$ $a = b = c$	One three-fold axis	$NaNO_3$, $CaCO_3$ (calcite)
7. Orthorhombic (Rhombic)	$\alpha = \beta = \gamma = 90°$ $a \neq b \neq c$	Three two-fold axes	Sulphur (rhombic), $BaSO_4$ (baryta), $PbCO_3$ (cerrusite)

• 6.9. LAW OF RATIONALITY OF INDICES (MILLER INDICES)

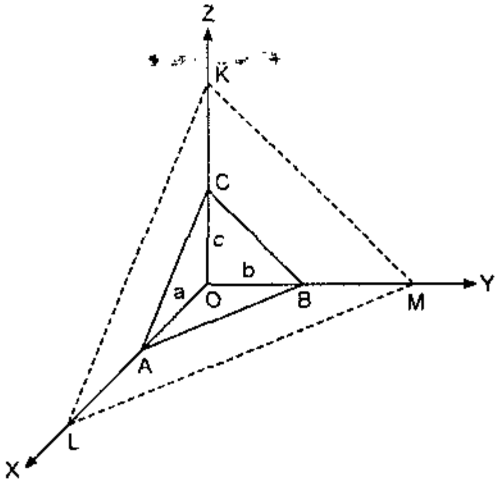


Fig. 9. Miller indices.

The geometry of a crystal may be defined in terms of coordinate axes all meeting at the origin. The number and inclination of these crystallographic axes are chosen in such a way that all the faces of the crystal either intersect them at a definite distance from the origin or are parallel to some of the axes, *i.e.*, intersecting at infinity. *According to law of rational indices, the intercepts of any face of a crystal along the crystallographic axes are either equal to the unit intercept (a, b, c) or some simple whole number multiples of them, e.g., la, mb and nc, where l, m and n are simple whole numbers.*

Let OX, OY and OZ represent the three crystallographic axes and let ABC be a unit plane (fig. 9) which cuts the three crystallographic axes with intercepts of lengths *a*, *b* and *c*. Suppose the other face KLM of the crystal makes intercepts *la*, *mb* and *nc*, where *l*, *m* and *n* are small integers, *i.e.*, 2, 2, 2 etc. In figure (9), the face KLM makes intercepts 2*a*, 2*b* and 2*c*, thus giving the value of 2, 2, 2 for *l*, *m* and *n*, respectively. The numbers *l*, *m* and *n* are called **Weiss indices** of corresponding plane which is described as *lmn* plane.

Weiss indices may have fractional values as well as infinity (an indefinite quantity). Weiss indices are, therefore, awkward in use and have consequently been replaced by Miller indices. Each face is represented by a set of 3 integers, *h*, *k* and *l*, called the **Miller indices**. Any particular face of a crystal is represented by the reciprocals of Weiss indices and multiplying throughout by the smallest number in order to make all reciprocals as integers. Thus, for the face KLM, the reciprocals are 1/2, 1/2, 1/2 which are in the ratio 1 : 1 : 1. The *Miller indices* of the face KLM are 1, 1, 1 which is designated as (111) face. Suppose a face cuts only two axes OY and OZ; intercepts being 2*b* and 3*c* and it does not cut the axis OX at all, being parallel to it. The reciprocals are 0 : 1/2 : 1/3. The ratio is thus 0 : 3 : 2. The Miller indices are thus (032). So, the *Miller indices of any crystal face are inversely proportional to the intercepts of that face on different axes.*

Ex. 1. ***Calculate the Miller indices of crystal planes which cut through the crystal axes at the following :***

(i) $(2a, 3b, c)$ ***(ii)*** (a, ∞, ∞)

(iii) $(6a, 3b\ 2c)$ ***(iv)*** $(2a, -3b, -4c)$

(i)	*a*	*b*	*c*	
	2	3	1	Intercepts
	1/2	1/3	1/1	Reciprocals
	3	2	6	Clear fractions

∴ Miller indices are **(326)**.

(ii)	*a*	*b*	*c*	
	1	∞	∞	Intercepts
	1	1/∞	1/∞	Reciprocals
	1	0	0	Clear fractions

∴ Miller indices are **(100)**.

(iii)	*a*	*b*	*c*	
	6	3	2	Intercepts
	1/6	1/3	1/2	Reciprocals
	1	2	3	Clear fractions

∴ Miller indices are **(123)**.

(iv)	*a*	*b*	*c*	
	2	− 3	− 4	Intercepts
	1/2	1/−3	1/−4	Reciprocals
	6	− 4	− 3	Clear fractions

∴ Miller indices are **$(6\bar{4}\bar{3})$***.

• 6.10. BRAGG'S EQUATION

Bragg pointed out that scattering of X-rays by crystals could be taken be equivalent to reflection from successive planes of atoms in the crystal. However, unlike reflecton of ordinary light, reflection of X-rays can take place only at certain angles which are dependent on wavelength of X-rays and the distance between the planes in the crystal. The fundamental equation which gives a simple relation between the wavelength of X-rays, the interplanar distance in the crystal and the angle of reflecton is known as ***Bragg's equation***. It can be derived as follows :

[I] Derivation of Bragg's Equation

The horizontal lines represent parallel planes in the crystal structure separated from one another by a distance d. Suppose a beam of X-rays incident at an angle θ, falls on the crystal. Some of them will be reflected from the uppermost plane at the same angle θ, while others will be absorbed and get reflected from successive planes as shown in figure (10). Let the two wavefronts be drawn perpendicular to the incident and reflected beam, respectively. The waves reflected from different layer planes will be in phase with one another only if the difference in the path lengths of the waves reflected from the successive planes is equal to an integral number of wavelengths. Drawing perpendiculars OL and OM to the incident and reflected beams, it will be seen that the difference in the wavelengths, say δ of the waves reflected from the first two planes is given by,

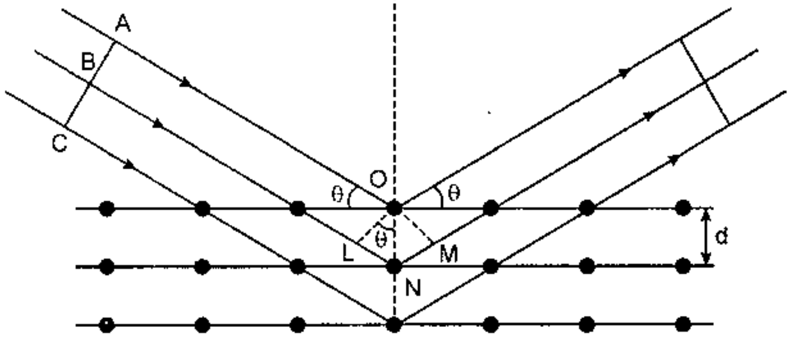


Fig. 10. Scattering of X-rays by a crystal.

$$\delta = \text{LN} + \text{MN}$$

This should be equal to a whole number multiple of wavelength, λ, *i.e.*,

$$n\lambda = \text{LN} + \text{MN}$$

Since the triangles OLN and OMN are congruent, LN = MN.

$$\therefore \quad n\lambda = 2\text{LN} = 2d \sin \theta \quad \ldots(1)$$

Equation is known as *Bragg's equation*.

If homogeneous X-rays are used, λ has a certain definite value. For a given set of lattice planes d will also have a fixed value. Thus, the possibility of getting maximum reflection (*i.e.*, possibility of getting reflected waves in phase with one another) depends upon θ. If θ is increased gradually, a number of positions will be obtained at which the reflections will be maximum. At these positions, n will have several values equal to 1, 2, 3, ... etc.

On the above basis, there are different orders of reflection, given by different values of n. The diffraction maxima are called *first, second, third, fourth etc. order* when $n = 1, 2, 3, 4, \ldots$ etc., respectively. Knowing the value of λ, we can calculate the value of d from which we can determine the internal structure of crystals. The following method can be employed for it.

Rotating crystal method : The study of the intensity of the X-ray spectrum will furnish the information as regards the arrangement of planes of different atoms in the given space lattice. Bragg obtained the positions of maximum reflection intensity by means of an *X-ray spectrometer* whose construction is shown in figure (11).

The spectrometer consists of an X-ray tube enclosed in a box coated with lead. The X-rays pass through the slit and finally allowed to strike a single crystal C mounted on the turn table. The crystal is rotated gradually by means of the turn table so as to increase the glancing angle at which the X-rays are incident at the exposed face of the crystal. The intensities of the reflected rays are measured on a recorder R, such as ionisation chamber or a photographic plate. The angles, for which the reflections are maximum, give the value of θ. The procedure is repreated for each plane of the crystal. The lowest angle at which the maximum reflection occurs corresponds to $n = 1$, *i.e.*, first

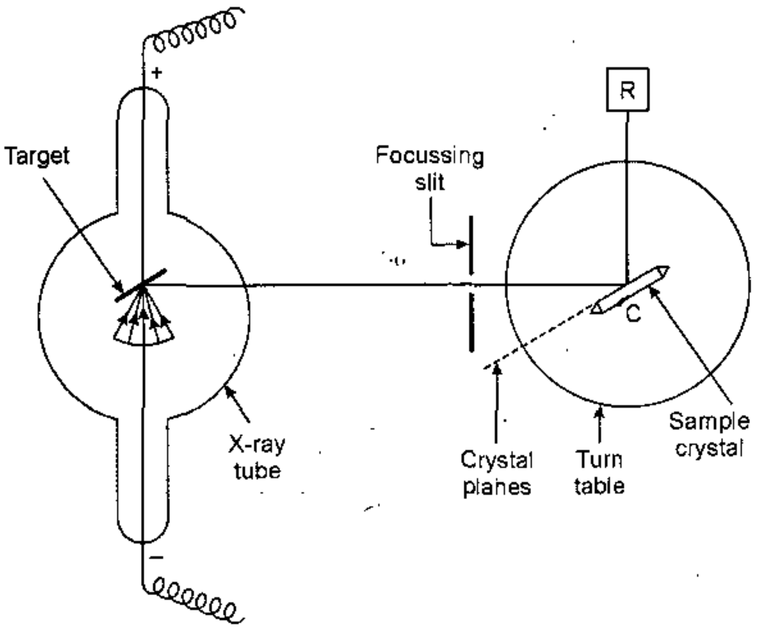


Fig. 11. Rotating crystal method.

order reflection. Similarly, the next higher angle at which the maximum reflection occurs again corresponds to $n = 2$. Generally, the angle for first order reflection is taken as θ, so that the value of n is set as 1.

The value of θ for the first order reflection from the three faces of NaCl crystal were found to be 5·9°, 8·4° and 5·2°, respectively. Applying Bragg's equation, ($d = n\lambda/2 \sin\theta$) and knowing that n and λ are the same in each case, the distance d between successive planes in the three faces will be in the ratio of :

$$\frac{1}{\sin 5{\cdot}9^\circ} : \frac{1}{\sin 8{\cdot}4^\circ} : \frac{1}{\sin 5{\cdot}2^\circ} = 9{\cdot}61 : 6{\cdot}84 : 11{\cdot}04$$
$$= 1{\cdot}00 : 0{\cdot}707 : 1{\cdot}141$$

This ratio corresponds to the spacings for the three planes of a face centred cubic lattice. So, we can say that sodium chloride crystal has a *face centred cubic structure*.

• 6.11. STRUCTURE OF SODIUM CHLORIDE (NaCl) CRYSTAL

The unit cell of sodium chloride is shown in figure (12). In the structure, the sodium and chloride ions are represented by hollow circles and solid circles, respectively.

The chloride ions (Cl^-) are arranged in *cubic close packing* or *face centred cubic arrangement*. In it, there are Cl^- ions at the corners of the cube as well as at the centre of each face. The sodium ions (Na^+) occupy all the octahedral sites. There is only one octahedral site per atom in a closed packed lattice. So, there will be one Na^+ ion for every Cl^- ion. This corresponds to 1 : 1 stoichiometry of sodium chloride crystal. In *the structure, each Na^+ ion is surrounded by* 6 Cl^- ions which are disposed towards the corners of a regular octahedron, as shown in figure (12). Similarly, each Cl^- ion is surrounded by 6 Na^+ ions. So, the coordination number of both Na^+ ion and Cl^- ion is 6.

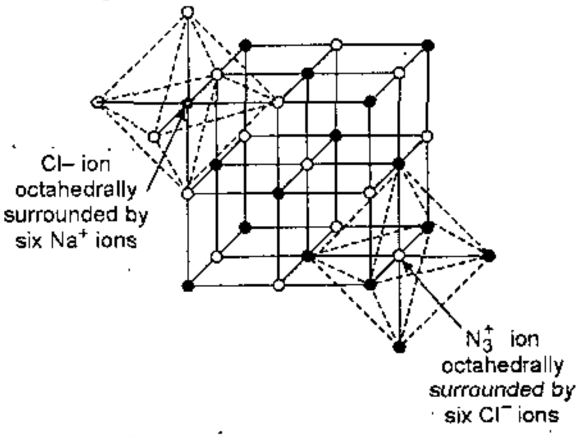


Fig. 12. Face centred cubic structure of NaCl crystal.

• SUMMARY

- In solids, atoms, ions and molecules are held together by relatively strong chemical forces — ionic bond, covalent bond or by intermolecular vander Waals forces. They do not translate *although they vibrate to some extent in their fixed positions. This explains why solids are rigid* and have definite shape.

- In a crystal, the atoms, molecules or ions are arranged in a regular, repeating three dimensional pattern called the crystal lattice, *e.g.*, sugar, glucose are crystalline solids.
- An amorphous solid (Greek : *amorphous = no form*) has atoms, molecules or ions, arranged at random and lacks the ordered crystalline lattice, *e.g.*, rubber, plastic, glass are amorphous solids.
- **Amorphous substances** are said to be isotropic, because they show the some value of any property in all directions. Thus, thermal and elctrical conductivities, refactive index, coefficient thermal expansion in amorphous solids are independent of the direction along which they are measured.
- **Crystalline substances** are anisotropic and the magnitude of a physical property changes with direction.
- The angles between the plane faces of the crystal are referred to as at interface angles.
- The consistency of interfacial angles is an essential characteristic of crystalline solids.
- A crystal is said to have a **plane of symmetry** if it can be divided by an imaginary plane into two equal parts, each of which is the exact mirror image of the other.
- An **axis of symmetry** is an imaginary line drawn through the crystal such that during rotation of the crystal through 360°, the crystal presents exactly the same appearance more than once.
- **Centre of symmetry** is a point at the centre of the crystal so that any line drawn through it will meet the surface of the crystal at equal distances on either side.
- A crystal may have a number of planes of symmetry or axis of symmetry, but it can have only one centre of symmetry.
- **Miller indices** of a plane may be defined as the reciprocals of the intercepts which the plane makes with the axes.
- The particles in crystals are arranged in regular pattern that extend in all directions. The overall arrangement of particles in a crystal is called the **crystal lattice, space lattice** or simply **lattice**.
- A crystal is made up of a large number of basic units. The simple basic unit or the building block of the crystal lattice is called the unit cell.
- The crystal lattice of substances may be categorised into seven types. These are called **Bravais lattices** and the corresponding unit cells are referred to as **Bravais unit cells**. The unit cells may be characterised by the parameters, *viz.*, (i) relative lengths of the edges along the three axes (a, b, c). (ii) the three angles between the edge (α, β, γ).
- **Types of cubic unit cells :** There are following three types of cubic unit cells :
  (i) *A simple cubic unit cell* is one in which the particles (atoms or ions) are occupying only the corners of the cube.
  (ii) *A face centred cubic unit cell* is one in which one particle is situated at the centres of each faces of the cube apart from the particles at the corners.
  (iii) *A body centred cubic unit cell* is one in which there is one particle at the centre of the cube in addition to the particles at the corners.
- **Bragg's equation :** It is given by $n\lambda + 2d \sin \theta$.

• STUDENT ACTIVITY

1. Mention the differences between crystalline and amorphous solids.

2. Define space lattice and unit cell.

3. Write a short note on Miller indices.

4. Derive Bragg's equation.

• TEST YOURSELF

1. Define crystalline and amorphous solids.
2. Mention the differences between crystalline and amorphous solids.
3. Explain isotropy and anisotropy.
4. Define interfacial angle.
5. State and explain the symmetry in a crystal system.
6. Discuss the types of crystal systems.
7. Write a note on Miller indices.
8. Explain the difference between Wiss indices and Miller indices by a suitable example.
9. Discuss the structure of sodium chloride crystal.
10. Derive the relation $n\lambda = 2d \sin \theta$ in crystallography.
11. Write a short note on Bravais lattices.
12. Explain space lattice and unit cell.
13. Discuss the types of Bravais lattices in a cubic crystal system.
14. Calculate the Miller indices of a crystal plane which is cut through the crystal axes 2a, – 3b, – c.
15. Define and explain the law of constancy of interfacial angles and the law of rational indices.
16. Total number of symmetry elements in a cubic crystal is :
(a) 8 (b) 9 (c) 11 (d) 13
17. Intercepts made by a plane on crystallgraphic axes are a, b, c. The plane is designated as :
(a) 1 1 1 (b) $\bar{1}$ 1 1 (c) $\bar{1}$ 1 $\bar{1}$ (d) $\bar{1}$ $\bar{1}$ $\bar{1}$
18. Intercepts made by a plane on crystallgraphic axes are $2a$, $3b$ and $2c$. The Miller indices are:
(a) 2, 3, 2 (b) 3, 2, 3 (c) 2, 2, 3 (d) 3, 2, 2
19. Bragg's equation is :
(a) $n\lambda = d \sin \theta$ (b) $2 n\lambda = d \sin \theta$
(c) $n\lambda = 2d \sin \theta$ (d) $n\lambda = \sin \theta$
20. The coordination numbers of Na^+ and Cl^- ion in NaCl are :
(a) 6, 8 (b) 6, 6 (c) 8, 8 (d) 8, 6
21. The elements of symmetry are :
(a) Plane of symmetry (b) Axis of symmetry
(c) Centre of symmetry (d) All of these

22. A crystalline solid does not have one of the following properties. It is :

(a) Anisotropy (b) Sharp melting points

(c) Isotropy (d) Definite and regular geometry

23. Fill in the blanks

(i) A substance which does not have a regularity of the structure is called .... solid.

(ii) For a .... system, $a = b = c$; $\alpha = \beta = \gamma = 90°$.

(iii) A solid does not have .... vapour pressure.

(iv) If there are 4 atoms in a unit cell in a cubic system, it is an example of .... centred cubic unit cell.

(v) The number of atoms per unit cell in a simple cubic, fcc and bcc are ...., ... and ...., respectively.

(vi) Rubber is an example of .... solid.

ANSWERS

16. (d), **17.** (b), **18.** (b), **19.** (c), **20.** (b), **21.** (d), **22.** (c),

23. **(i)** amorphous **(ii)** cubic **(iii)** high **(iv)** face **(v)** 1, 4, 2 **(vi)** amorphous

❑❑❑

UNIT

7

THERMODYNAMICS

LEARNING OBJECTIVES

- Terms Used in Chemical Thermodynamics
- Nature of Work and Heat
- Zeroth Law of Thermodynamics
- First Law of Thermodynamics
- Internal Energy
- Enthalpy
- Heat Capacity
- Work Done in an Isothermal Reversible Expansion of a Gas
- Work Done in Adiabatic Reversible Expansion of a Gas or Deduction of PV^{γ} = Constant
- Joule-Thomson Effect
- Second Law of Thermodynamics
- Carnot's Cycle
- Entropy
- Entropy Changes For Different Processes
- Criteria of Spontaneity of a Reaction
- Work Function
- Free Energy
- Gibbs-Helmholtz Equation
- Clapeyron Equation
- Clausius-Clapeyron Equation
- Nernst Heat Theorem
- Third Law of Thermodynamics
  - ☐ Summary
  - ☐ Student Activity
  - ☐ Test Yourself

Thermodynamics is that branch of natural science which deals with energy transformations accompanying the physical and chemical processes. Thermodynamics shows the quantitative relations between various forms of energy and heat. The subject is of theoretical nature but has proved of immense importance in physics, chemistry and engineering. The **advanced physical chemistry** is now often studied from the standpoint of thermodynamics. It also helps us to lay down the criteria for predicting feasibility of a process including a chemical reaction under a given set of conditions. In the other words, it helps us to predict whether a given process or a chemical reaction is possible under given conditions of pressure, temperature and concentration. Thermodynamics also helps us to determine the extent to which a process including a chemical reaction, can proceed before attainment of equilibrium.

• 7.1. TERMS USED IN CHEMICAL THERMODYNAMICS

In the study of thermodynamics, few terms are frequently used. These are described as follows:

1. Thermodynamic system. It is defined as *any specified portion of matter under study which is separated from the rest of the universe with a bounding surface.* A system may consist of one or more than one substance.

2. Surroundings. *The rest of the universe which might be in a position to exchange matter and energy with the system is called the surroundings.* For example, when a chemical reaction is carried out between two aqueous solutions in a beaker, the contents of the system form the system.

3. Types of systems. (a) A system which can exchange matter as well as energy with its surroundings is said to be an ***open system.*** (b) A system which can exchange energy but not matter with its surroundings is called a ***closed system.*** (c) A system which can exchange neither energy nor matter with its surroundings is called an ***isolated system.***

If a system is maintained at a constant temperature, it is termed an ***isothermal system***. If a system is so insulated from its surroundings that no heat flows in or out of the system, it is termed an ***adiabatic system.***

4. Homogeneous and heterogeneous systems. A system is said to be ***homogeneous*** if it is completely uniform throughout. In such a system, there is only one phase, *e.g.*, a pure solid, pure liquid or a mixture of gases.

A system is said to be ***heterogeneous,*** when it is not uniform throughout. In such a system there are two or more phases, e.g., a system consisting of two immiscibel solvents.

5. Macroscpic systems. A system is said to be ***macroscopic*** when it consists of a large number of molecules, atoms or ions. (The word macroscopic means *on a large scale* and is, therefore, used to convey the sense of appreciable quantities). The properties associated with macroscopic system are known as macroscopic properties, *e.g.*, pressure, temperature, volume, density, viscosity, surface tension etc.

6. State of a system. When macroscopic properties of a system hav fixed values, the system is said to be in a **definite state.** When there is any change in the property, the system changes into a different state. Therefore, the state of a system is fixed by its macroscopic properties.

7. Thermodynamic variables or state variables. The quantities whose values determine the state of a system are called its thermodynamic variables or state variables. The most important state variables are mass, composition, pressure, temperature and volume. It is, however, not necessary that we should always specify allthe variables, because some of them are inter-dependent. For a single pure gas, composition may not be one of the variables, as it remains only 100%. For one mole of an ideal gas, the gas equation $PV = RT$ is obeyed. Evidently, if only two out of the three variables (P, V, T) are known, the third can be easily calculated. The two variables generally specified are pressure and temperature. These are known as ***independent variables.*** The third variable, *viz.*, volume is known as ***dependent variable,*** as its value depends upon the values of pressure and temperature.

8. Extensive variable. The variable of a system which depends upon the amount of the substance or substances present in the system is known as extensive variable, *e.g.*, mass, volume, energy, etc.

9. Intensive variable. The variable of a system which is independent of the amount of the substance present in the system is known as intensive variable *e.g.*, pressure, temperature, viscosity, refractive index.

10. State functions and path functions. State variables which are determined by the initial and final states of the system ***only*** and not by the path followed are called ***state functions.*** These depend upon how the change from initial to the final state is carried out.

State variables, on the contrary which are determined or depend on the path followed are called ***path functions.***

Consider the expansion of a gas from P_1, V_1, T_1 to P_2, V_2 and T_2 (i) in steps and (ii) adiabatically. In adiabatic expansion, let the work done by the system be W and heat absorbed is zero.

In stepwise expansion, heat absorbed = Q and work done = W. Here $W \neq Q$ and the heat absorbed in the two cases are also different even though the system has undergone the same net change. Thus, W and Q are path functions and not the state functions. However, the change in internal energy (heat absorbed-work done) in the two cases will be seen to be constant. This is possible only if E_1 and E_2 have the same values in the two states of the system. Internal energy of a system is thus a state function. Entropy, free energy, enthalpy are other state functions.

11. Thermodynamic equilibrium. A system in which the macroscopic properties donot undergo and change with time is said to be in thermodynamic equilibrium. When an isolated system is left to itself and the pressure and temperature are measured at different points of the system, it is seen that although these quantities may initially change with time, the rate of change becomes smaller and smaller until no further observable change occurs. In such a state, the system is said to be in thermodynamic equilibrium.

Thermodynamic equilibrium means the existence of three kinds of equilibria in the system. These are termed *thermal equilibrium*, *mechanical equilibrium* and *chemical equilibrium*.

(a) Thermal equilibrium : A system is said to be in thermal equilibrium if there is no flow of heat from one part of the system to another. This is possible when the temperature remains the same throughout in all parts of the system.

(b) Mechanical equilibrium. A system is said to be in mechanical equilibrium if there is no mechanical work done by one part of the system or the other. This is possible when the pressure remains the same throughout in all parts of the system.

(c) Chemical equilibrium : A system is said to be in chemical equilibrium if the concentration of the various phases remain the same throughout in all parts of the system.

12. Thermodynamic process : A thermodynamic process is a path or an operation by which a system changes from one state of another. Four different thermodynamic processes are known which are as follows :

(a) Isothermal process : A process is said to be isothermal if the temperature of the system remains constant throughout the whole process. This is obtained by making a perfect thermal contact of th system with a thermostat of a large heat capacity.

(b) Adiabatic process : A process is said to be adiabatic if no heat is allowed to enter or leave the system during the whole process. In such a process, therefore, the temperature gets altered because the system is not in a position to exchange heat with the surroundings. It is obtained by having the will of the system made of perfect heat insulating substance.

(c) Isobaric process : A process is said to be isobaric if the pressure remains constant throughout the whole process.

(d) Isochoric process : A process is said to be isochoric if the volume remains constant throughout the whole process.

13. Reversible and irreversible processes : *A process which is carried out infinitesimally slowly so that the driving force is only infinitesimally greater than the opposing force is called a reversible process.* In a reversible process, the direction of the process can be reversed at any point by making a small change in a variable like pressure, temperature etc.

Any process which does not take place in the above way, i.e., a process which does not occur infinitesimally slowly, is termed an irreversible process.

A reversible process cannot be realised in practice, it would require infinite time for its completion. Hence, all those reactions which occur in nature or in laboratory are irreversible. A reversible process is thus *theoretical* and *imaginary*. The concept of reversibility can be understood as follows :

Consider a gas cylinder provided with a frictionless and weightless position upon which is kept some sand. At the beginning, when an equilibrium exists between the inside pressure of the gas and outside pressure of atmosphere plus sand, the piston is motionless. If we remove a grain of sand, the gas will expand slightly, but the equilibrium will be restored almost instantaneously. If the same grain of sand in replaced, the gas will return to its original volume and the equilibrium remains unchanged.

14. Exact and inexact differentials : An exact differential is one which integrates to a finite diffrence, $\int_A^B dE = E_B - E_A$, where E_A and E_B are the internal energy of the system in the initial and final states, respectively. It is independent of the path of integration. In a cyclic process, the final state is the same as the initial state, *i.e.*, $E_B = E_A$, the cyclic integral of an exact differential, $\oint dE = 0$. The difference, $E_B - E_A$ is denoted by ΔE.

An inexact differential is one which integrates to a total quantity depending upon the path of integration, *e.g.*,

$$\int_A^B \delta W = W$$

where W is the total quantity of work appearing during the change from initial state A to the final state, B. Small changes in path, independent of state functions are represented by symbols like dE, dEm, etc., while small changes in path dependent functions are represented by symbols like δq, δW etc. Finite changes inthe former are represented by symbols likes ΔE, ΔF etc., but symbols like $\Delta q, \Delta W$ are meaningless when we deal with path dependent functions. This is so, because the system in the two states is not associated with any heat or work. Heat and work appear during the process only. Moreover, the cyclic integral of an inexact differential is generally not zero.

• 7.2. NATURE OF WORK AND HEAT

It has been seen that when a system changes from one state to another, it is accompanied by change in energy. The change in energy may appear in the form of work, heat, light etc.

In CGS system, the unit of energy is *erg*. In SI system, the unit of work, heat and energy is *joule* (1 calorie = 4.184 joules = 4.184×10^7 ergs). An erg is defined as the *work done when a resistance of 1 ohm is moved through a distance of 1 cm.* As erg is a small quantity, a bigger unit.

called joule (1 joule = 10^7 erg) is used. Joule (1850) showed that there is a definite relationship between mechanical work done W and heat produced, H, *i.e.*,

$$W \propto H \text{ or } W = JH$$

where J is known as ***Joule mechanical equivalent of heat.***

Energy is made up of two factors, viz., (i) *Intensity factor* and (ii) *Capacity factor*. The product of these two factors gives the energy. Heat energy is measured by the product of temperature (*intensity factor*) and the heat capacity (*capacity factor*) of the system. The product gives the energy of the system. If a substance of mass m kg and specific heat s kJ per kg is heated through $t°$, the heat energy involved is given by mst kilojoules.

Similarly, when a body of mass m kg is moved through a height h m, the work done against gravity is obtained by multiplying the *intensity factor* (mg newtons) and capacity factor (h metres). The work done is mgh joules. This work is stored in the body as potential energy and is released when the body falls to its original position.

• 7.3. ZEROTH LAW OF THERMODYNAMICS

We know that temperature is one of the quantities necessary to define the state of a thermodynamic system. In other words, every thermodynamic system must possess a temperature. *This postulate of the existence of temperature is sometimes called the zeroth law of thermodynamics.* In other words, this law states that, ***if body A is in equilibrium with body C and body B is also in equilibrium with body C, then bodies A and B are in equilibrium with each other.***

Energy manifests itself not only in the form of mechanical work, but also as heat energy, electrical energy and chemical energy. Energy is composed of two factors viz., intensity factor and capacity factor. The product of these two factors gives the energy.

Heat energy is measured by the product of temperature (intensity factor) and heat capacity (capacity factor) of the system. The product gives the energy of the system. If a substance of mass m kg and specific heat is s kJ per kg is heated through t, the heat energy involved is given by mst kJ.

The precise experimental basis for this assumption is the law of thermal equilibrium from which it can be shown that in a thermodynamical system for every participant in equilibrium, there exists a certain single valued function f of the state variables, P and V, which have the same values for all participants. Mathematically, it can be expressed as,

$$f_1(P_1, V_1) = f_2(P_2, V_2) = f_3(P_3, V_3) = \ldots = T$$

where the subscripts 1, 2, 3 refer to different participants. The identical numerical value has been put down as T, which may be called the *temperature*, any one of the bodies being used as a thermometer reading the temperature T on a suitable scale. The above equation thus defines an empirical temperature. It is true that it has not been found possible to express the last equation in finite or closed form for most substances. Its existence for most substances will, however, be taken for granted.

• 7.4. FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics, also known as law of conservation of energy states that ***energy can neither be created nor destroyed, although it can be converted from one form to another.*** In other words, it can also be stated as '***the total energy of an isolated system always remains constant, although there may be change from one form to another.***' Thus, whenever energy in one form disappears, an equal amount of energy in some other form appears. This law was based on the failure to construct a perpetual motion machine, *i.e.*, a machine which could produce energy without expenditure of energy.

It is now known that energy can be produced by the destruction of mass according to Einstein's expression, $E = mc^2$, where E is the energy produced by the destruction of mass m and c is the velocity of light. In the light of this fact, the modified first law can be defined as, ***the total mass and energy of an isolated system remains constant.***

Mathematical statement of first law of thermodynamics : Let E_1 and E_2 be the energy of the system in state A and state B, respectively. Suppose a system while undergoing change from state A to state B absorbs heat Q from its surroundings and also performs some work W, either mechanical or electrical. On checking the amount of heat supplied and work done we find that Q is not equal to W.

According to first law of thermodynamics, the total energy must remain constant. In order to balance, we say that energy equivalent to $(Q - W)$ is stored in the system. It means that :

$Q - W$ = Energy of the system in its final state – Energy of the system in its initial state or $$\Delta E = Q - W \qquad \ldots(1)$$

When small changes are involved, equation (1) may be written as,

$$dE = dQ - dW \qquad \ldots(2)$$

Equations (1) and (2) are the ***mathematical statements*** of first law of thermodynamics.

• 7.5. INTERNAL ENERGY

Every substance is associated with a certain amount of energy, which depends upon its chemical nature, temperature, pressure and volume. This energy is known as ***internal*** or ***intrinsic energy***. The exact value of this energy is unknown because the chemical nature includes several indeterminant factors, *e.g.*, translational, rotational and vibrational motion of the molecules, the manner in which the molecules are put together, the nature of individual atoms, the energy possessed by the nucleus and the arrangement and number of electrons. Internal energy of a substance or system is, however, a definite quantity, and it is a function of the state of the system at the given instant, irrespective of the manner in which that state has been brought about. The absolute value of internal energy cannot thus be determined. However, in thermodynamics, it is the change in internal energy (ΔE) accompanying a physical or chemical process that is of importance. ΔE is a measurable quantity. Internal energy of a system is an extensive property, as its value depends upon the amount of the substance or system present.

If E_A and E_B be the internal energy of the system in the initial state (A) and final state (B), respectively then change in internal energy (ΔE) is given by ,

$$\Delta E = E_B - E_A$$

Internal energy (E) is related to enthalpy (H) according to the relation,

$$H = E + P\ V$$

where P and V are the pressure and volume, respectively.

From kinetic molecular theory, the internal energy of a given mass of an ideal gas at constant temperature is independent of value, *i.e.*, $\left(\frac{\partial E}{\partial V}\right)_T = 0$

If such a gas is expanded isothermally, *i.e.*, T is constant then $dT = 0$. Substituting these values in equation (2), we get

$$dE = 0.$$

So, the *change in internal energy when an ideal gas is expanded isothermally is* zero.

• 7.6. ENTHALPY

Suppose the change in the state of a system is carried out at constant pressure. In such a case, there will be a change in volume. Let the volume changes from V_A to V_B, at constant pressure P. The work done (W) by the system will be given by,

$$W = P\ (V_B - V_A) \qquad \ldots(1)$$

From first law of thermodynamics,

$$\Delta E = Q - W \qquad \ldots(2)$$

So, combining equations (1) and (2) we get,

$$\Delta E = Q - P\ (V_B - V_A)$$

or $$E_B - E_A = Q - P\ (V_B - V_A)$$

or $$Q = (E_B + P\ V_B) - (E_A + P\ V_A) \qquad \ldots(3)$$

The quantity $E + P\ V$ is known as **enthalpy** of the system. It is represented by H and shows the *total energy contained in the system*. Therefore,

$$H + E + P\ V$$

As, E, P and V are definite properties depending upon the state of the system, it follows that H is also a definite property depending upon the state of a system. From equation (3), therefore,

$$Q = H_B - H_A = \Delta H \qquad \ldots(4)$$

ΔH represents the increase in enthalpy of a system when it changes from state A to state B. Like ΔE, ΔH depends on the initial and final states of a system and it is a definite quantity. According to equation (4), the *change in enthalpy is equal to the heat absorbed when the change is carried out at constant pressure.*

From equations (1), (2) and (4), we get,

$$\Delta E = (H_B - H_A) - P\,(V_B - V_A)$$

or $$\Delta E = \Delta H - P\,\Delta V$$

or $$\Delta H = \Delta E + P\,\Delta V \qquad ...(5)$$

• 7.7. HEAT CAPACITY

The ***heat capacity*** or more accurately the ***mean heat capacity*** of a system is defined as the *quantity of heat required to raise the temperature of the system from a lower to higher temperature divided by the temperature difference.* The heat capacity of a system between temperatures T_1 and T_2 is given by,

$$C\,(T_2, T_1) = \frac{Q}{T_2 - T_1} \qquad ...(1)$$

As heat capacity varies with temperature, the true heat capacity is represented by the differential equation,

$$C = \frac{dQ}{dT}$$

For one mole of the gas, the heat capacity is called ***molar heat capacity*** *and is denoted by the symbol, C.*

Molar heat capacity of gases have two values, ***one at constant volume*** (C_V) and the other at ***constant pressure*** (C_P). At *constant* volume, no external work ($P\,\Delta V$) is done either by the system or on the system, as there is no change in volume. So, from first law of thermodynamics ($\Delta E = Q - W$),

$$Q = \Delta E$$

$$\therefore \qquad C_V\,(T_2, T_1) = \left(\frac{\Delta E}{T_2 - T_1}\right)_V \qquad \text{(From equation 1).}$$

or $$C_V = \left(\frac{\partial E}{\partial T}\right)_V \qquad ...(2)$$

So, *molar heat capacity of a system at constant volume is defined as the increase in internal energy of the system per degree rise in temperature.*

At constant pressure P, the heat supplied is used in raising the internal energy of the system and also in doing work by expansion. Let the volume increases by ΔV. So, ***the value of C_P is always greater than the value of C_V***. So, from first law of thermodynamics,

$$Q = \Delta E + W = \Delta E + P\,\Delta V$$

$$C_P\,(T_2, T_1) = \left(\frac{Q}{T_2 - T_1}\right)_P = \left(\frac{\Delta E + P\,\Delta V}{\Delta T}\right)_P = \left(\frac{\Delta H}{\Delta T}\right)_P$$

or $$C_P = \left(\frac{\partial H}{\partial T}\right)_P \qquad ...(3)$$

So, molar heat capacity of a system at constant pressure is defined as the increase in enthalpy of the system per degree rise in temperature.

Derivation of $C_P - C_V = R$

We know that,

$$\therefore \qquad C_P = \frac{dH}{dT} \text{ and } C_V = \frac{dE}{dT}$$

$$C_P - C_V = \frac{dH}{dT} - \frac{dE}{d\,T} = \frac{d\,(E + P\,V)}{dT} - \frac{dE}{dT} = \frac{dE}{dT} + \frac{d\,(P\,V)}{dT} - \frac{dE}{dT}$$

or
$$C_P - C_V = \frac{d\,(P\,V)}{dT} \qquad \ldots(4)$$

For an ideal gas, $PV = RT$. Differentiating this equation with respect to T, we get

$$\frac{d\,(PV)}{dT} = R$$

So, equation (4) becomes,

$$C_P - C_V = R.$$

• 7.8. WORK DONE IN AN ISOTHERMAL REVERSIBLE EXPANSION OF A GAS

A process is said to be reversible if the properties of the system at every instant remain uniform during the process. In a reversible process, the change from one equilibrium state to another is brought about *in infinitesimal steps so that the properties of each step change infinitesimally from* those of the next step. A reversible process is extremely slow and requires infinite time to complete. Reversible process is an ideal process which is difficult to be realised in actual practice. However, the reversible processes are very helpful in studying thermodynamics. From a reversible process maximum amount of work can be obtained from a given net process. This is explained as follows:

Consider a gas enclosed in a cylinder fitted with a weightless and frictionless piston. The pressure, volume and temperature of the gas be P_1, V_1 and T_1, respectively. Suppose the volume is expanded from V_1 to V_2 isothermally and reversibly. Let the final pressure be P_2. The work done (W_{rev}) in a reversible process is given by,

$$W_{\text{rev}} = nRT \log \frac{V_2}{V_1} = nRT \log \frac{P_1}{P_2} = nRT \log\left(1 + \frac{P_1 - P_2}{P_2}\right)$$

Expanding the logarithmic term and neglecting the higher powers of $(P_1 - P_2)/P_2$, as this quantity is small, we get

$$W_{\text{rev}} = nRT \frac{P_1 - P_2}{P_2} \qquad [\because \log(1 + x) = x] \quad \ldots(1)$$

When the work done by the same volume expansion from V_1 to V_2 is considered in an irreversible way by suddenly reducing the pressure from P_1 to P_2, the work done (W_{irr}) is given by,

$$W_{\text{irr}} = \text{External pressure } (P_2) \times \text{Volume change}$$

$$= P_2 (V_2 - V_1) = P_2 \left[\frac{nRT}{P_2} - \frac{nRT}{P_1}\right] = nRT\left(1 - \frac{P_2}{P_1}\right) \qquad \ldots(2)$$

Subtracting equation (2) from (1), we get

$$W_{\text{rev}} - W_{\text{irr}} = nRT\left[\frac{P_1 - P_2}{P_2} - \left(1 - \frac{P_2}{P_1}\right)\right] = nRT\left[\frac{P_1 - P_2}{P_2} - \frac{P_1 - P_2}{P_1}\right]$$

$$= nRT\,(P_1 - P_2)\left[\frac{1}{P_2} - \frac{1}{P_1}\right]$$

$$= \text{Positive quantity} \qquad (\because P_1 > P_2)$$

Thus, work done in a reversible isothemal process is definitely greater than the work done in an irreversible process. No other process will give greater amount of work than this. So, it proves that the work done in reversible expansion process is maximum.

Consider n moles of an ideal gas enclosed in a cylinder fitted with a weightless and frictionless piston. Let its pressure be P which in equilibrium state is equal to the external pressure on the piston. Keeping the temperature constant at T, the pressure is decreased by an infinitesimal amount dP, so that there is an infinitesimal increase in volume, dV. The very small amount of work done (dW) during this isothermal reversible expansion is,

$$dW = (P - dP)\,dV = P\,dV - dP\,.\,dV$$

or
$$dW = P\,dV \qquad (\text{Neglecting } dP\,.\,dV)$$

Since the step is reversible, the value dW corresponds to the maximum work. The maximum work, $W_{\max}$ for the isothermal expansion of the gas from volume V_1 to V_2 or pressure P_1 to P_2 will be :

$$W_{\max} = \int_{V_1}^{V_2} dW_{\max} = \int_{V_1}^{V_2} P dV \qquad \text{...(3)}$$

For n moles of an ideal gas, $PV = nRT$, *i.e.*, $P = nRT/V$

$$W_{\max} = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1} = 2.303\ nRT \log \frac{V_2}{V_1} \qquad \text{...(4)}$$

From Boyle's law, $P_1/P_2 = V_2/V_1$, therefore

$$W_{\max} = nRT \ln \frac{P_1}{P_2} = 2.303\ nRT \log \frac{P_1}{P_2} \qquad \text{...(5)}$$

For 1 mole of an ideal gas, equations (4) and (5) become

$$W_{\max} = RT \ln \frac{V_2}{V_1} = 2.303\ RT \log \frac{V_2}{V_1} \qquad \text{...(6)}$$

$$W_{\max} = RT \ln \frac{P_1}{P_2} = 2.303\ RT \log \frac{P_1}{P_2} \qquad \text{...(7)}$$

For n moles of an ideal gas, we can write equations (4) and (5) as,

$$W_{\max} = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2} \qquad \text{...(8)}$$

$$= 2.303\ nRT \log \frac{V_2}{V_1} = 2.303\ nRT \log \frac{P_1}{P_2} \qquad \text{...(9)}$$

• 7.9. WORK DONE IN ADIABATIC REVERSIBLE EXPANSION OF A GAS OR DEDUCTION OF PV^{γ} = CONSTANT

In adiabatic expansion, no heat is absorbed or evolved in the system, *i.e.*, $Q = 0$. So, from first law of thermodynamics,

$$\Delta E = -W$$

In adiabatic expansion, work is done by the system on the surroundings, so W must be positive. So, ΔE is negative, *i.e.*, there is a decrease in internal energy of the system. Thus, the temperature of the system falls.

Let P be the external pressure and ΔV be the increase in volume. The external work done by the system is equal to $P\,\Delta V$.

$$\therefore \qquad \Delta E = -W = -P\,\Delta V$$

If ΔT be the fall in temperature, then we know that,

$$\Delta E = C_V \Delta T \qquad \left(\because C_V = \frac{\Delta E}{\Delta T}\right)$$

or

$$C_V \Delta T = -P\,\Delta V = -W$$

or

$$W = P\,\Delta V = -C_V \Delta T$$

$$= -C_V (T_2 - T_1) \qquad \text{...(1)}$$

Equation (1) gives the maximum work involved.

For infinitesimally small quantities, equation (1) becomes

$$C_V\, dT = -P\, dV = -RT \frac{dV}{V}$$

or

$$C_V \cdot \frac{dT}{T} = -R \frac{dV}{V}$$

or

$$\int_{T_1}^{T_2} C_V \frac{dT}{T} = -\int_{V_1}^{V_2} R \frac{dV}{V}$$

or $$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} = R \ln \frac{V_1}{V_2} \qquad \text{...(2)}$$

Knowing $C_P - C_V = R$ and $C_P/C_V = \gamma$, equation (2) becomes

$$\ln \frac{T_2}{T_1} = \frac{R}{C_V} \ln \frac{V_1}{V_2} = \left(\frac{C_P - C_V}{C_V}\right) \ln \frac{V_1}{V_2} = \left(\frac{C_p}{C_v} - 1\right) \ln \frac{V_1}{V_2}$$

or $$\ln \frac{T_2}{T_1} = (\gamma - 1) \ln \frac{V_1}{V_2} = \ln \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

or $$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \qquad \text{...(3)}$$

As $P_1V_1 = RT_1$ and $P_2V_2 = RT_2$, it follows from equation (3)

$$\frac{P_2V_2/R}{P_1V_1/R} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

or $$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

or $$P_1V_1^{\gamma} = P_2V_2^{\gamma} \qquad \text{...(4)}$$

or $$PV^{\gamma} = \text{constant}.$$

Also, $$P_1^{1-\gamma} . T_1^{\gamma} = P_2^{1-\gamma} . T_2^{\gamma} \qquad \text{(From equations 3 or 4)}$$

$$\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{1-\gamma} \qquad \text{...(5)}$$

• 7.14. JOULE THOMSON EFFECT

[I] Joule-Thomson Effect

The behaviour of real gases was, investigated more systematically by Joule and Thomson. Their experimental procedure is shown in figure (1). When air or any other gas is permitted to pass from a region of one constant pressure, through a small orifice or porous plug to another region with a lower pressure which is also maintained constant, we have an expansion known as **porous plug expansion** in which the temperature falls. Such an expansion is also known as **'throttled adiabatic expansion'**. ***The change of temperature thus produced whenever a gas is made to expand from region of high pressure to a region of extremely low pressure through a porous plug is known as Joule-Thomson effect.***

[II] Joule-Thomson Effect For An Ideal Gas

Almost all gases behave in the above manner, *i.e.*, when subjected to porous plug expansion *the temperature of the gas falls.* Hydrogen and helium behave abnormally at ordinary temperatures. In other words, they get warmer instead of becoming cooled. It is, however, seen that if they are previously cooled (below −80°C for H_2 and below −240°C for He) they behave normally, *i.e.*, show the usual cooling behaviour.

The cooling effect is due to decrease in the kinetic energy of the gaseous molecules, since a part of this energy is used up in overcoming the vander Waals forces of attraction existing between the molecules. It has been observed that the Joule-Thomson effect is very small when a gas approaches ideal behaviour. ***In an ideal gas, the Joule-Thomson effect is zero.*** Therefore, when *an ideal gas expands in vacuum,* there is neither evolution nor absorption of heat, *i.e.,* $q = 0$. This is quite probable because in an ideal gas, the vander Waals forces are negligible and there is no expenditure of energy in overcoming these forces during expansion.

When an ideal gas expands in vacuum, it does no work because the pressure against which it expands is zero, *i.e.*, $w = 0$. From first law of thermodynamics, $\Delta E = q - w$, therefore, $\Delta E + 0 = 0$ or $\Delta E = 0$.

[III] Joule's law

When an ideal gas expands under adiabatic conditions in vacuum, there is no change in its internal energy. In other words, *the internal energy of a given amount of an ideal gas at constant temperature is independent of its volume, i.e.*.

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \qquad \ldots(1)$$

[IV] Inversion Temperature

The temperature at which the Joule-Thomson coefficient, i.e., change of temperature with pressure at constant enthalpy $\left[\left(\frac{\partial T}{\partial P}\right)_H\right]$***, changes its sign is known as the inversion temperature.*** At this temperature $\mu_{J.T.}$ is zero so that

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

or

$$T_i = \frac{2a}{Rb}$$

where T_i represents the inversion temperature. Thus, the inversion temperature depends upon the vander Waals constant a and b of the gas.

At critical point, $T_c = \frac{8a}{27bR}$

$$\therefore \qquad \frac{T_i}{T_c} = \frac{2a}{Rb} \times \frac{27bR}{8a} = \frac{27}{4} = 6.75$$

So, for any vander Waals gas, the ratio $\frac{T_i}{T_c}$ is always 6.75.

The calculated inversion temperature in case of hydrogen has been found to be rather high as compared to the observed value of −80°C. This may be attributed to an exceptionally low value of the constant a. The same is true for helium. In other gases, however, the calculated values are found to be fairly close to the observed values, keeping in view the various approximations involved in the derivation of equation $b = \frac{2a}{RT_c}$.

The inversion temperatures of most of the gases are very high (much higher than the room temperature). That is why, these gases undergo cooling on adiabatic expansion under ordinary conditions of temperature. On the other hand, the inversion temperatures of hydrogen and helium are very low, *i.e.*, −80°C and −240°C, respectively (being much below 0°C). So, these gases undergo heating on adiabatic expansion under ordinary conditions of temperature. However, if these gases are first cooled to temperatures below their inversion temperatures and then allowed to expand adiabatically, these gases also show cooling effect.

NUMERICAL PROBLEMS

Ex. 1. *Calculate Q, W, ΔE and ΔH for the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1 atm to a final pressure of 0.1 atm at a constant temperature of 273 K.*

Solution. Here $P_1 = 1$; $P_2 = 0.1$, $n = 1$, $R = 2$, $T = 273$.

$$W = 2.303\, nRT \log P_1/P_2 = 2.303 \times 1 \times 2 \times 273 \log \frac{1.0}{0.1}$$

$$= \mathbf{1257.43\ calories}$$

For an ideal gas expansion at constant temperature,

$$\Delta E = C_V\, dT = 0$$

From first law of thermodynamics,

$$\Delta E = Q - W = 0 \text{ or } Q = W$$

$$\therefore \qquad Q = \mathbf{1257.43\ calories.}$$

When temperature is constant, PV = constant, *i.e.*,

$$\Delta PV = 0.$$

$$\Delta H = \Delta E + \Delta PV = \mathbf{0}.$$

Ex. 2. *Calculate the work done when 1.0 mole of water at 100°C vaporises against an atmospheric pressure of 1.0 atm (assuming ideal gas behaviour).*

Solution. Work done, $W = P \times \Delta V = P\,(V_g - V_l)$

$$P = hdg = 76 \times 13.6 \times 981/\text{dyne cm}^{-2}$$

$$V_l = 18 \text{ ml} \qquad (\because V = m/d)$$

$$V_2 = \text{Volume of steam at } 100°\text{C} = \frac{22400 \times 373}{273} = 30600 \text{ ml} \qquad \left(\because \frac{V_1}{T_1} = \frac{V_2}{T_2}\right)$$

$$\therefore \quad W = 76 \times 13.6 \times 98\,(30600 - 18) \text{ erg}$$

$$= \frac{76 \times 13.6 \times 981 \times 30582}{4.184 \times 10^7} \text{ cal}$$

$$= \mathbf{741.4\ cal} \qquad (\because 4.184 \times 10^7 \text{ erg} = 1 \text{ cal})$$

Ex. 3. *Calculate the work that must be done at 25°C on two moles of CO_2 to compress them from a volume of 20 litres to a volume of 1 litre. (Assume ideal gas behaviour for CO_2).*

Solution. Here $V_1 = 20, V_2 = 1, n = 2, T = 298, R = 2.$

$$\therefore \quad W = 2.303\, nRT \log \frac{V_2}{V_1}$$

$$= 2.303 \times 2 \times 2 \times 298 \log \frac{1}{20}$$

$$= \mathbf{-\,3571.47\ calories.}$$

Ex. 4. *Calculate the work done during isothermal expansion of one mole of an ideal gas from 10 atm to 1 atm at 300 K.*

Solution. Here $n = 1, P_1 = 10, P_2 = 1, T = 300, R = 2.$

$$W = 2.303\, nRT \log P_1/P_2$$

$$= 2.303 \times 1 \times 2 \times 300 \log \frac{10}{1}$$

$$= \mathbf{1381.8\ calories.}$$

Ex. 5. *Calculate ΔE and ΔH when 10 litres of an ideal gas at STP is heated to 100°C in a closed container.* $\left(\text{Given } C_V = \frac{3}{2} R\right)$

Solution. We know that

$$C_V\,(T_2, T_1) = \left(\frac{\Delta E}{T_2 - T_1}\right)$$

or
$$\Delta E = C_V\,(T_2, - T_1) = \frac{3}{2} R \times (373 - 273)$$

$$= \frac{3}{2} \times 2 \times 100 = \mathbf{300\ calories.}$$

We know that, $\Delta H = \Delta E + P\,\Delta V$

or
$$\Delta H = \Delta E + R\Delta T \qquad \left\{\begin{matrix} \because PV_1 = RT_1, PV_2 = RT_2 \\ P\,(V_2 - V_1) = R\,(T_2 - T_1) \end{matrix}\right\}$$

$$= 300 + 2\,(373 - 273) = \mathbf{500\ calories.}$$

Ex. 6. *To what pressure must a given volume of nitrogen originally at 100°C and 1 atm. pressure be adiabatically compressed in order to raise its temperature to 400°C? (C_P/C_V for nitrogen = 1.4).*

Solution. For adiabatic expansion :

$$P_1^{1-\gamma}\, T_1^{\gamma} = P_2^{1-\gamma}\, T_2^{\gamma} \quad \text{or} \quad \left(\frac{P_2}{P_1}\right)^{1-\gamma} = \left(\frac{T_1}{T_2}\right)^{\gamma}$$

or
$$(1 - \gamma)\,(\log P_2 - \log P_1) = \gamma\,(\log T_1 - \log T_2)$$

Here $P_1 = 1, T_1 = 373, T_2 = 673, \gamma = 1.4, P_2 = ?$

$$\therefore \quad (1 - 1.4)(\log P_2 - \log 1) = 1.4(\log 373 - \log 673)$$

or $$\log P_2 = \frac{1.4}{0.4}(\log 673 - \log 373) = 3.5\,(2.8280 - 2.5717)$$

$$= 0.89705.$$

$$\therefore \quad P_2 = \text{antilog } 0.89705 = \mathbf{7.889\ atmospheres.}$$

Ex. 13. What is the enthalpy of NH_3 if,

$$N_2 + 3H_2 \rightarrow 2NH_3,\ \Delta H = -22\ kcal.$$

Solution. $\Delta H = 2H_{\mathrm{NH_3}} - (H_{\mathrm{N_2}} + 3H_{\mathrm{H_2}}) = 2H_{\mathrm{NH_3}} - (0 + 0)$

or $$-22 = 2\,H_{\mathrm{NH_3}} \text{ or } H_{\mathrm{NH_3}} = -\mathbf{11\ kcal.}$$

• 7.11. SECOND LAW OF THERMODYNAMICS

We know that first law of thermodynamics tells us about the relation between heat and work and their equivalence. It also tells us about the conservation of energy during all processes, physical and chemical. It does not, however, give us any idea about the extent of convertibility of one form of energy into another. It also does not give us an idea about the spontaneity of a reaction, *i.e.*, whether a given change is possible under given conditions of pressure and temperature or not.

If we study the relationship between work and heat, we see that whereas different forms of energy can be readily and completely converted into heat, it is not possible to completely reconvert heat into work. In order to represent the limitations on the convertibility of heat into work and to predict the direction of change of all naturally occurring processes, Kelvin, Clausius, etc. put forward a law, known as *second law of thermodynamics.* This law tells us the direction of change under given conditions of temperature and pressure.

Second law of thermodynamics states that, ***"whenever a spontaneous process occurs, it is accompanied by an increase in the total energy of the universe."***

Second law of thermodynamics can also be stated in a number of ways as follows :

(1) Planck's definition : *It is impossible to construct a machine working in cycles which can convert heat completely into an equivalent amount of work without producing any changes elsewhere.*

(2) Kelvin's definition : *It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cooler reservoir.*

(3) Clausius' definition : *It is impossible for a cyclic process to transmit heat from a body at a lower temperature to one at a higher temperature, without at the same time converting some work into heat.*

Second law of thermodynamics gives us an idea about free energy, entropy etc. which tell us about the spontaneity or feasibility of a process.

• 7.12. CARNOT'S CYCLE

When a system after completing a series of changes returns to its original state, it is said to have completed a cycle. The entire process is known as **cyclic process.** In a cyclic process, $\Delta E = 0$. So, from first law of thermodynamics, $\Delta E = q - w$

or $$0 = q - w$$

or $$q = w.$$

In other words, in a cyclic process the heat absorbed by a system is equal to the work done by it.

Carnot's Cycle

In order to calculate the maximum extent to which heat can be converted into work, Carnot used a cycle of processes which occurred under reversible conditions and is known as *Carnot's cycle.* The medium used in operating Carnot's engine was one mole of an ideal gas enclosed in a cylinder fitted with a frictionless and weightless piston.

The Carnot's cycle consists of four processes :

1. Isothermal reversible expansion

2. Adiabatic reversible expansion.
3. Isothermal reversible compression.
4. Adiabatic reversible compression.

The above four processes are shown in the diagram of Carnot cycle (Fig. 1).

1. First operation : *Isothermal reversible expansion :*

Let T_2, P_1 and V_1 be the temperature, pressure and volume, respectively of the gas enclosed in the cylinder initially. The gas is allowed to expand reversibly and isothermally at a higher temperature T_2, so that its volume increases from V_1 (at A) to V_2 (at B).

In an isothermal expansion of an ideal gas, $\Delta E = 0$, so the heat absorbed (q) is equal to the work done (w) by the system ($\because \Delta E = q - w$). Let q_2 be the heat absorbed by the system at temperature T_2 and W_1 be the work done by the system in this step, then

$$q_2 = W_1 = RT_2 \log_e \frac{V_2}{V_1}. \qquad \ldots(1)$$

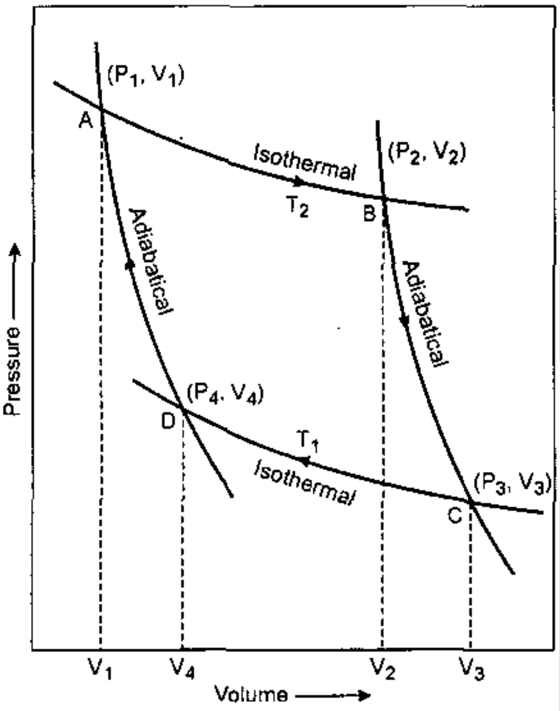


Fig. 1. Carnot's cycle

2. Second operation : *Adiabatic reversible expansion :*

The gas at B is allowed to expand reversibly and adiabatically, so that its volume increases from V_2 (at B) to V_3 (at C).

Under adiabatic conditions, there is no exchange of heat between the system and surroundings, *i.e.*, $q = 0$. So, according to first law of thermodynamics ($\Delta E = q - w$), we have

$$\Delta E = -w. \qquad \ldots(2)$$

As in adiabatic expansion, work *is always done by the system, i.e., w is always positive,* therefore, ΔE will always be negative. In other words, in this process, there will always be a fall in temperature. Let the temperature in this process falls from T_2 to T_1.

We know that : $$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\Delta E}{\Delta T}$$

or $$\Delta E = C_V \Delta T. \qquad \ldots(3)$$

Combining equations (2) and (3),

$$w = -C_V \,.\, \Delta T = -C_V (T_1 - T_2) = C_V (T_2 - T_1)$$

If the work done by the system in this step is W_2, then

$$W_2 = C_V (T_2 - T_1). \qquad \ldots(4)$$

3. Third operation : *Isothermal reversible compression :*

The gas at temperature T_1 is now allowed to compress reversibly and isothermally so that the volume decreases from V_3 (at C) to V_4 (at D). In this step, heat is given out by the system. If q_1 is the heat given out by the system and W_3 is the work done on the system then giving proper signs to q_1 and W_3, we can write

$$-q_1 = -W_3 = RT_1 \log_e \frac{V_4}{V_3}. \qquad \ldots(5)$$

4. Fourth operation : *Adiabatic reversible compression :*

The gas is now allowed to compress reversibly and adiabatically so that its volume decreases from V_4 (at D) to V_1 (at A). Thus, the system returns to its original state.

In this step, $q = 0$ and so from first law of thermodynamics ($\Delta E = q - w$),

$$\Delta E = -w = -(-w) = +w.$$

As in this step, work is done on the system, w is always negative. Therefore, ΔE will be positive, *i.e.*, temperature will increase, say from T_1 to T_2. We know that

$$w = \Delta E = C_V \Delta T = C_V (T_2 - T_1).$$

If W_4 be the work done on the system, then

$$W_4 = C_V (T_2 - T_1).$$

Giving proper sign to W_4, we have

$$-W_4 = -C_V (T_2 - T_1). \qquad \text{...(6)}$$

The net work done by the system,

$$W = W_1 + W_2 + (-W_3) + (-W_4)$$

$$= RT_2 \log_e \frac{V_2}{V_1} + C_V (T_2 - T_1) + RT_1 \log_e \frac{V_4}{V_3} - C_V (T_2 - T_1)$$

$$= RT_2 \log_e \frac{V_2}{V_1} + RT_1 \log_e \frac{V_4}{V_3}$$

or

$$W = RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_3}{V_4}. \qquad \text{...(7)}$$

For adiabatic process, we know that

$$C_V \log_e \frac{T_2}{T_1} = R \log_e \frac{V_1}{V_2}$$

For step II :

$$C_V \log_e \frac{T_2}{T_1} = R \log_e \frac{V_3}{V_2} \qquad \text{...(8)}$$

For step IV :

$$C_V \log_e \frac{T_2}{T_1} = R \log_e \frac{V_4}{V_1}. \qquad \text{...(9)}$$

From equations (8) and (9), we can write

$$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

or

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}.$$

So, equation (7) becomes

$$W = RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_2}{V_1}$$

or

$$W = R (T_2 - T_1) \log_e \frac{V_2}{V_1}. \qquad \text{...(10)}$$

The net heat absorbed by the system is given by

$$q = q_2 + (-q_1) = RT_2 \log_e \frac{V_2}{V_1} + RT_1 \log_e \frac{V_4}{V_3}$$

or

$$q = RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_3}{V_4} = RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_2}{V_1}$$

or

$$q = R (T_2 - T_1) \log_e \frac{V_2}{V_1}. \qquad \text{...(11)}$$

From equations (10) and (11), we can write

$$q = W \qquad \text{...(12)}$$

Thus, the essential condition for a cyclic process, *i.e.*, $w = q$ is fully satisfied.

Efficiency of a Heat Engine

Efficiency of a heat engine is defined as *the fraction of the heat absorbed which it can convert into useful work.* It is represented by η.

So,

$$\eta = \frac{W}{q_2} \qquad \text{...(13)}$$

Now

$$W = R (T_2 - T_1) \log_e \frac{V_2}{V_1} \qquad \text{[From equation (10)]}$$

and

$$q_2 = RT_2 \log_e \frac{V_2}{V_1} \qquad \text{[From equation (11)]}$$

$$\therefore \qquad \eta = \frac{R(T_2 - T_1)\log_e \frac{V_2}{V_1}}{RT_2 \log_e \frac{V_2}{V_1}} = \frac{T_2 - T_1}{T_2}$$

Moreover, $W = q = q_2 - q_1$ [From equation (12)]

So, from equation (13), we can write

$$\therefore \qquad \eta = \frac{q_2 - q_1}{q_2}$$

$$\text{So,} \qquad \eta = \frac{q_2 - q_1}{T_2} = \frac{T_2 - T_1}{T_2} \qquad \ldots(14)$$

As $\frac{T_2 - T_1}{T_2}$ or $\frac{q_2 - q_1}{q_2}$ is always less than unity, the efficiency of a heat engine will always be less than unity. In fact, *no heat engine has yet been constructed whose efficiency is equal to unity.*

Ex. 1. *Calculate the efficiency of a reversible engine working between 27°C and 127°C.*

Solution. We know that efficiency is given by

$$\eta = \frac{T_2 - T_1}{T_2} = \frac{400 - 300}{400}$$

$$(\because T_1 = 27 + 273 = 300 \text{ K}; T_2 = 127 + 273 = 400 \text{ K})$$

$$\because \qquad \eta = \frac{100}{400} = 0.25 \text{ or } 25\%.$$

Efficiency = **25%**

Ex. 2. *Heat supplied to a Carnot engine is 453.6 kcal. How much useful work can be done by the engine which works between 0°C and 100°C?*

Solution. $\eta = \frac{T_2 - T_1}{T_2} = \frac{373 - 273}{373} = \frac{100}{373}$

$\therefore$ Useful work = η × Heat supplied

$$= \frac{100}{373} \times 453.6 = \mathbf{121.6 \text{ kcal.}}$$

• 7.13. ENTROPY

Clausius (1850) introduced a new thermodynamic state function and termed it ***entropy***. From Carnot's cycle, we can show that

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \qquad \ldots(1)$$

where, q_2 is the heat absorbed at a higher temperature T_2 and q_1 is the heat evolved at a lower temperature T_1. From equation (1),

$$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

$$\text{or} \qquad \frac{q_1}{q_2} = \frac{T_1}{T_2} \quad \text{or} \quad \frac{q_1}{T_1} = \frac{q_2}{T_2}. \qquad \ldots(2)$$

Giving proper signs, *i.e.*, positive to heat absorbed and negative to heat evolved, we can write equation (2) as

$$\frac{-q_1}{T_1} = \frac{+q_2}{T_2}$$

$$\text{or} \qquad \frac{q_1}{T_1} + \frac{q_2}{T_2} = 0. \qquad \ldots(3)$$

Equation (3) shows that in a Carnot cycle, the summation of all q/T terms is zero. Any reversible cycle, say ABA, may be taken to be made up of a larger number of small Carnot cycles as shown in figure (2) (horizontals are adiabaticals and verticals are iso-thermals). For each Carnot cycle, the sum of two q/T terms involved is zero vide equation (3).

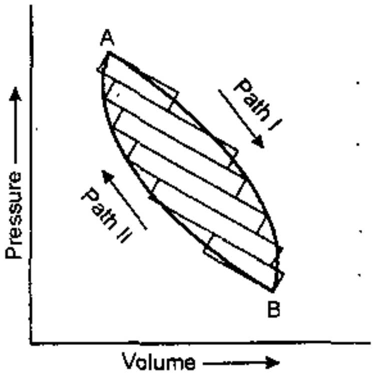


Fig. 2. Concept of entropy

or the complete reversible cycle ABA, we can write

$$\Sigma \frac{q}{T} = 0 \qquad \ldots(4)$$

For an infinitesimal change, equation (4) can be written as ,

$$\int \frac{dq}{T} = 0. \qquad \ldots(5)$$

The cycle ABA can be performed in two steps, *viz*, from A to B along path I and then from B to A along path II. We can thus write from equation (5),

$$\int \frac{dq}{T} = \int_A^B \frac{dq}{T} \text{(Path I)} + \int_B^A \frac{dq}{T} \text{(Path II)} = 0$$

or
$$\int_A^B \frac{dq}{T} \text{(Path I)} = -\int_B^A \frac{dq}{T} \text{(Path II)}$$

or
$$\int_A^B \frac{dq}{T} \text{(Path I)} = \int_A^B \frac{dq}{T} \text{(Path II)}.$$

This shows that $\int_A^B \frac{dq}{T}$ is the same and independent of the path taken from A to B. Its value depends only on the initial and final states, *i.e.*, A and B of the system. This quantity, like ΔE or ΔH, is dependent only on the states of the system. This function is called ***entropy*** and is denoted by S.

If S_A and S_B be the entropy of the system in the initial and final states, then change in entropy (ΔS) is given by

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T} \qquad \ldots(6)$$

For a finite change, equation (6) can also be written as,

$$\Delta S = \frac{q}{T} \qquad \ldots(7)$$

For an infinitesimally small change,

$$dS = \frac{dq}{T}. \qquad \ldots(8)$$

[i] Physical Significance of Entropy

Entropy of a substance is a real physical quantity and like pressure, temperature, internal energy, it is a definite function of the state of the body.

Entropy is also defined as the degree of disorder of a system.* Greater the disorder or randomness of a system, greater will be the entropy of the system.

Entropy is related to thermodynamic probability according to Boltzmann's equation,

$$S = k \log W + K$$

where k = Boltzmann's constant, K = another constant and W = thermodynamic probability. Planck (1912) showed that $K = 0$ and so

$$S = k \log W$$

This equation is known as **Boltzmann's-Planck equation.** It is not possible to evaluate the absolute value of entropy. It is only the entropy change which can be measured and is of great value as it provides valuable information regarding the spontaneity or feasibility of a process.

[II] Unit of Entropy

As entropy change (ΔS) is given by $\Delta S = q/T$, the unit of entropy will be *calorie per degree per mole* (in C.G.S. unit) or *joule per degree Kelvin per mole* (in S.I. unit). This unit is generally referred to as entropy unit (*e.u.*).

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*Second law of thermodynamics tells us that all the internal energy of any substance cannot be converted into useful work. The portion of this total energy which is used for doing useful work is called *available energy* and the remaining part which cannot be converted into useful work is called *unavailable* energy. *Entropy is thus a measure of this unavailable energy.* Entropy is thus the unavailable energy per unit temperature, *i.e.*,

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temperature}}.$$

[III] Entropy Change During Isothermal Expansion

Suppose one mole of an ideal gas is allowed to expand reversibly and isothermally from volume V_1 to volume V_2 at a constant temperature T.

The amount of work done when 1 mole of an ideal gas is allowed to expand isothermally from volume V_1 to volume V_2 is given by

$$w = 2.303\, RT \log_{10} \frac{V_2}{V_1}$$

In an isothermal process, $\Delta E = 0$ and so according to first law of thermodynamics ($\Delta E = q - w$), we have

$$0 = q - w$$

or

$$q = w = 2.303\, RT \log_{10} \frac{V_2}{V_1} \qquad \ldots(1)$$

We know that change in entropy (ΔS) is given by

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{2.303\, RT \log_{10} \frac{V_2}{V_1}}{T}$$

or

$$\Delta S = 2.303\, R \log_{10} \frac{V_2}{V_1} = 2.303\, R \log_{10} \frac{P_1}{P_2} \qquad \ldots(2)$$

($\because P_1 V_1 = P_1 V_2$, at constant temperature)

For n moles of an ideal gas, equation (2) can be written as

$$\Delta S = 2.303\, nR \log_{10} \frac{V_2}{V_1} = 2.303\, nR \log_{10} \frac{P_1}{P_2} \qquad \ldots(3)$$

[IV] Standard Entropy of a Gas

If the entropy of the gas at 1 atmospheric pressure and 298 K is expressed in terms of an ideal gas at the same pressure, then this value is referred to as the ***standard entropy*** of the gas.

• 7.14. ENTROPY CHANGES FOR DIFFERENT PROCESSES

[I] Entropy Change Accompanying Change from Solid to Liquid Phase

A solid changes into liquid state at its fusion point. The process requires absorption of heat (*i.e.*, latent heat of fusion).

Consider melting of 1 mole of a substance reversibly at fusion point T_f at constant pressure. Let ΔH be the molar heat of fusion. The entropy change (ΔS_f) will then be given by

$$\Delta S_f = \frac{\Delta H_f}{T_f} \qquad \ldots(1)$$

[II] Entropy Change Accompanying Change from Liquid to Vapour Phase

Suppose 1 mole of a substance changes from the liquid to vapour state reversibly at its boiling point, T_b under constant pressure. If ΔH_v be the molar heat of vaporisation, then the entropy change (ΔS_v) is given by,

$$\Delta S_v = \frac{\Delta H_v}{T_b} \qquad \ldots(2)$$

[As ΔH_f and ΔH_v are positive, hence processes of fusion and vaporisation are both accompanied by increase of entropy.]

(III) Entropy Changes in Reversible and Irreversible Processes

Suppose a system undergoes a change of state by a reversible process at constant temperature, T. The heat that it absorbs from the surroundings may be represented by q_{rev}. The increase in entropy of the system ΔS_{system} will be given by the equation

$$\Delta S_{\text{system}} = \frac{q_{\text{rev}}}{T} \qquad \ldots(3)$$

Since the surroundings have lost heat equal to q_{rev} reversibly at the same temperature T, the entropy change of surroundings, ΔS_{surr} will be given by the equation

$$\Delta S_{surr} = \frac{-q_{rev}}{T} \qquad \ldots(4)$$

As heat is lost by the surroundings, it is given a negative sign. The sum total of the entropy of the system and its surroundings during a reversible process is zero, *i.e.*,

$$\Delta S_{universe} = S_{system} + \Delta S_{surr}$$

$$= \frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0. \qquad \ldots(5)$$

Therefore, the ***net entropy change of the universe is constant in a reversible process.***

Suppose the same system undergoes the same change of state by irreversible or spontaneous process at constant temperature, T. The work done by the system will now be less and so the heat absorbed q_{irr} will be less than q_{rev}. Since entropy is a function of the state of the system, the increase in entropy of the system will be the same irrespective of the fact whether the change has been brought about reversibly or irreversibly. Hence, ΔS_{system} will remain the same as before, *i.e.*, equal to q_{rev} as given by equation (3). But as the work done by the system during irreversible process is less, the heat absorbed by the system will also be less, say equal to q_{irr}. It follows that the heat lost by the surroundings will be less than q_{rev}.

However, the loss of heat by the surroundings can be considered to take place infinitesimally slowly, *i.e.*, reversibly in view of an infinitely large size of the surroundings. So, the entropy change of the surroundings is given by,

$$\Delta S_{surr} = -\frac{q_{irr}}{T} \qquad \ldots(6)$$

The sum total of entropy change of the system and its surroundings during an irreversible process is given by,

$$\Delta S_{system} + \Delta S_{surr} = \frac{q_{rev}}{T} - \frac{q_{irr}}{T}$$

Since $$\frac{q_{rev}}{T} > \frac{q_{irr}}{T}$$

$$\therefore \quad \frac{q_{rev}}{T} - \frac{q_{irr}}{T} > 0$$

$$\therefore \quad \Delta S_{system} + \Delta S_{surr} > 0 \qquad \ldots(7)$$

Thus, we can conclude that entropy of the system and its surroundings taken together increases in a thermodynamically irreversible or spontaneous process at constant temperature, but it remains constant in a thermodynamically reversible process.

Combining equations (5) and (7), we get

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr} \geq 0.$$

An equal sign refers to a reversible process, while the greater sign refers to an irreversible process.

As most of the processes going on in nature are spontaneous and irreversible, it can be said that the ***"entropy of the universe always tends towards a maximum"***. So, ΔS also helps us in predicting whether a reaction is feasible or not. In case, ΔS is positive, the process is feasible or spontaneous.

Ex. 1. *Calculate the entropy increase in the evaporation of a mole of water at 100°C. Latent heat of evaporation of water is 540 calorie per gram.*

Solution. We know that

$$\Delta S = \frac{q}{T} = \frac{mL_e}{T_b}$$

where m = molecular weight, L_e = latent heat of evaporation per gram, T_b = boiling point

$$\therefore \quad \Delta S = \frac{18 \times 540}{373} = \mathbf{29.058\ cal\ deg^{-1}\ mole^{-1}.}$$

Ex. 2. *Calculate the entropy change during the formation of water from 1 gram mole of ice at 0°C. The latent heat of fusion of ice is 80 calorie per gram.*

Solution. $$\Delta S = \frac{q}{T} = \frac{mL_f}{T_f}$$

where L_f = Latent heat of fusion per gram, T_f = freezing point, m = molecular weight.

$$\therefore \qquad \Delta S = \frac{18 \times 80}{273} = \mathbf{5.274\ cal\ deg^{-1}\ mole^{-1}}.$$

Ex. 3. *Calculate the entropy change involved in the isothermal expansion of 5 moles of an ideal gas from a volume of 10 litres to a volume of 100 litres at 300 K in SI units.*

Solution. In an isothermal expansion,

$$\Delta S = 2.303\ nR \log_{10} \frac{V_2}{V_1}$$

$$= 2.303 \times 5 \times 8.314 \times \log_{10} \frac{100}{10}$$

$$= 2.303 \times 5 \times 8.314 \times 1 \qquad \left(\because \log \frac{100}{10} = \log 10 = 1\right)$$

$$= \mathbf{95.735\ JK^{-1}\ mole^{-1}}.$$

Ex. 4. *10 moles of H_2 gas having ideal behaviour at 300 K is expanded under isothermal and reversible conditions from 15 litres to 150 litres. Calculate w and ΔG ($R = 2$ cal).*

Solution.
$$W = 2.303\ nRT \log_{10} \frac{V_2}{V_1}$$

$$= 2.303 \times 10 \times 2 \times 300 \log \frac{150}{15}$$

$$= 2.303 \times 10 \times 2 \times 300 = \mathbf{13818\ cal.}$$

$$\Delta G = 2.303\ nRT \log_{10} \frac{V_1}{V_2}$$

$$= 2.303 \times 10 \times 2 \times 300 \log \frac{15}{150} = \mathbf{-13818\ cal.}$$

Ex. 5. *From the following values, calculate entropy change when 1.2 kg of diamond is converted into graphite at 300 K.*

(i) $C\ (graphite) + O_2 \rightarrow CO_2 \quad \Delta H = -94$ *kcal*

(ii) $C(diamond) + O_2 \rightarrow CO_2 \quad \Delta H = -91$ *kcal.*

Solution. Subtracting equation (i) from (ii), *i.e.*,

C (*diamond*) = C (*graphite*), $\Delta H = +3$ kcal.

Heat change when 12 *g* diamond is converted into graphite = 3 kcal

So, heat change when 1200 g diamond is converted into graphite = 300 kcal.

$$\Delta S = \frac{q}{T} = \frac{\Delta H}{T} = \frac{300 \times 1000\ \text{cal}}{300\ \text{K}}$$

$$= \mathbf{1000\ cal\ K^{-1}}.$$

Ex. 6. *Calculate the entropy change in 400 kg of water at 55°C when 75 J heat flows out of it into the surroundings at 20°C.*

Solution. ΔS = Loss in entropy of hot water + Gain in entropy of surroundings.

$$\text{Loss in entropy of hot water} = \frac{-q}{T} = \frac{-75}{328}$$

$$= -0.2286\ \text{JK}^{-1}.$$

$$\text{Gain in entropy of surroundings} = +q/T$$

$$= +\frac{75}{293} = +0.2559\ \text{JK}^{-1}$$

$$\Delta S = -0.2286\ \text{JK}^{-1} + 0.2559\ \text{JK}^{-1}$$

$$= \mathbf{0.0273\ JK^{-1}}.$$

• 7.15. CRITERIA OF SPONTANEITY OF A REACTION

The following are the thermodynamic conditions of spontaneity and equilibrium :

(1) Spontaneous change is uni-directional or irreversible. Now work has to be done for spontaneous change. It occurs by itself. On the other hand, reversible change is bi-directional. For a reversible change to occur, work has to be done.

(2) There is no time factor for spontaneous change; it may occur rapidly or very slowly.

(3) ***Conditions in terms of entropy change***

$$dS \geq \frac{dq}{T}$$

$$dq = dE + P\,dV \qquad \text{(First law of thermodynamics)}$$

$$\therefore \qquad TdS \geq dE + P\,dV \qquad \ldots(1)$$

If, $E =$ constant, then $dE = 0$

If, $V =$ constant, then $dV = 0$ ...(2)

So, from equations (1) and (2), we get

$$T\,(\partial S)_{E,\,V} \geq 0 \quad \text{or} \quad (\partial S)_{E,\,V} \geq 0 \qquad \ldots(3)$$

From equation (3), we conclude that

(a) If $(\partial S)_{E,\,V} = 0$, *i.e.*, S is ***maximum, then process is reversible, i.e., this is the condition of equilibrium.***

(b) If $(\partial S)_{E,\,V} > 0$ or positive, then the process is spontaneous.

(4) *Conditions in terms of internal energy change.*

$$dS \geq \frac{dq}{T}$$

or
$$dS \geq \frac{dE + PdV}{T}$$

or
$$TdS \geq dE + PdV$$

or
$$dE + PdV - TdS \leq 0 \qquad \ldots(4)$$

If $S =$ constant, then $dS = 0$

$V =$ constant, then $dV = 0$ ...(5)

From equations (4) and (5), we get

$$T\,(dE)_{S,\,V} \leq 0$$

or
$$(\partial E)_{S,\,V} \leq 0 \qquad \ldots(6)$$

Therefore, from equation (6), we can conclude that :

(a) If $(\partial E)_{S,\,V} = 0$, the process will be reversible. This is the condition of reversibility (equilibrium). When equilibrium state is reached, the internal energy becomes minimum.

(b) If $(\partial E)_{S,\,V} < 0$, then the process will be spontaneous. This is the condition of spontaneity.

(5) *Conditions in terms of enthalpy change.*

$$H = E + PV$$

$$\therefore \qquad dH = dE + PdV + VdP$$

or
$$dH - VdP = dE + PdV \qquad \ldots(7)$$

We know that $TdS \geq dE + PdV$ ...(8)

From equations (7) and (8), we get

$$TdS \geq dH - VdP$$

or
$$dH - VdP - TdS \leq 0 \qquad \ldots(9)$$

If $S =$ constant, then $dS = 0$

$P =$ constant, then $dP = 0$ ...(10)

From equations (9) and (10), we get

$$(dH)_{S,\,P} \leq 0$$

or
$$(\partial H)_{S,\,P} \leq 0 \qquad \ldots(11)$$

That is, in a real process $dH < 0$ or H diminishes. When equilibrium is reached, H is minimum. We can say,

(a) *For spontaneity* (irreversibility), $(\partial H)_{S,\,P} < 0$

(b) *For equilibrium,* $(\partial H)_{S,\,P} = 0$

(6) *Conditions in terms of work function (A) change.*

We know that, $A = E - TS$ or $dA = dE - TdS - SdT$

or
$$dA + SdT = dE - TdS$$

But
$$TdS \geq dE + PdV \qquad \ldots(12)$$

or
$$-PdV \geq dE - TdS \qquad \ldots(13)$$

From equations (12) and (13), we get

$$-P\,dV \geq dA + SdT$$

or $$dA + SdT + P\,dV \le 0$$

If, T = constant, then $dT = 0$ ...(14)

If, V = constant, then $dV = 0$ ...(15)

Hence, from equations (14) and (15), we get

$$(dA)_{T,V} \le 0$$

or $$(\partial A)_{T,V} \le 0 \qquad \ldots(16)$$

∴ **(a)** *For spontaneity (irreversibility).* $(\partial A)_{T,V} < 0$

(b) *For equilibrium (reversibility).* $(\partial A)_{T,V} = 0$

(7) ***Conditions in terms of Gibbs free energy (G) change.***

We know that, $G = H - TS$

$$dG = dH - TdS - SdT$$

$$= d\,(E + PV) - TdS - SdT$$

or $$dG = dE + PdV + VdP - TdS - SdT \qquad \ldots(17)$$

or $$dG - VdP + SdT = dE + PdV - TdS$$

Also $$TdS \ge dE + PdV$$

or $$0 \ge dE + PdV - TdS \qquad \ldots(18)$$

From equations (17) and (18), we get

$$dG - VdP + SdT \le 0 \qquad \ldots(19)$$

If P = constant, then $dP = 0$

T = constant, then $dT = 0$ ...(20)

From equations (19) and (20), we get

$$(dG)_{P,T} \le 0 \quad \text{or} \quad (\partial G)_{P,T} \le 0 \qquad \ldots(21)$$

(a) For spontaneity $(\partial G)_{P,T} < 0$

(b) For equilibrium, $(\partial G)_{P,T} = 0$

The criteria for spontaneity of a process can be summarised as follows :

S.No.	Spontaneity (Irreversibility)	Equlibrium (Reversibility)
1.	$(\partial S)_{E,V} > 0$	$(\partial S)_{E,V} = 0$
2.	$(\partial E)_{S,V} < 0$	$(\partial E)_{S,V} = 0$
3.	$(\partial H)_{S,P} < 0$	$(\partial H)_{S,P} = 0$
4.	$(\partial A)_{T,V} < 0$	$(\partial A)_{T,V} = 0$
5.	$(\partial G)_{P,T} < 0$	$(\partial G)_{P,T} = 0$

Usually, the physical or chemical changes occur at constant temperature and pressure. The direction of such changes can be predicted with the help of free energy change. We know that at constant pressure and constant temperature,

$$(\partial G)_{P,T} \le 0 \qquad \ldots(22)$$

From equation (22), it is clear that,

(a) When $(\partial G)_{P,T} = 0$, then process is reversible, *i.e.*, state of equilibrium exists.

(b) When $(\partial G)_{P,T} < 0$, *i.e.*, free energy change is negative, the process is non-spontaneous.

(c) When $(\partial G)_{P,T} < 0$, *i.e.*, free energy change is positive, the process is spontaneous.

The above conclusions can be used to predict whether a given process is possible or not, provided free energy change (ΔG or dG) is known. The value of ΔG can be calculated from the equation $G = H - TS$.

∴ At constant temperature, we can write

$$\Delta G = \Delta H - T\Delta S \qquad \ldots(2)$$

The equation (23) can be used to predict the possibility of chemical reactions. The following cases may arise :

Case 1. ***When ΔH = positive and ΔS = positive.***

Under such conditions, if $T\Delta S > \Delta H$, then only ΔG will be negative and so the process will occur spontaneously otherwise not.

Case 2. ***When ΔH = negative and ΔS = negative.***

Under such conditions, if $\Delta H > T\Delta S$, then only ΔG will be negative and so the process will occur spontaneously.

Case 3. ***When ΔH = positive and ΔS = negative.***

Under such conditions, ΔG will be positive and so the process or reaction can never take place.

Case 4. ***When ΔH = negative and ΔS = positive.***

Under such conditions, ΔG will be negative and so the process will take place spontaneously.

• 7.21. NERNST HEAT THEOREM

Nernst heat theorem gives the variation of enthalpy change (ΔH) and free energy change (ΔG) of a system with decrease of temperature. According to Gibbs-Helmholtz equation.

$$\Delta G = \Delta H + T\left(\frac{\partial (\Delta G)}{\partial T}\right)_P$$

From this equation, it is evident that at absolute zero, *i.e.*, when $T = 0$, $\Delta G = \Delta H$. However, Nernst observed that as the temperature is lowered towards absolute zero, the value of $\partial(\Delta G)/\partial T$ decreases and then approaches zero asymptotically. This means that ΔG and ΔH are not only equal to the absolute zero but the values approach each other asymptotically in the vicinity of this temperature. This result is known as *Nernst heat theorem.* Mathematically, it may be expressed as:

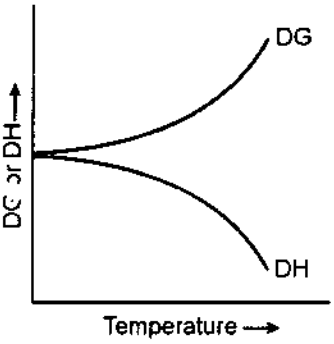

Fig. 3. Nernst heat theorem

$$\lim_{T \to 0} \frac{d(\Delta G)}{dT} = \lim_{T \to 0} \frac{d(\Delta H)}{dT} = 0 \qquad \ldots(1)$$

Graphically, the result may be represented by fig. (3). In fig. (3), ΔG has been shown to be greater than ΔH at temperature away from absolute zero. However, the reverse is also possible because $\partial(\Delta G)/\partial T$ can be both positive or negative.

Since gases do not exist at absolute zero, this means that the heat theorem is not applicable to gases. Similarly, it has been found to be inapplicable to liquids also. Nernst heat theorem is applicable to solids only.

• 7.22. THIRD LAW OF THERMODYNAMICS

[I] Third Law of Thermodynamics

According to third law of thermodynamics, *The entropy of all perfectly crystalline solids may be taken as zero at the absolute zero temperature.*

This law is also stated as follows :

Every substance has finite positive entropy but at the absolute zero of temperature, the entropy may become zero and in fact it does become zero in case of perfectly crystalline solids.

[II] Importance of Third Law of Thermodynamics

Calculation of absolute entropies from heat capacity data : It helps us in the calculation of the absolute entropies of chemical compounds at any desired temperature. This is shown as under:

The infinitesimal entropy change is given by

$$dS = \frac{dq}{T} \qquad \ldots(1)$$

But $C_P = \frac{dq}{dT}$ so that $dq = C_P\, dT$

Substituting this value in equation (1), we have

$$dS = \frac{C_P\, dT}{T}$$

Hence, the entropy change of a substance when its temperature changes from absolute zero to temperature (T) can be obtained from the equation

$$\int_{S=S_0}^{S=S} dS = \int_{T=0}^{T=T} C_P \frac{dT}{T}$$

or
$$S - S_0 = \int_0^T C_P \frac{dT}{T} \qquad \ldots(2)$$

where S_0 is the entropy of the substance at absolute zero and S is the entropy of the substance at temperature T.

According to third law of thermodynamics, $S_0 = 0$.

$$\therefore \qquad S = \int_0^T C_P \frac{dT}{T}$$
$$= \int_0^T C_P \, d \ln T \qquad \ldots(3)$$

Thus, the entropy (S) of the substance at temperature T can be calculated from the measurements of heat capacities (C_P) at a number of temperatures between 0 K to T K. The integral in equation (3) can be evaluated by plotting C_P vs $\ln T$, or 2.303 log T and then measuring the area under the curve between $T = 0$ to $T = T$ as shown in fig. (4).

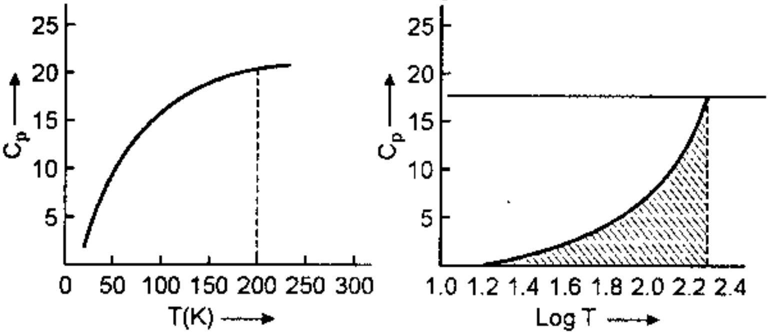

Fig. 4. Plot of heat capacities (C_P) *vs* T in the first case and *vs* log T in the second case.

If C_P is supposed to remain almost constant in the temperature range 0 to T K, equation (3) can be simplified to :

$$S = C_P \ln T = 2.303\, C_P \log T$$

This equation helps to calculate the value of S directly from the values of C_P and T.

For liquid and gaseous substances : The total absolute entropy of the substance at the given temperature will be the sum of all the entropy changes which the substance has to undergo in order to reach that particular state starting from the crystalline solid at absolute zero. Thus, if a substance is gaseous at 1 atm pressure and 25°C, the entropy of the gas at 25°C will be the sum of the following entropies involved at different stages :

(1) The entropy of heating the crystalline solid from $T = 0$ to $T = T_m$, the melting point;

(2) The entropy of melting, ΔH_m is latent heat of melting;

(3) The entropy of heating the liquid from T_m to T_b, the boiling point;

(4) The entropy of vaporization, $\frac{\Delta H_v}{T_b}$, where ΔH_v is latent heat of vaporisation;

(5) The entropy of heating the gas from T_b to 25°C (*i.e.*, 298 K).

Thus, the complete expression for the calculation of entropy at temperature T may be written as :

$$S = \underbrace{\int_0^{T_m} C_{P(s)}\, d \ln T}_{(1)} + \underbrace{\frac{\Delta H_m}{T_m}}_{(2)} + \underbrace{\int_{T_m}^{T_b} C_{P(l)}\, d \ln T}_{(3)} + \underbrace{\frac{\Delta H_v}{T_b}}_{(4)} + \underbrace{\int_{T_b}^{T} C_{P(g)}\, d \ln T}_{(5)}$$

• 7.23. WORK FUNCTION

[1] Helmholtz Function or Work Function

We know that the concept of entropy is the fundamental consequence of the second law of thermodynamics. There are two other functions, which utilize entropy in their derivations. These two functions are *'free energy function'* and *'work function.'* These functions like the internal energy, heat content and entropy are fundamental thermodynamic properties and depend upon the states of the system only.

We know that energy can be converted into work, but it is not always necessary that all the energy may be converted into work. So, any kind of energy which can be converted into useful work is called *'**available energy**'*, such as the operation of an engine or a motor. But the energy which cannot be converted into useful work is known as *'**unavailable energy**'*.

$\therefore$ Total energy = Isothermally available energy + Isothermally unavailable energy

It has also been explained before, that a part of internal energy of a system can be utilized at constant temperature to do useful work. *So, this fraction of internal energy which is isothermally available is called the '**work function**' of the system.* It is denoted by the symbol A.

The ***work function,*** A is defined by,

$$A = E - TS \qquad \ldots(1)$$

where, all the symbols have their usual significance. The work function A is seen to be a single valued function of the state of the system. Hence, likewise dA is a complete differential. Similarly, as E and S are extensive properties, A will also be extensive in nature.

[II] Physical Significance of Work Function

In order to obtain some understanding of the physical significance of the work function, consider an isothermal change from the initial state to the final state. The two states are represented by the subscripts 1 and 2, respectively. In such a case, equation (1) can be writen as,

$$A_1 = E_1 - TS_1 \qquad \ldots(2)$$

and

$$A_2 = E_2 - TS_2 \qquad \ldots(3)$$

temperature remains the same as the process is isothermal. Subtracting equation (2) from (3), we have,

$$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$$

or

$$\Delta A = \Delta E - T\,\Delta S \qquad \ldots(4)$$

where, ΔA is the increase in the work function, ΔE is the corresponding increase in internal energy and ΔS is the increase in entropy of the system.

Suppose the change is brought about reversibly at a constant temperature T, then the heat absorbed will be equal to Q_{rev} (say). Thus, the increase in entropy is given by,

$$\Delta S = \frac{Q_{\text{rev}}}{T}$$

Substituting this in equation (4), the result is

$$\Delta A = \Delta E - Q_{\text{rev}} \qquad \ldots(5)$$

From first law of the thermodynamics, $\Delta E = Q_{\text{rev}} - W$

or

$$-W = \Delta E - Q_{\text{rev}}$$

Combining this equation with equation (5), we have

$$W = -\Delta A \qquad \ldots(6)$$

Since the process is carried out reversibly, W represents the maximum work. It is clear from eqation (6) that the decrease in work function ($-\Delta A$) gives the maximum work that can be obtained from the system at a constant temperature. It is this fact, which justifies the use of the concerned term as ***work function***.

• 7.24. FREE ENERGY

[I] Free Energy Function

We know that the concept of entropy is the fundamental consequence of the second law of thermodynamics. There are two other functions, which utilize entropy in their derivations. These two functions are *'**free energy function**'* and *'**work function**'*. These functions like the internal energy, heat concept and entropy are fundamental thermodynamic properties and depend upon the states of the system only.

We know that energy can be converted into work, but it is not always necessary that all the energy may be converted into work. So, any kind of energy which can be converted into useful work is called *'**available energy**'*, such as the operation of an engine or a motor. But the energy which cannot be converted into useful work is known as *'**unavailable energy**'*.

$\therefore$ Total energy = Isothermally available energy + Isothermally unavailable energy

The isothermally available energy present in a system is called its free energy. It is denoted by the symbol G. Free energy is also known as ***thermodynamic potential or Gibbs' function.***

The function, G is defined by the equation,

$$G = E - TS + PV \qquad \ldots(1)$$

where, P, V, T as usual refer to the pressure, volume and temperature of the system, E is the energy content of the system whose entropy is S. As E, T and S depend only on the thermodynamic state and not on its previous history, it is clear that the same views must apply to G, the free energy function. Therefore, G may be regarded as single valued function of the state of the system. Hence dG, will be a complete differential. As E and S are extensive properties, therefore, G will also be extensive in character or in other words, the value of G will depend on the quantity of matter specified in the system. As $E + PV = H$, Equation (1) reduces to,

$$G = H - TS \qquad \ldots(2)$$

[II] Physical Significance of Free Energy

Consider an isothermal change from the initial state to the final state at constant temperature T. The two states are represented by the two subscripts 1 and 2 as before.

Therefore, equation (2) reduces as follows for both the states.

$$G_1 = H_1 - TS_1 \qquad \ldots(3)$$

$$G_2 = H_2 - TS_2 \qquad \ldots(4)$$

From equations (3) and (4), we have

$$(G_2 - G_1) = (H_2 - H_1) - T(S_2 - S_1)$$

or

$$\Delta G = \Delta H - T\Delta S, \qquad \ldots(5)$$

where, ΔG and ΔH represent the change in free energy and change in heat content, respectively.

At constant pressure, we know that,

$$\Delta H = \Delta E + P\Delta V$$

$$\therefore \quad \Delta G = \Delta E + P\Delta V - T\Delta S \qquad \ldots(6)$$

We know that, $\Delta A = \Delta E - T\Delta S$ ...(7)

Combining equations (7) and (6), we have

$$\Delta G = \Delta A + P\Delta V$$

or

$$-\Delta G = W - P\Delta V \qquad [\because\ -\Delta A = W] \quad \ldots(8)$$

Since $P\Delta V$ represents the quantity of work done by gas on expansion against the external pressure, therefore, $-\Delta G$ gives the maximum work which can be obtained from the system other than that due to change of volume, at constant temperature and pressure, ***The work other than that due to change of volume is called the net work.*** Hence,

$$\text{Net work} = W - P\Delta V$$

Therefore, $-\Delta G$ is a measure of the net work. In other words, the decrease in free energy ($-\Delta G$) is a measure of maximum net work that can be obtained from a system at constant temperature and pressure. G can also be defined as, ***'the fraction of total energy which is isothermally available for converting it into useful work'***. This decrease in free energy is of great importance in chemistry, especially in physical chemistry.

[III] Variation of Free Energy With Pressure and Temperature

We know that, $G = E + PV - TS$

On differentiation, we have,

$$dG = dE + PdV + VdP - SdT - TdS \qquad \ldots(9)$$

From first law of thermodynamics, we have

$$dE = dQ - dW$$

If the work is only due to expansion, then $dW = PdV$

Hence, $dE = dQ - PdV$

or $dQ = dE + PdV$

We also know that, $dS = \dfrac{dQ}{T}$

or $$TdS = dQ = dE + PdV \qquad \ldots(10)$$

Combining equations (9) and (10), we have

$$dG = VdP - SdT \qquad \ldots(11)$$

At constant temperature, $dT = 0$

$$\therefore \quad dG_T = VdP$$

or $$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \ldots(12)$$

Equation (12) represents the *variation of free energy with pressure.*

When pressure is constant, $dP = 0$. In such a case (11) reduces to,

$$dG_p = -SdT$$

or $$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \ldots(13)$$

Equation (13) represents the variation of free energy with temperature.

[IV] Change of Free Energy With Pressure for a Perfect Gas

For an isothermal change, $dT = 0$, so equation $dG = VdP - SdT$ reduces to

$$dG = VdP$$

On integration, we have,

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} VdP$$

For 1 mole of a perfect gas, $V = \frac{RT}{P}$

$$\therefore \quad \int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} \frac{RT}{P} dP$$

$$G_2 - G_1 = \Delta G = RT \log_e \frac{P_2}{P_1}$$

For n moles of perfect gas,

$$G_2 - G_1 = \Delta G = nRT \log_e \frac{P_2}{P_1} \qquad \ldots(14)$$

Equation (14) applies to a change occurring at constant temperature for a perfect gas. It also applies, whether the process is reversible or otherwise.

• 7.25. GIBBS-HELMHOLTZ EQUATION

From Gibbs free energy function, $G = H - TS$, a relation between the quantities, ΔG, ΔH and ΔS can be obtained. Similarly, the quantities ΔA, ΔE and ΔS can be related with the work function, $A = E - TS$.

The relations between the above thermodynamic functions lead to two important relations. Each of the two relations in known as ***Gibbs-Helmholtz equation.*** It is one of the most important relations in chemical thermodynamics, because it helps us towards a better understanding of the driving force behind chemical reactions. The two relations may be derived as under :

We know that $dG = VdG - SdT$. At constant pressure,

$$dG_P = -SdT_P$$

or $$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \ldots(1)$$

If the value of S is substituted in $G = H - TS$, we have

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P \qquad \ldots(2)$$

Similarly, from equation $dA = -PdV - SdT$, we have at constant volume,

$$dA_v = -SdT_v$$

or $$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \ldots(3)$$

Combining equation (3) with $A = E - TS$, we get,

$$A = E + T\left(\frac{\partial A}{\partial T}\right)_V \quad \dots (4)$$

Equations (2) and (3) are generally known as ***Gibbs-Helmholtz equations.***

Dividing equation (2) by T^2, we get

$$\frac{G}{T^2} = \frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P$$

This on rearrangement becomes,

$$\left[\frac{\partial (G/T)}{\partial T}\right]_P = -\frac{H}{T^2} \quad \dots (5)$$

Similarly, the following expression can also be derived from equation (4) after dividing it by T^2 and rearranging,

$$\left[\frac{\partial (A/T)}{\partial T}\right]_V = -\frac{E}{T^2} \quad \dots (6)$$

The above forms of Gibb-Helmholtz equations *viz., (5) and (6) are not frequently* used by scientists. Alternative forms which are frequently used can also be derived as follows :

For an isothermal process, equation $G = H - TS$ can be writen for initial and final states as :

$$G_1 = H_1 - TS_1 \quad \text{and} \quad G_2 = H_2 - TS_2$$

or

$$\Delta G = \Delta H - T\Delta S \quad \dots (7)$$

Similarly, equation (1) can be written as

$$\left(\frac{\partial G_1}{\partial T}\right)_P = -S_1 \quad \text{and} \quad \left(\frac{\partial G_2}{\partial T}\right)_P = -S_2$$

or

$$\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P = -S_2 + S_1 = -(S_2 - S_1) - \Delta S \quad \dots (8)$$

Combining equations (7) and (8), we get

$$\Delta G = \Delta H + T\left[\left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P\right]$$

$$\Delta G = \Delta H + \left(\frac{\partial (G_2 - G_1)}{\partial T}\right)_P$$

$$\Delta G = \Delta H + T\left[\frac{\partial (\Delta G)}{\partial T}\right]_P \quad \dots (9)$$

An expression analogous to equation (9) can be obtained from euation $A = E - TS$ and equation (3). It is represented as,

$$\Delta A = \Delta E + T\left[\frac{\partial (\Delta A)}{\partial T}\right]_V \quad \dots (10)$$

Equations (9) and (10) are useful forms of Gibbs-Helmholtz equation.

Dividing equation (9) by T^2, we get

$$\frac{\Delta G}{T^2} = \frac{\Delta H}{T^2} + \frac{1}{T}\left[\frac{\partial (\Delta G)}{\partial T}\right]_V \quad \dots (11)$$

On rearrangement, we obtain,

$$\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_P = -\frac{\Delta H}{T^2} \quad \dots (12)$$

Equation (12) represents the variation of $\Delta G/T$ with temperature.

Similarly from equation (10) we can obtain the expression

$$\left[\frac{\partial (\Delta A/T)}{\partial T}\right]_V = -\frac{\Delta E}{T^2} \quad \dots (13)$$

Equation (13) represents the variation of ΔA or $\Delta A/T$ with temperature.

[I] Integrated Form of Gibbs-Helmholtz Equation

On rearranging equation (11), we get

$$\frac{1}{T}\left[\frac{\partial(\Delta G)}{\partial T}\right]_P - \frac{\Delta G}{T^2} = -\frac{\Delta H}{T^2}$$

or
$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2}$$

or
$$\int d\left(\frac{\Delta G}{T}\right) = \int -\frac{\Delta H}{T^2}\,dT \qquad \ldots (14)$$

i.e.,
$$\frac{\Delta G}{T} = -\int \frac{\Delta H}{T^2}\,dT + X_P \qquad \ldots (15)$$

where,
$$X_P = f(P).$$

If equation (14) is integrated between limits T_1 and T_2, we get,

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H}{T^2}\,dT = \Delta H\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \ldots (16)$$

From equation (16) it is possible to calculate ΔG_2 at T_2 from the known values of ΔG_1 at T_1 and heat of reaction (ΔH). Equations (15) and (16) are known as integrated forms of Gibbs-Helmholtz equation.

[II] Significance of Gibbs-Helmholtz Equation

(i) It helps us to calculate the heat change in a reaction from the E.M.F.'s of galvanic cells. We know that the change in the free energy produced by the passage of n faradays, *i.e.*, nF coulombs through a reversible cell is given by, $-\Delta G = nFE$, where E denotes the reversible E.M.F. The negative sign implies that there is a decrease of free energy when the E.M.F. is positive. Hence, combining the last expression with equation (9), we get

$$E = -\frac{\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_P.$$

Whether the electrical work is greater than, equal to or less than ΔH depends on the sign of $(\partial E/\partial T)$, *i.e.*, temperature coefficient of E.M.F. It will thus be seen that if E and $(\partial E/\partial T)$ are known, the heat of reaction of the process occurring in the cell can be evaluated.

(ii) If the standard potential of an electrode is known at two or more temperatures, the entropy of the reversible ion can be determined by using a suitable form of Gibbs-Helmholtz equation.

(iii) By means of Gibb-Helmholtz equation, the entropy changes and enthalpy changes can also be calculated.

Problem 1. *The free energy change (ΔG) accompanying a given process is –85.77 kJ and 25°C and and –83.68 kJ at 35°C. Calculate the change in enthalpy (ΔH) for the process at 30°C.*

Solution. ΔG at 25°C = – 87.77 kJ

ΔG at 35°C = – 83.68 kJ

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = \frac{-83.68\text{ kJ} - (-85\text{ kJ}}{308\text{ K} - 298\text{ K}} = 0.209\text{ kJ K}^{-1}$$

ΔG at 30°C may be taken as the average of the values at 25°C and 35°C.

$$\therefore \qquad \Delta G \text{ at } 35^\circ\text{C} = \left(\frac{-85.77\text{ kJ} - 83.68\text{ kJ}}{2}\right) = -84.725\text{ kJ}$$

$$T = 30 + 273 = 303\text{K}$$

From $\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]$, we have

$$-84.725\text{ kJ} = \Delta H + (303\text{ K})(0.209\text{ kJ K}^{-1})$$

Hence, $\Delta H = $ **– 148.05 kJ.**

• 7.26. CLAPEYRON EQUATION

Suppose a single substance exists in two phases A and B in equilibrium with each other at constant temperature and pressure. If one mole of a substance is transferred from one phase A to the other phase B without altering the temperature and pressure, then there will be no work done other than that of expansion. So, from equation $dG = VdP - SdT$, we get,

$$dG = 0, \text{ as } dP = 0 \text{ and } dT = 0$$

i.e., $$G_B - G_A = 0 \quad \text{or} \quad G_A = G_B$$

In other words, the ***molar free energy of a substance is the same in the two phases which are in equilibrium.***

In a phase change, equation $dG = VdP - SdP$ can be written as

$$dG_A = V_A dP - S_A dT \qquad \dots (1)$$

and $$dG_B = V_B dP - S_B dT \qquad \dots (2)$$

Subtracting equation (1) from (2), we get

$$dG_B - dG_A = (V_B dP - S_B dT) - (V_A dP - S_A dT)$$

or $$0 = (V_B dP - S_B dT) - (V_A dP - S_A dT) \qquad (\text{As } G_A = G_B)$$

or $$V_B dP - S_B dT = V_A dP - S_A dT$$

or $$(V_B - V_A)\, dP = (S_B - S_A)\, dT$$

or $$\Delta V dP = \Delta S dT$$

or $$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

where, ΔS and ΔV have their usual significance.

Recognising further that at equilibrium we have,

$$\Delta S = \frac{\Delta H}{T} \qquad [\text{As } \Delta G = 0, \text{ at equilibrium}]$$

Therefore, $$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \qquad \dots (3)$$

Equation (3) was first derived by a French engineer Clapeyron in 1834. It gives the variation of the equilibrium pressure (P) wih temperature (T) for any two phases of a given substance.

Equation (3) is applicable to various equilihbria such as ***solid-liquid equilibria, liquid-vapour equilibria and equilibria between two solid modifications.*** The Clapeyron's equation for these various equilibria can be easily obtained as follows :

(1) Solid-liquid equilibrium

We know that solid and liquid forms of a substance can exist in equilibrium only at the freezing or melting point. Hence, in equation (3), T will be the freezing point at P will be the external pressure exerted on the system. So, euation (3) can also be written in a reversed form as :

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H} \qquad \dots (4)$$

If V_S and V_L represent the molar volumes of the solid and the liquid phases, respectively at temperature T and pressure P, then,

$$\Delta V = V_L - V_S$$

where, ΔV represents the increase in volume in transferring 1 mole of the substance from solid to liquid phase, ΔH the amount of heat absorbed may be replaced by ΔH_f, i.e., molar hat of fusion. So, making these changes in equation (4), we get the following Clapeyron equation

$$\frac{dT}{dP} = \frac{T(V_L - V_S)}{\Delta H_f} \qquad \dots (5)$$

(2) Liquid-vapour equilibrium

In this equilibrium, the increase in volume (ΔV) accompanying the transfer of one mole of liquid to the vapour state will be equal to $V_V - V_L$, where V_V and V_L represent the molar volumes of the vapour and liquid, respectively. ΔH may then be replaced by ΔH_V, i.e., molar heat of vaporisation.

From the above considerations, equation (4) becomes :

$$\frac{dT}{dP} = \frac{T(V_V - V_L)}{\Delta H_V} \qquad \dots (6)$$

It is a well known fact that the boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the external pressure. So, equation (6) represents the variation of boiling point of a liquid with pressure P. Thus equation (6) can also be written as :

$$\frac{dP}{dT} = \frac{\Delta H_V}{T\,(V_V - V_L)} \quad \ldots (7)$$

Equation (7) represents the rate of change of vapour pressure (P) of the liquid with temperature.

Note : The volume measured at the same temperature and pressure, *i.e.*, V_V and V_L are sometimes known as 'orthobaric volumes'.

(3) Equilibrium between two solid modifications

If α represents the stable form of a solid above the transition point and β the stable form of the solid below the transition point then equation (3) becomes :

$$\frac{dT}{dP} = \frac{T\,(V_\alpha - V_\beta)}{\Delta H_t} \quad \ldots (8)$$

where V_α and V_β represent the molar volumes of the two forms, respectively and ΔH_t is the molar heat of transition determined at T.

It is also possible to assume :

(In eqquation 5) : V_S and V_L as respective specific volumes of solid and liquid instead of molar volumes and ΔH_f the specific heat of fusion or heat of fusion per gram.

(In equation 7) : V_L and V_V as respective specific volumes of liquid and volume and ΔH_V the specific heat of vaporisation.

(In equation 8) : V_α and V_β as respective specific volumes of α and β forms and ΔH_t as specific heat of transition.

Applications of Clapeyron Equation

The Clapeyron equation can be applied in numerous ways to several physico-chemical problems.

(1) It can be used for predicting the effect of pressure on the volumes or densities of the solid and liquid phases (V_S and V_L) and heat of fusion (ΔH_f).

If $V_L < V_S$ then $(V_L - V_S)$ will be negative and so dT/dP will be negative. In other words, increase of pressure will decrease the melting point. This is observed in the ice-water equilibrum.

If $V_S > V_L$ then $(V_L - V_S)$ will be positive and dT/dP will be positive. In this case, increase of pressure will increase the melting point.

(2) It is also possible to calculate the heat of fusion (ΔH_f) of a substance from equation (5), if dT/dP or rather $\Delta T/\Delta P$ and specific volumes of the solid and liquid phases are known.

(3) Clapeyron equation can also predict the effect of pressure onthe transition temperature with the help of equation (8). Similarly, we can precisely calculate the heat of transition from the change in volume, *i.e.*, $(V_\alpha - V_\beta)$ and the value of dT/dP, from equation (8).

(4) The heat of vaporisation ΔH_V can also be calculated from equation (6) and we can also easily find the rate of change of boiling point from equation (6).

• 7.27. CLAUSIUS-CLAPEYRON EQUATION

If the temperature of the liquid is not too near the critical point then we can easily neglect the volume of the liquid (V_L), compared with that of the vapour (V_V). In such a case, equation (7) can be rearranged to give equation (9) on replacing P by p. So,

$$\frac{dp}{dT} = \frac{\Delta H_V}{T\Delta_V} \quad \ldots (9)$$

Furthermore, under such conditions the vapour pressure is very small, so it may be assumed that the vapour behaves as an ideal gas to which the equation $pV_V = RT$ is applicable.

$$\frac{dp}{dT} = p \cdot \frac{\Delta H_V}{RT^2}$$

∴ From equation (9), $\frac{1}{p}.\frac{dp}{dT}=\frac{\Delta H_V}{RT^2}$

or $$\frac{d\log p}{dT}=\frac{\Delta H_V}{RT^2} \quad \ldots (10)$$

Equation (10) is sometimes known as ***Clausius-Clapeyron equation*** and is generally spoken of as *first latent heat equation.* It was first derived by Clausius (1850) on the thermodynamic basis of Clapeyron equation.

Equation (8) is valid for evaporation and sublimation process, but not valid for transitions between solids or for the melting of solids. Clausius-Clapeyron equation is an approximate equation because the volume of the liquid have been neglected and the ideal behaviour of the vapour is also taken into account. It may thus be expected that results from equation (9) are less accurate than from equations (5), (7) and (8). However, equation (10) has the advantage of greater simplicity because in the calculation of the value of dp/dT or dT/dp, it is necessary to know the volumes of the liquid and vapour.

[I] Integrated Form of Clausius-Clapeyron Equation

Assuming the heat of vaporisation to be indpendent of temperature, if we integrate equation (10) between the limits T_1 to T_2 (for temperature) and p_1 to p_2 (for vapour pressure) we get,

$$\int_{p_1}^{p_2} d\log p=\int_{T_1}^{T_2}\frac{\Delta H_V}{RT^2}\,dT$$

or $$\log_e\frac{p_2}{p_1}=\frac{\Delta H_V}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

or $$\log_{10}\frac{p_2}{p_1}=\frac{\Delta H_V}{2.303R}\left(\frac{T_2-T_1}{T_1T_2}\right) \quad \ldots (11)$$

If ΔH_V is expressed in cal/mole and R = 1.987 cal/degree/mole, then equation (11) becomes

$$\log_{10}\frac{p_2}{p_1}=\frac{\Delta H_V}{4.576}\left(\frac{T_2-T_1}{T_1T_2}\right) \quad \ldots (12)$$

Equation (12) is the ***integrated form of Clausius-Clapeyron equation.*** If the integration is carried out indefinitely (without limits) then we can write the vapour-pressure equation (12) as,

$$\log_e p=-\frac{\Delta H_V}{RT}+C\text{ (constant)} \quad \ldots (13)$$

Ex. 1. *The vapour pressures of water at 95°C and 100°C are 634 and 760 mm, respectively. Calculate the latent heat of evaporation of water per gram between 95°C and 100°C.*

Solution. $$\log_e\frac{p_2}{p_1}=\frac{L_e}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]=\frac{L_e}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

or $$2.303\log_{10}\frac{p_2}{p_1}=\frac{L_e}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

where p_1 and p_2 are the vapour pressures at temperature T_1 and T_2, respectively and L_e is the latent heat of evaporation/mole. It is given that

$$P_1=634\text{ mm and }P_2=760\text{ mm}$$

$$T_1=95+273=368\text{K}\quad T_2=100+273=273\text{K}$$

So, $$2.303\log_{10}\frac{760}{634}=\frac{L_e}{1.987}\left[\frac{373-388}{368\times 373}\right]$$

or $$L_e=9886\text{ cal/mole}=9886/18=\mathbf{549.2\ cal/g.}$$

Ex. 2. *At what height must the barometer stand in order that water may boil at 99°C ? Given that latent heat of vaporisation of water per gram is 536 cal.*

Solution. As known, the integrated form of Clapyron-Clausius equation is

$$\log_e\frac{p_2}{p_1}=\frac{L_e}{R}\left[\frac{T_2-T_1}{T_1,T_2}\right]$$

or $p_1=76$ cm. mercury, $p_2=?$

$T_1 = 100 + 273 = 373\text{K}, T_2 = 99 + 273 = 372\text{K}$

$L_e = 536$ cal/gm $= 536 \times 18$ cal/mole

$$2.303 \log_{10} \frac{p_2}{76} = \frac{536 \times 18}{1.987}\left[\frac{372 - 373}{372 \times 373}\right] = -\frac{536 \times 18 \times 1}{1.987 \times 372 \times 373}$$

$$\log_{10} p_2 - \log_{10} 76 = -\frac{536 \times 18 \times 1}{1.987 \times 372 \times 373 \times 2.303}$$

or

$$\log_{10} p_2 = \log_{10} 76 - \frac{536 \times 18 \times 1}{1.887 \times 372 \times 373 \times 2.3030}$$

$$= 1.8808 - 0.0159 = \mathbf{1.8659}$$

Taking antilog we get, $p_2 =$ **73.43 cm. of mercury.**

• SUMMARY

- **System** is a specified portion of matter which is separated from the rest of the universe with a bounding surface.
- **Surroundings :** The rest of the universe which might be in a position to exchange matter and energy *with the system is called surroundings.*
- If a process is carried out infinitesimally slowly so that the driving force is only infinitesimally greater than the opposing force, it is called a reversible process.
- If the temperature of the system remains constant during each step of a process, it is called an isothermal process.
- If the heat neither enters nor leaves the system during any step of the process, it is called an adiabatic process.
- **First law of thermodynamics :** The total energy and mass of an isolated system remains constant, though one form *of energy can be converted into another form. Mathematically,*
  $$dE = dQ - dW$$
- The relation between ΔH and ΔE is $\Delta H = \Delta E + P\Delta V$.
- In an isothermal expansion of an ideal gas, the work done is given by
  $$W_m = 2.303\ nRT \log \frac{V_2}{V_1} = 2.303\ nRT \log \frac{P_1}{P_2}$$
- When a gas is made to expand from a region of high pressure to that of a low pressure through a porous plug, a change in temperature occurs. This effect is called *Joule-Thomson effect.*
- The temperature at which Joule-Thomson coefficient changes its sign is called inversion temperature.
- When a system after completing a series of changes returns to its original state, it is called a cyclic process.
- The fraction of heat absorbed by a heat engine which it can convert into useful work is called its efficiency. The efficiency of a heat engine is always less than unity.
- The degree of disorder of a system is called its entropy.
- The net entropy change of the universe is constant in a reversible process.
- The entropy of the universe always tends to a maximum.
- Work function, $A = E - TS$.
- Free energy function, $G = H - TS$.
- Gibbs-Helmholtz equation is given by, $\Delta G = \Delta H + T\left[\frac{\partial (\Delta G)}{\partial T}\right]_P$
- Clapeyron equation is given by $\frac{dp}{dT} = \frac{\Delta H}{T(V_2 - V_1)}$
- Clausius-Clapeyron equation is given by, $\frac{d \log_e p}{dT} = \frac{\Delta H}{RT^2}$
- Integrated form of Clausius-Clapeyron equation is given by $\log_{10} \frac{p_2}{p_1} = \frac{\Delta H}{2.303\, R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
- **Third law of thermodynamics :** Every substance has a funite entropy but at the absolute zero of temperature, the entropy may become zero and in fact it does become zero in case of perfectly crystalline solids.

• STUDENT ACTIVITY

1. State and explain first law of thermodynamics.

2. Define isothermal and adiabatic processes.

3. Define inversion temperature.

4. What is Joule-Thomson effect ?

5. State Nernst heat theorem.

6. State and explain third law of thermodynamics.

7. What are work function and free energy functions ?

• TEST YOURSELF

Answer the following questions :

1. Define thermodynamics. State its main objectives and limitations.
2. Differentiate between the terms 'isolated system' and 'closed system' as used in thermodynamics.

3. Explain the term 'isolated system'.
4. Distinguish clearly between extensive and intensive properties.
5. Write short note on the criteria for reversible and irreversible processes.
6. Explain what is a reversible process according to thermodynamics ?
7. Write if the following processes are reversible or not ?
   (i) mixing of gases by diffusion,
   (ii) dissolution of a solute in pure solvent.
   (iii) expansion of a gas in vacuum.
   (iv) melting of ice without rise in temperature
8. What are isothermal and adiabatic changes or differentiate clearly between isothermal and adiabatic processes ?
9. What is meant by an adiabatic change ?
10. Explain the difference between isobaric and isochoric processes.
11. Define a cyclic process.
12. Explain the terms :
    (i) Thermodynamic system
    (ii) Types of thermodynamic system.
13. Discuss the nature of work and heat.
14. State and explain first law of thermodynamics. Give its mathematical statement also.
15. Write a short note on first law of thermodynamics.
16. Write an explanatory note on the following :
    (i) Internal energy (ii) Enthalpy (iii) Heat capacity
17. Derive the relation $\Delta H = \Delta E + P\Delta V$.
18. Derive the relation $C_P - C_V = R$.
19. Derive an expression for maximum work done during an isothermal reversible expansion of n moles of an ideal gas.
20. Derive the expression $PV^{\gamma} =$ constant.
21. Derive the expression for the maximum work done in an adiabatic reversible expansion of an ideal gas.
22. What is Joule-Thomson effect ?: Show that for an ideal gas this effect is zero.
23. Define and explain inversion temperature.
24. State and explain second law of thermodynamics.
25. What is a cyclic process ? Deduce an expression for the efficiency of a Carnot's engine working between absolute temperatures T_1 and T_2.
26. State and explain entropy from the point of view of second law of thermodynamics.
27. Write a short note on entropy.
28. Discuss and derive the various entropy changes for the following processes :
    (i) Change from solid to liquid phase
    (ii) Change from liquid to vapour phase.
    (iii) Change for reversible and irreversible processes.
29. Discuss the criteria of spontaneity or irreversibility and conditions of equilibrium.
30. Write short notes on the following :
    (i) Work function (ii) Free energy
31. Derive Gibbs-Helmholtz equation.
32. Derive Clausius-Clapeyron equation. Give its integrated form also.
33. Describe Nernst heat theorem.
34. State and explain third law of thermodynamics.
35. Find the work done when 2 moles of an ideal gas expand isothermally from 2 litres to 5 litres against a constant pressure of 1 atm at 298 K.
36. Calculate the entropy change involved in isothermal expansion of 2 moles of the gas from a volume of 5 litres to a volume of 50 litres at 30°C.
37. Calculate the entropy increase in the evaporation of a mole of water at 100°C (Heat of vaporisation = 540 cal g^{-1}).
38. Thermodynamics is applicable to :
    (i) Microscopic systems only (ii) Macroscopic systems only
    (iii) Homogeneous systems only (iv) Heterogeneous systems only
39. A thermos flask is an example of :
    (i) Isolated system (ii) Closed system

(iii) Open system (iv) Heterogeneous system

40. Which of the following is not an intensive property ?
(i) Pressure (ii) Concentration
(iii) Density (iv) Volume

41. Which of the following condition holds good for an adiabatic process ?
(i) $dQ < 0$ (ii) $dQ > 0$ (iii) $dQ = 0$ (iv) $dQ = 1$

42. The enthalpy change of a reaction is independent of :
(i) State of the reactants and products
(ii) Nature of the reactants and products
(iii) Initial and final enthalpy change of the reaction
(iv) Different intermediate reactions

43. When the total energy change in an isothermal cycle is zero, it represents :
(i) A reversible cycle (ii) An adiabatic change
(iii) A thermodynamic equilibrium (iv) An irrerversible cycle

44. The work done when 1 mole of a gas expands reversibly and isothermally from 5 atm to 1 atm at 300 K is :
(i) – 4015 J (ii) + 4015 J (iii) Zero (iv) 150 J

45. Clausius–Clapeyron equation helps to calculate :
(i) Latent heat of varporisation (ii) Boiling point or freezing point
(iii) Vapour pressure at one temperature, if at another temperature is given
(iv) Allof the above

46. When water is cooled to ice, its entropy :
(i) Increases (ii) Decreases (iii) Remains the same (iv) Becomes zero

47. For a spontaneous process :
(i) $\Delta G > 0$ (ii) $\Delta G < 0$ (iii) $\Delta G = 0$ (iv) None of these

48. The change in free energy of a system is given by :
(i) $\Delta G = \Delta A + P\Delta V$ (ii) $\Delta G = \Delta H - T\Delta S$
(iii) $\Delta G = \Delta E + P\Delta V - T\Delta S$ (iv) All of these

49. Gibbs-Helmoholtz equation is applicable to all :
(i) Processes, physical or chemical
(ii) Processes, physical or chemical in a closed system
(iii) Chemical processes in a closed system
(iv) Physical processes in a closed system

50. Which is the correct unit for entropy ?
(i) kJ mol (ii) JK^{-1} mol (iii) JK^{-1} mol (iv) kJ mol^{-1}

51. A reaction proceeds with increase in both enthalpy and entropy. It will be spontaneous if :
(i) $\Delta H = T\Delta S$ (ii) $\Delta H > T\Delta S$ (III) $\Delta H < T\Delta S$ (iv) none of these

52. **Fill inthe blanks :**

(i) In a process ΔH = 100 kJ and ΔS = 100 JK^{-1} at 400 K. The value of ΔG will be ....
(ii) A spontaneous process occurs with a .... in free energy.
(iii) The change in free energy is a measure of net ....
(iv) For solid, liquid and gas, the entropy of the system increases in the order ....
(v) The entropy of a pure crystal is zero at absolute zero. This is a statement of .... law of thermodynamics.
(vi) Entropy is a measure of .... of the molecules of the system.
(vii) A spontaneous change is accompanied by .... of internal energy or enthalpy.
(viii) In an adiabatic process .... can flow into or out of the system.
(ix) In an adiabatic process .... must change.
(x) For the reaction $H_2 + I_2 = 2HI$, ΔH is equal to ....

ANSWERS

35. 1085 cal **36.** 38.29 JK^{-1} **37.** 26.06 cal K^{-1} mol^{-1} **38.** (ii) **39.** (i) **40.** (iv) **41.** (ii) **42.** (iv) **43.** (i) **44.** (i) **45.** (iv) **46.** (ii) **47.** (ii) **48.** (iv) **49.** (ii) **50.** (iii) **51.** (ii)
52. (i) 60 kJ (ii) decrease (iii) work done (iv) solid < liquid < gas (v) third (vi) randomness or disorder (vii) decrease (viii) no heat (ix) temperature (x) ΔE

UNIT

8

THERMOCHEMISTRY

LEARNING OBJECTIVES

- Heat of Reaction (Enthalpy of Raction)
- Heat of Formation (Enthalpy of Formation)
- Heat of Combustion (Enthalpy of Combustion)
- Heat of Transition (Enthalpy of Transition)
- Heat of Neutralisation (Enthalpy of Neutralisation)
- Heat of Solution (Enthalpy of Solution)
- Intrinsic Energy
- Exothermic and Endothermic Reactions and Compounds
- Thermochemical Equation
- Relation Between Heats of Reaction at Constant Pressure and olume
- Kirchoff's Equation
- Hess' Law of Constant Heat Summation
- Bond Enthalpy
  - ☐ Summary
  - ☐ Student Activity
  - ☐ Test Yourself

• 8.1. HEAT OF REACTION (ENTHALPY OF REACTION*)

Heat of reaction is defined as the, *"the amount of heat evolved or absorbed in a reaction when the number of moles of reactants as represented by the balanced equation have completely reacted."*

For example, $C(s) + O_2(g) = CO_2(g) + 94380$ calories

According to the equation, when 12 g of carbon reacts with 32 g of oxygen to form 44 g of carbon dioxide, 94,380 calories of heat is evolved. Thus, the heat of reaction is 94,380 calories.

Similarly, in the equation :

$$C(s) + 2S(s) = CS_2(l) - 20{,}000 \text{ calories}$$

When 12 g of carbon reacts with 64 g of sulphur to form 76 g of carbon disulphide, 20,000 calories of heat is absorbed. Thus, the heat of reaction is –20,000 cals.

Heat of reaction depends on the following factors :

(i) Physical state of substances : Heat of reaction is different for different physical state of substances, *e.g.*,

$$C(\text{diamond}) + O_2(g) = CO_2(g) + 94380 \text{ cals.}$$

$$C(\text{graphite}) + O_2(g) = CO_2(g) + 94700 \text{ cals.}$$

(ii) Temperature : The heat of reaction varies with temperature due to variation in its specific heat and is related by Kirchoffs equation, *i.e.*,

$$\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1)$$

where, ΔH_1 and ΔH_2 are the heats of reaction at temperatures T_1 and T_2, ΔC_P is difference in the heat capacities of products and reactants.

(iii) The heat of reaction depends on the fact whether the reaction is carried out at constant pressure (ΔH) or at constant volume (ΔE). The two are related by the expression :

---

* **Enthalpy of reaction :** It is defined as the *enthalpy change when the number of gram moles of the substances as specified by the chemical reaction have completely reacted.*

$$\Delta H = \Delta E + \Delta nRT$$

where, Δn = Difference in the number of moles of gaseous products and gaseous reactants.
T = Absolute temperature.

• 8.2. HEAT OF FORMATION (ENTHALPY OF FORMATION)

Heat of formation is defined as the, *"amount of heat evolved or absorbed (or enthalpy change) when one mole of a compound is formed from its constituent elements."*

For example :

(i) $C(s) + O_2(g) = CO_2(g) + 94380$ cals.
(ii) $H_2(g) + (1/2)\, O_2(g) = H_2O(l) + 68400$ cals.
(iii) $C(s) + 2H_2(g) = CH_4(g) + 17900$ cals.

The heats of formation of $CO_2(g)$, $H_2O(l)$ and $CH_4(g)$ are 94380 cals, 68400 cals and 17900 cals, respectively.

In the equation :

$$H_2(g) + Cl_2(g) = 2HCl(g) + 44000 \text{ cals.}$$

The heat of formation of HCl is not 44000 cals., but 44000/2, *i.e.*, 22,000 cals, as one mole of HCl is formed by the evolution of 22,000 cals, of heat.

Standard heat of formation or standard enthalpy of formation. The standard enthalpy of formation of compound is the *enthalpy change when one mole of a compound is formed from its elements, all substances being in their standard states*. It is represented by $\Delta H°_f$. The standard state of any substance is taken as its natural state at 298 K and under one atmospheric pressure.

By convention, the standard heat of formation of all elements is taken as zero.

• 8.3. HEAT OF COMBUSTION (ENTHALPY OF COMBUSTION)

Heat of combustion is defined as the, *"amount of heat evolved (or enthalpy change) when 1 mole of a compound is burnt completely in excess of air or oxygen at a given temperature and under normal pressure."*

For example :

$$C(s) + O_2(g) = CO_2(g) + 94380 \text{ cals.}$$

$$H_2(g) + (1/2)\, O_2(g) = H_2O(l) + 68400 \text{ cals.}$$

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) = 12CO_{12}(g) + 11H_2O(l) + 13{,}49{,}000 \text{ cals.}$$

The heats of combustion of carbon, hydrogen and cane sugar are 94380 cals., 68400 cals., and 1349000 cals., respectively.

[I] Determination of Heat of Combustion

The calorimeter used to carry out the determination of heat of combustion is called a **bomb calorimeter** (fig. 1). The inner vessel or the bomb is a strong walled tight fitting air tight vessel

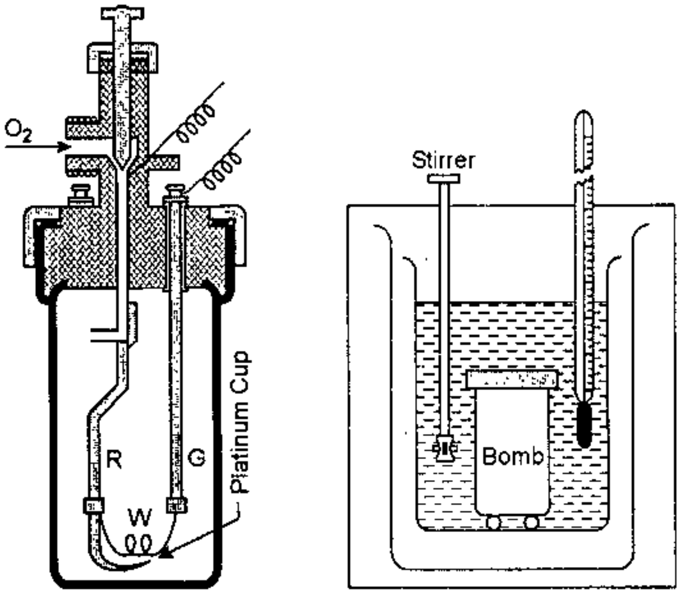

Fig. 1. Bomb calorimeter

coated inside with gold or platinum or some other non-oxidisable material. The cover can be fitted tightly to the vessel by means of a metal lid screwed down on a lead washer. A weighed quantity of the substance is taken in a platinum cup C which is supported on a rod R. This bomb is placed inside a double jacketed polished and metallic calorimeter and the substance is burnt electrically by passing a current through a copper wire W from which heat is conducted to the substance through a platinum loop touching it. A mechanical stirrer is also provided as shown.

When the current is passed, the temperature of water starts rising. The rise in temperature of water in the calorimeter is noted by means of an accurate thermometer, upto an accuracy of $\pm 0.01°$. The difference between the final and initial temperatures gives the rise of temperature. The heat capacity of the calorimeter system is obtained by taking and burning a known weight of a substance, whose heat of combustion is known. Generally, we take benzoic acid of very high purity, whose heat of combustion is taken to be 771.2 kcal.

If the heat capacity of the calorimeter system is Z and ΔT is the rise in temperature produced by burning w g of the given substance of molecular weight M, then

$$\text{Heat of combustion} = Z \times \Delta T \times \frac{M}{w} \text{ calories}$$

[II] Applications of Heat of Combustion

(i) Calculation of heat of formation : The heats of combustion of organic compounds can be determined very easily, so these values are used to calculate their heats of formation. The direct determination of these is often impossible.

(ii) Calculation of heat of transition : Suppose we want to calculate the heat of transition of diamond into graphite. It is done as follows :

$$\text{C (diamond)} + O_2(g) = CO_2(g) + a \text{ cals.}$$

$$\text{C (graphite)} + O_2(g) = CO_2(g) + b \text{ cals.}$$

On subtracting the two equations, we get,

$$\text{C (diamond)} = \text{C (graphite)} + (a - b) \text{ cals.}$$

$$\therefore \quad \text{Heat of transition} = (a - b) \text{ cals.}$$

(iii) Determination of calorific values of foods and fuels : The heat of combustion helps us in calculating the calorific values* of foods and fuels.

(iv) In deciding constitution : Heat of combustion of organic compounds is to a large extent an additive property and so has proved very valuable in deciding their chemical constitution.

• 8.4. HEAT OF TRANSITION (ENTHALPY OF TRANSITION)

Heat of transition is defined as the, *"heat change (or enthalpy change) when 1 mole of an element changes from one allotropic form to another"* *e.g.*, diamond to graphite. The heat of transition is really a measure of the difference in heat contents of the two forms of matter at the transition temperature.

The heats of combustion of diamond and graphite are given as follows :

$$\text{C (diamond)} + O_2(g) = CO_2(g);\ \Delta H = -94.4 \text{ kcal.}$$

$$\text{C (graphite)} + O_2(g) = CO_2(g);\ \Delta H = -94.7 \text{ kcal.}$$

By subtraction and rearranging, we get

$$\text{C (diamond)} = \text{C (graphite)};\ \Delta H_t = -94.4 + 94.7 = +0.3 \text{ kcal.}$$

In other words, the heat of transition (ΔH) of diamond to graphite is 0.3 kcal.

• 8.5. HEAT OF NEUTRALISATION (ENTHALPY OF NEUTRALISATION)

Heat of neutralisation is defined as the *"heat change (or enthalpy change) at a given temperature when one gram equivalent of an acid is neutralised by one gram equivalent of a base or vice versa in dilute solution."*

Some heats of neutralisation are given as follows :

$$HCl(aq) + NaOH(aq) = NaCl(aq) + H_2O + 13.7 \text{ kcal.} \qquad (\text{or } \Delta H = -13.7 \text{ kcal.})$$

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* The amount of heat produced in calories (or joule) when 1 g of a substance is completely burnt. It is expressed in cal g^{-1}, kcal g^{-1} or kJ g^{-1}.

$$HNO_3(aq) + NaOH(aq) = NaNO_3(aq) + H_2O + 13.7 \text{ kcal.} \qquad (\text{or } \Delta H = -13.7 \text{ kcal.})$$

$$HCl(aq) + KOH(aq) = KCl(aq) + H_2O + 13.7 \text{ kcal.} \qquad (\text{or } \Delta H = -13.7 \text{ kcal.})$$

Thus, we see that when both the acid and base are strong, the heat of neutralisation is always *nearly equal to –13.7 kcal. This can be explained as follows on the basis of complete dissociation* of both acid and the base :

Suppose the acid and base are represented by HA and BOH, respectively, then we can write,

$$H^+ + A^- + B^+ + OH^- = B^+ + A^- + H_2O + 13.7 \text{ kcal.}$$

or

$$H^+ + OH^- = H_2O + 13.7 \text{ kcal.}$$

Hence, the heat of neutralisation is really the heat of formation of 1 mole of water from 1g ion of hydrogen and 1g ion of hydroxyl ions, and as every neutralisation reaction involves this formation, the heat of neutralisation of strong acid and a strong base is always 13.7 kcal.

If, however, the acid or base or both are weak, the heat of neutralisation will be less than 13.7 kcal. In such cases, the neutralisation process involves not only the combination of hydrogen and hydroxyl ions but also the dissociation of the weak acid or base. The measured heat of neutralisation is, therefore, equal to the heat given out in the combination of $H^+(aq)$ and $OH^-(aq)$ ions plus the heat accompanying the dissociation of weak acid or/and weak base. The neutralisation of CH_3COOH and NaOH, for example can be represented as :

$$CH_3COOH(aq) + NaOH(aq) = CH_3COONa(aq) + H_2O + 13.2 \text{ kcal.} \qquad (\text{or } \Delta H = -13.2 \text{ kcal.})$$

The heat of neutralisation (ΔH) between formic acid and ammonium hydroxide is –11.7 kcal.

$$HCOOH(aq) + NH_4OH(aq) = HCOONH_4(aq)\ H_2O;\ \Delta H = -11.7 \text{ kcal.}$$

Determination of Heat of Neutralisation

The heat of neutralisation of an acid by a base can be determined by a simple calorimeter. For this, we take one small beaker placed inside another big beaker, the space between the two being filled with some insulating substance. The small beaker contains a stirrer and a thermometer.

First of all we measure the *water equivalent* (w) of calorimeter including stirrer and thermometer. For this, m_1 g of hot water at temperature t_1°, is added to m_2 g of cold water at temperature t_2° taken in the calorimeter. The mixture is stirred and the final temperature t_3° is noted.

$$\because \quad \text{Heat given} = \text{Heat taken}$$

$$\therefore \quad m_1(t_1 - t_3) = (m_2 + w)(t_3 - t_2)$$

or

$$w = \frac{m_1(t_1 - t_3)}{(t_3 - t_2)} - m_2$$

To measure the heat of neutralisation, we take a known volume of an acid of known concentration in a *calorimeter* and same volume of a base of the same concentration is taken in another exactly similar calorimeter. The temperature of both are noted. Now acid is added to alkali with constant stirring and final temperature is noted.

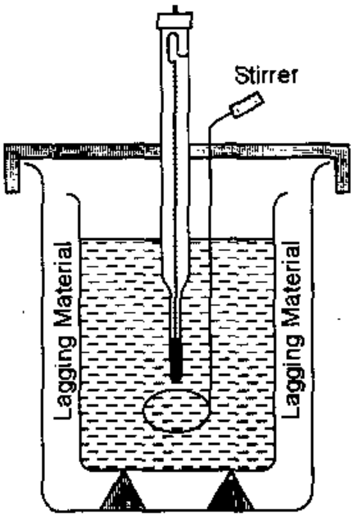


Fig. 2. Apparatus for measuring heat of neutralisation.

Suppose 100 ml of 0.5*N* HCl is taken in a calorimeter of water equivalent w. Let its temperature be t_4°. Similarly, 100 ml of 0.5*N* NaOH is taken in another calorimeter. Let its temperature be t_5°. So, temperature of the mixture may be taken as $\frac{t_4 + t_5}{2}$. After complete neutralisation, let the final temperature be t_6°.

$\therefore$ Heat evolved for neutralising 100 ml of 0.5*N* acid

$$= (200 + w) \times 4{\cdot}184 \times \left[t_6 - \left(\frac{t_4 + t_5}{2}\right)\right]$$

$$= H \text{ joules (say)}$$

$$\therefore \quad \text{Heat of neutralisation} = \frac{H \times 1000 \times 1}{0.5 \times 100} \text{ joules.}$$

• 8.6. HEAT OF SOLUTION (ENTHALPY OF SOLUTION)

Heat of solution is defined as the *"heat change (or enthalpy change) when one mole of a substance is dissolved in a solvent so that further dilution does not produce any change in enthalpy or heat change."* It is also called as integral heat of solution.

For example :

$$KCl(s) + aq = KCl(aq) - 4400 \text{ cals.}$$

$$MgSO_4(s) + aq = MgSO_4(aq) + 24{,}000 \text{ cals.}$$

The heat of solution of an electrolyte may be due to energy change involved during ionisation or some hydrate formation as in case of sulphuric acid. Usually, heat is absorbed when ions are torn apart from each other in the process of dissolution and heat is evolved during hydrate formation. In case of sodium chloride, that heat of separation of ions just equals the heat of hydration and so there is very little heat effect.

• 8.7. INTRINSIC ENERGY

Intrinsic energy is defined as, *"additional amount of energy in calories or joules which one gram mole of the compound possesses above that of its constituent elements."*

Consider the equation :

$$C(s) + O_2(g) = CO_2(g) + 94380 \text{ cals.}$$

As 1 mole of CO_2 is formed with the evolution of 94380 cals of heat, it is clear that energy of 1 mole of CO_2 is 94380 cals less than the sum of energies of its elements. This is due to the fact that total energy of the system before and after the reaction must be the same. Thus, the intrinsic energy of CO_2 is –94380 cals.

The intrinsic energy is not the absolute value of internal energy of the compound, but it is the difference between the internal energies of the compound and its constituent elements. If we arbitrarily fix the values of intrinsic energies of the elements as zero, the intrinsic energy of the compound can be calculated in terms of its heat of formation, *e.g.*,

$$C(s) + O_2(g) = CO_2(g) + 94380 \text{ cals.}$$

or $$E_C + E_{O_2} = E_{CO_2} + 94380 \text{ cals.}$$

or $$0 + 0 = E_{CO_2} + 94380 \text{ cals.}$$

or $$E_{CO_2} = -94380 \text{ cals.}$$

$\therefore$ Intrinsic energy = – Heat of formation.

• 8.8. EXOTHERMIC AND ENDOTHERMIC REACTIONS AND COMPOUNDS

A chemical reaction which is accompanied by the evolution of heat is known as an ***exothermic reaction*** and the compound so formed is known as an ***exothermic compound.***

In an exothermic reaction, ΔH ($\Delta H = H_{\text{products}} - H_{\text{reactants}}$) is negative, *i.e.*, sum of enthalpies of the products is less than that of the reactants and the difference in enthalpy is given out in the form of heat.

Example : $C(s) + O_2(g) = CO_2(g) + 94380$ cals.

$H_2(g) + (1/2)O_2(g) = H_2O(l) + 68400$ cals.

$CO_2(g)$ and $H_2O(l)$ are exothermic compounds for which ΔH are –94380 and –68400 cals., respectively.

A chemical reaction which is accompanied by the absorption of heat is known as an ***endothermic reaction*** and the compound so formed is known as an ***endothermic compound.***

In an endothermic reaction, ΔH is positve, *i.e.*, the sum of enthalpies of the products is greater than that of the reactants and the difference in enthalpy is absorbed by the system from the surroundings.

Example : $C(s) + 2S(s) = CS_2(l) - 20{,}000$ cal.

$CS_2(l)$ is an endothermic compound as $\Delta H = 20{,}000$ cal. Since exothermic compounds are formed from their elements with evolution of heat, they contain less energy than their constituent elements and are, therefore, stable. Similarly, endothermic compounds are formed with an absorption of heat, hence they contain more energy than their constituent elements and are, therefore, unstable.

• 8.9. THERMOCHEMICAL EQUATION

An equation which shows the amount of heat change (evolved or absorbed) in the chemical reaction is called a *thermochemical equation.*

$$C(s) + O_2(g) = CO_2(g) \qquad \text{[Chemical equation]}$$

$$C(s) + O_2(g) = CO_2(g) + 94380 \text{ cals.} \qquad \text{[Thermochemical equation]}$$

A thermochemical equation must essentially : (i) be balanced, (ii) mention the physical state of the reactants and products. The physical states are represented by the symbols (s), (l), (g) and (aq) for solid, liquid, gas and aqueous states, respectively, (iii) gives the values of ΔH or ΔE corresponding to the quantitites of substances given by the equation. Such an equation can be multiplied, added or subtracted just like simple algebraic equations.

• 8.10. RELATION BETWEEN HEATS OF REACTION AT CONSTANT PRESSURE AND VOLUME

Problem 2 : *Derive a relation between the heat of reaction at constant pressure and constant volume.*

The heat of reaction at constant pressure or enthalpy change (ΔH) and heat of reaction at constant volume or internal energy change (ΔE) are related by the equation :

$$\Delta H = \Delta E + P\Delta V \qquad \ldots(1)$$

where, ΔV = Change in volume due to expansion or contraction at constant pressure, P.

Consider the gaseous reaction :

$$n_1A + n_2B \longrightarrow m_1C + m_2D$$

Change in number of moles, Δn

$$= \text{(No. of moles of products)} - \text{(No. of moles of reactants)}$$

$$= (m_1 + m_2) - (n_1 + n_2)$$

Let the volume occupied by one mole of the gas be V, then

Change in volume, ΔV = Change in number of moles × Volume occupied by one mole of the gas

or $\Delta V = \Delta n.V$

or $P\Delta V = P.(\Delta n.V) = PV.\Delta n$

For 1 mole of a gas, $PV = RT$

$\therefore$ $P\Delta V = \Delta n.RT$

Substituting the value of $P\,\Delta V$ in equation (1), we get,

$$\Delta H = \Delta E + \Delta nRT \qquad \ldots(2)$$

or

$$\Delta H = \Delta E + 2\Delta nT \qquad (\because R = 2 \text{ cals deg}^{-1}\text{ mol}^{-1}) \quad \ldots(3)$$

The value of R may also be taken in joules per degree per mol, *i.e.*, 8.314 joules.

Equation (2) or (3) is the required relation between heats of reaction at constant pressure and constant volume.

• 8.11. KIRCHOFF'S EQUATION

Heat of reaction, in general, varies with temperature and its variation with temperature can be deduced as follows :

Let x_1 moles of a substance A react with x_2 moles of B to form y_1 moles of M, at a constant temperature; each substance being in a certain specific state. Thus,

$$x_1A + x_2B \rightarrow y_1M$$

The enthalpy of the reactants (H_1) is given by,

$$H_1 = x_1H_A + x_2H_B$$

The enthalpy of the products (H_2) is given by,

$$H_2 = y_1H_M$$

The increase in enthalpy (ΔH) for the change at constant pressure is,

$$\Delta H = H_2 - H_1 = y_1 H_M - x_1 H_A - x_2 H_B \qquad \ldots(1)$$

Similarly, the increase in internal energy (ΔE) at constant volume is,

$$\Delta E = E_2 - E_1 = y_1 E_M - x_1 E_A - x_2 E_B \qquad \ldots(2)$$

where, E terms represent the respective internal energy.

Differentiating equation (1) with respect to temperature, at constant pressure, and differentiating equation (2) with respect to temperature at constant volume, we get,

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = y_1\left(\frac{\partial H_M}{\partial T}\right)_P - x_1\left(\frac{\partial H_A}{\partial T}\right)_P - x_2\left(\frac{\partial H_B}{\partial T}\right)_P \qquad \ldots(3)$$

$$\left[\frac{\partial(\Delta E)}{\partial T}\right]_V = y_1\left(\frac{\partial E_M}{\partial T}\right)_V - x_1\left(\frac{\partial E_A}{\partial T}\right)_V - x_2\left(\frac{\partial E_B}{\partial T}\right)_V \qquad \ldots(4)$$

We know that,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \text{ and } C_v = \left(\frac{\partial E}{\partial T}\right)_V$$

Therefore, equations (3) and (4) reduce to,

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = y_1\,(C_p)_M - x_1\,(C_p)_A - x_2\,(C_p)_B = \Delta C_p \qquad \ldots(5)$$

$$\left[\frac{\partial(\Delta E)}{\partial T}\right]_V = y_1\,(C_v)_M - x_1\,(C_v)_A - x_2\,(C_v)_B = \Delta C_v \qquad \ldots(6)$$

where, ΔC_p and ΔC_v refer to overall changes in heat capacities in the reaction, *i.e.*, to their algebraic sum. Expressions (5) and (6) are ***mathematical forms of Kirchoff's equation*** and represent the *variation of heat content and internal energy of the reactants and products with temperature.*

Integrating equations (5) and (6) between proper limits, we have

$$\int_{H_1}^{H_2} d\,(\Delta H) = \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p.d\,T$$

Assuming ΔC_p to be independent of temperature, we get

$$\Delta H_2 - \Delta H_1 = \Delta C_P\,(T_2 - T_1) \qquad \ldots(7)$$

where, ΔH_1 and ΔH_2 are the heats of reaction at constant pressure at temperatures T_1 and T_2, respectively.

Integrating equation (6) between proper limits, we get

$$\int_{E_1}^{E_2} (d\,\Delta E) = \int_{T_1}^{T_2} \Delta C_v.dT$$

or

$$\Delta E = \Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_v.dT$$

Assuming ΔC_v to be independent of temperature, we get

$$\Delta E_2 - \Delta E_1 = \Delta C_v\,(T_2 - T_1) \qquad \ldots(8)$$

where, ΔE_1 and ΔE_2 are the heats of reaction at constant volume, at temperatures T_1 and T_2, respectively.

Kirchoff's law is valid for physical and chemical changes and is independent of nature and complexity of the systems. For an extended range of temperature, it is necessary to take into account the variation of heat capacities with temperature. The above expressions (5) and (6) may be used quite accurately over a range of temperature for which mean heat capacities remain constant.

• 8.12. HESS' LAW OF CONSTANT HEAT SUMMATION

Hess (1840) experimentally discovered a law which was a direct consequence of the first law of thermodynamics. According to it,

"If any change is brought about by two or more methods, in one step or more steps, the total amount of heat evolved or absorbed will be the same, no matter by which method the change is brought about."

For example, carbon can be burnt into carbon dioxide directly or it may first be changed to carbon monoxide and then oxidised to carbon dioxide.

First method : $C + O_2 = CO_2 + 94{,}380$ cals.

Second method : (i) $C + (1/2)O_2 = CO + 26{,}380$ cals.

(ii) $CO + (1/2)O_2 = CO_2 + 68{,}000$ cals.

Thus, the total heat evolved in second method is also 94,380 calories, which is the same as the heat evolved in the first method.

Theoretical Derivation of Hess' Law :

The Hess' law can be theoretically derived on the basis of first law of thermodynamics. Consider the conversion of A into B. When it occurs in one step let the heat evolved be Q_1 cals.

$$A \to B + Q_1 \text{ cals.}$$

Now let the change be carried out in a number of steps as follows :

$$A \to C \to D \to B$$

The thermochemical equations may be written as :

(i) $A \to C + q_1$ cals. (ii) $C \to D + q_2$ cals. (iii) $D \to B + q_3$ cals.

The heat evolved $= q_1 + q_2 + q_3 = Q_2$ cals.

According to Hess' law, $Q_1 = Q_2$. If $Q_1 \neq Q_2$ then either $Q_1 > Q_2$ or $Q_1 < Q_2$. Suppose $Q_1 > Q_2$, it means that by changing A into B in one step (first method) and then by changing B into A in three steps (second method), there would be again of heat equivalent to $(Q_1 - Q_2)$ calories. By repeating this cycle a great number of times a large amount of heat will be evolved in an isolated system. This is against the first law of thermodynamics. So, Q_1 cannot be greater than Q_2.

Similarly, we can prove that Q_1 cannot also be less than Q_2, because in this case, a large amount of heat will be absorbed by repeating the above cycle a great number of times. So, Q_1 must be equal to Q_2.

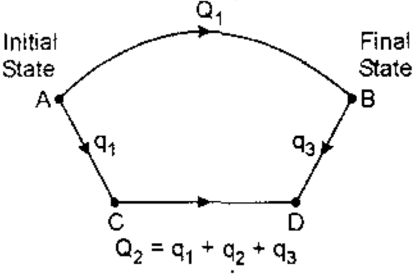


Fig. 3

Applications of Hess' Law

(i) Determination of heat of formation of substances which otherwise cannot be measured experimentally : The substances like methane, benzene, CO etc., cannot be prepared by uniting their elements. Therefore, it is not possible to measure heats of formation of such compounds directly. These can be determined indirectly by using Hess' law.

(ii) Determination of heat of transition : Hess' law is used in calculating the heat of transition, *i.e.*, conversion of one allotropic form into another. For example, conversion of C (diamond) into C (graphite) can be calculated as follows :

$$\text{C (diamond)} + O_2(g) = CO_2(g) + a \text{ cals.}$$

$$\text{C (graphite)} + O_2(g) = CO_2(g) + b \text{ cals.}$$

On subtracting the above equations, we get,

$$\text{C (diamond)} - \text{C (graphite)} = (a - b) \text{ cals.}$$

or $$\text{C (diamond)} = \text{C (graphite)} + (a - b) \text{ cals.}$$

$\therefore$ Heat of transition $= (a - b)$ cals.

(iii) Determination of heats of various reactions : By using Hess' law we can calculate the heat or enthalpy changes of many reactions which otherwise cannot be measured directly.

• 8.13. BOND ENTHALPY

Heat of formation of a bond or bond enthalpy is defined as the *average amount of energy required to break all the bonds of a particular type in one mole of a substance*. It is also known as ***bond energy***.

The bond energy of H—H bond is the energy required to break all bonds in one mole of a gas. It is expressed in kcal mole^{-1} or kJ mol^{-1}, *e.g.*, the bond energy of H—H bond is 433 kJ mol^{-1} or 103.58 kcal mol^{-1}. ***Bond breaking is an endothermic process, i.e.,*** ΔH is negative. Bond energy helps us to calculate the heat of formation of a compound or in calculating heats of reaction for gaseous reactions for which no thermal data is available and which involves substances having co-valent bonds.

For the reaction $H_2C = CH_2\,(g) + H_2\,(g) \to H_3C - CH_3\,(g)$, four C—H bonds, one C=C bond, one H—H bond are broken, while six C—H bonds and one C—C bond are formed. If the bond enthalpies of C—C, C—H, C = C and H — H bonds are 83, 99, 147 and 104 k cal mol^{-1}, respectively. we can write for ΔH,

$$\begin{aligned}\Delta H &= [4 \times 99 + 1 \times 147 + 1 \times 104] - [6 \times 99 + 1 \times 83] \\ &= 647 - 677 = -30 \text{ kcal.}\end{aligned}$$

∴ Heat of reaction = **– 30 kcal mole^{-1}.**

NUMERICAL PROBLEMS

Ex. 1. *Calculate the heat of formation of ethylene from the following data :*

(1) $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -94.0$ *kcal.*

(2) $H_2(g) + (1/2)\, O_2(g) \rightarrow H_2O(l)$; $\Delta H = -64.4$ *kcal.*

(3) $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$; $\Delta H = -337.0$ *kcal.*

Solution. We should aim at :

$$2\mathrm{C}(s) + 2\mathrm{H}_2(g) = \mathrm{C}_2\mathrm{H}_4(g); \qquad \Delta H = ?$$

Multiplying equation (1) by 2, equation (2) by 2 and reversing equation (3) and adding, we get,

$$\begin{array}{rl} 2\mathrm{C}(s) + 2\mathrm{O}_2(g) \rightarrow 2\mathrm{CO}_2(g); & \Delta H_1 = -188.0 \text{ kcal.} \\ 2\mathrm{H}_2(g) + \mathrm{O}_2(g) \rightarrow 2\mathrm{H}_2\mathrm{O}(l); & \Delta H_2 = -128.8 \text{ kcal.} \\ 2\mathrm{CO}_2(g) + 2\mathrm{H}_2\mathrm{O}(l) \rightarrow \mathrm{C}_2\mathrm{H}_4(g) + 3\mathrm{O}_2(g); & \Delta H_3 = +337.0 \text{ kcal.} \\ \hline 2\mathrm{C}(s) + 2\mathrm{H}_2(g) = \mathrm{C}_2\mathrm{H}_4(g);\ \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 & \end{array}$$

or

$$\begin{aligned}\Delta H &= (-188.0 - 128.8 + 337.0) \text{ kcal.} \\ &= +20.2 \text{ kcal.}\end{aligned}$$

∴ Heat of formation of ethylene, ΔH = **20.2 kcal.**

Ex. 2. *Calculate the heat of formation of methane from the following data :*

(1) $CH_4 + 4O \rightarrow CO_2 + 2H_2O + 213.3$ *kcal.*

(2) $C + O_2 \rightarrow CO_2 + 96.9$ *kcal.*

(3) $H_2 + O \rightarrow H_2O + 68.4$ *kcal.*

Solution. We should aim at :

$$\mathrm{C} + 4\mathrm{H} \rightarrow \mathrm{CH}_4 \pm \text{Heat}$$

Multiplying equation (3) by 2, reversing equation (1) and adding both with equaation (2), we get,

$$\begin{array}{c} 2\mathrm{H}_2 + 2\mathrm{O} \rightarrow 2\mathrm{H}_2\mathrm{O} + 136.8 \text{ kcal.} \\ \mathrm{CO}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{CH}_4 + 4\mathrm{O} - 213.3 \text{ kcal.} \\ \mathrm{C} + \mathrm{O}_2 \rightarrow \mathrm{CO}_2 + 96.9 \text{ kcal.} \\ \hline \mathrm{C} + 2\mathrm{H}_2 \rightarrow \mathrm{CH}_4 + (136.8 - 213.3 + 96.9) \text{ kcal.} \end{array}$$

or

$$\mathrm{C} + 2\mathrm{H}_2 \rightarrow \mathrm{CH}_4 + 20.4 \text{ kcal.}$$

∴ Heat of formation of methane = **20.4 kcal.**

Ex. 3. *Calculate the heat of formation of ethyl alcohol, given that ΔH for combustion of ethyl alcohol, ΔH for formation of carbon dioxide and water are –326.7, –94.05 and –68.3 kcal. respectively.*

Solution. We should aim at :

$$2\mathrm{C} + 3\mathrm{H}_2 + \mathrm{O} = \mathrm{C}_2\mathrm{H}_5\mathrm{OH} \pm Q \text{ kcal.}$$

Given :

$$\begin{array}{lll} (1) & \mathrm{C}_2\mathrm{H}_5\mathrm{OH} + 3\mathrm{O}_2 = 2\mathrm{CO}_2 + 3\mathrm{H}_2; & \Delta H = -326.7 \text{ kcal.} \\ (2) & \mathrm{C} + \mathrm{O}_2 = \mathrm{CO}_2; & \Delta H = -94.05 \text{ kcal.} \\ (3) & \mathrm{H}_2 + \frac{1}{2}\mathrm{O}_2 = \mathrm{H}_2\mathrm{O}; & \Delta H = -68.3 \text{ kcal.} \end{array}$$

Multiplying equation (2) by 2, equation (3) by 3, reversing equation (1) and adding, we get,

$$\begin{array}{ll} 2\mathrm{C} + 2\mathrm{O}_2 = 2\mathrm{CO}_2; & \Delta H_1 = -188.10 \text{ kcal.} \\ 3\mathrm{H}_2 + \frac{3}{2}\mathrm{O}_2 = 3\mathrm{H}_2\mathrm{O}; & \Delta H_2 = -204.90 \text{ kcal.} \\ 2\mathrm{CO}_2 + 3\mathrm{H}_2\mathrm{O} = \mathrm{C}_2\mathrm{H}_5\mathrm{OH} + 3\mathrm{O}_2; & \Delta H_3 = +326.70 \text{ kcal.} \\ \hline 2\mathrm{C} + 3\mathrm{H}_2 + \mathrm{O} = \mathrm{C}_2\mathrm{H}_5\mathrm{OH};\quad \Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 & \end{array}$$

$$\begin{aligned} &= (-188.10 - 204.90 + 326.70) \text{ kcal.} \\ &= -66.30 \text{ kcal.}\end{aligned}$$

∴ Heat of formation of ethyl alcohol, $\Delta H = -$ **66.3 kcal.**

Ex. 4. *If the heats of combustion of benzene, carbon and hydrogen are q_1, q_2 and q_3 cal. respectively, what will be the heat of fromation of benzene?*

Solution. Given that,

(1) $C_6H_6 + \frac{15}{2}O_2 = CO_2 + 3H_2O + q_1$ cal

(2) $C + O_2 = CO_2 + q_2$ cal

(3) $H_2 + \frac{1}{2}O_2 = H_2O + q_3$ cal

We should aim at :

$$6C + 3H_2 = C_6H_6$$

Multiplying equation (2) by 6, (3) by 3, reversing equation (1) and then adding, we get,

$$6C + 6O_2 = 6CO_2 + 6q_2 \text{ cal.}$$

$$3H_2 + \frac{1}{2}O_2 = 3H_2O + 3q_3 \text{ cal.}$$

$$6CO_2 + 3H_2O = C_6H_6 + \frac{15}{2}O_2 - q_1 \text{ cal.}$$

$$\overline{6C + 3H_2 = C_6H_6 + (6q_2 + 3q_3 - q_1) \text{ cal.}}$$

∴ Heat of formation of benzene = $\boldsymbol{(6q_2 + 3q_3 - q_1)}$ **cal.**

Ex. 5. *Calculate the heat of formation of hydrocarbon C_xH_y, if its heat of combustion is a cals and the heats of formation of CO_2 and H_2O are b and c cals, respectively.*

Solultion. We should aim at :

$$xC + \frac{y}{2}H_2 = C_xH_y \pm Q \text{ cals.}$$

Given :

(1) $C_xH_y + \left(x + \frac{y}{4}\right)O_2 = xCO_x + \frac{y}{2}H_2O + a$ cals.

(2) $C + O_2 = CO_2 + b$ cals.

(3) $H_2 + \frac{1}{2}O_2 = H_2O + c$ cals.

Multiplying equation (2) by x, equation (3) by $y/2$, reversing equation (1) and adding we get,

$$xCO_2 + \frac{y}{2}H_2O = C_xH_y + \left(x + \frac{y}{4}\right)O_2 - a \text{ cals.}$$

$$xC + xO_2 = xCO_2 + xb \text{ cals.}$$

$$\frac{y}{2}H_2 + \frac{y}{4}O_2 = \frac{y}{2}H_2O + \frac{y}{2}c \text{ cals.}$$

$$\overline{xC + \frac{y}{2}H_2 = C_xH_y + \left(xb + \frac{y}{2}c - a\right) \text{cals.}}$$

∴ Heat of formation of $C_xH_y = \boldsymbol{\left(xb + \frac{y}{2}c - a\right)}$ **cals.**

Ex. 6. *Calculate the heat of reaction :*

$$CO_2 + H_2 = H_2O + CO$$

The heats of formation of CO, CO_2, and H_2O are 25.4, 90.5 and 55.0 cal.. respectively.

Solution. Given :

(1) $C + \frac{1}{2}O_2 = CO + 25.4$ kcal. (2) $C + O_2 = CO_2 + 90.5$ kcal.

(3) $H_2 + \frac{1}{2}O_2 = H_2O + 55.0$ kcal.

Reversing equation (2) and adding it with equations (1) and (3), we get,

$$CO_2 = C + O_2 - 90.5 \text{ kcal.}$$

$$C + \frac{1}{2}O = CO + 25.4 \text{ kcal.}$$

$$H_2 + \frac{1}{2} O_2 = H_2O + 55.0 \text{ kcal.}$$

$$\overline{CO_2 + H_2 = CO + H_2O + (25.4 + 55.0 - 90.5) \text{ kcal.}}$$

or $$CO_2 + H_2 = CO + H_2O - 10.1 \text{ kcal.}$$

Heat of reaction = **– 10.01 kcal.**

Ex. 7. *Given the following thermochemical equations :*

$$C \text{ (graphite)} + O_2(g) \rightarrow CO_2(g);\ \Delta H = -94.1 \text{ kcal.}$$

$$C\text{(graphite)} \rightarrow C\text{(diamond)};\ \Delta H = -0.5 \text{ kcal.}$$

(i) Calculate ΔH for burning of diamond to CO_2.

(ii) Calculate the quantity of graphite that must be burned to evolve 1000 kcals. of heat.

Solution.

(i) $C \text{ (graphite)} + O_2(g) \rightarrow CO_2(g);$ $\Delta H = -94.1$ *kcal.*

$C\text{(diamond)} \rightarrow C\text{(graphite)};$ $\Delta H = -0.5$ *kcal.*

Adding the above equations,

$C \text{ (diamond)} + O_2(g) \rightarrow CO_2(g);$ $\Delta H = (-94.1 - 0.5)$ *kcal.*

$$\Delta H = \mathbf{-94.6 \text{ kcal.}}$$

(ii) According to the equation,

$$C \text{ (graphite)} + O_2(g) \rightarrow CO_2(g);$$

94.1 kcal. of heat is evolved by the burning of 1g atom or 12 g of C (graphite).

So, quantity of graphite required to evolve 1000 kcals. of heat on burning

$$= \frac{12 \times 1000}{94.1} \text{ g}$$

$$= \mathbf{127.52 \text{ g.}}$$

Ex. 8. *At 17°C, the heat of combustion at constant pressure of amorphous carbon into CO_2 is 96,960 cals and that of CO into CO_2 is 67,970 cals. Determine the heat of formation of CO at constant volume.*

Solution. The heat of formation of CO is given by :

$$\underset{\text{Negligible vol}}{C(s)} + \underset{1/2 \text{ vol}}{\frac{1}{2} O_2(g)} = \underset{1 \text{ vol}}{CO(g)} + \text{Heat}$$

Given (At constant pressure) :

(1) $C + O_2 = CO_2 + 96{,}960$ cals.

(2) $CO + \frac{1}{2} O_2 = CO_2 + 67{,}970$ cals.

Subtracting equation (2) from (1), we get,

$$C + \frac{1}{2} O_2 = CO + (96{,}960 - 67{,}970) \text{ cals.}$$

or $$C + \frac{1}{2} O_2 = CO + 28{,}990 \text{ cals.}$$

∴ Heat of formation of CO at constant pressure = 28,990 cals.

or $$\Delta H = -28{,}990 \text{ cals.}$$

We know that, $\Delta H = \Delta E + \Delta nRT$ ...(1)

Given : $\Delta H = -28{,}990$ cal, $\Delta n = 1 - \frac{1}{2} = \frac{1}{2}$, $R = 2$ cals., $T = 290\ K$

Putting the above values in equation (1), we get

$$-28990 = \Delta E + \frac{1}{2} \times 2 \times 290$$

or $$\Delta E = -28990 - 290 = -29{,}280 \text{ cals.}$$

∴ Heat of formation of CO at constant volume = **29,280 cals.**

Ex. 9. *At 27°C and constant volume, the heat of combustion of ethylene is –335.8 kcal. Calculate the heat of combustion at constant pressure at the same temperature. ($R = 2$ cal deg^{-1} mole^{-1})*

Solution. The heat of combustion of ethylene is represented as :

$$\underset{1\ vol}{C_2H_4(g)} + \underset{3\ vol}{3O_2(g)} = \underset{2\ vol}{2CO_2(g)} + \underset{Negligible\ vol}{2H_2O(l)}$$

Given : $\Delta E = 335.8$ kcal. $\Delta n = 2 - 4 = -2$, $T = 300\ K$, $R = -0.002$ kcal. $\Delta H = ?$

We know that, $\Delta H = \Delta E + \Delta nRT$

$\therefore$ $\Delta H = -335.8 + (-2) \times 0.002 \times 300 = -335.8 - 1.2 = -337.0$

Heat of combustion at constant pressure $(\Delta H) = -$ **337 kcal.**

Ex. 10. *Heat of combustion of glucose at constant pressure and at 17°C was found to be –6,51,000 cals. Calculate the heat of combustion of glucose at constant volume considering water to be in gaseous state.*

Solution. The heat of combustion of glucose is represented as :

$$\underset{Negligible\ vol}{C_6H_{12}O_6(s)} + \underset{6\ vol}{6CO_2(g)} = \underset{6\ vol}{6CO_2(g)} + \underset{6\ vol}{6H_2O(g)}$$

Given : $\Delta H = -6{,}51{,}000$ cal. $\Delta n = 12 - 6 = 6$.

$T = 17 + 233 = 290\ K$, $R = 2$ cal deg^{-1} $mole^{-1}$, $\Delta E = ?$

We know that, $\Delta H = \Delta E + \Delta nRT$

or $-6{,}51{,}000 = \Delta E + (6) \times 2 \times 290$

or $\Delta E = -6{,}51{,}000 - (6) \times 2 \times 290$

$= -6{,}5{,}000 - 3{,}480$

$= -6{,}54{,}480.$

$\therefore$ Heat of combustion at constant volume = **– 6,54,480 cals.**

Ex. 11. *If the bond energies for H—H, O═O and O—H bonds are 104, 118 and 111 kcal mol^{-1}, respectively, calculate the heat of the reaction,*

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

Solution. In this reaction, two O—H bonds are formed and one H—H bond is broken. So we can write for ΔH,

$$\Delta H = -2\Delta H\ (O—H) + \Delta H\ (H—H) + \frac{1}{2}\Delta H\ (C═O)$$

$$= (-2 \times 111) + 104 + \left(\frac{1}{2} \times 118\right)$$

$$= -222 + 104 + 59 = -59\ \mathbf{kcal.\ mol^{-1}}$$

Ex. 12. *Calculate the bond energy of HCl, if the H—H bond energy is 433 kJ mol^{-1}, Cl—Cl bond energy is 242 kJ mol^{-1} and H_f for HCl is – 91 kJ mol^{-1}.*

Solution. Given :

(1) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)$ $\Delta H = -91$ kJ

(2) $H_2(g) \rightarrow 2H(g)$ $\Delta H = +433$ kJ

(3) $Cl_2(g) \rightarrow 2Cl(g)$ $\Delta H = +242$ kJ

Multiplying equation (1) by 2, we get,

(4) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ $\Delta H = -182$ kJ

Adding equations (2) and (3) we get,

(5) $H_2(g) + Cl_2(g) \rightarrow 2H(g) + 2Cl(g)$ $\Delta H = +675$ kJ

Subtracting equation (4) from (5), we get

$2HCl(g) \rightarrow 2H(g) + 2Cl(g)$ $\Delta H = +857$ kJ

Dividing the last equation by 2, we get

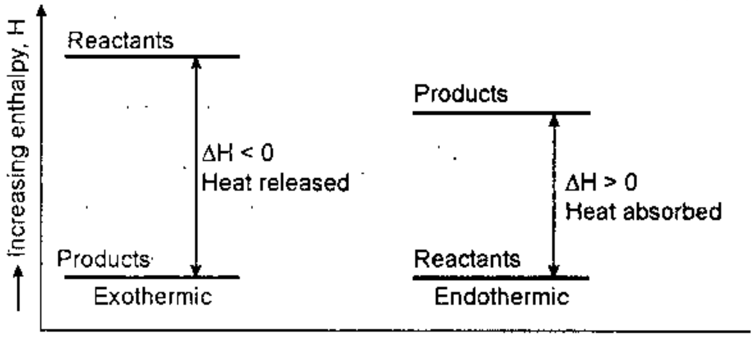
$HCl(g) \rightarrow H(g) + Cl(g),$ $\Delta H = +428{\cdot}5$ kJ

$\therefore$ Bond energy of H—Cl bond is **428·5 kJ.**

• SUMMARY

- Thermochemistry is that branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.
- In an exothermic reaction heat is evolved and the internal energy of reactants is greater than the internal energy of the products.
- In an endothermic reaction, heat is absorbed and the internal energy of reactants is less than the internal energy of the products.

- The change in internal energy (ΔE) is the heat change accompanying a chemical reaction at constant volume because no external work is performed.
- While the heat change in a process is equal to its change in internal energy (ΔE) at constant volume, it gives at constant pressure the enthalpy change (ΔH), *i.e.*, ΔE = Heat change in a reaction at constant volume, ΔH = Heat change in a reaction at constant pressure.



- Heat of reaction may be defined as the amount of heat evolved or absorbed in a reaction when the number of moles of reactants as represented by the balanced chemical equation change completely into products.
- Kirchoff's equation may be represented as

  (i) $\dfrac{d(\Delta E)}{dT} = (C_V)_2 - (C_V)_1 = \Delta C_V$

  i.e., change in heat of reaction at constant volume per degree change in temperature is equal to the difference in heat capacities at constant volume of products and reactants.
- (ii) $\dfrac{d(\Delta H)}{dT} = (C_P)_2 - (C_P)_1 = \Delta C_P$

  i.e., change in heat of reaction at constant pressure per degree change in temperature is equal to the difference in heat capacities at constant pressure of products and reactants.
- Heat of formation is defined as the change in enthalpy that takes place when one mole of the compound is formed from its elements.
- Heat of combustion is defined as the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.
- Heat of combustion of a substance (ΔH_C) is always negative.
- Heat of solution is defined as the change in enthalpy when one mole of a substance is dissolved in a specified amount of solvent at a given temperature.
- Heat of neutralisation is defined as the change in enthalpy of the system when one gram equivalent of an acid is neutralised by one gram equivalent of an alkali or vice versa in dilute solution.
- The heat of neutralisation of a strong acid and strong base is –13.7 k cal, no matter which acid or base is used.
- The heat of neutralisation of an acid and a base is merely the heat of formation of water from hydrogen and hydroxyl ions.
- **Hess' law of constant heat summation :** If a chemical change can be made to take place in two or more different ways whether in one step or two or more steps, the amount of total heat change is the same no matter by which method the change is brought about.
- Bond energy is defined as the average amount of energy required to break all bonds of a particular type in one mole of the substance.

• STUDENT ACTIVITY

1. Describe the factors on which heat of reaction depends.

2. State and explain heat of combustion.

3. Define heat of neutralisation. Why heat of neutralisation of a strong acid and strong base is always constant ?

4. State and explain Hess' law.

5. Defin heat of formation.

6. State and explain heat of solution.

7. Write Kirchoff's equation.

• TEST YOURSELF

Answer the following questions :

1. Define or explain the following terms :
    - (a) Thermochemistry
    - (b) Heat of reaction
    - (c) Heat of formation
    - (d) Standard heat of reaction
    - (e) Standard heat of formation
    - (f) Heat of solution
    - (g) Heat of combustion
    - (h) Heat of neutralisation
    - (i) Heat of transition
    - (j) Hess' law
    - (k) Bond energy
    - (l) Thermochemical equation
2. Explain the terms : heat of reaction at constant pressure and heat of reaction at constant volume. How are they related ?

3. State and explain heat of combustion with examples.

4. How will you determine the heat of combustion experimentally ?

5. Derive Kirchoff's equation.

6. Discuss the variation of heat of reaction with temperature.

7. Mention the factors on which heat of reaction depends.

8. State and explain heat of neutralisation. How it is experimentally determined ?

9. Explain why the heat of neutralisation of a strong acid and a strong base is always constant, equal to −13.7 k cal ?

10. Define bond energy.

11. State and explain Hess' law.

12. When 100 ml of 1 N HCl is neutralised by an equivalent amount of NaOH, 5273 kJ of heat is evolved. Calculate the heat of neutralisation of HCl.

13. The heat of formation of methane at 27°C is −19.3 k cal, when the measurements are made at constant pressure. What will be the heat of formation at constant volume ?

14. In the reaction,

$$C(s) + O_2(g) \rightarrow CO_2(g) + 94{\cdot}5 \text{ kcal., } 94{\cdot}5 \text{ kcal. is}$$

(i) Heat of formation of $CO_2(g)$ (ii) Heat of combustion of $CO_2(g)$
(iii) Heat of solution of $CO_2(g)$ (iv) Heat of reaction of $CO_2(g)$

15. If the heat of formation of a compound is − 100 kJ, its intrinsic energy will be :
(i) − 100 kJ (ii) − 50 kJ (iii) 50 kJ (iv) 100 kJ

16. Which is correct equation for ΔH and ΔE ?
(i) $\Delta E = \Delta H + \Delta nRT$ (ii) $\Delta H = \Delta E + \Delta nRT$
(iii) $\Delta E = \Delta H + nRT$ (iv) $\Delta H = \Delta E + nRT$

17. The enthalpy of neutralisation of a strong acid and strong base is :
(i) 13·7 kcal (ii) − 13·7 kcal
(iii) Less than 13·7 kcal (iv) Greater than 13·7 kcal

18. From the following data,

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + 571{\cdot}831 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) + 285{\cdot}906 \text{ kJ}$$

the enthalpy of combustion (ΔH) of hydrogen will be :
(i) − 285·925 kJ (ii) − 185·91 kJ (iii) 285·925 kJ (iv) 185·91 kJ

19. Hess' law is used to determine :
(i) Heat of formation of substances which are otherwise difficult to measure
(ii) Heat of transition
(iii) Heat of various other reactions like dimerisation
(iv) All of the above

20. The thermochemical equations may be :
(i) Multiplied (ii) Added (iii) Subtracted (iv) All of the above

21. **Fill in the blanks :**
(i) Greater the heat of fusion of a substance, ... is the magnitude of intermolecular forces.
(ii) The heat of neutralisation of a weak acid by a strong base is .... than that of a strong acid by a strong base.
(iii) The fuel efficiency of methane (mol. mass = 16) is .... that of ethane (mol. mass = 30).
(iv) In an exothermic reaction, the heat energy is .... while in an endothermic reaction it is ....
(v) For exothermic reaction, ΔH is ...., while for endothermic reaction it is ....
(vi) The calorific value is defined as the amount of heat produced in calories when ...... of a substance is completely burnt.

ANSWERS

12. 52.73 kJ **13.** 18.70 k cal **14.** (i) **15.** (iv) **16.** (ii) **17.** (ii) **18.** (i) **19.** (iv) **20.** (iv)
21. (i) higher (ii) lesser (iii) greater (iv) released, absorbed
(v) negative, positive (vi) one gram.

❑❑❑

UNIT

9

PHASE EQUILIBRIUM

LEARNING OBJECTIVES

- Phase
- Component
- Degree of Freedom or Variance
- Statement of Phase Rule
- One Component System
- Water System
- Two Component System
- Lead-Silver System
- Henry's Law
- Distribution Law
  - ☐ Summary
  - ☐ Student Activity
  - ☐ Test Yourself

9.1. PHASE

A phase is defined as *"any homogeneous, physically distinct part of a system which is mechanically separable and bounded by a definite surface.* A phase can exist in either state of matter, *viz.*, solid, liquid or gas. A system may consist of one phase or more than one phases.

Examples

1. Pure substances : A pure substance (*s*, *l* or *g*) made of one chemical species only has one phase, *e.g.*, oxygen (O_2), ice (H_2O), alcohol (C_2H_5OH) etc.

2. Mixture of gases : A mixture of gases, say H_2, N_2 and O_2 contributes one phase only as all gases mix freely to form a homogeneous mixture.

3. Miscible liquids : Two or more completely miscible liquids give a uniform solution. *e.g.*, a solution of water and ethanol has one liquid phase.

4. Non-miscible liquids : A mixture of non-miscible liquids forms as many number of liquid phases as that of liquids, because on standing they form separate layers, *e.g.*, a mixture of water and chloroform forms two liquid phases.

5. Aqueous solutions : An aqueous solution of a solid substance such as NaCl is uniform throughout. So, there is only one liquid phase.

6. Mixture of solids : A mixture of two or more solid substances contains as many phases. Each of these substances have different physical and chemical properties and form a separate phase. Thus, a mixture of calcium carbonate and calcium oxide has two solid phases.

7. In the dissociation of calcium carbonate there will be three phases, *viz.*, two solid phases ($CaCO_3$ and CaO) and one gaseous phase (CO_2).

8. In water system, there are three phases, *viz.*, ice (solid), water (liquid) and vapours (gas). Similarly, in sulphur system, there are four phases, *viz.*, rhombic sulphur and monoclinic sulphur (solids), liquid sulphur (liquid) and vapour sulphur (gas).

9.2. COMPONENT

The number of components of a system is defined as, *"the smallest number of independently variable constituents by means of which the composition of each phase can be represented by means of a chemical equation."*

Constituents can either be elements or compounds. While writing the chemical equations, we can use zero as well as negative quantities of the constituents, besides the positive ones (as is the convention).

Examples

1. Water system : We know that water system consists of three phases, ***viz., solid*** (ice), ***liquid*** (water) and ***gas*** (water vapours). Each of the three phases is nothing else but water. Hence, all the three phases can be represented in terms of the composition of only one constituent, water *i.e.*, by the formula H_2O.

$$\text{Ice } (s) = H_2O;\ \text{Water } (l) = H_2O;\ \text{Vapour } (g) = H_2O$$

So, water system is a ***one component system.***

2. Dissociation of calcium carbonate : The case of dissociation of calcium carbonate is rather complicated. Its equilibrium can be represented as :

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The composition of all the three phases can be expressed in terms of either of the two components. Any two out of three substances can be chosen as the two components. This is clearly understood as follows :

(a) When $CaCO_3$ and CaO are the two components :

Phase $\rightleftharpoons$ **Components**

$CaCO_3 = CaCO_3 + 0.CaO$

$CaO = 0.CaCO_3 + CaO$

$CO_2 = CaCO_3 - CaO$

(b) When $CaCO_3$ and CO_2 are the two components :

$CaCO_3 = CaCO_3 + 0.CO_2$

$CaO = CaCO_3 - CO_2$

$CO_2 = 0.CaCO_3 + CO_2$

(c) When CaO and CO_2 are the two components :

$CaCO_3 = CaO + CO_2$

$CaO = CaO + 0.CO_2$

$CO_2 = 0.CaO + CO_2$

Hence, from the above three cases, it is crystal clear that only two constituents are needed to express the composition of each of the three phases. Hence, it is a ***two component system.***

3. Dissociation of ammonium chloride : The case of dissociation of ammonium chloride is very interesting. It dissociates as follows :

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

There are two phases, *viz.*, one solid and one gas. The system will be a ***one component or two component system*** depending upon the relative quantities of HCl and NH_3 formed.

(a) When NH_3 and HCl are in equivalent quantities :

Gaseous phase Component

$NH_3 + HCl = NH_4Cl$

Solid phase

$NH_4Cl = NH_4Cl$

So, we see that the composition of both the phases has been expressed in terms of only one substance, *viz.*, NH_4Cl. So, the system is a ***one component system.***

(b) When NH_3 and HCl are not in equivalent quantities :

Suppose :

$$NH_4Cl(s) \rightleftharpoons x\,NH_3(g) + y\,HCl(g) \qquad (x > y)$$

The composition of the solid phase can only be represented by NH_4Cl, but the composition of the gaseous phase cannot be represented by NH_4Cl, but in terms of NH_3 and NH_4Cl as follows:

Gas phase : $xNH_3 + yHCl = yNH_3 + yHCl + (x - y)\,NH_3$

$= yNH_4Cl + (x - y)\,NH_3$

Solid phase : $NH_4Cl = NH_4Cl + 0.NH_3$

Hence, in this case the two components are NH_4Cl and NH_3. If HCl is present in excess over NH_3, then the two components will be NH_4Cl and HCl. However, the system remains a ***two component system.***

• 9.3. DEGREE OF FREEDOM OR VARIANCE

There are three variable factors, *viz.*, temperature, pressure and concentration, on which the equilibrium of a system depends. In some cases, we have to mention only one factor to define the system completely, sometimes two or three. So, the degree of freedom (or variance) of a system is defined as, ***the least number of variable factors such as temperature, pressure or concentration which must be specified so that the remaining variables are fixed automatically and the system is completely defined.***

System having degrees of freedom three, two, one or zero are known as ***trivariant, bivariant, univariant*** (or monovariant) and ***non-variant*** systems, respectively.

Examples

1. For ice-water-vapour system, F = 0 : In the system, ice $\rightleftharpoons$ water $\rightleftharpoons$ vapour, the three phases co-exist at the freezing point of water. As the freezing temperature of water has a fixed value, the vapour pressure of water also has a definite value. The system has two variables (T and P) and both these are already fixed. So, the system is completely defined automatically and there is no need to specify any variable. So, it has no degree of freedom, *i.e.*, $F = 0$.

2. For saturated NaCl solution, F = 1 : The saturated solution of sodium chloride in equilibrium with solid NaCl and water vapour, *i.e.*,

$$NaCl(s) \rightleftharpoons NaCl\text{ (solution)} \rightleftharpoons \text{Water vapour}$$

is completely defined if we specify temperature only. The other two variables, *i.e.*, composition of NaCl solution and vapour pressure have a definite value at a fixed temperature. So, the system has one degree of freedom.

3. For a pure gas, F = 2 : For a sample of pure gas, $PV = RT$. If the values of P and T are specified, volume (V) can have only one definite value or that the volume, *i.e.*, third variable is fixed automatically. Any other sample of the gas under the same pressure and temperature as specified above will be identical with the first one. So, the system containing a pure gas has two degrees of freedom.

• 9.4. STATEMENT OF PHASE RULE

Phase rule as given by W.J. Gibbs, is defined as follows :

"If any heterogeneous system in equilibrium is not affected by electrical or magnetic forces or by gravity, then the degrees of freedom (*F*), number of components (*C*) and number of phases (*P*) are connected by means of the equation,

$$F = C - P + 2."$$

The mass of the phase does not enter into the equation, as it has no effect on the state of equilibrium.

• 9.5. ONE COMPONENT SYSTEM

For a one component system, we can write the phase rule equation as :

$$F = C - P + 2 = 0 = 1 - P + 2 = 3 - P$$

Three cases may arise :

Case 1. When only **one phase** is present,

$$F = 3 - 1 = 2$$

Thus, the system is **bivariant.** It can be completely defined by specifying the two variables *viz.*, temperature and pressure. Or that, both the temperature and pressure can be varied independently. Therefore, a single phase is represented by an area on P, T-graph.

Case 2. When **two phases** are in equilibrium,

$$F = 3 - 2 = 1$$

The system then has one degree of freedom and is termed **monovariant** or **univariant.** This means that if we change the temperature the pressure cannot be changed independently. The pressure is fixed automatically for a given temperature. A two phase system is represented by a line on a P, T-graph.

Case 3. When **three phases** are in equilibrium,

$$F = 3 - 3 = 0$$

The system then has zero degree of freedom and is termed **nonvariant** or **invariant.** This special condition can be obtained at a definite temperature and pressure. Therefore, the system is defined completely and no further statement of external conditions is necessary. A three phase system is represented by a point on the P, T-graph. At this point, the three phases (solid, liquid, vapour) are in equilibrium. Therefore, this point is known as **triple point.**

In a one component system four phases cannot co-exist in equilibrium. The reason is that in a one component system, $C = 1$ and, therefore, the phase rule equation ($F = C - P + 2$) becomes:

$$F = 1 - P + 2 = 3 - P.$$

The minimum degree of freedom in any system can be zero, *i.e.* $F = 0$ and so,

$$0 = 3 - P_{\max} \text{ or } P_{\max} = 3.$$

Thus, not more than three phases can co-exist in equilibrium in a one component system.

• 9.6. WATER SYSTEM

Water exists in three phases, *viz.* (a) ***solid***—ice, (b) ***liquid***—water, (c) ***gas***—vapour.

The system is a one component system, as the composition of all the three phases can be expressed in terms of only one constituent, H_2O. The phase diagram for the water system is as shown in figure (1). A phase diagram is a plot showing the conditions of pressure and temperature under which two or more physical states can exist together in a state of dynamic equilibrium.

The salient features of the phase diagram are as follows :

(1) The curves AO, OB, OC.

(2) The triple point, O.

(3) The areas AOB, BOC, AOC.

The significance of each of these features is discussed below.

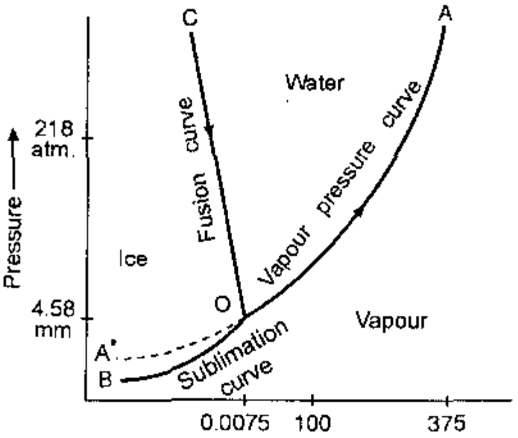


Fig. 1. Phase diagram of water system

(i) Curve AO : It is known as ***vapour pressure curve or vaporisation curve of liquid water.*** The two phases in equilibrium along AO are water and water vapour. Hence, the curve is univariant. It also follows from the phase rule equation,

$$F = C - P + 2 = 1 - 2 + 2 = 1.$$

From the curve it is also clear that in order to define the system along it, we have to mention either temperature or pressure. This is because for one value of temperature there can only be one value of pressure. The curve AO terminates at O the critical point of water (374°C).

(ii) Curve OB : It is known as the ***vapour pressure curve or sublimation curve of ice.*** The two phases in equilibrium along OB are solid ice and water vapour and so the curve is univariant ($F = C - P + 2 = 1 - 2 + 2 = 1$). This also follows from the curve, because there is only one value of pressure for any value of temperature.

The curve OB extends to B, which is nearly absolute zero where no vapour exists.

(iii) Curve OC : It is known as ***freezing point curve of water or fusion curve of ice.*** The two phases, ice and water, are in equilibrium along OC. So, the curve is univariant ($F - C - P + 2 = 1 - 2 + 2 = 1$).

This curve shows the effect of pressure on the melting point of ice* or freezing point of water. As the curve OC slopes towards the pressure axis, the melting point is lowered as the pressure is increased. This fact can also be predicted by Le-Chatelier's principle, as ice melts with decrease in volume.

(iv) Triple point : The curves OA, OB and OC meet at point O, where all the three phases, *viz.*. liquid water, ice and water vapour exist in equilibrium. So, it is known as a ***triple point.***

Applying phase rule to triple point, we have

$$F = C - P + 2 = 1 - 3 + 2 = 0.$$

So, this point is non-variant, *i.e.*, in order to define the system at O, we have not to mention any variable factor, *i.e.*, the system is self-defined.

---

* Normal melting point of a substance is defined as the temperature at which the solid and liquid are in equilibrium at atmospheric pressure.

The triple point, posseses fixed values for pressure and temperature, *i.e.*, 4.58 mm. of Hg and +0.0075°C, respectively. (It is clear that O is not the actual melting point of ice. *i.e.*, 0°C. Its value has been increased due to the fact that 0°C is the normal melting point of ice at 760 mm of Hg and decrease of pressure will increase the melting point of ice. Since a decrease of pressure by 1 atmospheric pressure or 760 mm of Hg increases the melting point by 0.008°C, therefore, a decrease of pressure to 4.58 mm will raise the melting point to +0.0075°C.)

(v) Areas : The diagram consists of three areas *viz.*, *AOB*, *BOC* and *AOC*, which show the conditions of temperature and pressure under which a single phase—water vapour, ice and water respectively, is capable of stable existence.

Applying phase rule to different areas, we have

$$F = C - P + 2 = 1 - 1 + 2 = 2,$$

i.e, the systems are bivariant. This also follows from the diagram, because in order to define the system completely at any point within the area, we have to express both the variable factors—pressure and temperature—making the system bivariant.

Metastable Equilibrium : Fahrenheit observed that under certain conditions, water can be cooled to −9°C, without the separation of ice at 0°C. Similarly, every liquid can be cooled below *the freezing point without the separation of the solid phase. So, water* cooled below its freezing point is known as ***supercooled water***. But as soon as the equilibrium is disturbed either by stirring or by adding a small piece of ice, supercooled water immediately changes into ice. Therefore, it can be said that such water is in itself stable, but becomes unstable on disturbing the equilibrium. Such an equilibrium is known as ***metastable equilibrium***. It can be defined as, ***"an equilibrium which in itself is stable but becomes unstable on being disturbed by stirring or adding a piece of the solid phase."***

From the diagram, it is clear that if water is cooled along AO undisturbed, then at O, no ice separates out, as should have happened. In such a case, the curve AO merely extends to A′. The phases along OA′ will be water and vapour, in metastable equilibrium, as water normally should not exist below O. The curve OA′ which is known as ***metastable curve*** will be univariant. As soon as the equilibrium is disturbed by stirring or adding a piece of ice, the curve OA′ immediately merges into OB with liquid water changing into solid ice. The curve OA′ is in accordance with the general principle that the vapour pressure of the metastable phase is always higher than the stable phase. This is evident because the curve OA′ lies above the curve OB. *Below O, ice is the stable phase and water is the metastable phase.*

Table 1. Salient features of water system

Curve/Region/ Point		Name	Phases : Solid (S), Liquid (L) and Vapour (V)	Variance
1.	Curve OA	Vaporisation curve of water	$L \rightleftharpoons V$	1
2.	Curve OB	Sublimation curve of ice	$S \rightleftharpoons V$	1
3.	Curve OC	Fusion curve of ice	$L \rightleftharpoons S$	1
4.	Region AOB	—	Vapour	2
5.	Region AOC	—	Liquid	2
6.	Region BOC	—	Solid	2
7.	Point 'O'	Triple point	$S \rightleftharpoons L \rightleftharpoons V$	0
8.	Curve OA′	Metastable vaporisation curve of water	$L \rightleftharpoons V$	1

• 9.7. TWO COMPONENT SYSTEM

A two component system is that system in which the composition of each phase present in it can be represented in terms of two substituents, *e.g.*, lead-silver system, potassium iodide–water system etc.

Phase rule when applied to a two component system becomes

$$F = C - P + 2 = 2 - P + 2 = 4 - P$$

Since the minimum number of phases in any system is *one*, it is evident from the above equation that the maximum degree of freedom in a two component system is **three**. Therefore, in addition to temperature and pressure, a third variable, namely composition, has also to be taken into account. In order to represent such an equilibrium graphically, it is, therefore, necessary to have three coordinate axes at right angles to one another. This will lead to three dimensional or space models which cannot be easily represented on paper (figure 2-a). Therefore, it is customary to choose any two of the three variables for graphical representation, assuming the third variable to remain constant. Thus, we get three types of curves as shown in (figure 2 b, c, d).

[I] Condensed Phase Rule Equation

When in a system, one variable out of pressure, temperature or concentration is taken as constant, the number of degrees of freedom is reduced by one. In that case, phase rule equation ($F = C - P + 2$) becomes,

$$F = (C - P + 2) - 1$$

or $$F = C - P + 1$$

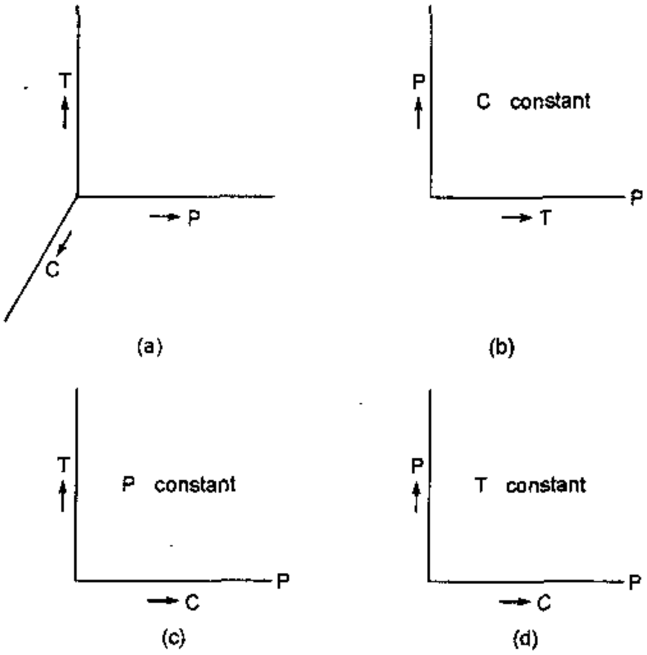


Fig. 2

This equation is known as ***condensed*** or ***reduced phase rule equation***.

[II] Condensed State or Phase

In ***solid-liquid system***, a negligible change in pressure produces no change in equilibrium as the vapour pressure of solid is negligible. Therefore, in such a system, the pressure variable may be taken as nearly constant. So, a system in which vapour phase is ignored is known as a ***condensed system.*** For such a system, we apply the condensed phase rule equation, $F = C - P + 1$.

• 9.8. LEAD-SILVER SYSTEM

The two metals lead and silver mix together in the liquid form but do not form any chemical compound. The phase diagram is as shown in figure (4). It is explained as follows :

1. Curve AC : Pure lead melts at 327°, while silver at 961°. Point A represents the melting point of pure lead. By the gradual addition of silver, the freezing point of lead decreases along AC. The curve AC is thus known as ***freezing point or melting point curve of lead***. The phases present along AC are solid lead and its solution with silver. Thus, it is a univariant curve as.

$$F = C - P + 1 = 2 - 2 + 1 = 1$$

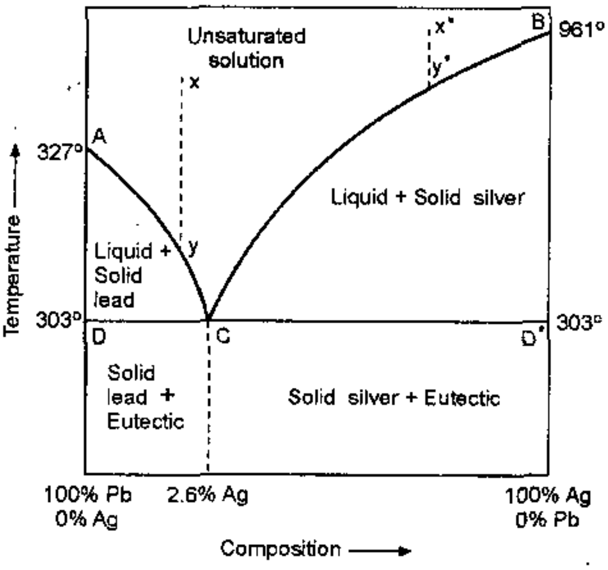


Fig. 3. Phase diagram of Pb–Ag system.

2. Curve BC : Similarly, B represents the melting point of pure silver. By the addition of lead to it, the freezing point of silver decreases along BC and we get a solution of it with lead. The curve BC is known as the ***freezing point or melting point curve of silver.*** The two phases present along it are solid silver and a solution of it with lead. It is, therefore, a univariant curve as,

$$F = C - P + 1 = 2 - 2 + 1 = 1.$$

3. Point C : The two curves AC and BC meet at a common point C. Therefore, C gives conditions of temperature and composition under which three phases, *viz*., solid silver, solid lead and solution co-exist in equilibrium. It is thus a non-variant point as,

$$F = C - P + 1 = 2 - 3 + 1 = 0.$$

The point C is known as *eutectic point* of the system. The temperature and composition corresponding to eutectic point are known as eutectic temperature and eutectic composition, respectively. The eutectic temperature and composition are 303° and 2.6% Ag and 97.4% Pb, respectively.

4. Areas : In the area above the curves AC and BC, the two components are present in the form of one homogeneous liquid phase. The system becomes bivariant as,

$$F = C - P + 1 = 2 - 1 + 1 = 2.$$

In other areas the phases are present as shown in the figure.

Effect of cooling : Consider the phase changes which occur on cooling a liquid mixture. Suppose a liquid mixture of composition x is cooled at constant temperature. The temperature will fall without any change in the composition until the point y on the curve yC is reached. At this point, lead will begin to separate out. The system becomes univariant, as it consists of two phases. The temperature will now fall with a change in the composition of the liquid mixture along AC. As cooling continues, Pb keeps on separating out while the solution becomes richer and richer in silver. When the eutectic temperature (303°) is reached, the second solid phase, *viz.*, silver begins to crystallise out. The system thus becomes non-variant at C. The two solids lead and silver will separate out together in a fixed ratio on further cooling, so that the composition of the solution remains constant as shown by point C. The temperature also remains constant. When the solution phase has completely disappeared as solid, the system consists only of a mixture of solid Ag and Pb. The system becomes univariant and further cooling will lower the temperature below solidus DD′. In area below DD′ two solid phases Pb and Ag will co-exist.

If a liquid solution of composition represented by a point x′ is cooled its temperature will fall without change in the composition along x′y′. At y′, solid Ag begins to crystallise out and the system becomes univariant. Further cooling will shift the equilibrium along y′C, when Ag goes on separating out and the solution becomes richer and richer in Pb. When the eutectic temperature is reached, Pb also begins to crystallise out. Further cooling will not change the temperature as well as the composition as long as three phases are present at C. When solution phase solidifies, only then the temperature falls below solidus DD′ within which two solid phases Pb and Ag co-exist.

Pattinson's process of desilverisation of lead : This process consists of increasing the relative percentage of silver in ores of lead called ***argentiferous lead ores*** containing very small amounts of silver, say 0.1%. Its relative content can be increased by taking a liquid solution of the ore and increasing it to a high temperature. It is then cooled and the temperature falls along xy. At y, solid lead begins to crystallise out which can be removed by ladels. Further cooling will shift the equilibrium along yC, making the solution richer and richer in Ag. Along yC, lead will go on separating out which is continuously removed. At C, the percentage of silver increases to 2.6% (starting from 0.1%).

• 9.9. DISTRIBUTION LAW

Nernst found that ***if a substance is present in two immiscible solvents in a system at equilibrium then the solute distributes itself between the two immiscible solvents in such a way that at constant temperature, the ratio of its concentrations in the two solvents is constant, whatever the total amount of the solute may be.***

If C_1 and C_2 represent the concentration of a solute in the two solvents, then

$$\frac{C_1}{C_2} = \text{constant} = K,$$

where K is known as ***distribution*** or ***partition coefficient***.

Nernst found that the ratio C_1/C_2 is constant only when the solute has the same molecular species in both the solvents. If a solute associates to form double molecules in one solvent and not in the other, the equilibrium cannot exist between double molecules present in one solvent and single molecules present in the other. The law is valid only if the ratio of concentrations of single molecules in the two solvents is taken into consideration. The distribution law as enunciated by Nernst does not hold good in cases where the solute undergoes dissociation or association in any of the solvents. For example, if a solute remains unaltered in one solvent and undergoes partial dissociation in another, the ratio of total concentrations in the two solvents will not be constant, but the ratio of concentration of undissociated molecules in the two solvents would be constant.

Thus, the ***distribution law*** in its proper form may be stated as,

'When a solute distributes itself between two immiscible solvents in contact with one another, there exists for similar molecular species at a given temperature, a constant ratio of concentration between the two solvents, irrespective of any other species which may be present.'

Thus, in the above equation, $C_1/C_2 = K$, the terms C_1 and C_2 refer to concentrations of similar molecular species in the two liquids at constant temperature.

As the solubility of a solute changes with temperature, and as the magnitude of the change in the two solvents may not be the same, the distribution coefficient (K) is found to vary with change in temperature.

[I] Limitations of Distribution Law

The important conditions to be satisfied for the application of the distribution law are as follows :

(i) Constant temperature : The temperature should be kept constant throughout the experiment.

(ii) Same molecular state : The molecular state of the solute should be the same in both the solvents. The law fails if the solute dissociates or associates in one of the solvents.

(iiii) Non-miscibility of solvents : The two solvents should be non-miscible or only slightly soluble in each other. The extent of mutual solubility of the solvents remains unchanged by addition of solute to them.

(iv) Dilute solutions : The concentration of the solute in the two solvents should be low. The law fails when the concentrations are high.

(v) Equilibrium concentrations : The concentrations of the solute should be noted after the equilibrium has been established.

[II] Applications of Distribution Law

Distribution law helps us in calculating the degree of dissociation or association of a solute. Distribution indicators also involve the principle of distribution law.

(1) The process of extraction : The most common and important application of distribution law is the ***solvent extraction*** of substances by solvents. Organic compounds are more soluble in organic solvents like CCl_4, C_6H_6 etc., than in water and so in the laboratory, this principle is used for the removal of a dissolved substance from aqueous solution by using organic solvents. Since organic compounds have their distribution ratio largely in favour of organic phase, most of the organic substances would pass into non-aqueous layer. Finally, this non-aqueous layer is removed and distilled to obtain the pure compound.

In solvent extraction, it is advisable to use a given volume of an extracting liquid in small lots in successive stages rather than in one single operation at a time. ***The greater the distribution ratio is in favour of the organic solvent, the greater will be the amount extracted in any one operation.***

Suppose a solute A is present in 100 c.c. water and that 100 c.c. of benzene is used for its extraction. Let the distribution coefficient of A between benzene and water be 4.

$$\therefore \qquad K = \frac{\text{Concentration of A in benzene}}{\text{Concentration of A in water}} = 4$$

(i) When the whole of benzene (100 c.c.) is used at a time for extraction, suppose x_1 g of solute pass into benzene layer and x_2 g is left in aqueous layer, so

$$\frac{x_1/100}{x_2/100} = 4;$$

$$i.e., \qquad \frac{x_1}{x_2} = 4 \quad \text{or} \quad \frac{x_1}{x_1 + x_2} = \frac{4}{5}$$

In other words, 100 c.c. benzene has separated 4/5 or 80% of the solute originally present.

(ii) Now let us use 100 c.c. benzene in two successive extractions, using 50 c.c. each time. Then in the first extraction,

$$\frac{x_1/50}{x_2/100} = 4;$$

$$\frac{x_1}{x_2} = 2 \quad i.e., \quad \frac{x_1}{x_1 + x_2} = \frac{2}{3}$$

In other words, in the first extraction (2/3)rd, *i.e.*, 66.6% is extracted. Hence, (1/3)rd or 33.4% of the original amount is still retained in aqueous medium. In the second extraction using 50 c.c.

of benzene, we shall further extract (2/3)rd, of (1/3)rd, *i.e.*, (2/9)th of the original amount. So, in both the extractions, using 100 c.c. benzene we can separate $(2/3 + 2/9) = 8/9$ or 88.9% of the original amount of the solute. Thus, a two stage extraction is more efficient. If we use four or five extractions, the operation will still be more efficient.

Derivation of general formula of Extraction : It is possible to derive a general expression for the amount remaining unextracted after a given number of operations. Let V c.c. of a solution containing W g of the substance be extracted with v c.c. of a solvent. Let W_1 g of substance remain unextracted in aqueous layer. Then

$$\text{Concentration of substance in solvent } = \frac{W - W_1}{v}$$

$$\text{Concentration of substance in water } = \frac{W_1}{V}$$

$$\therefore \qquad \text{Distribution coefficient,} \quad K = \frac{W_1/V}{\dfrac{W - W_1}{v}}$$

$$\text{or} \qquad W_1 = \frac{KV\,(W - W_1)}{v} = W \cdot \frac{KV}{KV + v}$$

If W_2 be the amount remaining unextracted at the end of the second extraction with v c.c. of the solvent, then

$$W_2 = W_1 \frac{KV}{KV + v} = W \frac{KV}{KV + v} \cdot \frac{KV}{KV + v} = W\left(\frac{KV}{KV + v}\right)^2$$

Similarly, after nth extraction, the amount remained unextracted will be given by,

$$W_n = W\left(\frac{KV}{KV + v}\right)^n \qquad \text{...(8)}$$

If the entire quantity of the extracting solvent is used in one lot, then unextracted amount (W') will be given by,

$$W' = W\left(\frac{KV}{KV + v}\right) \qquad \text{...(9)}$$

Since the quantity within the bracket is less than unity, (8) is smaller than (9) and W_n will be smaller, the greater the value of n. Hence the efficiency of extraction increases by increasing the number of extractions using only a small amount of the extracting solvent each time. It must be remembered that the value of K, the partition coefficient in equations (8) and (9) is that of the substance between the solvent (A) in which the substance is already dissolved and the solvent (B) which is used for extraction.

(2) Determination of association : When a solvent is associated in solvent 1 and exists as single molecules in solvent 2, the distribution law is written as,

$$\frac{\sqrt[n]{C_1}}{C_2} = K$$

where n = number of molecules which combine to form an associated molecule. Thus, knowing the values of C_1, C_2 and K, we can calculate the value of n.

(3) Determination of dissociation : Suppose a solute is dissociated in aqueous solvent 1 and exists as single molecule in solvent 2. If α is the degree of dissociation of the solute, the distribution law is written as :

$$\frac{C_1\,(1 - \alpha)}{C_2} = K$$

Thus, α can be calculated.

(4) Confirmatory test for bromide and iodide : The salt solution is treated with chlorine water, when a small quantity of Br_2 or I_2 is liberated. This solution is then shaken with CCl_4 or $CHCl_3$. On standing, the CCl_4 or $CHCl_3$ layer forms the lower layer. The free Br_2 or I_2 being more soluble in CCl_4 or $CHCl_3$ concentrates into the lower layer, making it brown for bromine and violet for iodine.

(5) Determination of solubility : If the concentration of a solute in solvents 1 and 2 be C_1 and C_2, then distribution coefficient (K) is given by,

$$K = C_1/C_2.$$

As concentration and solubility (S) are proportional to each other, we can write,

$$K = S_1/S_2.$$

If solubility (S_1) of a solid in one solvent is known then solubility (S_2) in other solvent can be calculated.

(6) Distribution indicators : In iodine titrations, the end point is indicated by adding starch solution which turns blue. A greater sensitivity is obtained by adding a distribution indicator. A few drops of an immiscible organic solvent say CCl_4 is added to the solution. The bulk of any iodine present passes into CCl_4 layer making its colour more intense.

Besides, distribution law is applicable in deducing the formula of a complex ion, in desilverisation of lead, partition chromatography etc.

[III] Distribution Law in Case of Association of the Solute in One of the Solvents

Let A represents the normal formula of the solute. It does not associate in solvent I, but associates in solvent II to give molecules of the type A_n (figure 5). Let C_1 be the concentration of solute A in solvent I and C_2 be its total concentration in solvent II.

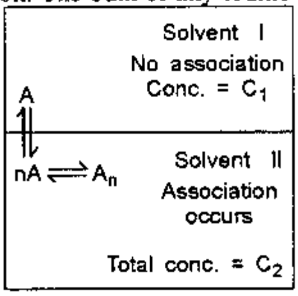


Fig. 5. Association of solute

In solvent II, the associated molecules exist in equilibrium with single molecules, *viz.*,

$$A_n \rightleftharpoons nA$$

According to the law of mass action,

$$K = \frac{[A]^n}{[A_n]}$$

or $$[A] = \{K \cdot [A_n]\}^{1/n} = \text{constant} \times [A_n]^{1/n}. \quad \ldots(1)$$

If the solute exists largely as associated molecules in solvent II, the concentration of the associated molecules (A_n) may be taken to be equal to C_2, *i.e.*,

$$[A_n] = C_2$$

Therefore, from equation (1), we get

$$[A] = \text{constant} \times (C_2)^{1/n} = kC_2^{1/n}.$$

Applying the distribution law to similar molecular species, we have,

$$K = \frac{\text{Concentration of A in solvent I}}{\text{Concentration of A in solvent II}}$$

or $$K = \frac{C_1}{k\,(C_2)^{1/2}}$$

or $$\frac{C_1}{(C_2)^{1/2}} = K \,.\, k = \text{constant}.$$

Such a case is observed in the distribution of benzoic acid between water and benzene.

NUMERICAL PROBLEMS

Ex. 1. *The following data shows the distribution of phenol between water and chloroform :*

Concentration (c_1) in water :	*0.094*	*0.163*	*0.254*	*0.436*
Concentration (c_2) in chloroform :	*0.254*	*0.761*	*1.85*	*5.43*

Calculate the partition coefficient between water and chloroform. What conclusions can be drawn from these results concerning the molecular condition of phenol in chloroform layer?

Solution. Phenol in chloroform may be present either as normal molecules or in the form of associated molecules. In the former case, c_1/c_2 should be constant, whereas in the latter $c_1/c_2^{1/n}$ should be constant, where n is the number of molecules of phenol associate to give a single associated molecule.

The value of c_1/c_2 in the four cases are given as follows :

(i) $\frac{c_1}{c_2} = \frac{0.094}{0.254} = 0.3701,$ (ii) $\frac{c_1}{c_2} = \frac{0.163}{0.761} = 0.2142,$

(iii) $\frac{c_1}{c_2} = \frac{0.254}{1.85} = 0.1373,$ (iv) $\frac{c_1}{c_2} = \frac{0.436}{5.43} = 0.0833.$

Since values of c_1/c_2 are not constant, so phenol does not exist as single molecules in chloroform.

Now, the values of $\frac{c_1}{\sqrt{c_2}}$ are given as follows :

(i) $\frac{c_1}{\sqrt{c_2}}=\frac{0.094}{\sqrt{(0.254)}}=0.1865,$ (ii) $\frac{c_1}{\sqrt{c_2}}=\frac{0.163}{\sqrt{(0.761)}}=0.1868,$

(iii) $\frac{c_1}{\sqrt{c_2}}=\frac{0.254}{\sqrt{(1.85)}}=0.1867,$ (iv) $\frac{c_1}{\sqrt{c_2}}=\frac{0.436}{\sqrt{(5.43)}}=0.1870,$

Since $c_1/\sqrt{c_2}$ values are constant, therefore, phenol exists as double molecules in chloroform.

Ex. 2. *Calculate how much succinic acid would be extracted from 100 c.c. of water containing 5 g of succinic acid if extracted with 50 c.c. of ether. The partition coefficient of succinic acid between water and ether is 5.5 Succinic acid has normal molecular weight in both the solvents.*

Solution. Let x g of succinic acid passes over into 50 c.c. of ether, then the amount left unextracted in 100 c.c.water will be $(5-x)$ g.

$\therefore$ Concentration of solute dissolved in ether = x g per 50 c.c.

Concentration of solute left in water = $(5-x)$ g per 100 c.c.

From the distribution law, $K=\frac{C_1}{C_2}$

or $5.5=\frac{(5-x)/100}{x/50}$

or $x=0.4166$ g.

Amount of succinic acid extracted = **0.4166 g**

Ex. 3. *At 20°C, SO_2 was permitted to distribute between 200 c.c. of chloroform and 75 c.c. water. At equilibrium, the chloroform layer contained 0.14 mole of SO_2 and water layer 0.05 mole. Calculate the distribution coefficient of SO_2 between water and chloroform.*

Solution. $C_W=\frac{0.05}{75}$ moles per c.c.

$$C_{CHCl_3}=\frac{0.14}{200}\text{ moles per c.c.}$$

$$K=\frac{C_W}{C_{CHCl_3}}=\frac{0.05\times 200}{75\times 0.14}=\mathbf{0.953}$$

Ex. 4. *If the distribution coefficient of benzoic acid between water and C_6H_6 is 0.304 at 20°C, calculate the number of moles of benzoic acid which may be extracted from 100 c.c. of 0.02 molar aqueous solution by 10 c.c. of C_6H_6.*

Solution. Let x moles of acid remain unextracted. The concentration of the acid in benzene will be

$$\frac{0.02-x}{10}\text{ per c.c.}$$

Also the concentration of the acid in the original aqueous solution is $x/100$.

$\therefore$ $K=\frac{x/100}{(0.02-x)/10}$

or $0.304=\frac{x}{100}\times\frac{10}{(0.02-x)}=\frac{x}{0.02-10x}$

$\therefore$ $x=0.015$ mole

$\therefore$ Number of moles of acid extracted

$=(0.02-0.015)$

$=\mathbf{0.005}$

Ex. 5. *The solubility of a substance is twice as great in ether as in water. Compare the quantities extracted from 100 c.c. of aqueous solution by using :*

(i) 100 c.c. ether in single operation.

(ii) 50 c.c ether in successive operations.

Solution. **(i) By using 100 c.c. ether at a time.**

Let 1 g of substance be present in 100 c.c. aqueous layer and let by using 100 c.c. ether at a time, x g of it passes over into ethereal layer.

Then from distribution law,

$$K=\frac{C_1}{C_2}$$

or $$2 = \frac{x}{1-x} \qquad (\because K = 2 \text{ given})$$

$\therefore$ $$x = \mathbf{0.66\ g}$$

(ii) By using 50 c.c. ether in two instalments.

In first instalment : Let by using 50 c.c. ether x_1 g of substance passes over from 100 c.c. aqueous layer.

Concentration of substance dissolved in ether

$$= x_1 \text{ g per 50 c.c.}$$

Concentration of substance left in aqueous layer

$$= (1 - x_1) \text{ g per 100 c.c.}$$

Hence from distribution law,

$$K = \frac{C_1}{C_2}$$

$$2 = \frac{\frac{x_1}{50}}{\frac{(1-x_1)}{100}}$$

or $$x_1 = \mathbf{0.5\ g}$$

In second instalment : The amount of substance now left in aqueous layer is 1 – 0.5 g, *i.e.*, 0.5 g. Consider by using next 50 c.c., x_2 g of substance passes over from 100 c.c. aqueous layer.

Then, concentration of substance dissolved in ether

$$= x_2 \text{ g per 50 c.c.}$$

Concentration of substance left in aqueous layer

$$= (0.5 - x_2) \text{ g per 100 c.c.}$$

Hence, from distribution law, $K = C_1/C_2$

or $$2 = \frac{\frac{x_2}{50}}{\frac{(0.5-x_2)}{100}}$$

or $$x_2 = \mathbf{0.25\ g}$$

So, total amount of substance extracted in two instalments

$$= 0.5 + 0.25 = \mathbf{0.75\ g}$$

Thus, it is clear that it is more advantageous to use 50 c.c. ether in two instalments (as it extracts 0.75 g) rather than 100 c.c. in one instalment (as it extracts only 0.66 g).

Ex. 6. *1 g of I_2 is in 50 ml of CS_2. 1000 ml of water is added into it. Calculate the amount of I_2 extracted into water. Partition coefficient of I_2 in CS_2 and H_2O is 200.*

Solution. Suppose x g of I_2 is extracted into water. Then, amount of I_2 left behind in 50 ml of CS_2 will be $(1 - x)$ g.

$\therefore$ $$K = \frac{\text{Conc. of } I_2 \text{ in } CS_2}{\text{Conc. of } I_2 \text{ in } H_2O} = \frac{\frac{(1-x)}{50}}{\frac{x}{1000}}$$

$\therefore$ $$200 = \frac{\frac{(1-x)}{50}}{\frac{x}{1000}} \quad \text{or} \quad x = 0.0909 \text{ g}$$

So, amount of I_2 extracted in water = **0.0909 g**

Ex. 7. *At 25°C, the distribution coefficient of iodine between CCl_4 and water is 85. If at 25°C, the solubility of iodine in water is 0.33 g/litre, determine the solubility of iodine in CCl_4*

Solution. $$K = \frac{\text{Conc. of } I_2 \text{ in } CCl_4}{\text{Conc. of } I_2 \text{ in } H_2O} = \frac{\text{Solubility of } I_2 \text{ in } CCl_4\ (S_1)}{\text{Solubility of } I_2 \text{ In } H_2O\ (S_2)}$$

or $$85 = \frac{S_1}{0.33 \text{ g/litre}}$$

or $$S_1 = 85 \times 0.33 \text{ g/litre}$$

$$= \mathbf{28.05 \text{ g/litre}}$$

• 9.10. HENRY'S LAW

Henry's law states that *'at a constant temperature, the solubility of a gas in a liquid is proportional to the pressure of the gas above it.* Mathematically, Henry's law can be expressed as

$$C = kP$$

where C is the solubility (or concentration), k is a constant and P is the pressure of the gas. The constant k is called **Henry's constant.**

Explanation : Henry's law is, in fact, a form of distribution law. If a vessel containing a liquid and a gas is shaken then at equilibrium the gas can be regarded as distributed between the liquid (phase A) and the space above (phase B).

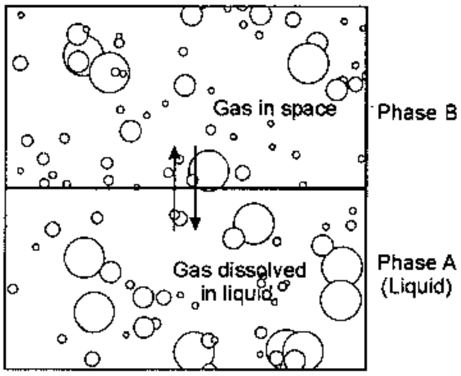


Fig. 6

The influence of partial pressure on solubility is used in making carbonated beverages like champagne, beer and several soft drinks. So called *soda water* is bottled under carbon dioxide pressure of about 4 atm. When the bottle is opened to the air, the partial pressure of CO_2 above the solution is decreased (to about 0.001 atm.) and CO_2 bubbles out.

Let C_1 be the concentration of the gas in phase B and C be the concentration of the gas in phase A. Applying the distribution law,

$$\frac{C}{C_1} = K_D \quad \text{(a constant)}$$

We know that the molar concentration of gas is proportional to its pressure, P. Therfore,

$$\frac{C}{P} = k \text{ (a constant)}$$

or $$C = kP$$

This is Henry's law equation.

Like distribution law, Henry's law holds good for dilute solutions of gases, which do not react with the solvent. If a mixture of gases is in contact with a liquid, the partial pressure of an individual gas, not their total pressure, determines the mass of each gas dissolving. In such a case, *the solubility of each gas is proportional to its partial pressure.*

Ex. 1. *The solubility of pure oxygen in water at 20°C and 1.00 atm pressure is* 1.38×10^{-3} *mol* L^{-1}. *Calculate the concentration of oxygen (mol* L^{-1}*) at 20°C and a partial pressure of* 0.21 *atm.*

Solution. Henry's constant, $$k = \frac{\text{Conc. of } O_2}{\text{Pressure of } O_2}$$

or $$k = \frac{1.38 \times 10^{-3} \text{ mol L}^{-1}}{1.00 \text{ atm.}}$$

$$= 1.38 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1}$$

Calculation of concentration of O_2 :

$$C = k \times P$$

$$\text{Conc. of } O_2 = (1.38 \times 10^{-3} \text{ mol L}^{-1} \text{ atm}^{-1}) \times (0.21 \text{ atm.})$$

$$= \mathbf{2.9 \times 10^{-4} \text{ mol L}^{-1}}.$$

• SUMMARY

- A phase is defined as any homogeneous part of a system having all physical and chemical properties the same throughout.

- A component is defined as the least number of independent chemical constituents in terms of which the composition of every phase can be expressed by means of a chemical equation.
- The degree of freedom is defined as the least number of variable factors (concentration, pressure, temperature) which must be specified so that the remaining variables are fixed automatically and the system is completely defined.
- According to phase rule, if any heterogeneous system in equilibrium is not affected by electrical or magnetic forces or by gravity, the sum of degree of freedom (F) and number of phases (P) is given by the number of component (C) plus 2. Mathematically,

$$F + P = C + 2$$

or

$$F = C - P + 2$$

- Water system has three phases, viz., solid (ice), liquid (water) and gas (vapour).
- The triple point has $F = 0$. For water system, the values of temperature and pressure at triple point are 0.0076° and 4.58 atm, respectively.
- In a two component system, like lead-silver, it is necessary to take into account the two variables *viz.*, temperature and concentration, the pressure is assumed to be constant. Such a solid/liquid system with the gas phase absent is called a condensed system.
- If a solute X distributes itself between two immiscible solvents A and B at constant temperature, and X is in the same molecular condition in both the solvents, then

$$\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = K_D$$

where K_D is known as distribution coefficient or partition coefficient.

- **Henry's law :** At constant temperature, the solubility of a gas in a liquid is proportional to the pressure of the gas above it. Mathematically,

$$C = kP$$

where C = concentration or solubility of the gas and P = pressure of the gas. The constant k is known as Henry's constant.

• STUDENT ACTIVITY

1. Define phase with two examples.

2. State phase rule.

3. State and explain one component system.

4. Write a note on triple point.

5. Define Henry's law.

6. Write three applications of distribution law.

• TEST YOURSELF

1. Define phase with suitable examples.
2. State and explain component.
3. State and explain degree of freedom.
4. State the phase rule.
5. Can four phases co-exist in equilibrium at any time in a one component system ?
6. Apply phase rule to water system with a neat labelled diagram.
7. Write a note on triple point.
8. What is a condensed system ?
9. Apply phase rule to lead-silver system with a labelled diagram.
10. Explain Pattinson's process for the desilverisation of lead ores on the basis of Pb-Ag system.
11. Dtermine the number of phases and components in the following systems :
   (i) Water in a beaker at room tmperature.
   (ii) A solution of ethanol with water which is in equilibrium with vapours.
   (iii) $(NH_4Cl\ (s) \rightleftharpoons NH_4Cl\ (vap.) \rightleftharpoons NH_3\ (g) + HCl\ (g)$
   (iv) HCl gas is passed from outside in equilibrium (iii).
12. What will be the degree of freedom in the following closed systems ?
   (i) Liquid water and water vapours.
   (ii) Liquid water and water vapours at 25°C.
   (iii) Dilute solution of NaCl filled partially in a closed vessel.
   (iv) Saturated solution of NaCl filled partially in a closed vessel.
   (v) A gaseous mixture of N_2, O_2 and H_2.
13. Determine the number of phases, components and degree of freedom of the following systems:
   (i) Sodium chloride and water
   (ii) A mixture of nitrogen and hydrogen gases in a vessel.
   (iii) $2H_2S(g) \rightleftharpoons 2H_2O(g) + S_2(g)$
   (iv) $H_2O(s) \rightleftharpoons H_2O(g)$
   (v) $Na_2SO_4 . 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(l)$
   (vi) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
14. Derive distribution law when the solute associates in one of the solvents.
15. Define eutectic point.
16. For a one component system, the triple point is an invariant point. Discuss.
17. State and explain Henry's law.
18. State and explain distribution law.
19. Mention the limitations of distribution law.
20. Describe the applications of distribution law.
21. State distribution law and give the conditions under which the law is applicable.
22. *In a one component system, the maximum number of phases which can exist in equilibrium* at a point is :
   (i) 0 (ii) 1 (iii) 2 (iv) 3
23. In water system, the triple point has the values of :
   (i) 0°C, 1 atm (ii) 0°C, 4.58 mm
   (iii) 0.0075°C, 1 atm (iv) 0.0075°C, 4.58 mm

24. At eutectic point, a system has :
(i) Only two phases (ii) Highest melting point
(iii) Minimum melting point (iv) Uncertain composition

25. Henry's law is not applicable to :
(i) H_2 (ii) O_2 (iii) CO_2 (iv) He

26. In lead-silver system, the percentage of silver at the eutectic point is :
(i) 0% (ii) 2.6% (iii) 97.4% (iv) 100%

27. The dissociation of $CaCO_3$ is a :
(i) One component system (ii) Two component system
(iii) Three component system (iv) Two phase system

28. A mathematically constant ratio exists between concentrations of similar molecular species in any two phases in contact with each other at a constant temperature. This law is known as :
(i) Boyle's law (ii) Charles law (iii) Distribution law (iv) Dilution law

29. Which one of the statements is false for distribution law ?
(i) Temperature must remain constant
(ii) The two solvents must be mutually immiscible
(iii) The concentration of the solute in two solvents must be kept very high
(iv) The concentration of the solute in two solvents must be very low

30. When a solute is shaken with water and a solvent X in which it forms a dimer, the concentrations were found to be C_w and C_s in water and solvent, respectively. Which one of the following expression will be correct between water and X ?
(i) $\frac{C_s}{C_w}$ (ii) $\frac{C_w}{\sqrt{C_s}}$ (iii) $\frac{C_w}{C_s}$ (iv) $\frac{\sqrt{C_s}}{C_w}$

31. Distribution law cannot be applied for the system in which I_2 is distributed between :
(i) H_2O and CS_2 (ii) H_2O and CCl_4
(iii) H_2O and ether (iv) H_2O and alcohol

32. In a pair of immiscible liquids a common solute dissolves in both and equilibrium is reached, then the concentration of the solute in the upper layer is :
(i) In fixed ratio with that in the lower layer
(ii) Same as in lower layer
(iii) Less than in the lower layer (iv) None of these

33. A 95°C, an aqueous solution of iodine containing 0.0156 lit^{-1} is in equilibrium with a CCl_4 solution containing 4.412 g lit^{-1}. If the solubility of I_2 in water at 90°C is 0.34g lit^{-1}, then its solubility in CCl_4 is :
(i) $\frac{4.412 \times 0.0516}{0.34}$ (ii) $\frac{0.0516 \times 0.34}{4.412}$
(iii) $\frac{4.412 \times 0.34}{0.0516}$ (iv) $\frac{0.0516}{4.412 \times 0.34}$

34. The solubility of iodine in water is 0.8 g/litre. If the partition coefficient of iodine between water and carbon tetrachloride is 82, the solubility of iodine in carbon tetrachloride is :
(i) 102.5 g/litre (ii) 65.6 g/litre (iii) 0.009 g/litre (iv) 81.2 g/litre

35. The condition under which Nernst distribution law will not hold true is :
(i) Temperature is constant
(ii) Molecular state of the solute is same in both solvents
(iii) The solute does not cause any change in the mutual solubility of the two solvents
(iv) None of them

36. You are given 100 mL of CCl_4 to extract iodine from 200 mL of its aqueous solution for extracting maximum amount of iodine. Which one of the following processes would you use?
(i) All 100 mL of CCl_4 (ii) 50 mL of CCl_4 twice
(iii) 10 mL of CCl_4 ten times (iv) 25 mL of CCl_4 four times

37. **Fill in the Blanks :**
(i) Phase rule was given by ....
(ii) Dissociation of NH_4Cl in a closed vessel is a .... component system.
(iii) Phase rule equation is given by ....
(iv) In a two component system, the maximum degree of freedom is ....
(v) In a system of H_2, O_2, N_2 gases, the number of phases will be ....
(vi) The eutectic temperature of Pb-Ag system is ....
(vii) Benzoic acid .... as double molecules in benzene.

(viii) The temperature during the distribution law experiment should be ....
(ix) Distribution law was given by ....
(x) When iodine is distributed between water and CCl_4, the solute exists in the .... molecular state in both the liquids.

ANSWERS

11. (i) Components = 1; Phases = 2 (ii) Components = 1; Phases = 2
(iii) Components = 1; Phases = 2 (iv) Components = 2; Phases = 2
12. (i) One ($F = 1 - 2 + 2 = 1$) (ii) One ($F - 1 - 2 + 2 = 1$)
(iii) Two ($F = 2 - 2 + 2 = 2$) (iv) Four ($F = 3 - 1 + 2 = 4$)
13. (i) **Sodium chloride water system**
Phases = 2; Components = 2 (NaCl and H_2O); Degree of freedom = 2
(ii) **System of N_2 and H_2 gases**
Number of phases = 1; Components = 2 (H_2, N_2); Degree of freedom = 3.
(iii) Phases = 1, Componnt = 1, Degree of freedom = 2
(iv) Phases = 2, Component = 1, Degree of freedom = 1
(v) Phases = 3, Component = 2, Degree of freedom = 1
(vi) Phases = 3, Components = 2, Degree of freedom = 1.
22. (iv) **23.** (iv) **24.** (iii) **25.** (iii) **26.** (ii) **27.** (ii) **28.** (iii) **29.** (iii) **30.** (ii) **31.** (iv)
32. (i) **33.** (iii) **34.** (iii) **35.** (iv) **36.** (iii)
37. (i) Gibbs (ii) one (iii) $F = C - P + 2$ (iv) three (v) one (vi) 303°C
(vii) associates (viii) constant (ix) Nernst (x) same.

❑❑❑

UNIT

10

ELECTROCHEMISTRY-I

LEARNING OBJECTIVES

- Electrical Conductance
- Migration of Ions
- Transport Number
- Kohlrausch's Law
- Applications of Conductivity Measurements
  - ☐ Summary
  - ☐ Student Activity
  - ☐ Test Yourself

• 10.1. ELECTRICAL CONDUCTANCE

[I] Specific Conductivity

The resistance (R) offered by a metallic conductor to the passage of electric current is proportional to its length (l) and inversely proportional to its area of cross-section (A), *i.e.*,

$$R \propto \frac{l}{A} \quad \text{or} \quad R = \rho \cdot \frac{l}{A}$$

where ρ is a constant known as *specific resistance* of the substance. If $l = 1$ cm and $A = 1\ \text{cm}^2$ then $\rho = R$ ohm.

So, specific resistance is defined as the *resistance in ohms of a conductor 1 cm in length and 1 cm^2 cross section or it is the resistance of 1 cm^3 of the conductor.* In solutions, we use the term conductivity which shows the ease with which the current flows through a conductor.

The reciprocal of specific resistance is known as ***specific conductivity***, (κ). *i.e.*, $\kappa = \frac{1}{\rho}$ · So, specific conductivity is defined as the *conductivity of* 1 *cm^3 of a solution placed between electrodes.*

The unit of specific conductivity is ohm^{-1} cm^{-1} S cm^{-1} (where S = Siemen).

[II] Equivalent Conductivity

Equivalent conductivity is defined as the *conductivity of a solution containing 1 g equivalent of an electrolyte when placed between two large electrodes placed 1 cm apart.*

It is represented by λ or Λ. If 1 g equivalent of an electrolyte is dissolved in V c.c. of solution, its equivalent conductivity is written as λ_v or Λ_c. Its unit is ohm^{-1} cm^2 equivalent^{-1}.

[III] Molecular Conductivity

Molecular conductivity is defined as the *conductivity of a solution containing 1 g mole of an electrolyte when placed between two large electrodes placed 1 cm apart.*

It is represented by μ. If 1 g mole of an electrolyte is dissolved in V c.c. of solution, its molecular conductivity is written as μ_v. Its unit is ohm^{-1} cm^2 mole^{-1}.

[IV] Relation between Specific Conductivity, Equivalent Conductivity and Molecular Conductivity

Suppose 1 c.c. of a solution of an electrolyte is placed between two large electrodes 1 cm apart. The cross-sectional area of solution will thus be 1 cm^2. The conductivity of the solution will thus be equal to specific conductivity, because we have 1 cm^3 of the solution. Suppose 1 c.c. of the solution contains 1 gram equivalent of the electrolyte. According to definition, the conductivity of the solution will be equal to its equivalent conductivity also.

$\therefore$ Conductivity = Specific conductivity = Equivalent conductivity.

Suppose the solution is now diluted to 100 c.c. We will now have 100 cm cubes of the solution. The conductivity of the solution will now be 100 times of its specific conductivity. But as the solution contains only 1 gram equivalent of the electrolyte, the total conductivity of the solution will remain equal to equivalent conductivity.

∴ Equivalent conductivity = 100 × Specific conductivity.

In general, if the solution is diluted to V c.c., then

Equivalent conductivity = Specific conductivity × V

Similarly, if 1 g mole of an electrolyte is dissolved in V c.c. of solution, then

Molecular conductivity = Specific conductivity × V.

[V] Effect of Dilution on Conductivities

The conductivity of a solution depends on the number of ions present in it. On dilution, the degree of dissociation of an electrolyte increases, whereby the number of ions increases. So, the conductivity increases with dilution. The decrease in interionic attractive forces and viscosity with dilution also helps in increasing the conductivity.

Specific conductivity of a solution decreases with dilution. This is due to the fact that the number of ions per c.c. of the solution decreases with dilution. The increase in number of ions is much less than the increase in volume of the solution. As specific conductivity is the conductivity of 1 cm^3 of the solution *i.e.*, it depends on the number of ions per cm^3 of the solution. Therefore, the specific conductivity decreases with dilution.

The equivalent conductivity and molecular conductivity increase with dilution. The decrease in specific conductivity with dilution is more than compensated by the increase in volume of the solution. The equivalent conductivity is the product of specific conductivity and dilution, therefore, the equivalent conductivity increases with dilution. Similarly, molecular conductivity also increases with dilution.

When the electrolyte is completely dissociated at a certain dilution, the equivalent conductivity attains a maximum value. Further dilution will not make any change in equivalent conductivity of the solution. This dilution is known as **infinite dilution** and the maximum value of equivalent *conductivity of the solution is known as* ***equivalent conductivity at infinite dilution.*** It is represented by λ_∞.

[VI] Measurement of Equivalent Conductivity

The conductivity of a solution placed between two electrodes can be expressed in terms of its resistance as follows :

$$R = \rho \times \frac{l}{A} \qquad \ldots (1)$$

(where, ρ = specific resistance, l = distance between the two electrodes and A = area of cross section of electrodes).

Equation (1) can also be expressed as

$$\frac{1}{\text{Observed conductivity}} = \frac{1}{\text{Specific conductivity}} \times \frac{l}{A}$$

or $$\text{Specific conductivity} = \text{Observed conductivity} \times \frac{l}{A}$$

For a given cell, l and A are constants and so l/A is constant, known as ***cell constant*** (x). First of all, the specific conductivity of the solution is measured as follows :

(i) Determination of observed conductivity of the solution

(ii) Determination of cell constant.

(1) Determination of observed conductivity of the solution : The observed conductivity of a solution is measured by measuring its resistance by using Wheatstone's bridge. If direct current is passed through the solution, the electrolysis occurs. This produces the following two difficulties:

(a) Polarisation occurs, *i.e.*, products of electrolysis deposit at the electrodes and develop a back E.M.F.

(b) Concentration of the solution changes.

The above difficulties can be removed by using alternating current (A.C.). The polarisation produced due to the passage of current in one direction is counter-balanced by the polarisation produced due to the passage of current in the other direction. Thus, concentration of the solution also remains unchanged. In laboratory, A.C. is produced by induction coil. By using A.C., galvanometer cannot be used for determining the null point. It is then replaced by a head phone, in which null point is determined by the point of minimum sound.

Method : The solution whose conductivity is to be measured is taken in a cell, known as **conductivity cell** . It is made of pyrex glass and is fitted with freshly platinised platinum plates sealed into glass tubes. These constitute electrodes. The electrodes are fixed in an ebonite cover so that the distance between the electrodes may not change during the experiment. The circuit is completed by inserting copper wires in mercury taken in glass tubes.

A schematic diagram of the apparatus is shown in figure (1). AB is a uniform wire. The conductivity cell, resistance box R, headphone, induction coil and jockey are connected as shown in figure (1).

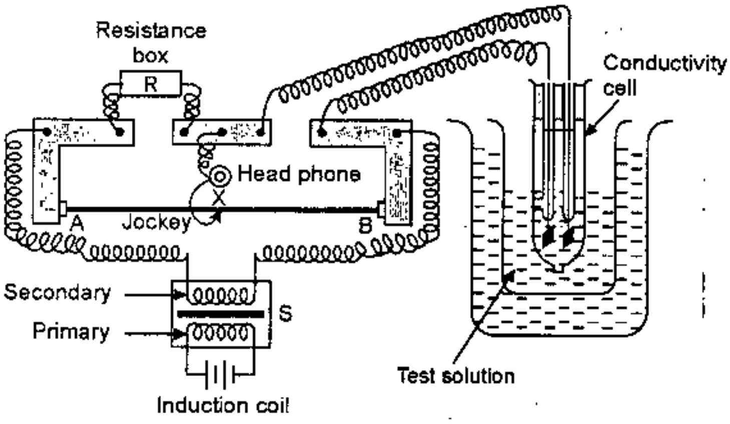


Fig. 1. Apparatus for measuring conductance

By moving the jockey over the wire AB and after taking out some resistance from the resistance box, a point X is found on the wire AB when the sound in the head phone is minimum. According to Wheatstone's principle,

$$\frac{\text{Resistance of solution}}{\text{Resistance, } R} = \frac{\text{Resistance of BX}}{\text{Resistance of AX}} = \frac{\text{Length BX}}{\text{Length AX}}$$

$$\therefore \text{ Resistance of solution } = \frac{\text{BX}}{\text{AX}} \times \text{Resistance, } R$$

$$\therefore \text{ Observed conductivity of solution} = \frac{\text{AX}}{\text{BX}} \times \frac{1}{\text{Resistance, } R}$$

The observed conductivity of the solution will be equal to its specific conductivity, if the distance between the electrodes is 1 cm and area of cross section is 1 cm^2. But it is not always possible. So, observed conductivity of the solution will not be equal to its specific conductivity. Thus, observed conductivity of the solution has to be multiplied by the cell constant to obtain its specific conductivity.

(2) Determination of cell constant : The ratio of the distance (l cm) between the two electrodes and the cross-sectional area (A) of the electrodes for a particular cell is constant and is known as ***cell constant.*** As already discussed,

$$\text{Observed conducitivity} \times \text{Cell constant} = \text{Specific conductivity}$$

$$\text{or} \qquad \text{Cell constant} = \frac{\text{Specific conductivity}}{\text{Observed conductivity}}$$

For determining the cell constant, N/50 KCl solution is taken in the conductivity cell and its observed conductivity is determined as usual. The specific conductivity of N/50 KCl solution at 25°C is 0.002765 $\text{ohm}^{-1}\ \text{cm}^{-1}$.

$$\therefore \qquad \text{Cell constant} = \frac{0.002765 \text{ ohm}^{-1} \text{ cm}^{-1}}{\text{Observed conductivity of N/50 KCl}}$$

(3) Determination of equivalent conductivity : The equivalent conductivity of the solution is calculated from the following relation :

$$\lambda_V = k_V \times V$$

where V = volume in c.c. of the solution containing 1 g equivalent of an electrolyte.

Ex. 1. *At 25°C, the specific conductivity of N/10 KCl solution is 0.002780 ohm^{-1}. The resistance of this solution placed in the cell is 500 ohms. Calculate the cell constant.*

Solution. $\text{Cell constant} = \dfrac{\text{Specific conductivity}}{\text{Observed conductivity}}$

$$= \frac{0.002780}{1/500} = 0.002780 \times 500 = \mathbf{1.39}.$$

Ex. 2. *When a solution whose specific conductivity was 1.342×10^{-2} ohm^{-1} cm^{-1} was placed in a cell, its resistance was found to be 170.5 ohm. The area of cross-section of the electrode was 1.86 sq cm. Calculate the distance between the electrodes and cell constant.*

Solution. $\text{Cell constant} = \dfrac{\text{Specific conductivity}}{\text{Observed conductivity}}$

$$= \frac{1.342 \times 10^{-2}}{1/170.5} = 1.342 \times 10^{-2} \times 170.5$$

$$= \mathbf{2.288}$$

$$\text{Cell constant} = \frac{\text{Distance between the electrodes } (l)}{\text{Area of cross section of electrodes } (A)}$$

or $$2.288 = \frac{l}{1.86}$$

or $$l = 2.288 \times 1.86 = \mathbf{4.255\ cm}$$

Ex. 3. *0.5 N solution of salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq cm in area was found to offer a resistance of 25 ohms. Calculate the equivalent conductivity of the solution.*

Solution. $\because$ Cell constant $= \frac{l}{A} = \frac{2.1}{4.2} = 0.5$

$\because$ Specific conductivity = Observed conductivity × Cell constant

$$= \frac{1}{25} = 0.5 = 0.02$$

$\therefore$ Equivalent conductivity = Specific conductivity × Volume in c.c. containing 1 g eq. of an electrolyte

$$= 0.02 \times 2000 = \mathbf{40\ ohm^{-1}\ cm^2\ eq^{-1}}$$

$(\because$ For $0.5N$, $V = 2 \times 1000$ c.c.$)$

• 10.2. MIGRATION OF IONS

A U-tube (Fig. 2a) is partly filled (3/4) with a dilute solution of agar-agar containing KCl and a small amount of phenolphthalein. Potassium chloride is added to increase the conductivity of the solution. A drop of dilute HCl solution is added in the left limb, while a drop of dilute NaOH solution is added in the right limb. The agar-agar solution becomes colourless in the left limb and pink in the right limb. The solution of agar-agar is then allowed to set to form a gel. A small amount of powdered charcoal is added on the surface of the solution in each limb to mark the position of the boundary.

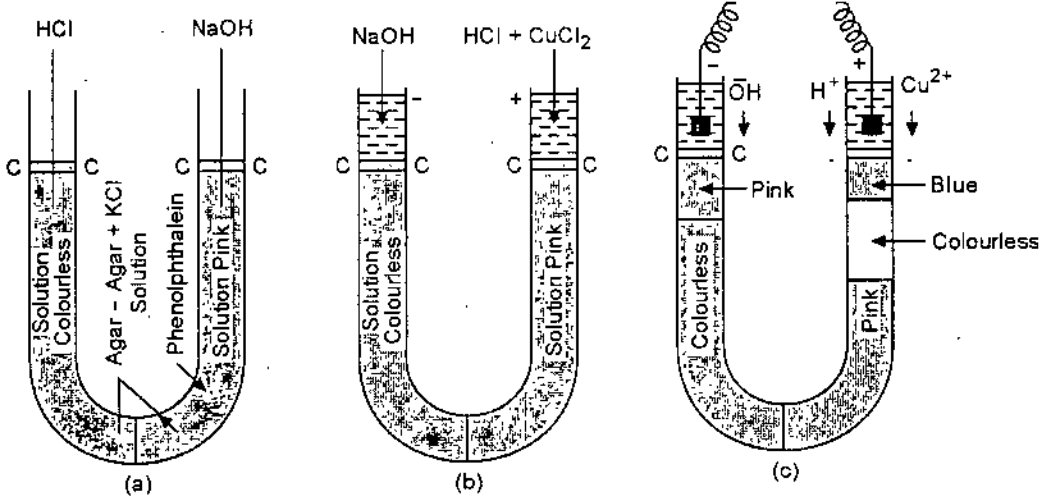


Fig. 2. Apparatus for depecting migration of ions

A solution of NaOH is carefully added in the left limb, while a solution of HCl and cupric chloride is added in the right limb (Fig. 2b). Metallic electrodes are dipped in each limb, cathode in the left limb, while anode in the right limb. On passing an electric current, H^+ ions and Cu^{2+} ions move towards the left limb, while OH^- ions move towards the right limb. Due to the migration of H^+ ions, the pink colour in the right limb disappears, while due to the migration of Cu^{2+} ions, a blue colour is formed. In the left limb, the pink colour appears again due to the migration of OH^- ions.

The above experiment shows that :

(i) Ions do not move with the same speed.

(ii) The speeds of H^+, Cu^{2+} and OH^- ions are in the following order :

$$H^+ > OH^- > Cu^{2+}$$

Discharge of Ions in Equivalent Amounts

Suppose an electrolytic cell contains an anode A and cathode B. This cell is divided into three chambers by putting imaginary partitions at C and D. Before electrolysis, cell contains 14 pairs, out of which 5 pairs each are in anodic and cathodic chambers and 4 pairs in the central chamber (Fig. 3-I). On passing electric current, suppose :

(i) Only cations move (Fig. 3-II). On passing electric current let 3 cations move towards the cathode. So, there will be three unpaired cations in the cathodic chamber. There will also be three unpaired anions left in the anodic chamber. As unpaired ions get discharged at the respective electrodes, so three cations and three anions, *i.e., the same number* are discharged at cathode and anode, respectively.

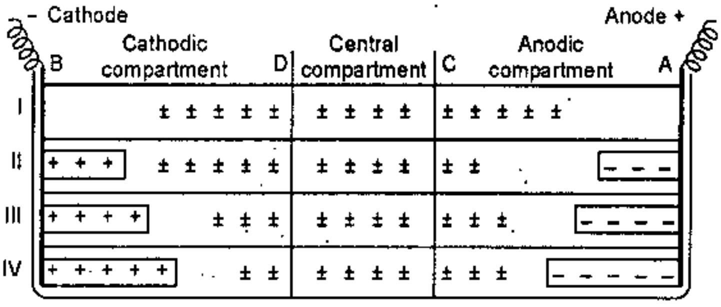


Fig. 3

(ii) Both cations and anions move with the same speed (Fig. 3-III). On passing electric current, let 2 cations move towards the cathode and during the same time 2 anions move towards the anode. Thus, there will be 4 unpaired cations and 4 unpaired anions in the cathodic and anodic chambers, respectively. So, four cations and four anions, *i.e., the same number* will be discharged at the respective electrodes.

(iii) Both cations and anions move with different speeds (Fig. 3-IV). On passing electric current, let 2 cations move towards the cathode and during the same time 3 anions move towards the anode. In this case, five unpaired cations and five unpaired anions, *i.e., the same number* will be discharged at the respective electrodes.

From the above, it is clear that $\frac{\text{speed of cation}}{\text{speed of anion}}$ is 2/3, as during the same time 2 cations and 3 anions move towards cathode and anode, respectively. From fig. 3-(IV), it is clear that fall in concentration round anode is 2 (from 5 to 3 ions) and fall in concentration round cathode is 3 (from 5 to 2 ions). Thus, the ratio of fall in concentration round anode and fall in concentration round cathode is also 2/3.

$$\therefore \quad \frac{\text{Fall in concentration round anode}}{\text{Fall in concentration round cathode}} = \frac{\text{Speed of cation}}{\text{Speed of anion}}$$

In other words, the fall in concentration round an electrode is proportional to the speed of that ion which moves away from it.

• 10.3. TRANSPORT NUMBER

During electrolysis, the ions of an electrolyte move towards the opposite electrode with different speeds. The electric current flows due to the movement of ions. The amount of current carried by an anion will also be different, due to their different speeds. So, ***the fraction of the total current carried by an ion is known as its transport number or Hittorf number.*** It is generally expressed by t or n.

$$\therefore \text{ Transport number of cation, } t_c = \frac{\text{Current carried by cation}}{\text{Total current carried}} \quad \ldots(1)$$

$$\text{Transport number of anion, } t_a = \frac{\text{Current carried by anion}}{\text{Total current carried}} \quad \ldots(2)$$

If u_a and u_c be the speed of anion and cation, respectively, then

Current carried by cation $\propto u_c$ and current carried by anion $\propto u_a$.

Total current carried $\propto u_a + u_c$.

$$\therefore \text{ From equation (1),} \qquad t_c = \frac{u_c}{u_a + u_c}$$

$$\text{From equation (2),} \qquad t_a = \frac{u_a}{u_a + u_c}$$

$$\therefore \qquad t_a + t_c = \frac{u_a}{u_a + u_c} + \frac{u_c}{u_a + u_c} = 1$$

Thus, if the transport number of one of the ions is known, then that of the other can be easily calculated.

The transport number of an ion is not constant for an ion as it depends on the nature of the ion or transport number of the other ion with which it is associated.

Principle of Determination of Transport Number

We know that the fall in concentration round any electrode is proportional to the speed of the ion moving away from it. Therefore,

$$\frac{\text{Fall in concentration round anode}}{\text{Fall in concentration round cathode}} = \frac{\text{Speed of cation}}{\text{Speed of anion}} = \frac{u_c}{u_a}$$

Adding 1 on both sides,

$$\frac{\text{(Fall in concentration round cathode + Fall in concentration round anode)}}{\text{Fall in concentration round cathode}} = \frac{u_a + u_c}{u_a}$$

On reversing it,

$$\frac{\text{Fall in concentration round cathode}}{\text{Fall in concentration round both electrodes}} = \frac{u_a}{u_a + u_c} = t_a$$

Similarly,

$$\frac{\text{Fall in concentration round anode}}{\text{Fall in concentration round both electrodes}} = \frac{u_c}{u_a + u_c} = t_c$$

$$\therefore \qquad t_c = \frac{\text{Fall in concentration round anode}}{\text{Total fall in concentration}}$$

Total fall in concentration is equal to the amount of silver deposited in the silver voltameter (connected in series).

$$\therefore \qquad t_c = \frac{\text{Fall in concentration round anode}}{\text{Amount of silver deposited in silver voltameter}}$$

From the above equation, we can calculate the transport number of Ag^+ ions in a solution of $AgNO_3$.

• 10.4. KOHLRAUSCH'S LAW

The equivalent conductivities at infinite dilution at 18°C of some pairs of electrolytes having the same cation or anion are given below :

Electrolyte	λ_∞	Difference	Electrolyte	λ_∞	Difference
KCl	130.0	21.1	KCl	130.0	18.8
NaCl	108.9		KF	111.2	
KF	111.2	21.1	NaCl	108.9	18.8
NaF	90.1		NaF	90.1	

From the above, it is clear that the replacement of potassium ion by sodium ion in any of the electrolytes produces the same difference, *i.e.*, 21.1 in equivalent conductivity at infinite dilution, irrespective of the nature of the anion. Similarly, the replacement of chloride ion by fluoride ion in any of the electrolytes produces the same difference, *i.e.*, 18.8 in equivalent conductivity at infinite dilution, irrespective of the nature of the cation. These observations led Kohlrausch to formulate a law, known as ***Kohlrausch's law***. According to this law,

"At infinite dilution, each ion makes a definite contribution towards equivalent conductivity of the electrolyte, irrespective of the nature of the other ion with which it is associated and that the equivalent conductivity at infinite dilution for any electrolyte is the sum of the contributions of the two ions."

Mathematically, Kohlrausch's law is expressed as,

$$\lambda_\infty = \lambda_a + \lambda_c$$

where, λ_a and λ_c are the ionic conductances of anion and cation, respectively.

Applications of Kohlrausch's Law

(1) Calculation of equivalent conductivity at infinite dilution for weak electrolytes. The value of λ_∞ for strong electrolytes can be determined graphically by extrapolation. But the value of λ_∞ for weak electrolytes like CH_3COOH, NH_4OH etc. cannot be determined directly, as they are weakly ionised. Thus, the value of λ_∞ for acetic acid can be calculated from the determination of λ_∞ values for strong electrolytes, hydrochloric acid, sodium acetate and sodium chloride. Suppose the values are x, y and z. According to Kohlrausch's law,

$$\lambda_{\infty\,(CH_3COOH)} = \lambda_{H^+} + \lambda_{CH_3COO^-}$$

$$\lambda_{\infty\,(HCl)} = \lambda_{H^+} + \lambda_{Cl^-} = x \qquad \ldots(1)$$

$$\lambda_{\infty\,(CH_3COONa)} = \lambda_{CH_3COO^-} + \lambda_{Na^+} = y \qquad \ldots(2)$$

$$\lambda_{\infty\,(NaCl)} = \lambda_{Na^+} + \lambda_{Cl^-} = z \qquad \ldots(3)$$

Subtracting equation (3) from the sum of equations (1) and (2), we get

$$\lambda_{H^+} + \lambda_{Cl^-} + \lambda_{CH_3COO^-} + \lambda_{Na^+} - \lambda_{Na^+} - \lambda_{Cl^-} = x + y - z$$

or $$\lambda_{H^+} + \lambda_{CH_3COO^-} = x + y - z$$

or $$\lambda_{\infty\,(CH_3COOH)} = x + y - z$$

Thus, the value of λ_∞ can be calculated*.

Ex. 1. *If the equivalent conductivities at infinite dilution for HCl, NaCl and CH_3COONa are 380.5, 109 and 78.5, calculate the value of λ_∞ for acetic acid.*

Solution. $\lambda_\infty\, CH_3COOH = \lambda_{CH_3COO^-} + \lambda_{H^+}$

$$\lambda_\infty\, HCl = \lambda_{H^+} + \lambda_{Cl^-} = 380.5 \qquad \ldots(i)$$

$$\lambda_\infty\, NaCl = \lambda_{Na^+} + \lambda_{Cl^-} = 109 \qquad \ldots(ii)$$

$$\lambda_\infty\, CH_3COONa = \lambda_{Na^+} + \lambda_{CH_3COO^-} = 78.5 \qquad \ldots(iii)$$

Subtracting equation (ii) from the sum of equations (i) and (iii), we get

$$\lambda_{H^+} + \lambda_{Cl^-} + \lambda_{Na^+} + \lambda_{CH_3COO^-} - \lambda_{Na^+} - \lambda_{Cl^-}$$
$$= 380.5 + 78.5 - 109$$

or $$\lambda_{H^+} + \lambda_{CH_3COO^-} = 350.0$$

$$\lambda_\infty\, CH_3COOH = \mathbf{350.0}$$

Ex 2. *At 298 K, the equivalent conductivities at infinite dilution of sodium propionate, HCl and NaCl are 85.9, 426.1 and 126 $ohm^{-1}\, cm^2\, eq^{-1}$, respectively. Calculate the equivalent conductivity at infinite dilution of propionic acid.*

Solution. $\lambda_\infty\, C_2H_5COOH = \lambda_{H^+} + \lambda_{C_2H_5COO^-}$

$$\lambda_\infty\, C_2H_5COONa = \lambda_{C_2H_5COO^-} + \lambda_{Na^+} = 85.9 \qquad \ldots(i)$$

$$\lambda_\infty\, HCl = \lambda_{H^+} + \lambda_{Cl^-} = 426.1 \qquad \ldots(ii)$$

$$\lambda_\infty\, NaCl = \lambda_{Na^+} + \lambda_{Cl^-} = 126 \qquad \ldots(iii)$$

Subtracting equation (iii) from the sum of equations (i) and (ii), we get

$$\lambda_{C_2H_5COO^-} + \lambda_{H^+} = \lambda_\infty\, C_2H_5COOH$$
$$= 85.9 + 426.1 - 126$$

or $$\lambda_\infty\, C_2H_5COOH = \mathbf{386.0\ ohm^{-1}\, cm^2\, eq^{-1}}$$

(2) Calculation of ionic conductance. At a constant temperature, the value of ionic conductance (λ_a or λ_c) is constant and is proportional to the speed of the respective ion, *i.e.*,

$$\lambda_a \propto u_a \text{ or } \lambda_a = ku_a \qquad \ldots(4)$$

$$\lambda_c \propto u_c \text{ or } \lambda_c = ku_c \qquad \ldots(5)$$

Adding euation (4) and (5), we get

---

* For λ_∞ value of NH_4OH,

$$\lambda_{\infty\,(NH_4OH)} = \lambda_{NH_4^+} + \lambda_{OH^-} = \lambda_{\infty\,(NH_4Cl)} + \lambda_{\infty\,(NaOH)} - \lambda_{\infty\,(NaCl)}$$
$$= (\lambda_{NH_4^+} + \lambda_{Cl^-}) + (\lambda_{Na^+} + \lambda_{OH^-}) - (\lambda_{Na^+} + \lambda_{Cl^-})$$

If the λ_∞ values for NH_4Cl, NaOH and NaCl be x, y and z, then

$\lambda_\infty\, (NH_4OH) = (x + y - z)$.

$\lambda_a + \lambda_c = k\,(\mu_a + u_c)$ or $\lambda_\infty = k\,(\mu_a + u_c)$ [Accord ingto Kohlrausch's law]

$$\therefore \qquad \frac{\lambda_c}{\lambda_\infty} = \frac{u_c}{u_a + u_c} = t_c$$

or $\qquad \lambda_c = t_c \times \lambda_\infty$

Similarly, $\qquad \lambda_a = t_a \times \lambda_\infty$.

So, ionic conductance of an ion can be obtained by multiplying its transport number by the equivalent conductivity at infinite dilution of an electrolyte containing that ion.

(3) Calculation of absolute velocity of ions or absolute ionic mobility. Absolute ionic mobility of an ion is the ionic mobility of an ion in cm/sec under a potential gradient of 1 volt cm^{-1} [Potential gradient is defined as the ratio of EMF of the cell (in volts) and the distance between the electrodes in cm].

We know that, ionic conductance of an ion is proportional to ionic mobility, *i.e.*,

$\lambda_a \propto u_a$ or $\lambda_a = ku_a$ where, k = constant.

$\lambda_c \propto u_c$ or $\lambda_c = ku_c$

$$\therefore \qquad u_a = \frac{\lambda_a}{k} \quad \text{and} \quad u_c = \frac{\lambda_c}{k}$$

When the potenital gradient is 1 volt/cm, then the value of constant, k is found to be 96500 coulomb, *i.e.*, one faraday.

$$\therefore \qquad u_a = \frac{\lambda_a}{F} = \frac{\lambda_a}{96500}$$

$$u_c = \frac{\lambda_c}{F} = \frac{\lambda_c}{96500}$$

$$\therefore \quad \text{Absolute ionic mobility} = \frac{\text{Ionic mobility}}{96500}$$

Ex. 3. *The equivalent conductivity of a dilute solution of KCl is 130.1 ohm^{-1}. The transport number of K^+ ion in this solution is 0.496. Calculate the absolute velocities and ionic conductances of K^+ and Cl^- ions.*

Solution. $\qquad \lambda_a = t_a \times \lambda_\infty$

$$\therefore \qquad \lambda_{K^+} = t_{K^+} \times \lambda_{\infty\,KCl}$$

$$= 0.496 \times 130.1 = \mathbf{64.529\ ohm^{-1}}$$

$$\lambda_{\infty\,KCl} = \lambda_{K^+} + \lambda_{Cl^-}$$

or $\qquad 130.1 = 64.529 + \lambda_{Cl^-}$

$$\therefore \qquad \lambda_{Cl^-} = 130.1 - 64.529 = \mathbf{65.571\ ohm^{-1}}$$

Absolute velocity of K^+

$$= \frac{64.529}{96500} = \mathbf{6.686 \times 10^{-4}\ cm/sec}$$

Absolute velocity of Cl^-

$$= \frac{65.571}{96500} = \mathbf{6.794 \times 10^{-4}\ cm/sec}$$

(4) Calculation of degree of dissociation of weak electrolytes. We know that the degree of dissociation (α) can be obtained from the following expression :

$$\alpha = \frac{\lambda_V}{\lambda_\infty} = \frac{\lambda_V}{\lambda_a + \lambda_c}$$

Ex. 4. *If the equivalent conductivities at infinite dilution of NaCl, HCl and CH_3COONa are 126.45, 426.16 and 91.0, respectively, calculate the value of λ_∞ for CH_3COOH. If the equivalent conductivity of the given solution of acetic acid is 48.15 at 25°C, calculate its degree of dissociation.*

Solution. $\lambda_\infty\ CH_3COOH = \lambda_\infty\ CH_3COONa + \lambda_\infty\ HCl - \lambda_\infty\ NaCl$

$$= 91.0 + 426.16 - 126.45 = \mathbf{390.71}$$

$$\text{Degree of dissociation,} \quad \alpha = \frac{\lambda_V}{\lambda_\infty} = \frac{48.15}{390.71} = 0.1232$$

$\therefore$ Degree of dissociation = **12.32%**.

Ex. 5. *The molecular conductivity of a weak monobasic acid at infinite dilution is 387 ohm^{-1}. If at the same temperature, N/50 solution of the acid has a specific conductivity 0.00033 ohm^{-1} cm^{-1}, calculate the degree of dissociation of N/50 acid.*

Solution. For monobasic acid,

$$\mu_\infty = \lambda_\infty = 387$$

$$\therefore \quad \lambda_V = \kappa_V \times V = 0.00033 \times 50{,}000 = 16.5$$

$$\therefore \quad \alpha = \frac{\lambda_V}{\lambda_\infty} = \frac{16.5}{387} = 0.0426$$

∴ Degree of dissociation = **4.26%.**

(5) Calculation of solubility of sparingly soluble stalts. Certain salts like AgCl, $BaSO_4$, $PbCrO_4$ etc. which are assumed to be insoluble, are actually sparingly soluble in water. The solubility in such cases cannot be determined by the usual methods. However, Kohlrausch's law helps us in determining the solubility of sparingly soluble salts by conductivity measurements.

Suppose, it is required to determine the solubility of AgCl in water. At 25°C, some AgCl is added to water. A very small amount of salt passes into the solution and the rest settles down. The conductivity is determined as usual by placing the conductivity cell in the saturated solution. The conductivity of water used in the experiment is also determined. The difference between the two multiplied by the cell constant gives the specific conductivity of the solution due to dissolved AgCl. Let the specific conductivity be κ.

As the solubility of AgCl is very small, the minute quantity, that is dissolved may be considered to be present at infinite dilution and so the determined equivalent conductivity (λ_V) may be taken as the equivalent conductivity at infinite solution (λ_∞).

$$\therefore \quad \lambda_V = \lambda_\infty = \lambda_a + \lambda_c \qquad \text{(According to Kohlrausch's law)}$$

$$\text{and} \quad \lambda_V = \kappa \times V$$

where, V = volume in c.c. containing 1 g equivalent of an electrolyte.

$$\therefore \quad \lambda_a + \lambda_c = \kappa \times V$$

$$\text{or} \quad V = \frac{\lambda_a + \lambda_c}{\kappa}$$

Thus, V can be calculated.

$$\because \quad V \text{ c.c. of solution contains electrolyte} = 1 \text{ g eq}$$

$$\therefore \quad 1000 \text{ c.c. of solution contains electrolyte} = \frac{1000}{V} \text{ g eq}$$

$$\therefore \quad \text{Solubility of AgCl} = \frac{1000}{V} \text{ g eq/litre} = \frac{1000 \times E}{V} \text{ g/litre}$$

where, E = equivalent weight of AgCl.

Ex. 6. *The specific conductivity of a saturated solution of silver chloride is 1.33 × 10^{-6} ohm^{-1}. If the ionic conductances of Ag$^+$ and Cl$^-$ ions are 59 and 74 respectively, calculate the solubility of AgCl.*

Solution. $\lambda_\infty \text{ AgCl} = \lambda_{Ag^+} + \lambda_{Cl^-}$

$$= 59 + 74 = 133 \text{ ohm}^{-1}$$

For sparingly soluble salt,

$$\lambda_V = \lambda_\infty = \kappa_V \times V$$

$$\text{or} \quad 133 = 1.33 \times 10^{-6} \times V$$

$$\text{or} \quad V = \frac{133}{1.33 \times 10^{-6}} = 10^8 \text{ c.c.}$$

$$\because \quad 10^8 \text{ c.c. of the solution contain AgCl} = 1 \text{ g eq}$$

$$\therefore \quad 1000 \text{ c.c. of the solution contain AgCl} = \frac{1000}{10^8} \text{ g eq}$$

$$= 10^{-5} \text{ g eq}$$

$$\therefore \quad \text{Solubility} = 10^{-5} \times 143.5 \text{ g/litre}$$

$$= \mathbf{1.435 \times 10^{-3}} \textbf{ g/litre.}$$

Ex. 7. *At 25°C, the specific conductance of a saturated solution of AgCl is 3.41×10^{-6} ohm^{-1} cm^{-1} and that of used water is 1.61×10^{-6} ohm^{-1} cm^{-1}. The ionic conductances of Ag^+ and Cl^+ ions at 25°C are 61.92 and 76.34 ohm^{-1} cm^2 eq^{-1}. Calculate the solubility in g per litre of AgCl at the same temperature.*

Solution. $\lambda_\infty \text{AgCl} = \lambda_{\text{Ag}^+} + \lambda_{\text{Cl}^-}$

$$= 61.92 + 76.34 = 138.26$$

Specific conductivity of AgCl

= Specific conductivity of saturated solution of AgCl
– Specific conductivity of water

$$= 3.41 \times 10^{-6} - 1.61 \times 10^{-6} = 1.80 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$$

For sparingly soluble salt, AgCl, we can write,

$$\therefore \quad \lambda_V = \lambda_\infty = \kappa_V \times V$$

$$\text{or} \quad 138.26 = 1.80 \times 10^{-6} \times V$$

$$\text{or} \quad V = \frac{138.26}{1.80 \times 10^{-6}} \text{ c.c.}$$

$\because$ $\dfrac{138.26}{1.80 \times 10^{-6}}$ c.c. of the solution contain AgCl = 1 g eq

$\therefore$ 1000 c.c. of the solution contain AgCl

$$= \frac{1000 \times 1.80 \times 10^{-6}}{138.26} \text{ g eq}$$

$$= 1.30 \times 10^{-5} \text{ g eq}$$

$$\therefore \quad \text{Solubility} = 1.30 \times 10^{-5} \times 143.5 \text{ g/litre}$$

$$= \mathbf{1.86 \times 10^{-3} \text{ g/litre.}}$$

• 10.5. APPLICATIONS OF CONDUCTIVITY MEASUREMENTS

(1) Determination of basicity of organic acids : Ostwald showed that if the equivalent conductivity of a sodium salt of an organic acid is determined at dilution 32 litres and 1024 litres, then the difference between the two values is 10.8 times the basicity of the acid (*B*), *i.e.*,

$$\frac{\lambda_{1024} - \lambda_{32}}{10.8} = B$$

(2) Determination of degree of hydrolysis : The degree of hydrolysis (*h*) of salts like NH_4Cl, $CuSO_4$ can be determined from the following equation :

$$h = \frac{\lambda_V - \lambda'_V}{\lambda_\infty - \lambda'_V}$$

where, λ_V = equivalent conductivity of the solution at dilution *V*, λ'_V = equivalent conductivity of the unhydrolysed salt, λ_∞ = equivalent conductivity of the strong acid at infinite dilution.

(3) Conductometric titrations : Conductivity measurements are used to determine the end points of acid-alkali, precipitation titrations etc. It is based on the principle that conductivity depends on the number and mobility of ions.

In the titration of strong acid with a strong base (HCl and NaOH), the acid is taken in the conductivity cell and alkali in the burette. The conductivity of HCl is due to H^+ and Cl^- ions. As NaOH is gradually added, the fast moving H^+ ions are replaced by slow moving Na^+ ions, *e.g.*,

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$

On continued addition of sodium hydroxide the conductivity goes on decreasing till the acid has been completely neutralised. After end point, addition of NaOH will introduce fast moving OH^- ions and the conductivity will again start rising. On plotting the conductivity (X-axis) and volume of alkali added (Y-axis), two straight lines AB and CD are obtained. The point of intersection X of these lines represents the end point (See figure 4).

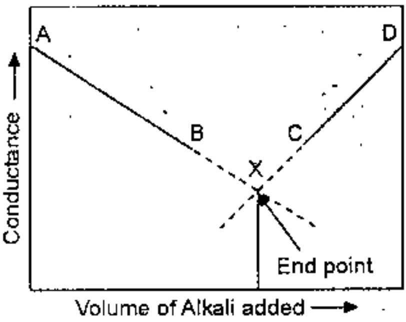


Fig. 4. Titration curve of strong acid and strong base.

Similarly, in the titration of weak acid and strong base (CH_3COOH and NaOH), the conductivity of the acid will be low because of its poor ionisation. On adding alkali, the conductivity begins to increase due to the formation of highly ionised sodium acetate.

$$CH_3COOH + Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O$$

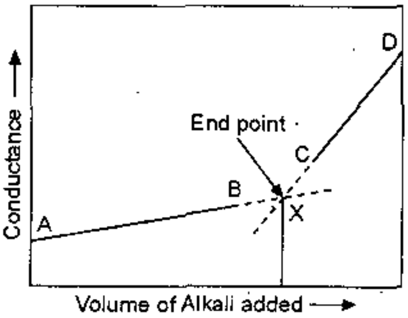


Fig. 5. Titration curve of week acid and strong base.

On complete neutralisation of the acid, further addition of alkali introduces fast moving OH^- ions. The conductivity of the solution starts increasing even more sharply than before. On plotting the conductivity values and volume of alkali added, we get two straight lines, the point of intersection X, of which shows the end point (Fig. 5).

Similarly, we can titrate strong acid and weak alkali (HCl and NH_4OH), mixture of acids, *e.g.*, HCl and CH_3COOH against alkali say NaOH. Conductivity measurements have also been used in precipitation titrations, *e.g.*, titration of $AgNO_3$ against KCl.

In order to get good results, the change of volume during the titration should be as small as possible. It is done by taking the titrating solution in the burette nearly 5 to 10 times stronger than the solution taken in the conductivity cell.

Conductometric titrations can be used in coloured solutions also and also in titrating weak acids againt weak alkalis (CH_3COOH and NH_4OH) where usual methods fail to give accurate results.

• SUMMARY

- Specific resistance is defined as the resistance in ohms of a substance 1 cm in length and 1 cm^2 cross-section or it is the resistance of 1 cm^3 of the substance.
- Specific conductivity is defined as the conductivity of 1 cm^3 of a solution of an electrolyte.
- The unit of specific conductivity is ohm^{-1} cm^{-1} or S cm^{-1}.
- Equivalent conductivity is defined as the conductivity of a solution containing 1 g equivalent of an electrolyte when placed between two large electrodes placed 1 cm apart.
- The unit of equivalent conductivity is ohm^{-1} cm^2 $equivalent^{-1}$.
- Molecular conductivity is defined as the conductivity of a solution containing 1 g mole of an electrolyte when placed between two large electrodes placed 1 cm apart.
- The unit of molecular conductivity is ohm^{-1} cm^2 $mole^{-1}$.
- Equivalent conductivity = Specific conductivity × Volume in c.c. of a solution containing 1 g equivalent of an electrolyte.
- The specific conductivity of a solution decreases with dilution, while equivalent and molecular conductivities increase with dilution.
- $$\text{Cell constant} = \frac{\text{Specific conductivity}}{\text{Observed conductivity}} = \frac{0.002765}{\text{Observed conductivity of N/50 KCl solution}}$$
- The ions are always discharged in equivalent amounts, no matter what their relative speeds are.
- Fall in concentration round an electrode is proportional to the speed of the ion moving away from it.
- At infinite dilution, the equivalent conductivity for any electrolyte is the sum of the contribution of the two ions.
- The fraction of the total current carried by an ion is known as its transport number.
- The sum of the transport numbers of both the ions of an electrolyte is always one.

• STUDENT ACTIVITY

1. Define specific and equivalent conductance.

2. How is cell constant of a conductivity cell ?

3. State and explain transport number.

4. Explain Kohlrausch's law.

5. Write a note on conductometric titrations.

• TEST YOURSELF

1. Define the terms, specific conductivity, equivalent conductivity and molecular conductivity.
2. What are the units of different conductivities ?
3. What is the relation between different conductivities ?
4. What is the effect of dilution on different conductivities ?
5. How will you determine the equivalent conductivity of an electrolytic solution ?

6. What is cell constant and how it is determined ?

7. The specific conductivity of N/50 solution of KCl at 25°C is 0.002765 mhos. If the resistance of the same solution placed in the cell is 2000 ohm, calculate the cell constant.

8. The molecular conductivity of N/32 acetic acid is 9.625 ohm^{-1} and at infinite dilution is 385 ohm^{-1}. Calculate the degree of dissociatin of N/32 acetic acid.

9. The observed conductivity of a 0.01 N solution of an electrolyte with cell constant of 0.5 is 0.001185 ohm^{-1}. Calculate its equivalent conductance.

10. Show that ions migrate towards oppositely charged electrodes with different velocities.

11. Define transport number. Mention the principle for its determination.

12. State and explain Kohlrausch's law.

13. With the help of Kohlrausch's law, how will you determine ?

(i) Equivalent conductivity at infinite dilution for weak electrolytes.
(ii) The ionic conductances of ions of an electrolyte.
(iii) The degree of dissociation of weak electrolytes.
(iv) The solubility of sparingly soluble salts.

14. Write a note on conductometric titrations.

15. Discuss in brief the applications of conductivity measurements.

16. The conductivity of 1 cm^3 of an electrolytic solution is known as :

(a) Specific conductivity (b) Equivalent conductivity
(c) Molecular conductivity (d) None of the above

17. If the distance between the electrodes is 2 cm and area of cross-section is 4 cm^2, the cell constant is :

(a) 2 (b) 0.2 (c) 0.5 (d) 8

18. The sum of ionic conductances is written as :

(a) λ_v (b) λ_∞ (c) μ_v (d) κ_v

19. The conductivity of a solution depends on :

(a) Number of ions (b) Number of moleculs
(c) Number of prarticles (d) All of the above

20. The sum of transport numbers of both ions of an electrolyte is :

(a) Zero (b) One (c) Infinite (d) None of the abvoe

21. **Fill in the blanks :**

(i) $\text{Resistance} = \ldots\ldots\ldots \times \dfrac{\text{Distance between electrodes}}{\text{Area of cross section of electrodes}}$

(ii) The unit of specific conductivity is ....

(iii) $\ldots\ldots\ldots = \dfrac{\text{Specific conductivity}}{\text{Observed conductivity}}$

(iv) $\lambda_a + \lambda_c = \ldots\ldots\ldots$

(v) $t_a + t_c = \ldots\ldots\ldots$

ANSWERS

7. 5.53 **8.** 2.5% **9.** 59.25 $\text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$ **16.** (a) **17.** (c) **18.** (b) **19.** (d) **20.** (b)
21. (i) specific resistance (ii) $\text{ohm}^{-1}\ \text{cm}^{-1}$ (iii) cell constant (iv) λ_∞ (v) one

U N I T

11

ELECTROCHEMISTRY-II

LEARNING OBJECTIVES

- Hydrolysis of Salts
- Hydrogen Ion Concentration or pH Value
- Buffer Solutions
- Terms Used in Electrochemistry
- Galvanic Cells
- Reversible and Irreversible Cells
- *Reversible Electrodes*
- Relation Between Free Energy Change and Electrical Energy
- Nernst's Equation for E.M.F. of a Reversible Cell
- Electrode Potential
- Oxidation-Reduction Potential
- Reference Electrodes
- Concentration Cells
- Applications of Concentration Cells
  - □ Summary
  - □ Student Activity
  - □ Test Yourself

• 11.1. HYDROLYSIS OF SALTS

Pure water is neutral, as the concentrations of H^+ and OH^- ions are the same. When water reacts with any salt and makes the solution either acidic or alkaline, then this phenomenon is called ***salt hydrolysis***. It is defined as :

"The phenomenon of the interaction of salt with water giving acidic or alkaline solution is known as salt hydrolysis.

We can explain the salt hydrolysis by taking the following examples.

[I] Salts of Weak Acid and Strong Base

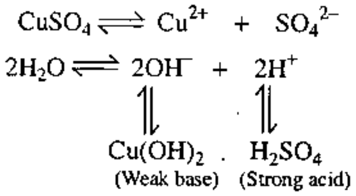
Salts like Na_2CO_3, $NaHCO_3$, CH_3COONa, KCN etc. belong to this category. For example, sodium acetate (salt) is obtained by the combination of weak acid (CH_3COOH) and strong base (NaOH). In solution, this salt gives CH_3COO^- and Na^+ ions which combine with H^+ and OH^- ions, respectively, furnished by water, as follows :

$$\begin{array}{rcccl} CH_3COONa & \rightleftharpoons & CH_3COO^- & + & Na^+ \\ H_2O & \rightleftharpoons & H^+ & \rightleftharpoons + & OH^- \\ & & \upharpoonleft\downharpoonright & & \upharpoonleft\downharpoonright \\ & & \underset{\text{(Weak acid)}}{CH_3COOH} & & \underset{\text{(Strong base)}}{NaOH} \end{array}$$

The base NaOH thus formed, being strong, ionises to a large extent, while the acid CH_3COOH formed, being weak, ionises to a very small extent. Thus, the solution contains an excess of free OH^- ions, whereby the solution becomes ***alkaline.*** So, aqueous solution of all salts belonging to this category is alkaline in nature, *i.e.*, turns red litmus to blue.

[II] Salts of Strong Acid and Weak Base

Salts like NH_4Cl, $CuSO_4$, $FeCl_3$, aniline hydrochloride etc. belong to this category. For example, copper sulphate (salt) is obtained by the combination of strong acid (H_2SO_4) and weak base [$Cu(OH)_2$]. In solution, this salt gives Cu^{2+} and SO_4^{2-} ions which combine with OH^- and H^+ ions, respectively, furnished by water, as follows :

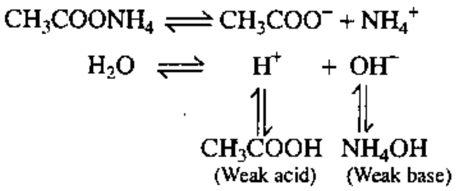


$$\begin{array}{ccccc} CuSO_4 & \rightleftharpoons & Cu^{2+} & + & SO_4^{2-} \\ 2H_2O & \rightleftharpoons & 2OH^- & + & 2H^+ \\ & & \updownarrow & & \updownarrow \\ & & Cu(OH)_2 & & H_2SO_4 \\ & & \text{(Weak base)} & & \text{(Strong acid)} \end{array}$$

The acid H_2SO_4 thus formed, being strong, ionises to a large extent, while the base $Cu(OH)_2$ formed being weak, ionises to a very small extent. Thus, the solution contains an excess of H^+ ions, whereby the solution becomes acidic. So, aqueous solution of all salts belonging to this category is acidic in nature, *i.e.*, turns blue litmus to red.

[III] Salts of Weak Acid and Weak Base

Salts like $(NH_4)_2CO_3$, CH_3COONH_4, aniline acetate belong to this category. For example, ammonium acetate (salt) is obtained by the combination of weak acid (CH_3COOH) and weak base (NH_4OH). In solution, this salt gives CH_3COO^- and NH_4^+ ions which combine with H^+ and, OH^- ions, respectively, furnished by water as follows :



$$\begin{array}{ccccc} CH_3COONH_4 & \rightleftharpoons & CH_3COO^- & + & NH_4^+ \\ H_2O & \rightleftharpoons & H^+ & + & OH^- \\ & & \updownarrow & & \updownarrow \\ & & CH_3COOH & & NH_4OH \\ & & \text{(Weak acid)} & & \text{(Weak base)} \end{array}$$

Both the acid (CH_3COOH) and base (NH_4OH) formed are weak and so are feebly ionised. Thus, the solution contains neither an excess of H^+ ions nor OH^- ions. So, the solution remains almost neutral. If the acid is slightly more ionised than the base, the solution will be acidic and if the base is slightly more ionised than the acid, the solution will be alkaline.

Sodium chloride reacts with water as follows :

$$\underset{}{NaCl + H_2O} \longrightarrow \underset{\text{Strong base}}{NaOH} + \underset{\text{Strong acid}}{HCl}$$

The acid and base formed due to hydrolysis are both strong and so they are completely ionised. The solution thus contains neither an excess of H^+ ions nor excess of OH^- ions. Therefore, the solution will be neutral. In other words, salts of strong acid and strong base do not hydrolyse.

• 11.2. HYDROGEN ION CONCENTRATION OR pH VALUE

We know that pure water is neutral, so it follows that it contains equal concentrations of hydrogen and hydroxyl ions. At a certain temperature, the product of the concentration of H^+ and OH^- ions in pure water is known as ***ionic product of water***. The ionic product of water at 25°C is approximately equal to 1×10^{-14}.

$$\therefore \qquad [H^+][OH^-] = 1 \times 10^{-14}$$

$$\text{or} \qquad [H^+]^2 = 1 \times 10^{-14} \ \{\text{since } [H^+] = [OH^-]\}$$

$$[H^+] = 1 \times 10^{-7} = [OH^-].$$

It means that in pure water the concentration of H^+ and OH^- ions is 10^{-7} g ion per litre each. Therefore, both degree of acidity and degree of alkalinity of a solution can be expressed quantitatively in terms of hydrogen ion concentration.

In neutral solution, $[H^+] = [OH^-] = 10^{-7}$

In acidic solution, $[H^+] > 10^{-7}$

In alkaline solution, $[H^+] < 10^{-7}$.

The above method of expressing the acidity or alkalinity of a solution has given place to another still more simple and convenient method. It was introduced by Sorensen in 1909. In this method, hydrogen ion concentration is expressed in terms of ***hydrogen ion exponent***, *i.e.*, a number obtained by giving a positive value to the negative power of 10 in the expression 1×10^{-n}. This was originally represented as pH but now most suitably written as pH. Thus,

pH of a solution is numerically equal to the negative power to which 10 must be raised in order to express the hydrogen ion concentration.

For example, if $[H^+] = 10^{-x}$; then pH = x. Thus, we have a scale in which degree of acidity can be expressed in terms of pH.

	Acidic solution					Neutral solution	Alkaline solution				
$[H^+] =$	10^{-0}	10^{-1}	10^{-2}	10^{-3}	10^{-4}...	10^{-7}	...10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
pH =	0	1	2	3	4 ...	7	...10	11	12	13	14

Mathematically, we can write

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

or

$$\log [H^+] = -\text{pH} \log 10$$

$$\text{pH} = \frac{-\log [H^+]}{\log 10} = -\log [H^+] \qquad [\because \log 10 = 1]$$

$$= \log \frac{1}{[H^+]}$$

Thus, pH may also be defined as the *logarithm of the reciprocal of the hydrogen ion concentration.*

Since the pH value of pure water (neutral) is 7, any solution having pH less than 7 will be acidic and greater than 7 will be alkaline.

Ex. 1. *Calculate the pH of N/1000 HCl and N/1000 NaOH, assuming both to be completely ionised.*

Solution. For $N/1000$ HCl, $[H^+] = \frac{N}{1000}$ g eq/litre = 10^{-3} g ion/litre

$$\therefore \quad \text{pH} = 3$$

For $N/1000$ NaOH, $[OH^-] = \frac{N}{1000}$ g eq/litre = 10^{-3} g ion/litre

$$\therefore \quad \text{pOH} = 3$$

$$\therefore \quad \text{pH} = 14 - \text{pOH} = 14 - 13 = \mathbf{11}$$

Ex. 2. *Calculate the pH of 0.001 N acetic acid, if it is 10% ionised.*

Solution. $[H^+]$ = Degree of dissociation × Normality

$$= \alpha \,.\, N = \frac{10}{100} \times 0.001 = 10^{-4}$$

$$\therefore \quad \text{pH} = \mathbf{4.}$$

Ex. 3. *Calculate the pH of a solution containing 4g/litre of NaOH.*

Solution. Normality of NaOH solution $= \frac{4}{40} N = \frac{N}{10}$

For 0.1 N NaOH solution, $[OH^-] = 10^{-1}$. $\therefore$ pOH = 1

$$\therefore \quad \text{pH} = 14 - \text{pOH} = 14 - 1 = \mathbf{13.}$$

Ex. 4. *Calculate the pH of a solution containing 2 g/litre of NaOH (Na = 23 : $\log_{10} 2 = 0.3010$).*

Solution. Normality of NaOH solution $= \frac{2}{40} N = \frac{N}{20}$

$$\therefore \quad [OH^+] = 1/20 \text{ g ion/litre}$$

$$\because \quad [H^+]\,[OH^-] = 10^{-14}$$

or

$$[H^+] \times 1/20 = 10^{-14}$$

$$\therefore \quad [H^+] = 20 \times 10^{-14} = 2 \times 10^{-13}$$

$$\therefore \quad \text{pH} = -\log [H^+] = -\log (2 \times 10^{-13})$$

$$= 13 - \log 2 = 13 - 0.3010$$

or

$$\text{pH} = \mathbf{12.6990}$$

Ex. 6. *Calculate the pH of a solution for which the hydrogen ion concentration is 0.005 g/litre.*

Solution.

$$\text{pH} = -\log [H^+] = -\log (0.005)$$

$$= -\log (5 \times 10^{-3})$$

or

$$\text{pH} = 3 - \log 5 = 3 - 0.6990 = \mathbf{2.3010}$$

• 11.3. BUFFER SOLUTIONS

The pH value of pure water is 7, but it gradually changes on standing either due to the absorption of atmospheric CO_2 or impurities of the vessel. Moreover, the addition of a drop of HCl or NaOH in 1 litre of water, increases its H^+ ion or OH^- ion concentration considerably.

But it is observed that the addition of HCl to a solution containing a mixture of weak acid and a salt of it with a strong base (*i.e.*, $CH_3COOH + CH_3COONa$) is very slightly influenced and its pH value remains nearly the same. Similarly, a mixture of weak base and a salt of it with a strong acid (*i.e.*, $NH_4OH + NH_4Cl$) is very slightly influenced and it maintains its pH value. Such combinations possess the following characteristics :

(i) They possess a definite pH value.

(ii) The pH value remains steady on keeping it for a long time or on dilution.

(iii) The pH value is not appreciably changed on the addition of suitable quantity of either an acid or a base to the buffer solution.

So, those solutions which have both reserve acidity and alkalinity are called buffer solutions.

Buffer solutions are of two types :

(i) Acidic buffer solution : It is a mixture of weak acid and a salt of it with a strong base, *e.g.*, mixture of acetic acid and sodium acetate. The pH of this buffer solution is always less than 7.

(ii) Basic buffer solution : It is a mixture of weak base and a salt of it with a strong acid, *e.g.*, mixture of ammonium hydroxide and ammonium chloride. The pH of this buffer solution is always greater than 7.

Explanation : An acidic buffer solution like $CH_3COOH + CH_3COONa$ contains a very small concentration of H^+ ions. The formation of common acetate ion further suppresses the dissociation of acetic acid.

$$\begin{array}{rcl}
CH_3COONa \rightleftharpoons & CH_3COO^- & + Na^+ \\
HCl \rightleftharpoons & H^+ & + Cl^- \\
 & \Updownarrow & \\
 & CH_3COOH & \\
 & \text{Slightly ionised} &
\end{array}$$

When a drop of an alkali, say NaOH, is added to the solution, it reacts with CH_3COOH to form CH_3COONa and water. Thus, the OH^- ions of the base are removed and the pH value of the solution remains nearly the same.

Moreover, the addition of NaOH to a basic buffer solution containing $NH_4OH + NH_4Cl$ does not change its pH value because the OH^- ions produced from it readily combine with NH_4^+ ions obtained from NH_4Cl to form slightly ionised NH_4OH.

$$\begin{array}{rcl}
NH_4Cl \rightleftharpoons & NH_4^+ & + Cl^- \\
NaOH \rightleftharpoons & OH^- & + Na^+ \\
 & \Updownarrow & \\
 & NH_4OH & \\
 & \text{Slightly ionised} &
\end{array}$$

Therefore, buffer solution contains actually a very small concentration of H^+ or OH^- ions, but they possess a large reserve of opposite ions. Hence, they are known as solutions with ***reserve acidity and reserve alkalinity.***

Buffer solutions find several applications in laboratory as well as in industries. A few important applications are given below :

(i) In determining pH of unknown solution.

(ii) In studying the rate of chemical reactions.

(iii) In the removal of phosphate radical in qualitative analysis.

(iv) In preparing cultures in biological specimens.

(v) In the manufacture of ethyl alcohol from molasses (pH lies between 5 and 6.8)

(vi) In paper manufacture, sugar manufacture, leather tanning etc.

Calculation of pH Value of Buffer Mixture (Henderson-Hassel Equation)

Consider an acidic buffer solution of a weak acid (HA) and a salt (AB) of it with a strong base (BOH). Let c_1 and c_2 be the molar concentrations of the acid and the strongly ionised salt (AB), respectively.

Consider the dissociation of a weak acid HA as follows :

$$HA \rightleftharpoons H^+ + A^-$$

Applying the law of mass action,

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

or $$[H^+] = K_a \cdot \frac{[HA]}{[A^-]} \qquad \ldots(1)$$

where, K_a = ionisation constant of the acid.

The feeble dissociation of the weak acid is further suppressed by the presence of A^- ions with the result that the concentration of the unionised acid may be taken to be equal to the concentration of the total acid, *i.e.*, $[HA] = c_1$. The concentration of $[A^-]$ ions may be taken to be equal to the concentration of the salt, as it is nearly totally dissociated, *i.e.*, $[A^-] = c_2$.

∴ From equation (1),

$$[H^+] = K_a \cdot \frac{c_1}{c_2} = K_a \cdot \frac{[\text{Acid}]}{[\text{Salt}]}$$

Taking logarithm and then reversing the sign, we get

$$-\log [H^+] = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

or $$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \qquad \ldots(2)$$

Equation (2) is known as *Henderson-Hassel equation* from which we can calculate the pH of any acidic buffer solution.

Similarly, for a mixture of a weak base and its salt, Henderson-Hassel equation may be written as,

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

where, K_b = ionisation constant of the base.

Knowing pOH, we can calculate the value of pH, from the equation, $\text{pH} + \text{pOH} = \text{p}K_w = 14$

Ex. 1. *What will be the pH value of a solution obtained by mixing 0.20 moles per litre sodium acetate with 0.15 moles per litre acetic acid? Dissociation constant of acetic acid is 1.8×10^{-5}.*

Solution. From Henderson's equation,

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

$$= -\log 1.8 \times 10^{-5} + \log \frac{0.20}{0.15}$$

$$= 4.7448 + 0.1249 = \mathbf{4.8697}$$

Ex. 2. *Prove that the pH of a solution of an acid with dissociation constant K and degree of dissociation α is given by*

$$pH = \log_{10} \frac{1}{K} + \log_{10} \frac{\alpha}{1-\alpha}$$

Solution. Consider the dissociation of an acid HA which occurs as follows :

$$\underset{1-\alpha}{HA} \rightleftharpoons \underset{\alpha}{H^+} + \underset{\alpha}{A^-} \qquad (\alpha = \text{degree of dissociation})$$

On applying the law of mass action,

$$K = \frac{[H^+][A^-]}{[HA]} \qquad (K = \text{dissociation constant})$$

or $$\log_{10} K = \log_{10} [H^+] + \log_{10} \frac{[A^-]}{[HA]}$$

or $$-\log_{10}[H^+] = -\log_{10} K + \log_{10}\frac{[A^-]}{[HA]}$$

or $$pH = \log_{10}\frac{1}{K} + \log_{10}\frac{\alpha/V}{(1-\alpha)/V}$$

or $$pH = \log_{10}\frac{1}{K} + \log_{10}\frac{\alpha}{1-\alpha}$$

• 11.4. TERMS USED IN ELECTROCHEMISTRY

(1) Electrochemical cells : ***Those cells in which the electrical current results from a chemical reaction and in which oxidation occurs at one electrode, while reduction at the other are known as electrochemical cells.***

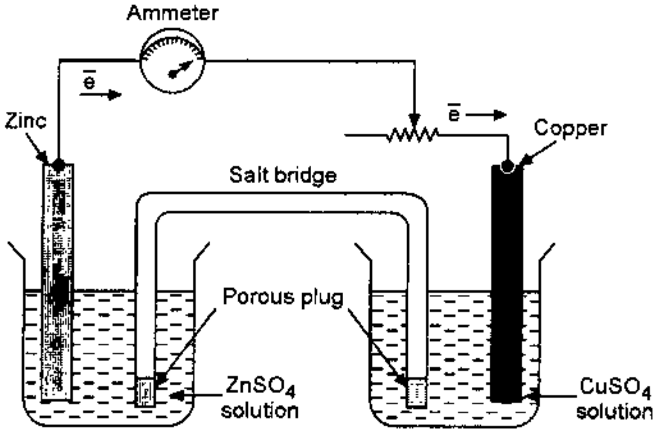


Fig. 1. Electrochemical cell

(2) Electrode reactions : Consider an electrochemial cell in which zinc rod is dipped in an aqueous solution of $ZnSO_4$ taken in one beaker and a copper rod is dipped in an aqueous solution of $CuSO_4$ taken in another beaker. The two solutions are joined by means of a salt bridge (a glass tube filled with gelatin or agar-agar gel containing either KCl, KNO_3 or NH_4NO_3 etc.). One of the metal rods, say zinc is connected to one terminal of an ammeter and the other rod, say copper is connected to the other terminal of the same ammeter through a variable resistance, as shown in figure (1).

If the metal rods are not connected or if the salt bridge is taken out, no current flows through the ammeter and no reaction occurs in the cell. But when the connection is made, the current starts flowing as shown by the reading in the ammeter. It is observed that due to the passage of electricity, the zinc rod has lost in weight, while the copper rod has gained in weight. The loss in weight of zinc rod is due to the passing of zinc metal into solution as Zn^{2+} ions.

$$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^- \qquad \ldots (1)$$

This is known as ***oxidation half reaction.*** The electrons so released accummulate on the zinc rod, move into the ammeter and then through the resistance enter the copper rod. These electrons are taken up by Cu^{2+} ions which are discharged as copper metal on the copper electrode, viz.,

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad \ldots (2)$$

This is known as ***reduction half reaction.***

The direction of flow of electrons (negative electricity) is indicated by the direction in which the ammeter needle deflects. In the present cell, the electrons are flowing from zinc electrode to copper electrode. So, the direction of flow of positive electricity, which is regarded as the direction of flow of conventional current, is from copper electrode to zinc electrode.

(3) Oxidation and reduction electrodes : According to convention, the electrode at which oxidation occurs is known as ***negative electrode,*** whereas the electrode at which reduction occurs is known as ***positive electrode.*** Thus, zinc electrode and copper electrode negative and positive electrodes, respectively. The reason for this nomenclature is that oxidation is accompanied by liberation of electrons which are given up to that electrode. This electrode thus acquires a negative charge. Reduction is accompanied by absorption of electrons by a reactant in solution from the electrode, which thus acquires a positive charge.

(4) Cell reaction : The ***overall reaction*** or ***cell reaction*** occurring in the cell is the redox reaction obtained by adding the oxidation half reaction and reduction half reaction occurring at each electrode. Thus, in the present cell the cell reaction is obtained by adding reactions (1) and (2), *i.e.,*

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

During this reaction, no heat is evolved, whereby it can be inferred that the decrease in potential energy appears as electrical energy in the present case.

So an electrochemical cell can also be defined as follows :

"*Electrochemical cell is a device in which a redox reaction occurs indirectly and the decrease in potential energy of the reaction appears largly in the form of the electrial energy.*"

• 11.5. GALVANIC CELLS

A galvanic cell is a device which converts chemical energy (or potential energy) into electrical energy due to the redox reaction occurring within the cell.

One of the simplest galvanic cell is a **Daniell cell.** In it, zinc sulphate is placed in a porous pot, in which a zinc rod is dipped. Copper sulphate solution is taken in a glass vessel in which a copper rod is dipped. The porous pot is then placed in the glass vessel. In it, the two solutions seep through the porous pot and, therefore, come in contact with each other at once. The reactions occurring at each electrode are :

At zinc electrode : $Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$ (Oxidation)

At copper electrode : $Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ (Reduction)

Thus, the cell reaction is represented as :

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

The electrical energy produced by a cell is given by the product of its E.M.F. (E) and quantity of electricity (nF) passed, where n is the valency of the metal. If E.M.F. is measured in volts and the quantity of electricity in coulombs, the electrial energy is obtained in volt-coulombs or joules.

In Daniell cell, the cell reaction occurs due to passage of 2 faradays, *i.e.*, 2×96500 coulombs of electricity. So, the electrical energy produced in the Daniell cell $= 2 \times 96500 \times 1{\cdot}1 = 212{,}300$ volt coulombs or joules.

• 11.6. REVERSIBLE AND IRREVERSIBLE CELLS

A cell is said to be thermodynamically reversible if it sends out infinitesimally small current so that the cell reaction always remains virtually in an equilibrium state.

For finding out whether the given cell is reversible or not, it is connected to an external source of E.M.F. working in opposite direction. If the cell satisfies the following conditions, the cell is reversible.

(a) If the opposing E.M.F. is exactly equal to that of the cell itself, no current is given out by the cell and the cell reaction does not occur.

(b) If the opposing E.M.F. is infinitesimally smaller than that of the cell itself, an extremely small current is given out by the cell and a correspondingly small amount of cell reaction occurs.

(c) If the opposing E.M.F. is infinitesimally greater than that of the cell itself, an extremely small current starts flowing in the opposite direction and the corresponding small amount of cell reaction is also reversed.

A cell which does not satisfy the above conditions, is an **irreversible cell.**

Daniell cell is a reversible cell, whose E.M.F. is 1·1 volt. If an external E.M.F. equal to 1·1 volt is applied, no current flows in the cell. If the external E.M.F. is infinitesimally smaller than 1·1 volt, the cell sends a very small current and the following cell reaction occurs.

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

If the external E.M.F. is infinitesimally greater than 1·1 volt, the cell starts sending the current in the opposite direction and the above cell reaction is reversed.

• 11.7. REVERSIBLE ELECTRODES

Every reversible cell consists of two reversible electrodes. These are of following types :

(a) Metal-metal ion electrode : It consists of a metal rod dipping in a solution of its own ions, *i.e.*, metallic rod dipping in $ZnSO_4$ solution and a copper rod dipping in $CuSO_4$ solution etc.

$$M(s) \rightleftharpoons M^+(aq) + e^-$$

If the metal rod (M) behaves as a positive electrode (*i.e.*, electrode reaction involves reduction), the above equilibrium shifts to the left, *i.e.*, concentration of M^+ ions in solution decreases. If the metal rod behaves as a negative electrode (*i.e.*, electrode reaction involves oxidation), the above equilibrium shifts to the right, *i.e.*, concentration of M^+ ions in solution increases. So, the above *electrode is reversible with respect to* M^+ *ions.*

For a metal of valency *n*, the electrode reaction will be :

$$M(s) \rightleftharpoons M^{n+}(aq) + ne^-$$

(b) Gas electrode

(i) Hydrogen electrode : This consists of hydrogen gas bubbling in a solution of an acid, say HCl. The electrode reaction will be :

$$\frac{1}{2} H_2(g) \rightleftharpoons H^+(aq) + e^-$$

This electrode is reversible with respect to H^+ ions. As hydrogen gas is non-conducting, platinum or some metal which comes quickly in equilibrium with hydrogen is used to make electrical contact (Fig. 2) This electrode is represented as : Pt, $H_2(g) \mid H^+$.

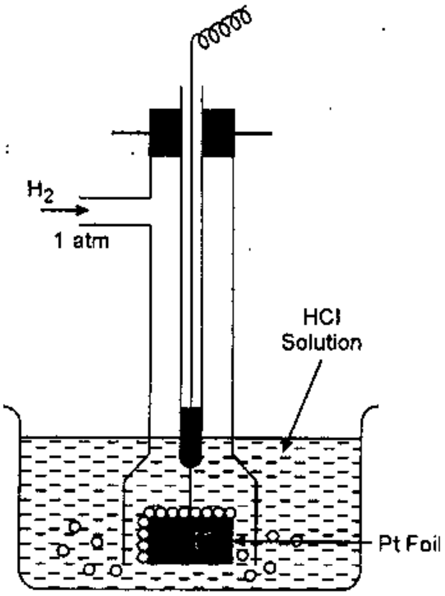


Fig. 2. Hydrogen electrode

(ii) Chlorine electrode : This electrode consists of chlorine gas bubbling at a given pressure into a solution of HCl. It is represented as,

$$Pt, Cl_2(g) \mid Cl^-$$

The electrode reaction is :

$$\frac{1}{2} Cl_2(g) + e^- \rightleftharpoons Cl^-(aq)$$

This electrode is reversible with respect to chloride ions.

(c) Metal-metal salt ion electrode : It consists of a metal and a sparingly soluble salt of the same metal dipping in a solution of a soluble salt having the same anion. One important electrode of this type is *calomel electrode.*

Calomel electrode consists of mercury, solid mercurous chloride and a solution of potassium chloride. It is represented as,

$$Hg \mid Hg_2Cl_2(s), KCl(aq).$$

It is set up by taking mercury at the bottom of a glass tube having a side tube. It is covered by a paste of mercurous chloride (calomel). A solution of KCl is added through the tube over the paste. The solution of KCl may be normal, decinormal or saturated. The solution also fills the side tube ending in a jet on one. A platinum wire sealed in a glass tube serves to make electrical contact of the electrode (Fig. 3).

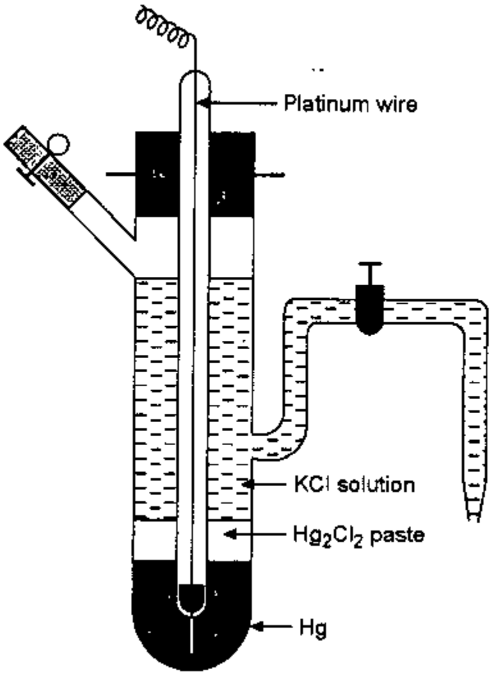


Fig. 3. Calomel electrode

If the electrode reaction involves oxidation, mercury would liberate electrons to send mercurous (Hg_2^{2+}) ions into the solution. These ions then combine with chloride ions (given by KCl) to form insoluble mercurous chloride. Thus, the concentration of chloride ions decreases in the solution. The electrode reactions involved are :

$$\begin{array}{c} 2Hg(l) \rightleftharpoons Hg_2^{2+} + 2e^- \\ \underline{Hg_2^{2+} + 2Cl^- \rightleftharpoons Hg_2Cl_2(s)} \\ 2Hg(l) + 2Cl^- \rightleftharpoons Hg_2Cl_2(s) + 2e^- \end{array}$$

If the electrode reaction involves reduction, the Hg_2^{2+} ions given by sparingly soluble mercurous chloride get discharged at the electrode. So, more calomel will pass into the solution. Thus, the concentration of chloride ions increases in the solution. The electrode reactions involved are :

$$\begin{array}{c} Hg_2Cl_2(s) \rightleftharpoons Hg_2^{++} + 2Cl^- \\ \underline{Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg(l)} \\ Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^- \end{array}$$

This electrode is thus reversible with respect to chloride ions.

(d) Oxidation reduction electrode : That electrode in which the potential is developed due to the tendency of transfer of ions from one valency or oxidation state to a more stable valency or oxidation state constitutes an *oxidation-reduction electrode*. For example, when Pt wire is immersed in a solution containing Fe^{2+} and Fe^{3+} ions, we get an oxidation-reduction (or redox) electrode. It may be represented as :

$$\text{Pt} \mid Fe^{2+}, Fe^{3+}$$

The electrode reacton is :

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

The platinum wire is used to accept the electrons and to make electrical contact.

• 11.8. RELATION BETWEEN FREE ENERGY CHANGE AND ELECTRICAL ENERGY

If the cell reaction in a given cell occurs due to the passage of n electrons, then the amount of electricity produced for the cell reaction will be n faradays, (*i.e.*, nF coulombs). If the E.M.F. of the cell is E volt and G is the free energy, then

$$\text{Electrical energy of the cell} = -\Delta G = nFE \quad \ldots(1)$$

According to Gibbs-Helmholtz equation, the change in free energy of a system (ΔG) at constant pressure is given by the following equation :

$$-\Delta G = -\Delta H - T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \quad \ldots(2)$$

where, ΔH is the enthalpy change or heat of reaction for the cell reaction at constant pressure.

Substituting the value of ΔG from equation (1) in (2), we get

$$nFE = -\Delta H + T\left[\frac{\partial(nFE)}{\partial T}\right]_P$$

As n and F are constants, we can also write

$$nFE = -\Delta H + nFT\left(\frac{\partial E}{\partial T}\right)_P$$

or

$$\Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P . \quad \ldots(3)$$

This permits the calculation of heat of reaction (enthalpy change) from the measured EMF of the cell and the sign of temperature coefficient of E.M.F. of the reaction, *i.e.*, $\left(\frac{\partial E}{\partial T}\right)_P$.

(i) If $\left(\frac{\partial E}{\partial T}\right)_P = 0$, then from equation (3),

$$\Delta H = -nFE$$

It means that the cell while working, will not undergo any heat change.

(ii) If $\left(\frac{\partial E}{\partial T}\right)_P$ is positive, *i.e.*, the E.M.F. of the cell increases with increase of temperature, $nFE > \Delta H$, *i.e.*, the electrical energy is greater than the heat of reaction and the cell will take heat from the surroundings.

(iii) If $\left(\frac{\partial E}{\partial T}\right)_P$ is negative, *i.e.*, the E.M.F. of cell decreases with increase of temperature, $nFE < \Delta H$, *i.e.*, the electrical energy is less than the heat of reaction and the cell will give heat to the surroundings.

• 11.9. NERNST'S EQUATION FOR E.M.F. OF A REVERSIBLE CELL

Suppose the reaction occurring in a reversible cell is represented by the equation

$$aA + bB \rightleftharpoons cC + dD$$

The decrease in free energy, $-\Delta G$ accompanying the process is given by the following thermodynamic equation,

$$-\Delta G = -\Delta G^o - RT \ln K \quad \ldots(1)$$

where, $-\Delta G^\circ$ is the decrease in free energy accompanying the same process when all the reactants and products are in their standard states of unit concentration and K is equilibrium constant for the reaction. The value of ΔG° is given by, $\Delta G^\circ = -nFE^\circ$, where, E° = standard emf of the cell.

E° is defined as ***the E.M.F. of the cell when the concentration of each reactant and product of the cell reaction is equal to unity.***

Substituting the value of K in equation (1), we get,

$$-\Delta G = -\Delta G^\circ - RT \ln \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b} \qquad \ldots (2)$$

If the E.M.F. of the cell is E volts and the cell reaction occurs for the passage of n faradays, *i.e.*, nF coulombs, the electrical work done by the cell is nFE volt-coulombs or joules. As decrease in free energy ($-\Delta G$) is given by the relation, $-\Delta G = nFE$, we have,

$$nFE = -\Delta G^\circ - RT \ln \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b}$$

or
$$nFE = nFE^\circ - RT \ln \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b}$$

or
$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b}$$

or
$$E = E^\circ - \frac{2{\cdot}303\,RT}{nF} \log \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b} \qquad \ldots (3)$$

Equation (3) is known as general equation for the E.M.F. of a reversible cell. This equation is known as ***Nernst equation.***

• 11.10. ELECTRODE POTENTIAL

Each cell is made up of two electrodes also known as ***half cells.*** At one electrode, oxidation occurs (*i.e.*, electrons are evolved), while at the other electrode, reduction occurs (*i.e.*, electrons are taken up). The tendency of an electrode to lose or gain electrons, when it is brought in contact with its own ions in solution is called ***single electrode potential.*** As the tendency to lose electrons is the tendency to get oxidised, this tendency is called ***oxidation potential.*** The tendency to gain electrons means to get reduced and so this tendency is called ***reduction potential.*** The oxidation potential and reduction potential are inverse of each other.

[I] Determination of Single Electrode Potential

It is not possible to determine experimentally the potential of a single electrode. It is only the difference of potentials between two electrodes that we can measure by combining them to get a complete cell. If the potential of one electrode is known then that of the other can be calculated. The electrode whose electrode potential is known as called a ***reference electrode.*** One such reference electrode is a hydrogen electrode, in which the hydrogen gas at one atmospheric pressure is bubbled through a solution of hydrogen ions of unit concentration. The potential of such reversible hydrogen electrode is arbitrarity taken as zero and is also known as ***standard hydrogen electrode*** and is represented as, Pt, H_2 (1 atm) | H^+ (c = 1).

If it is required to find the electrode potential of say zinc electrode dipping in $ZnSO_4$ solution, then it is combined with a standard hydrogen electrode to get the following complete cell.

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+}(aq) \mid \mathrm{H}^+ (c = 1) \mid \mathrm{H_2}\ (1\ \mathrm{atm}), \mathrm{Pt}$$

The E.M.F.* of the cell is determined potentiometrically, and is equal to the potential of the electrode (on H_2 scale) as the potential of standard hydrogen electrode is taken as zero.

[II] Nernst's Equation for Single Electrode Potential

Consider a cell in which the following reaction occurs :

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

---

*The standard E.M.F. of a cell (E°_{cell}) is equal to the standard electrode potential of the right hand electrode minus the standard electrode potential of the left hand electrode. So,

$$E^\circ_{cell} = E^\circ_{el}\ (\text{right}) - E^\circ_{el}\ (\text{left})$$

Both half cell reactions are taken as reduction half reactions. So,

E°_{cell} = Reduction potential of the right electrode – Reduction potential of the left electrode.

According to Nernst's equation, for the emf of the cell,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\mathrm{C}]^c [\mathrm{D}]^d}{[\mathrm{A}]^a [\mathrm{B}]^b} \quad \ldots(1)$$

where, E° is standard E.M.F. of the reversible cell.

Consider an electrode consisting of a metal M in contact with a solution of its own cations, M^{n+}, The following equilibrium is established assuming that the left to right reaction involves reduction.

$$\mathrm{M}^{n+}(aq) + n\mathrm{e}^- \rightleftharpoons \mathrm{M}(s).$$

According to equation (1), for the above electrode reaction, the electrode potential $E_{(\mathrm{M}^{n+},\,\mathrm{M})}$ is given by,

$$E_{(\mathrm{M}^{n+},\,\mathrm{M})} = E_{(\mathrm{M}^{n+},\,\mathrm{M})} - \frac{RT}{nF} \ln \frac{[\mathrm{M}]}{[\mathrm{M}^{n+}]}$$

where, $E^\circ_{\mathrm{M}^{n+},\,\mathrm{M}}$ is the standard electrode potential, n is the number of electrons for which the electrode reaction occurs.

Since M is solid, it can be considered to be in its standard state of unit concentration. So, the above equation becomes,

$$E_{(\mathrm{M}^{n+},\,\mathrm{M})} = E^\circ_{(\mathrm{M}^{n+},\,\mathrm{M})} - \frac{RT}{nF} \ln \frac{1}{[\mathrm{M}^{n+}]}$$

$$E_{(\mathrm{M}^{n+},\,\mathrm{M})} = E^\circ_{(\mathrm{M}^{n+},\,\mathrm{M})} + \frac{RT}{nF} \ln\ [\mathrm{M}^{n+}] \quad \ldots(1)$$

$$E_{(\mathrm{M}^{n+},\,\mathrm{M})} = E^\circ_{(\mathrm{M}^{n+},\,\mathrm{M})} + \frac{2.303\ RT}{nF} \log\ [\mathrm{M}^{n+}] \quad \ldots(2)$$

$$\left\{\text{For } 25^\circ\text{C or 298 K, } \frac{2.303\ RT}{F} = \frac{2.303 \times 8.314\ \mathrm{JK^{-1}\ mole^{-1}} \times 298\ \mathrm{K}}{96500\ \text{coulomb mole}^{-1}}\right\}$$

$$= 0.0591\ \text{volt}\ \ \mathrm{K}\ (\text{joule} = \text{volt} - \text{coulomb})$$

∴ At 298 K, equation (2) becomes,

$$E_{(\mathrm{M}^{n+},\,\mathrm{M})} = E^\circ_{(\mathrm{M}^{n+},\,\mathrm{M})} + \frac{0.0591}{n} \log\ [\mathrm{M}^{n+}] \quad \ldots(3)$$

Equations (2), (3) and (4) are known as Nernst's equations for a single electrode potential.

[III] Effect of Electrolyte Concentration on Electrode Potential

If the concentration of the electrolyte is increased 10 times then according to equation (3), the electrode potential is increased by $0.0591/n$ volts. Similarly, for every 10^x times increase in electrolyte concentration, the electrode potential will be increased by $0.0591 \times x/n$ volts.

[IV] Sign Convention of Electrode Potential

According to latest convention, the electrode potential is given a positive sign if the electrode reaction involves reduction, when connected to a standard hydrogen electrode and a negative sign if the electrode reaction involves oxidation when connected to a standard hydrogen electrode.

When zinc electrode is connected to a standard hydrogen electrode, oxidation occurs at zinc electrode, so potential *of zinc electrode is negative. But when copper electrode is connected to a* standard hydrogen electrode, reduction occurs at copper electrode, so potential of copper electrode is positive.

(V) Standard Electrode Potential (E°_{el})

As is known, the electrode potential at a given temperature, depends on the concentration of the ions in the solution. If the concentration of the ions is unity and the temperature is 25°C, the potential of the electrode is called *standard electrode potential.*

The magnitude of the standard electrode potential is a measure of the tendency of the half cell reaction to occur in the direction of reduction.

• 11.11. OXIDATION-REDUCTION POTENTIAL

As discussed earlier, oxidation-reduction electrode is only used for those electrodes in which the potential is developed from the presence of ions of the same substance in two different oxidation states. Thus, when an unattackable metal, say Pt wire is inserted into a solution containing Fe^{2+} and Fe^{3+} ions or Sn^{2+} and Sn^{4+} ions, it is seen that the wire acquires a potential. ***The potential at the***

electrode arising from the tendency of the ions in one oxidation state to change into another more stable oxidation state is known as oxidation-reduction potential or redox potential.

In case of Fe^{3+}, Fe^{2+} electrode, the equilibrium is represented as,

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}$$

The oxidation-reduction potential, $E_{(Fe^{3+}, Fe^{2+})}$ is given by,

$$E_{(Fe^{3+}, Fe^{2+})} = E^{\circ}_{(Fe^{3+}, Fe^{2+})} - \frac{RT}{F} \ln \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$= E^{\circ}_{(Fe^{3+}, Fe^{2+})} + \frac{RT}{F} \ln \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

where $E^{\circ}_{(Fe^{3+}, Fe^{2+})}$ is known as standard oxidation-reduction potential.

In general, we can write the elecrode reaction as :

$$\text{Oxidised state} + ne \rightleftharpoons \text{Reduced state}$$

The oxidation-reduction potential (E_{el}) is given by

$$E_{el} = E^{\circ}_{el} - \frac{RT}{F} \ln \frac{[\text{Reduced state}]}{[\text{Oxidised stated}]}$$

or $$E_{el} = E^{\circ}_{el} + \frac{RT}{F} \ln \frac{[\text{Oxidised state}]}{[\text{Reduced stated}]}$$

where, E°_{el} is known as standard oxiation-reduction potential.

When [Reduced state] = [Oxidised state], then $E^{\circ}_{el} = E_{el}$.

So, standard oxidation-reduction or redox potential is defined as the ***oxidaion-reduction or redox potential when the concentrations of oxidised and reduced states are equal.***

• 11.12. REFERENCE ELECTRODES

It is not possible to find the single electrode potential directly. It is only the difference of potentials between two electrodes that we can measure exeperimentally by combining to get a complete cell. If the potential of one electrode is known then that of the other can be calculated. The electrode whose potential is known is termed as ***reference electrode***. Reference electrodes are of two types :

(i) Primary reference electrode and (ii) Secondary reference electrode.

Standard hydrogen electrode is a *primary reference electrode*. But it is not always convenient to set up standard hydrogen electrode. The difficulties involved are in maintaining the concentration of hydrogen ions at unity and in keeping the pressure of H_2 uniformly at 1 atmosphere. The electrode also gets poisoned due to the presence of traces of impurities in hydrogen gas. To overcome this, some other electrodes, called *secondary reference electrodes* are used. These are :

(a) Calomel electrode : It is widely used and can be easily set up. The potential of calomel electrode, on the hydrogen scale, has been measured by connecting it to a standard hydrogen electrode. The value of electrode potential changes with the concentration of KCl solution used. The reduction potentials of different calomel electrodes at 25°C are given below :

(i) Decinormal calomel electrode.

Hg | Hg_2Cl_2 (*s*), 0.1 *N* KCl $E^{\circ} = +0.3335$ volt

(ii) Normal calomel electrode.

Hg | Hg_2Cl_2 (*s*), 0.1 *N* KCl $E^{\circ} = +0.2810$ volt

(iii) Saturated calomel electrode.

Hg | Hg_2Cl_2 (*s*), satd. KCl $E^{\circ} = +0.2422$ volt

Suppose it is required to find the electrode potential of zinc electrode immersed in 0.1 M solution of $ZnSO_4$. The zinc electrode is connected to say decinormal calomel electrode by means of a salt bridge. The cell formed as is shown below*

$$Zn(s) \mid ZnSO_4\ (0.1\ M) \parallel 0.1\ N\ KCl, Hg_2Cl_2\ (s) \mid Hg(l)$$

The E.M.F. of the cell measured experimentally has been found to be 1.0022 volt at 25°C. According to convention,

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*The calomel electrode is written on the left as reduction occurs at this electrode.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cl}}\,(\text{right}) - E^{\circ}_{\text{el}}\,(\text{left})$$

or $$1.0022 = 0.3335 - E^{\circ}_{(\text{Zn}^{2+},\,\text{Zn})}$$

$$E^{\circ}_{(\text{Zn}^{2+},\,\text{Zn})} = 0.3335 - 1.0022 = -\,0.6687 \text{ volt.}$$

∴ Reduction potential of zinc electrode is – 0.6687 volt, at 25°C.

(b) Silver-silver chloride electrode : It consists of a silver wire coated with a layer of silver chloride which is then dipped in a solution of an electrolyte containing chloride ions (*e.g.*, KCl or HCl) of unit concentration. This electrode represented as below has a reduction potential of + 0.2224 volt.

$$\text{Ag} \mid \text{AgCl}\,(s),\, \text{KCl}\,(aq)\,(c = 1)$$

• 11.13. CONCENTRATION CELLS

Concentration cells are those cells in which the electrical energy is produced due to the transfer of a substance from a solution of higher concentration around one electrode to a solution of lower concentration around another electrode.

Concentration cells are of two types as shown below :

(a) Electrode concentration cells or amalgam cells. In this, the extreme electrodes are of different concentrations. This can be achieved by making the solution of metal electrode in mercury (called amalgam) of different concentrations *e.g.*,

$$\text{Zn} - \text{Hg}\,(c_1) \mid \text{ZnSO}_4\,(aq) \mid \text{Zn} - \text{Hg}\,(c_2)$$

When the cell works, the electrode reactions will be :

At left electrode : $\text{Zn} - \text{Hg}\,(c_1) \rightleftharpoons \text{Zn}^{2+}\,(aq) + 2e^-$

At right electrode : $\text{Zn}^{2+}\,(aq) + 2e^- \rightleftharpoons \text{Zn} - \text{Hg}\,(c_2)$

Cell reaction : $\text{Zn} - \text{Hg}\,(c_1) \qquad \text{Zn} - \text{Hg}\,(c_2)$.

The total E.M.F. (E) of the cell is given by,

$$E = \frac{RT}{2F} \log \frac{c_1}{c_2} = \frac{2.303\,RT}{2F} \log_{10} \frac{c_1}{c_2}$$

It means that E.M.F. of the cell is dependent upon the concentration ratio of the two amalgams.

(b) Gas concentration cells. In these cells, the gas electrode is generally made up of gas materical at different concentrations and are dipped in a solution of gas ions. Generally, gases like hydrogen, chlorine etc. are dipped in hydrogen and chloride ions, respectively. The potential of such cells depends on the pressure of the gases and the concentration of their ions in solution.

An example of a gas concentration cell is a cell in which two hydrogen electrodes at partial pressures p_1 and p_2 are dipped in a solution of H^+ ions of concentration C_{H^+} or $[\text{H}^+]$

$\text{Pt, H}_2\,(p_1) \mid \text{Solution of HCl} \mid \text{H}_2\,(p_2)\text{, Pt}$

When the cell works, the following electrode reactions will occur :

At left electrode : $\frac{1}{2}\text{H}_2\,(p_1) \rightleftharpoons \text{H}^+ + e^-$ **(Oxidation)**

At right electrode : $\text{H}^+ + e^- \rightleftharpoons \frac{1}{2}\text{H}_2\,(p_1)$ **(Reduction)**

Cell reaction : $\frac{1}{2}\text{H}_2\,(p_1) \rightleftharpoons \frac{1}{2}\text{H}_2\,(p_2)$

So, the electrical energy is produced due to the transfer of hydrogen gas at pressure p_1 to pressure p_2.

The total E.M.F. (E) of the cellis given by,

$$E = \frac{2.303\,RT}{2F} \log_{10} \frac{p_1}{p_2}$$

(c) Electrolyte concentration cells. These type of cells are further divided into two types:

(a) Concentration cells without transport or transference : In such cells, there is no direct transfer of electrolytes from one solution to another. The transfer occurs due to the result of chemical reaction. In general,

"A concentration cell without transport can be constructed if two simple cells with electrodes reversible with respect to each of the ions constituting the electrolyte are oppositely combined."

Consider one cell in which the electrodes are reversible with respect to H^+ and Cl^- ions, as

H_2 (1 atm) | HCl (c_1), AgCl (s) | Ag (s)

When the cell woks, the hydrogen at LHE dissolves to form H^+ ions, whereas silver is deposited from silver chloride at RHE, *i.e.*,

Left hand electrode : $\frac{1}{2}H_2\,(1\text{ atm}) \rightleftharpoons H^+(c_1) + e^-$

Right hand electrode : $AgCl\,(s) + e^- \rightleftharpoons Ag\,(s) + Cl^-(c_1)$

Cell reaction :

$$\frac{1}{2}H_2\,(1\text{ atm}) + AgCl\,(s) \rightleftharpoons H^+(c_1) + Ag\,(s) + Cl^-(c_1) \rightleftharpoons HCl\,(c_1) + Ag\,(s)$$

The total E.M.F. (E) if such a cell is given by

$$E = \frac{RT}{F}\log_e\frac{c_2}{c_1} = \frac{2.303\,RT}{F}\log_{10}\frac{c_2}{c_1} \qquad ...(3)$$

As $c_2 > c_1$, there occurs a transfer of elecrolyte from concentrated to dilute solution.

(b) Concentration cell with transport or transference : In such cells, the liquid junction potential between the junction of two solutions is taken into consideration.

H_2 (1 atm) | HCl (c_1) $\vdots$ HCl (c_2) | H_2 (1 atm)

The two solutions of HCl are in direct contact wih each other and so there is a direct transfer of HCl from more concentrated solution (c_2) to the less concentrated solution (c_1). In general,

"When two solutions of the elecrolyte of two concentrations are placed together and an electrode reversible with respect to one of the ions of electrolyte is dipped in each solution, we get a concentration cell with transport."

In the above notation, the dotted line shows a liquid junction potential. The electrode reactions will be :

At left electrode : $\frac{1}{2}H_2 \rightleftharpoons H^+\,(c_1) + e$

At right electrode : $H^+\,(c_2) + e \rightleftharpoons \frac{1}{2}H_2$

Cell reaction : $H^+\,(c_2) \rightleftharpoons \frac{1}{2}H_2 + (c_1)$ ...(1)

From the above, it follows that electrons will flow from left ot right. As the current is constituted by H^+ and Cl^- ions, it means and H^+ ions are moving from left to right and Cl^- ions are moving from right to left.

The total E.M.F of such a cell is given by,

$$E = (2\nu_a + \nu_c)\,t_a \cdot \frac{2.303RT}{F}\log\frac{c_2}{c_1}$$

where ν term indicates the number of respective ion.

• 11.14. APPLICATIONS OF CONCENTRATION CELLS

[I] Determination of Solubility of Sparingly Soluble Salts

Suppose the solubility of AgCl is to be measured, then the following cell is constructed.

Ag | AgCl (s), 0.1 M KCl (aq) || 0.1 M $AgNO_3$ ((aq) | Ag

$[Ag^+] = C$ $\qquad$ $[Ag^+] = 0.1$

The salt bridge shown by || consists of a saturated solution of KNO_3 or NH_4NO_3. The cell is set up by dipping one of the silver electrodes in 0.1M solution of $AgNO_3$ and the other in 0.1 M KCl solution and the two solutions are connected through a salt bridge. A drop of silver nitrate solution is added to KCl solution. The small amount of silver chloride formed is sufficient to obtain its saturated solution.

The above concentration cell is reversible with respect to silver ions. One Ag electrode is in contact with Ag^+ ions of known concentration (0.1M), assuming silver nitrate to be completely ionised, while the other Ag electrode is in contact with a much lower unknown concentration of Ag^+ ions (given by the ionisation of sparingly soluble AgCl). The E.M.F. of the cell at 25°C is given by,

$$E = \frac{2.303\,RT}{nF}\log\frac{[\mathrm{Ag}^+]_r}{[\mathrm{Ag}^+]_l}$$

or $$E = 0.0591\log\frac{0.1}{C}, \text{ at } 25°\mathrm{C}$$

where, C is unknown concentration of silver ions given by AgCl. Knowing the value of E, we can calculate C. As the concentration of chloride ions is 0.1, the solubility product of AgCl is given by,

$$K_s\,(\mathrm{AgCl}) = [\mathrm{Ag}^+]\,[\mathrm{Cl}^-] = C \times 0.1$$

The solubility (S) of AgCl is then given by,

$$S = \sqrt{K_s}\,(\mathrm{AgCl}) \text{ moles/litre}$$
$$= \sqrt{K_s}\,(\mathrm{AgCl}) \times 143.5 \text{ g/litre}$$

($\because$ Molecular weight of AgCl = 143.5).

[II] Determination of Valency of Ions

The valency of doubtful ions can be established by E.M.F. measurements, *e.g.*, the valency of mercurous ion was established by setting and determining the E.M.F. of the following concentration cell.

Hg	Mercurous nitrate (aq) C_1	NH_4NO_3 Salt bridge	Mercurous nitrate (aq) C_2	Hg

The E.M.F. of the cell is given by,

$$E = \frac{RT}{nF}\ln\frac{C_2}{C_1}$$

where n = valency of mercurous ion and $C_2 > C_1$.

At 25°C $$E = \frac{0.0591}{n}\log\frac{C_2}{C_1}$$

When $C_2/C_1 = 10$, the E.M.F. was found to be 0.0295 volt. So, $n = 2$ and thus mercurous ion may be represented as Hg_2^{++}.

[III] Determination of pH value

(1) By using hydrogen electrode. The potential of a hydrogen electrode in contact with a solution of H^+ ions which involves the reaction.

$$\mathrm{H}^+ + e \rightleftharpoons \frac{1}{2}\mathrm{H}_2\,(1 \text{ atm})$$

is given by,

$$E_{(\mathrm{H}^+,\,\mathrm{H}_2)} = E^\circ_{(\mathrm{H}^+,\,\mathrm{H}_2)} + \frac{RT}{F}\ln[\,\mathrm{H}^+\,] \qquad (\because\ n = 1)$$

At 25°C, $$E_{(\mathrm{H}^+,\,\mathrm{H}_2)} = E^\circ_{(\mathrm{H}^+,\,\mathrm{H}_2)} + 0{\cdot}0591\log[\mathrm{H}^+]$$

By convention, $E^\circ_{(\mathrm{H}^+,\,\mathrm{H}_2)} = 0$, so the last equation becomes

$$E_{(\mathrm{H}^+,\,\mathrm{H}_2)} = 0{\cdot}0591\log[\mathrm{H}^+] = -0{\cdot}0591\text{ pH}$$

Thus, the potential of a hydrogen electrode depends on the pH value of the solution with which it is in contact. Thus, pH of a solution can be determined by combining a hydrogen electrode with calomel electrode (reference electrode), to get the following cell.

$$\mathrm{Pt, H_2(1\ atm)}\ |\ \mathrm{H^+}\ (c = \text{unknown})\ \|\ 0.1\ N\ \mathrm{KCl}(aq), \mathrm{Hg_2Cl_2}(s)\ |\ \mathrm{Hg}$$

The E.M.F. of the cell is determined potentiometrically and is given by,

$$E_{\text{cell}} = E_{\text{el}}\text{ (right)} - E_{\text{el}}\text{ (left)}$$

or E_{cell} = Reduction potential of right electrode – Reduction potential of left electrode

$$E_{\text{cell}} = +\,0{\cdot}3335 - (-\,0{\cdot}0591\text{ pH})$$

or $$0{\cdot}0591\text{ pH} = E_{\text{cell}} - 0{\cdot}3335$$

or $$\text{pH} = \frac{E_{\text{cell}} - 0{\cdot}3335}{0{\cdot}0591}$$

or $$\text{pH} = \frac{E_{\text{cell}} - \text{Reduction potential of calomel electrode}}{0.0591}$$

Hydrogen electrode can be used over entire pH range, but it cannot be used in solution containing strong reducing agents or in presence of reducible ions, having positive electrode potentials, *e.g.*, Cu, Ag, Au etc.

(2) By using quinhydrone electrode. Quinhydrone electrode is preferred over H_2 electrode, as it can be set up easily by simply adding a pinch of quinhydrone to the unknown solution and dipping a clean platinum electrode to make electrical contact. Quinhydrone is an equimolecular compound of quinone (Q) and hydroquinone (QH_2), *i.e.*,

$$\underset{\text{Quinhydrone}}{C_6H_4O_2 \,.\, C_6H_4(OH)_2} \rightleftharpoons \underset{\text{Quinone (Q)}}{C_6H_4O_2} + \underset{\text{Hydroquinone }(QH_2)}{C_6H_4(OH)_2}$$

The quinone-hydroquinone system involves the following equilibrium :

$$\underset{Q}{C_6H_4O_2} + 2H^+ + 2e^- \rightleftharpoons \underset{QH_2}{C_6H_4(OH)_2}$$

The electrode potential is given by,

$$E_{(H^+,\,Q,\,QH_2)} = E^{\circ}_{(H^+,\,Q,\,QH_2)} + \frac{2.303\,RT}{2F}\log\frac{[Q][H^+]^2}{[QH_2]}$$

$$= E^{\circ}_{(H^+,\,Q,\,QH_2)} + \frac{2.303\,RT}{2F}\log\frac{[Q]}{[QH_2]} + \frac{2.303\,RT}{F}\log[H^+] \qquad \ldots(1)$$

QH_2 is a weak acid and its ionisation is very small, so if the pH is less than 7, the concentration of QH_2 is the same as that of Q *i.e.*, $[Q]/[QH_2] = 1$. So, from (1), at 25°C

$$E^{\circ}_{(H^+,\,Q,\,QH_2)} = E^{\circ}_{(H^+,\,Q,\,QH_2)} + 0.0591\log[H^+]$$

or $$E^{\circ}_{(H^+,\,Q,\,QH_2)} = E^{\circ}_{(H^+,\,Q,\,QH_2)} - 0.0591\text{ pH}$$

or $$E_{(H^+,\,Q,\,QH_2)} = +0.6996 - 0.0591\text{ pH} \qquad \ldots(2)$$

($\because$ Standard reduction potential of quinhydrone electrode = + 0.6996 volt)

Thus, the potential of quinhydrone electrode depends upon the pH of the solution. It may be connected with a calomel electrode (reference) to get the following complete cell.

$$\text{Hg} \mid Hg_2Cl_2\,(s),\ 0.1\text{ N KCl}\,(aq) \parallel H^+\text{ (unknown conc.)},\qquad Q, QH_2 \mid \text{Pt}$$

The E.M.F. of the cell is given by,

E_{cell} = Reduction potential of R.H. electrode – Reduction potential of L.H. electrode

$$E_{\text{cell}} = [0.6996 - 0.0591\text{ pH}] - [+0.3335]$$

or $$\text{pH} = \frac{0{\cdot}6996 - 0{\cdot}3335 - E_{\text{cell}}}{0.0591}$$

or $$\text{pH} = \frac{\text{Red. potential of quinhydrone electrode} - \text{Red. potential of calomel electrode} - E_{\text{cell}}}{0.0591}$$

Quinhydrone electrode cannot be used for solutions having pH greater than 8, because hydroquinone ionises considerably as an acid and also gets oxidised partly by atmospheric oxygen.

(3) By using glass electrode. Glass electrode can usually be used for pH between 0 and 9 even in presence of strong oxidising agents. It is easy to operate.

It is seen that a difference of potenial is developed at the interface between glass and a solution containing H^+ ions, the magnitude of which depends on the concentration of H^+ ions. At 25°, it is given by,

$$E_G = E^{\circ}_G + 0.0591\log[H^+]$$

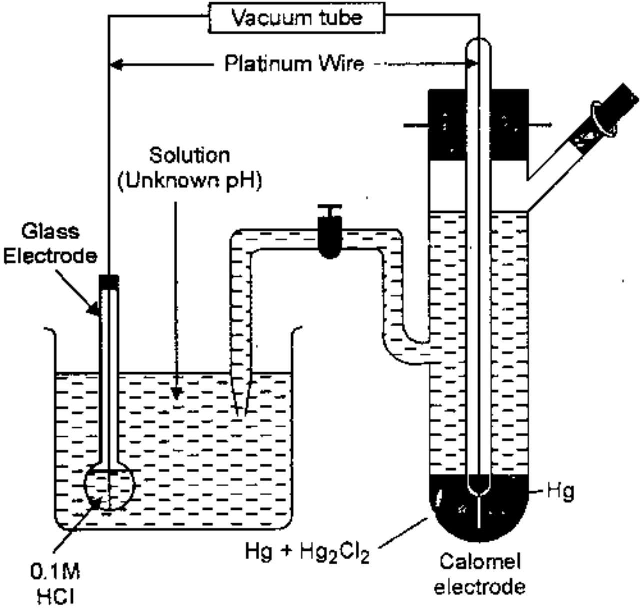


Fig. 4. Determination of pH by glass electrode

or $$E_G = E_G^o - 0.0591 \text{ pH}$$

E_G^o is constant for a given glass electrode. The electrode involves the reduction of H^+ ions.

The glass electrode (Fig. 4) is made of special glass of low melting point and high electrical conductivity. It is blown into a bulb and then sealed to the bottom of a glass tube. A solution of 0.1 *N* HCl is placed inside the bulb (0.1 *N* HCl gives a constant H^+ ion concentration). A platinum wire or Ag–AgCl electrode is dipped to make elecrical contact. The glass elecrode is then connected with a calomel electrode to get the following complete cell.

$$\text{Hg} \mid Hg_2Cl_2\,(s),\ 0.1\ \text{N KCl}(aq) \parallel \text{Experimental solution} \mid \text{Glass} \mid \quad 0.1\ N\ \text{HCl}\ (aq)\ \text{Pt}$$

The E.M.F. of the cell is measured by means of a potentiometer and is given by,

$$E_{cell} = \text{Reduction potential of R.H. electrode} - \text{Reduction potenial of L.H. electrode}$$

$$E_{cell} = [E_G^o - 0.0591 \text{ pH}] - [+0.3335]$$

or $$\text{pH} = \frac{E_G^o - 0.3335 - E_{cell}}{0.0591} \qquad \ldots(1)$$

$$\text{pH} = \frac{\text{Red. potential of glass electrode} - \text{Red. potential of } \textit{calomel electrode} - E_{cell}}{0.0591}$$

The value of E_G^o is first obtained by working with solutions of known pH values. So, the value of pH can be calculated from equation (1).

• SUMMARY

- Salt hydrolysis is the process in which a salt reacts with water to form either an acidic or alkaline solution.
- Salts of strong acids and strong bases do not hydrolyse as they form neutral solutions. The pH of such solutions is 7.
- The product of the concentration of H^+ and OH^- ions in pure water is known as ionic product of water (K_W) at that temperature. Its value is nearly 1.0×10^{-14} at 25°C.
- The pH of a solution is numerically equal to the negative power to which 10 must be raised in order to express the hydrogen ion concentration, *i.e.*, if $[H^+] = 10^{-x}$, then pH = x.
- The pH of an acid, alkali and neutral solution will be less than 7, greater than 7 and 7, respectively.
- A solution with reserve acidity and reserve alkalinity is known as a buffer solution.
- *Buffer mixture is generally a mixture* of weak acid and a salt of it with a strong base, *e.g.*, $CH_3COOH + CH_3COONa$. It can also be a mixture of weak base and a salt of it with a stong acid, *e.g.*, $NH_4OH + NH_4Cl$.
- The pH of a buffer solution is given by Henderson-Hassel equation, *i.e.*,

$$\text{pH} = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \qquad \text{[For acidic buffer solution]}$$

$$\text{pOH} = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \qquad \text{[For basic buffer solution]}$$

- A cell in which electrical energy is produced due to a chemical reaction is known as an electrochemical cell.
- A galvanic cell is a device which converts chemical energy or potential energy into electrical energy due to a redox reaction.
- A cell is said to be thermodynamically reversible if it sends out infinitesimally small current so that the cell reaction always remain virtually in an equilibrium state.
- The tendency of an electrode to lose or gain electrons, when it is brought in contact with its own ions in solution is known as single electrode potential.
- When the concentration of the ions is unity and the temperature is 25°C, the electrode potential is known as standard electrode potential.
- Hydrogen electrode and calomel electrode are used as reference electrodes.
- Concentration cells are used to determine the solubility of sparingly soluble salts, pH of solution etc.

- The pH of a solution can be determined by using glass electrode, hydrogen electrode, quinhydrone electrode etc.

• STUDENT ACTIVITY

1. Explain why NaCl does not hydrolyse ?

2. Explain the buffer action.

3. Define electrochemical cell and galvanic cell.

4. Explain calomel electrode.

5. Define standard electrode potential.

• TEST YOURSELF

1. Explain the term hydrolysis. Explain the phenomenon by taking :
(a) Salts of strong acid and weak base
(b) Salts of weak acid and strong base
(c) Salts of weak acid and weak base.
2. Explain why salts of strong acid and strong base do not hydrolyse ?
3. Explain the term pH. How it is determined by using an electrode ?
4. State and explain buffer solutions. Describe the types of buffers and the buffer action.
5. Derive an equation for the determination of pH of a buffer solution.
6. Explain the following terms :
(i) Electrochemical cells (ii) Electrode reactions (iii) Cell reaction
(iv) Oxidation and reduction electrode (v) Reversible and irreversible cells
(vi) Oxidation-reduction potential (vii) Reference electrodes
(viii) Hydrogen electrode (ix) Calomel electrode (x) Galvanic cells
7. What are reversible electrodes ? Explain the different types of reversible electrodes.
8. Derive Nernst's equation for E.M.F. of a reversible cell.
9. State and explain single electrode potential. How it is determined ? Derive Nernst equation for a single electrode potential.
10. What is the effect of electrolyte concentration on single electrode potential ?
11. What are concentration cells ? Classify them.
12.

How concentration cells are used to determine :
(i) Solubility of a sparingly soluble salt
(ii) Valency of an ion
(iii) pH of a solution.

13. Write short notes on the following :
(i) Glass electrode (ii) Quinhydrone electrode (iii) Hydrogen electrode

14. The pH of 0.05 N solution of HCl is :
(a) 0.5 (b) 1.3 (c) 3.0 (d) 5.0

15. Which of the following salts when dissolved in water will hydrolyse?
(a) NaCl (b) KCl (c) NH_4Cl (d) Na_2SO_4

16. When 0.4 g NaOH is dissolved in 1 litre of solution, the pH is :
(a) 2 (b) 6 (c) 10 (d) 12

17. The pH of 10^{-8} M solution of HCl in water is :
(a) 8 (b) – 8 (c) Between 7 and 8 (d) Between 6 and 7

18. The pOH of a solution is 5, the H^+ ion concentration will be :
(a) 10^4 (b) 10^{10} (c) 10^{-4} (d) 10^{-10}

19. Which of the following is a buffer solution ?
(a) KOH + KCl (b) $HNO_3 + NaNO_3$
(c) HCl + NaCl (d) Basic acid + Borax

20. Fill in the blanks :
(i) The cathode is the electrode at which —occurs
(ii) The anode is the electrode at which — occurs.
(iii) In a galvanic cell — energy is generated at the expense of —energy.
(iv) In an electrolytic cell the—energy is generated at the expense of—energy.
(v) In a redox system, the potential when the oxidised and reduced forms have the same concentration is known as—potential.
(vi) In the cell, $H_2 \mid H^+ \| 0.1\ N\ AgNO_3 \mid Ag$

the anode is on the—side, while the cathode is on the—side.

ANSWERS

14. (b) **15.** (c) **16.** (d) **17.** (d) **19.** (d)
20. (i) Reduction (ii) Oxidation (iii) Electric, chemical (iv) Chemical, electric
(v) Standard, redox (vi) Left, right.

❑❑❑

UNIT

12

SPECTROSCOPY

LEARNING OBJECTIVES

- Introduction
- Electromagnetic Radiations
- Regions of Spectrum
- Ultraviolet Spectroscopy
- Rotational Spectrum
- Infrared Spectrum
- Vibrational Spectrum
- Raman Spectrum
  - ☐ Summary
  - ☐ Student Activity
  - ☐ Test Yourself

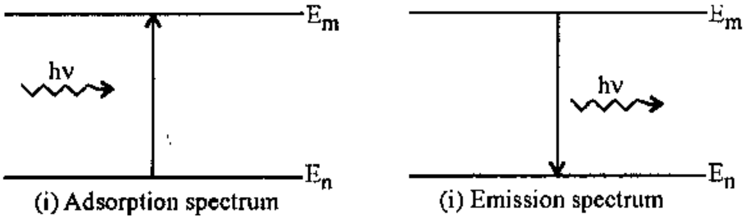
• 12.1. INTRODUCTION

In organic chemistry, the most commonest and most important job is to determine the structural formula of a compound just synthesised or isolated from a natural source. The compound will fall into one of the two groups though at first we shall not know which group? It will be either (i) a previously reported compound, which we must identify or (ii) a new compound, whose structure we must prove.

If the compound has already been reported by some other chemists, then a description of its properties will be found somewhere in the chemical literature. We then have to show that the compound prepared is identical with the one previously described. If, on the contrary, our compound is a new one that has never before been reported then we must carry out a much more elaborate proof of its structure. To carry out our investigations, we first purify the compound and determine its physical properties like melting point, boiling point, density, refractive index and solubility in different solvents. In the laboratory today, we would measure various spectra of the compound, in particular, the infrared spectrum and the NMR spectrum because spectroscopic examination gives us a wealth of informations.

Spectroscopy is a technique ***which deals with the transitions that a molecule undergoes between its energy levels upon absorption of suitable radiations determined by quantum mechanical selection rules.***

Quantum mechanics tells us that the energy levels of all systems are quantized which are given by suitable quantum numbers. These energy levels are obtained by solutions of the time-independent Schrödinger wave equation. We now consider how a spectrum arises ? In figure (1), the two molecular energy levels are shown as E_n and E_m. If a photon of frequency ν falls on a molecule in the ground state and its energy $h\nu$ is exactly equal to the energy difference ΔE $(= E_m - E_n)$ between the two molecular energy levels, then the molecule undergoes a transition from the lower energy level to a higher energy level due to absorption of a photon of energy, $h\nu$. The spectrum thus obtained is known as **absorption spectrum**. If on the contrary, the molecule undergoes a transition from the excited energy level to the ground state with the emission of a photon of energy, $h\nu$, the spectrum thus obtained is known as **emission spectrum**.



(i) Adsorption spectrum (i) Emission spectrum

Fig. 1. Spectroscopic transitions between molecular energy levels.

The instruments most directly concerned with our primary interest, molecular structure, are the *spectrometers*–measures of spectra. The spectroscopic methods have several advantages over the classical methods of analysis which are as follows :

(a) Spectroscopic methods take much less time.

(b) For spectroscopic analysis, only a very small amount of the substance, say 1 mg or even less, is sufficient.

(c) The substances remain generally unaffected or unchanged during spectroscopic examination and can be re-used for other tests, if required.

(d) *The spectroscopic methods are comparatively much reliable in establishing the structure* and identity of a compound.

Table 1 : Symbols used in spectroscopy

Symbol	Definition
ν	Frequency in Hz (cycles per second)
λ	Wavelength
μ	Micrometre, as micron (μ), 10^{-6} m
nm	Nanometre, as millimicron (mμ), 10^{-9} m
Å	Angstrom, 10^{-10} m or 10^{-1} nm
cm^{-1}	Wave number, Frequency in reciprocal cm or $\frac{1}{\lambda} = \text{cm}^{-1}$

• 12.2. ELECTROMAGNETIC RADIATIONS

We are already familiar with different kinds of electromagnetic radiation of light (visible, *ultraviolet, infrared*), *X-rays, radio* and *radar waves*. These are simply different parts of a broad spectrum that stretches from gamma rays, whose wavelengths are measured in fractions of an angstrom, to radiowaves, whose wavelengths are measured in metres or even kilometres. All these have the same velocity, 3×10^{10} centimetre per second.

Mathematically, wavelength (λ) of a radiation is related to its frequency (ν) by the expression $\lambda = \frac{c}{\nu}$, where c is the velocity of the radiation and is equal to 3×10^{10} cm/sec. As λ and ν are inversely related to each other, the shorter the wavelength, the higher the frequency and vice-versa.

Table 2 : Wavelength of electromagnetic radiations

Radiation	Wavelength (Å)		
Cosmic rays	Zero	to	0.001
Gamma rays	0.001	to	0.1
X-Rays	0.1	to	150
Ultraviolet rays	150	to	3800
Visible rays	3800	to	7600
Infrared rays	7600	to	6×10^6
Microwaves	6×10^6	to	3×10^9
Radiowaves	3×10^9	to	3×10^{13}

When a beam of electromagnetic radiation is passed through a substance, the radiation can be either absorbed or transmitted, depending upon its frequency and the structure of the molecules it encounters. Electromagnetic radiation is energy, and so when a molecule absorbs radiation, it gains energy. Just how much energy it gains, depends upon the frequency of the radiation. The higher the frequency (the shorter the wavelength) the greater the gain in energy. The gain in energy (ΔE) and frequency of radiation are connected by the following relation

$$\Delta E = h\nu$$

where h is Planck's constant (6.626×10^{-27} erg sec). As ΔE and ν are directly related, radiation with higher frequency (or shorter wavelength) leads to a greater gain in energy. In other words, the shorter the *wavelength of a radiation, the more energetic it is.*

Units to Express Wavelengths of Radiations

The units commonly used to express the wavelengths of ultraviolet, visible and infrared radiations are Greek symbols, **micron** (μ) and **millimicron** ($m\mu$).

$$1\mu = 1000\ \text{m}\mu = 10^{-4}\ \text{cm}.$$

Occasionally, the unit **Angstrom** (Å) is used to denote especially ultraviolet and visible radiations.

$$1\ \text{Å} = 0.1\ \text{m}\mu = 10^{-4}\ \mu = 10^{-8}\ \text{cm}.$$

More recently, the wavelength of ultraviolet and visible radiations are expressed in **nanometres (nm).**

$$1\ \text{nm} = 1\ \text{m}\mu = 10^{-3}\mu = 10\ \text{Å}.$$

The frequency is usually expressed in **Hertz** (Hz), or cycle/second.

$$1\ \text{Hz} = 1\ \text{cycle/second}.$$

Sometimes, molecular spectra are expressed in frequency units which are **reciprocal centimetres** (cm^{-1}). A reciprocal centimetre shows the number of wavelengths per centimetre and is known as **wave number** ($\bar{\text{v}}$).

Wavelength in μ units can be converted into wave numbers (cm^{-1}) by the following expression:

$$\text{Wave number } (\text{cm}^{-1}) = \frac{10^4}{\lambda\ (\text{in } \mu)}$$

The approximate range of wavelengths, frequencies and energies of different types of radiations are given in table 3.

Table 3

Types of radiation	Wavelength (Å) (Upper limit)	Frequency (Hz or s^{-1})	Energy (kJ mol^{-1})
Cosmic rays	0.001	3×10^{21}	1.2×10^9
Gamma rays	1	3×10^{16}	1.2×10^6
X-rays	150	2×10^{16}	8.98×10^3
Ultraviolet	38.0	7.9×10^{14}	3.16×10^2
Visible	7600	3.95×10^{14}	1.58×10^2
Infrared	6×10^6	5×10^{11}	1.99×10^{-1}
Microwaves	3×10^9	10^9	3.99×10^{-4}
Radiowaves	3×10^{13}	10^5	3.99×10^{-8}

• 12.3. REGIONS OF SPECTRUM

[I] Origin and Regions of Electronic Spectra

Electronic spectra can be classified into two types, viz., emission spectra and absorption spectra.

(a) Emission spectra : When a substance is subjected to a large amount of heat or to an electric discharge, its atoms or molecules absorb energy and are excited. When these excited species return to their ground state, they may emit radiation which on passing through a prism gives rise to a spectrum, known as **emission spectrum**. If such a spectrum is recorded on a photographic plate, the atoms in it appear as bright lines on a dark background, and that of molecule appear as bands.

(b) Absorption spectra : If we place a coloured substance between the prism and the source of light, a portion of the light in the continuous spectrum may be absorbed and we get black bands. If, for example, a sodium flame is placed between white light source and the prism, the continuous spectrum of white light is crossed by two dark lines in the yellow region. If white light source is now removed, the whole of continuous spectrum disappears leaving behind only two bright yellow lines occupying the position of the two dark lines in the former case. These dark lines are called ***absorption line spectrum*** or simply ***absorption spectrum.***

During absorption, some of the molecules in the path of incident light collide with photons of radiant energy. However, only those photons get absorbed whose energy exactly equals the difference in energy, ΔE between the ground and excited states of the molecules.

[II] Types of Absorption Spectra

The internal energy of a molecule may be considered to be the sum of electronic, vibratioal, rotational and translational energies, *i.e.*,

$$E_{\text{internal}} = E_{\text{elect}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{trans}}$$

Translational energy is not quantized so it is negligibly small and we can neglect it, hence

$$E_{\text{internal}} = E_{\text{elect}} + E_{\text{vib}} + E_{\text{rot}}$$

(1) Ultraviolet (UV) spectroscopy : For each electronic level within the molecule there is an energy separation of nearly 10^5 cal mole^{-1}. Therefore, electronic excitation requires energetic photons of $\lambda \sim 286$ nm from ultraviolet range (200-400 nm). This is called *ultraviolet (UV) spectroscopy.*

(2) Infrared (IR) spectroscopy : We find a number of associated vibrational levels between two successive electronic levels X and Y, the energy separation between the former levels is one tenth to a hundredth of that between X and Y. Further, each vibrational level is associated with a set of rotational states and the energy separation is of the order of a hundredth of that between two vibrational levels.

Photons from IR range (2000 to 20,000 nm) possess sufficient energy to excite the molecule from one vibrational level to another. In IR spectroscopy, the radiation absorbed produce *stretching* and *bending* of organic bonds.

(3) Nuclear magnetic resonance (NMR) spectra : The wavelength of radiations absorbed by atomic nuclei are under the influence of strong magnetic fields. Thus, NMR spectra span the radio-frequency regions, *viz.*, 5–100 MHz which induce transitions between the nuclear spin energy levels of a molecule.

• 12.4. ULTRAVIOLET SPECTROSCOPY

Ultraviolet spectroscopy is a technique which is at present commonly used in the detection of impurities in organic compounds. It is also employed in determining the molecular weights, dissociation constants of acids and bases, in the study of kinetics of certain reactions in the ultraviolet range.

The ultraviolet range can be divided into two spectral regions :

(i) The region between 2000 to 4000Å which is known as *near ultraviolet region.*

(ii) The region below 2000Å which is known as *far* or *vacuum ultraviolet region.*

As already mentioned, the wavelengths in the UV region is expressed in nanometre (1 nm = 10^{-7} cm) or angstrom (1 Å = 10^{-8} cm). The absorption is generally expressed in wave numbers ($\bar{\nu} = \text{cm}^{-1}$).

This spectroscopic technique is not useful below 200 mμ because in this region absorption occurs by oxygen and nitrogen. To study absorption below this region, the whole path length is evacuated. Hence, this region is called vacuum ultraviolet region.

[I] Origin and Theory of Ultraviolet Spectra

The ultraviolet absorption spectrum occurs due to transition of electron within a molecule or an ion from a lower to a higher electronic energy level. The ultraviolet emission spectra occurs due to the reverse type of transition. If the radiation is to cause electronic excitation, it must be in the ultraviolet region of the electromagnetic spectrum.

If a molecule after absorbing ultraviolet radiation of frequency ν sec^{-1}, undergoes transition from a lower to a higher energy level, the energy difference is given by $\Delta E = h\nu$ erg, where h is Planck's constant.

The actual amount of energy required depends on the difference in the energy between the ground state E_1 and excited state E_2 of the electrons. The above equation now becomes, $E_2 = E_1 = h\nu$.

The spectra of simple molecules in the gaseous state have narrow absorption peaks, where each peak represents a transition from a particular combination of vibrational and rotational levels in the electronic ground state to a corresponding combination in the excited state. In ultraviolet range, the absorbed energy produces changes in the valency electrons of the molecules. The electrons involved in organic molecules are as mentioned below :

(i) π-Electrons : These electrons are involved in unsaturated hydrocarbons. Some typical compounds containing π-bonds are trienes and aromatic compounds.

(ii) σ-Electrons : These electrons are involved in saturated bonds between carbons and hydrogens as in paraffins. These bonds are also known as σ-bonds. The amount of energy required to excite electrons in σ-bonds is much more than that produced by ultraviolet light. Compounds containing such bonds, therefore, do not absorb ultraviolet radiation. For this reason, paraffin compounds are usually used as solvents.

(iii) n-Electrons : These electrons are not involved in bonding between atoms in the molecules, *e.g.*, organic compounds containing nitrogen, oxygen, sulphur or halogens. As n-electrons can be excited by ultraviolet radiation, any compound containing nitrogen, oxygen, sulphur or halogens or unsaturated hydrocarbons may absorb ultraviolet radiations.

[III] Components of Ultraviolet Spectrometer

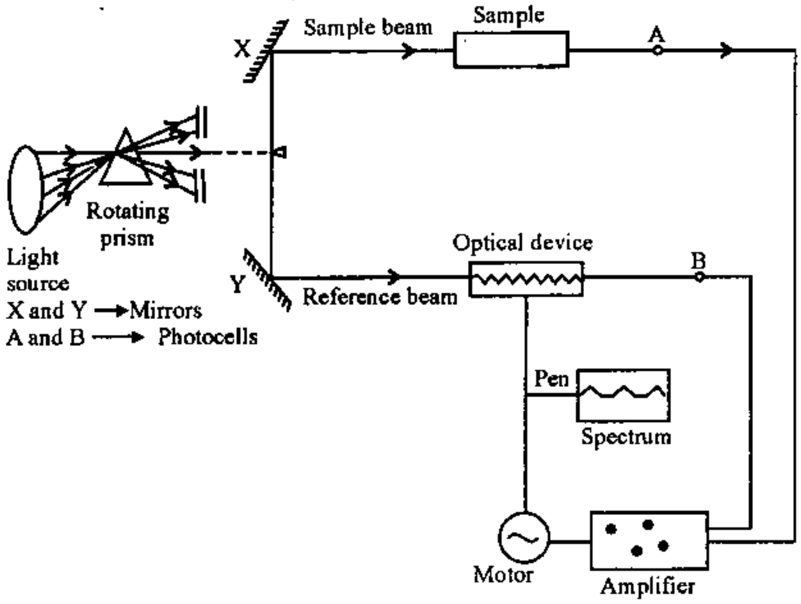


Fig. 2. UV spectrophotometer

The main components of an ultraviolet spectrophotometer (Fig. 2) are mentioned below :

(1) Radiation source : Generally, a hydrogen-discharge lamp is the source for ultraviolt radiations (200-400 nm), while a tungsten filament lamp is commonly used to produce visible radiations (400-800 nm).

(2) Monochromator : It is used to disperse radiation according to a desired wavelength.

(3) Sample cells : These cells are used to contain samples for analysis. A cell is made up of that material which does not absorb light in the region being studied. Generally, quartz cells are used in the ultraviolet and visible regions.

(4) Detectors : Generally, barrier layer cell, photocell, photo multiplier tube are used.

(5) Recording system : The unknown compound is first dissolved in a suitable solvent at a proper concentration. The solution is then placed in a suitable cell. An identical cell containing only the solvent is used at the same time to serve as the control cell. The cell containing the sample is then exposed to UV or visible radiation of appropriate wavelength. The instruments are so designed that they directly measure the optical density of the solution at the desired wavelength. The wavelength of radiation is then changed, and a new value of optical density is measured. In this way, a number of values of optical density are recorded over a range of wavelengths. A graph is plotted between wavelengths as abscissa and optical density readings (or molar extinction coefficients, ε, as optical density = $\varepsilon, c \,.\, l$) as ordinate. The resulting graph is known as *ultraviolet spectrum*, which may consist of one or more broad peaks or humps. The wavelength corresponding to the top of the peak is taken to be the value of λ_{max}. The values of λ_{max} and ε at the wavelength are shown, while giving UV spectral data of a compound.

In a self recording spectrophotometer, the plotting of graph is done automatically by the movement of a pen on a chart.

[III] Applications of Ultraviolet Spectroscopy

Some important applications of ultraviolet spectroscopy are as follows :

(1) Qualitative analysis : Identification of compounds can be done by comparing absorption spectrum with known compound. A curve is plotted between wavelengths (λ) and degree of absorption (ε).

(2) Quantitative analysis : The technique is also used for quantitative analysis of compounds. This is based on Beer's law. In the determination of concentration of an unknown compound, wavelength of maximum absorption for compound is selected. Then optical densities are measured for some known compounds. Now the optical density is plotted against concentration of solute over a range of concentrations. A straight line is obtained and from this graph, the concentration of unknown solution is evaluated.

(3) Chemical kinetics : The technique is helpful for studying the kinetics of a reaction. Here change in concentration of either a reactant or product with time is measured. As absorbance is proportional to concentration, so this technique can be used to follow the course of a reaction.

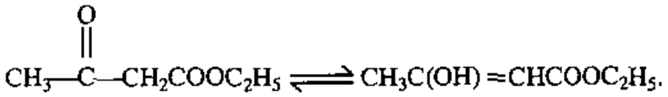
(4) Molecular weight determination : Molecular weights of compounds can easily be determined by this technique provided suitable derivatives of these compounds could be prepared.

Take a picrate and change it into aminopicrate. A known concentration of it is dissolved in one litre of solution and its optical density measured at $\lambda_{max} = 380$ nm. The concentration c is determined by the formula

$$c = \frac{\log \frac{I_0}{I_t}}{\varepsilon_{max} \times l}$$

From this, c is calculated. The weight w of aminopicrate is known. From c and w, molecular weight of aminopicrate can be calculated. From it, the molecular weight of parent compound can be determined.

(5) Tautomeric equilibrium : The technique has been proved very helpful in determining the percentages of keto and enol forms in tautomeric equilibrium. Take an example of ethyl acetoacetate.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2COOC_2H_5 \rightleftharpoons CH_3C(OH)=CHCOOC_2H_5.$$

The keto form has $\lambda_{max} = 275$ nm and $\varepsilon = 16$, while enol form has $\lambda_{max} = 244$ *nm and* $\varepsilon = 16000$.

From strength of 244 nm band, we can measure proportions of tautomers present in ethyl acetoacetate.

(6) Detection of impurities : The impurities present in organic compounds can easily be detected by UV absorption spectroscopy. The main reasons for the superiority of this method are :

(i) The bands due to impurities are very intense.

(ii) The organic compounds can be classified into saturated compounds having little absorption, while the unsaturated compounds have strong absorption bands.

• 12.5. ROTATIONAL SPECTRUM

[I] Rotational Energy of a Diatomic Molecule

On the basis of wave mechanics, it can be seen that if a *diatomic molecule is considered* to be a rigid rotator, *i.e.*, like a rigid dumb bell joined along its line of centres by a bond equal in length to the distance r_0 between the two nuclei (Fig. 3), then the allowed rotational energy of the molecule around the axis passing through the centre of gravity and perpendicular to the line joining the nuclei is given by

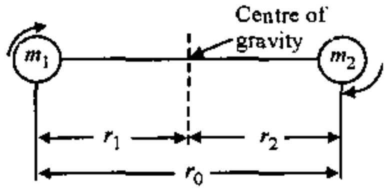


Fig. 3. Rigid rotator.

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1)$$

where J is the rotational quantum number. It can have values 0, 1, 2, 3 etc. The term I is the moment of inertia of the molecule about the axis of rotation, and is given by,

$$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) r_0^2 = \mu r_0^2$$

where m_1 and m_2 are the atomic masses of the two atoms of the diatomic molecule and μ is known as reduced mass, given by,

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

[II] Expression For Rotational Energy

We know that the centre of gravity of a diatomic molecule is the point which satisfies the following condition

$$m_1 r_1 = m_2 r_2 \qquad \ldots (1)$$

The moment of inertia of the diatomic molecule is given by.

$$I = m_1 r_1^2 + m_2 r_2^2 \qquad \ldots (2)$$

$$= m_2 r_2 r_1 + m_1 r_1 r_2 = r_1 r_2 (m_1 + m_2)$$

But $\quad r_1 + r_2 = r_0$

From equation (1), $m_1 r_1 = m_2 (r_0 - r_1)$ or $m_1 r_1 = m_2 r_0 - m_2 r_1$

or $\quad m_1 r_1 + m_2 r_1 = m_2 r_0$ or $(m_1 + m_2) r_1 = m_2 r_0$

or

$$r_1 = \frac{m_2 r_0}{m_1 + m_2}$$

Similarly,

$$r_2 = \frac{m_1 r_0}{m_1 + m_2}$$

Substituting the values of r_1 and r_2 in equation (2), we get

$$I = \frac{m_1 m_2^2}{(m_1 + m_2)^2} r_0^2 + \frac{m_1^2 m_2}{(m_1 + m_2)^2} r_0^2$$

$$= \frac{m_1 m_2 (m_1 + m_2)}{(m_1 + m_2)^2} r_0^2 = \frac{m_1 m_2}{m_1 + m_2} r_0^2$$

$$= \mu r_0^2 \qquad \left(\text{where } \mu = \frac{m_1 m_2}{m_1 + m_2} \right)$$

Now, by definition, the angular momentum of a rotating molecule is given by

$$L = I\omega$$

where ω is the angular velocity (just as linear momentum is given by the product of mass and velocity).

However, angular momentum is quantized whose values are given by

$$L = \sqrt{J(J+1)} \frac{h}{2\pi} \qquad \ldots (3)$$

where $J = 0, 1, 2, 3 \ldots$, called the *rotational quantum numbers.*

Further the energy of a rotating molecule is given by $E = \frac{1}{2} I\omega^2$.

$\therefore$ The quantized value of the rotational energy will be given by

$$E_r = \frac{1}{2} I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \qquad \ldots (4)$$

Substituting the value of L from equation (3) in equation (4), we get

$$E_r = J(J+1) \frac{h^2}{4\pi^2} \times \frac{1}{2I}$$

or

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) \qquad \ldots (5)$$

Putting $J = 0, 1, 2, 3$ etc. in equation (5), pattern of the rotational energy levels obtained will be as shown in figure (4). It is clear that the spacing between the energy levels increases as J increases, because of the factor $J(J+1)$ in equation (5).

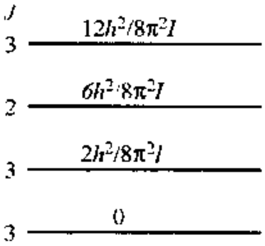


Fig. 4. Rotational energy levels of a diatomic molecule treating it as a rigid rotator.

[III] Frequency and Wave Number of Rotational Lines

We know that the allowed rotational energies are given by the expression

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1)$$

As $E = h\nu$, therefore, in terms of frequency, we can write

$$\nu = \frac{h}{8\pi^2 I} J(J+1) \qquad \ldots (6)$$

Further we know that, $c = \nu\lambda = \nu/\bar{\nu}$ (because wave number $\bar{\nu} = 1/\lambda$). Therefore, in term of wave numbers, equation (6) can be written as

$$\bar{\nu} = \frac{h}{8\pi^2 Ic} J(J+1) = BJ(J+1) \qquad \ldots (7)$$

where $B = h/8\pi^2 Ic$ and is called *rotational constant.*

Putting $J = 0, 1, 2, 3$ etc. in equation (7), the wave numbers of the different rotational levels will be 0, $2B, 6B, 12B, 20B, 30B$ ...., and so on. When a transition takes place from a lower rotational level with rotational quantum number J to a higher rotational level with rotational quantum number J', the energy absorbed will be given by

$$\Delta E_r = E_r' - E_r \quad (\text{or } E_{J'} - E_J) = \frac{h^2}{8\pi^2 I} J'(J'+1) - \frac{h^2}{8\pi^2 I} J(J+1)$$

or

$$\Delta E_R = \frac{h^2}{8\pi^2 I} [J'(J'+1) - J(J+1)] \qquad \ldots (8)$$

However, according to the rotational selection rules, only those rotational transitions are allowed for which $\Delta J = \pm 1$. Therefore, in the present case $J' = J + 1$. Substituting this value in equation (8), we get

$$\Delta E_r = \frac{h^2}{8\pi^2 I} [(J+1)(J+2) - J(J+1)] = \frac{h^2}{8\pi^2 I} 2(J+1) \qquad \ldots (9)$$

To express in terms of wave numbers, we put

$$\Delta E_r = h\nu = h\frac{c}{\lambda} = hc\bar{\nu} = \frac{h^2}{8\pi^2 I} \times 2(J+1) \qquad \text{[From eq. 9]}$$

or

$$\bar{\nu} = \frac{h}{8\pi^2 Ic} \times 2(J+1) = 2B(J+1) \qquad \ldots (10)$$

where $B = \dfrac{h}{8\pi^2 Ic}$ and is rotational constant. The value of $\bar{\nu}$ in equation (10) represents the wave numbers of the spectral lines which are obtained as a result of the transitions between the rotational levels. Putting $J = 0, 1, 2, 3$ *etc.* (*i.e.*, for the transitions $J = 0$ to $J' = 1$; $J = 1$ to $J' = 2$ etc.) or in general from J to $J + 1$ (involving absorption of energy), the wave numbers of the lines obtained will be $2B, 4B, 6B, 8B, \ldots$, and so on.

We find that the most important fact of the pure rotational spectrum is that every two successive lines have a constant difference of wave number equal to $2B$. This is known as **frequency separation** (or more strictly **wave number separation**). Thus, the various lines in the rotational spectra will be equally spaced as shown in figure (5).

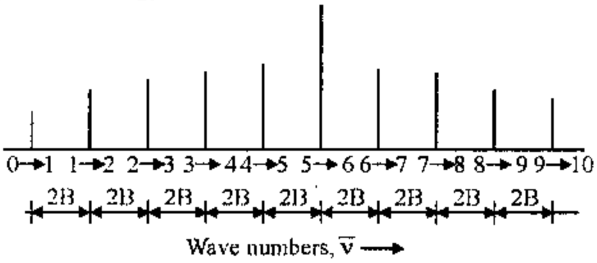


Fig. 5. Appearance of a rotational spectrum.

Any two successive lines will have the difference in wave number given by

$$\Delta\bar{\nu} = 2B = \frac{h}{4\pi^2 Ic}$$

Another important feature of spectra is that the intensities of different transitions are not equal. The intensities increase with increasing J, pass through a maximum and then decrease as J increases further.

[IV] Selection Rules for Rotational and Vibrational Spectra

Atomic spectrum as well as molecular spectrum are obtained due to the transition taking place between energy levels. However, such transitions can occur only between definite energy levels and not between just any two energy levels. ***The restrictions thus applied on the transition are governed by certain rules which are called the selection rules.*** If the selection rules are followed, the transition can occur and it is called an **allowed transition.** If these are not followed, the transition cannot take place and it is called a **forbidden transition.** The selection rules to be followed depend upon the type of transition.

The selection rules are generally expressed in terms of changes in quantum numbers for the allowed transitions. For example, for the pure rotational transition, the selection rule is $\Delta J = \pm 1$, where J represents rotational quantum number ($\Delta J = +1$ corresponds to absorption and $\Delta J = -1$ corresponds to emission). Similarly, for pure vibrational transition, the selection rule is $\Delta v = \pm 1$, where v represents the vibrational quantum number.

• 11.6. INFRARED SPECTRUM

[I] Introduction

Infrared spectroscopy is one of the most powerful analytical techniques which gives us the possibility of chemical identification. Radiations in the infrared region from about 800 to 20,000 nm are not energetic enough to cause electronic excitations in most organic molecules. IR radiations cause stretching and bending of organic bonds. In all organic molecules, the bonds, which join different atoms, can stretch and bend and all of them absorb infrared radiations. After absorption of IR radiations, the molecules thus give rise to close packed absorption bands known as *infrared absorption spectrum.* This may extend over a wide wavelength range. A number of bands may be present in infrared spectrum corresponding to the characteristic functional groups and bonds present in the substance. There, we say that *infrared spectrum of a chemical compound is a finger print for its identification.*

[II] Units Used and Range in Infrared Radiation

Infrared spectra are generally expressed in terms of the frequencies of radiations absorbed rather than wavelengths. This is due to the reason that frequency is directly proportional to the energy of the radiation, whereas wavelength is inversely proportional to energy. The most common unit used in infrared study is wave number $\bar{\nu}$, which shows the number of vibrations of radiation per centimetre (cm^{-1}). Wavelengths in μm can be converted into wave numbers, according to the relation, $\bar{\nu} = 10^4/\lambda$ because $1\ \mu = 10^{-6}$ m $= 10^{-4}$ cm.

The infrared radiation lies between the visible microwave regions of the electromagnetic spectrum. This region may be divided into the following three types.

(i) ***Near infrared region*** : It is the region which extends from 0.8 to 2.5 μm (12500 to 4000 cm^{-1}). It is also known as ***vibration-rotation region.***

(ii) ***Far infrared region*** : It is the region which extends from 15 to 200 μm (667 to 50 cm^{-1}). It is also known as ***rotation region.***

(iii) ***Ordinary infrared region*** : It is the region which extends from 2.5 to 1.5 μm (4000 to 667 cm^{-1}).

[III] Molecular Vibrations in Infrared Spectrum

The atoms in a molecule are always in motion, which may be of different types. Consider a simple diatomic molecule A-B. The only vibrations which can occur in such a molecule are the compression or extension along the A-B bond. This may be compared to the compression or stretching of a coiled spring as shown in figure (7). This type of vibrational movement is referred to as *bond stretching, i.e.*, in these vibrations the distance between two atoms increases or decreases, but the atoms remain in the same bond axis. Such a mode of vibration does not cause any dipole change in the symmetrical molecule, *e.g.*, O =C= O and, therefore, it is not ***infrared active vibration.***

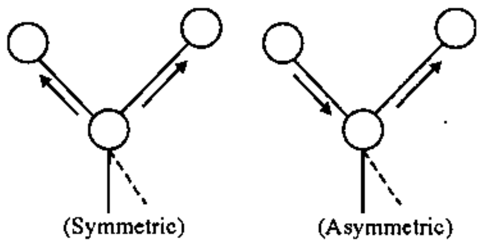


Fig. 6. Kinds of stretching vibrations.

When the stretching and compression occur in a symmetrical fashion, we call it ***symmetric stretching.*** But when one bond is compressing, while the other is stretching, then it is known as ***asymmetric stretching.***

In bending or deformation vibrations, atoms move in and out of the bond axis plane. So, these vibrations involve change in bond angle or a movement of a group of atoms with respect to the rest of the molecule, without movement of atom in the group with respect to one another. Therefore, the bending mode of vibrations involves oscillations of atom perpendicular to its chemical bond. The bending modes are of four types :

(i) Rocking : In this mode of vibration, the two atoms joining a central atom, move back and forth in the plane of the molecule [Fig. (7)].

(ii) Scissoring : In this deformation, the two atoms, joined to a central atom, move towards and away from each other. In this mode, the bond angle changes [Fig. (8)].

(iii) Twisting : In this deformation, the structural unit rotate about the bond, which joins it to the rest of the molecule [Fig. (9)].

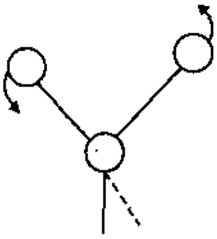


Fig. 7. Rocking mode of vibration.

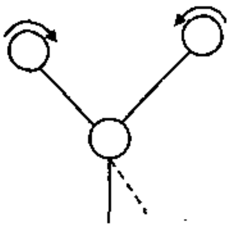


Fig. 8. Scissoring mode of vibration.

(iv) Wagging : In this kind of vibration, the structural unit moves back and forth, out of the plane of molecule [Fig. (10)].

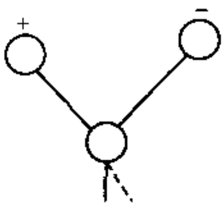


Fig. 9. Twisting mode of vibration. + or – sign signifies vibrations perpendicular to the plane of paper.

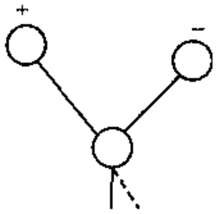


Fig. 10. Wagging mode of vibration. The + sign means vibrations perpendicular to the plane of paper.

[III] Parts of Infrared Spectrophotometer

The instrument used for recording infrared spectra is called ***infrared spectrometer or infrared spectrophotometer***. Most of the instruments have a range of 2μ to 15μ (5000 – 667 cm^{-1}). The general parts of a spectrophotometer and their functions are mentioned below :

(a) Radiation source : The source of infrared radiation is primarily an incandescent solid material, which follows the characteristics of a black body radiator. The tungsten filament lamp is the usual source of near infrared region. It is maintained at red hot by means of an electric current. The most recent source is the invention of K.H. Opperman (Fig. 11). It operates at 2.8 volts and 30 watts. It provides radiant infrared energy from 2.5 μ (4000 cm^{-1}) to 25 μ (400 cm^{-1}).

(b) Infrared monochromator : Prisms and gratings are generally used as monochromators. A combination of prism and grating is also used for this purpose. The most common prism material used is NaCl (rock salt) for the region 2.5 to 15.4 μ (4000 – 650 cm^{-1}). KBr (1000-4000 cm^{-1}) and CsI (1000-260 cm^{-1}) are also commonly used.

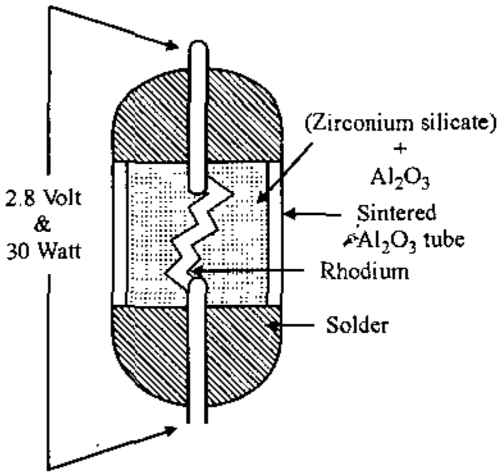


Fig. 11. Source developed by K.H. Opperman

(c) Cell compartment : It is the portion where the cells in which the sample under examination is placed. They are usually made of rock salt (NaCl) or other similar substances.

Sampling : It is important that substances are sampled suitably for infrared spectral studies:

(i) Gaseous substances : Gaseous substances are examined as such in the apparatus.

(ii) Liquid substances : Liquid substances are examined by placing a thin film between the rock salt plates of a liquid cell. A drop of the liquid substance is put on a rock salt plate of a liquid cell and the other plate of the cell is put on it so that the liquid forms a thin film between the two plates.

(iii) Solid substances : Solid substances can be examined in the form of a potassium bromide disc (or pellet) or a Nujol mull or a solution in a suitable solvent.

(a) KBr pellet or disc : The solid is ground with 10-100 times its bulk of pure KBr and the mixture so obtained is passed into a disc using a special mould through a hydraulic press. The pellet must be transparent.

(b) Nujol mull : Nujol is a highly purified liquid fraction petroleum known as liquid paraffin. The substance (1 mg) is finely ground with *nujol* in a small agate pestle mortar to form a translucent mull of the substance. A drop or two of this mull is taken as the liquid sample.

(c) Solution : The given compound is dissolved to give 1-5% solution in CCl_4, carbon disulphide or chloroform free from alcohol. This solution is introduced into a special cell, 0.1 to 1 mm. thick, made of sodium chloride. A second cell of equal thickness, but containing pure solvent, is placed in path of other beam of spectrometer in order that solvent absorptions should be balanced. Spectra taken in such dilute solution in non-polar solvents are generally more desirable since intramolecular forces which are strong in crystalline state are reduced to minimum error. On the other hand, it is found that many compounds which are not soluble in non-polar solvents absorb in infrared region. In this case, where solvent absorption exceeds 65% of incident light, the spectra cannot be taken, while in case of CCl_4 or $CHCl_3$ the absorption takes place above 65% of incident light.

[IV] Principle of Infrared Spectrophotometer

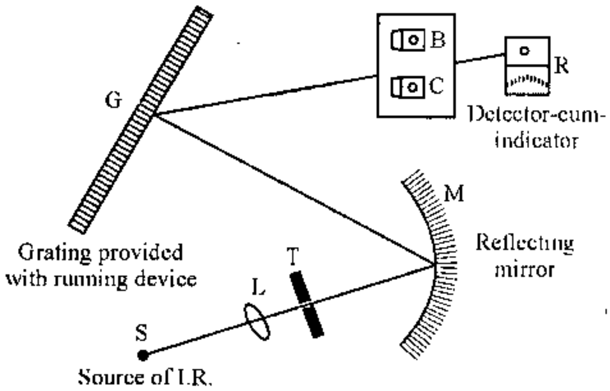


Fig. 12. Flow sheet diagram of I.R. spectrophotometer.

The flow sheet diagram of the infrared spectrophotometer is shown in figure (12). The beam of infrared radiation from the source S is allowed to pass by means of lens L through a narrow slit T. This beam is then focussed by means of a mirror M on the grating G, which is provided with a rotating device. The radiations of a desired wavelength emerge from G. Such radiations are allowed to pass through a cell B, containing the solution under examination and from there to the detector-cum-indicator R. The intensity of the thermo-electric current, which is a measure of the intensity of radiation, is recorded. The cell B is then replaced by a cell C containing pure solvent and again the intensity of radiation is recorded as before. If I and I_0 reprsent the intensity of radiation when the radiation passes through the solution and intensity of the same radiation when it passes through the solvent, then

$$I / I_0 = \text{Transmittance or transmittancy.}$$

The transmittance is determined at different wavelengths and thus infrared spectra is obtained. The frequency of a given stretching vibration in an infrared spectrum can be related to two factors, namely (i) the masses of the bonded atoms–light atoms vibrate at higher frequencies than heavier ones-and (ii) the relative stiffness of the bond. Triple bonds are stiffer (and vibrate at higher frequencies) than double bonds and double bonds are stiffer (and vibrate at higher frequencies) than single bonds. The stretching frequencies of groups involving hydrogen (a light atom) such as C—H, N—H and O—H all occur at relatively high frequencies.

[V] Applications of Infrared Spectroscopy

Some important applications of infrared spectroscopy are as follows :

(1) Qualitative analysis : The qualitative analysis can easily be done by comparing the spectrum of unknown sample with the standard one.

(2) Quantitative analysis : The quantitative determination is based on the determination of concentration of one of functional groups of compound being estimated. Suppose there is a mixture of hexane and hexanol and then the concentration of hexanol can be determined by measuring the absorption of OH bond. The following formula is used for calculating the concentration

$$A = -\log I/I_0 = abc$$

where, A = absorbance, I = intensity of radiation after leaving the sample, I_0 = intensity of radiation before entering the sample, a = absorptivity of cell (It is a property of molecular species being transmitted), b = initial path length of sample cell, and c = concentration of solution.

If a and b are constants then $A \propto c$.

Hence, c can be measured by knowing A. The different values of A are plotted against respective concentrations to get calibration curve from which the concentration of unknown solution is evaluated.

(3) Determination of purity : As impurity reduces the sharpness of individual bands and causes appearance of extra bands and blurring of spectrum. Hence purity can easily be estimated.

(4) Presence of water in a sample : If sample contains water, it gives bands at 3600 to 200 cm^{-1} region, in 1650^{-1}cm region and in 600-300 cm^{-1} region. If anyhow, water is coordinated to a metal ion, an additional band can be seen in the range 880-650 cm^{-1} region.

(5) Calculation of force constant : Taking a simple case where a diatomic molecule may be considered as a simple harmonic oscillator, *i.e.*, an oscillator in which the restoring force (F) is directly proportional to the displacement, in accordance with Hooke's law, we have $F = -kx$, where x is the displacement and is equal to the distance (R) to which the atoms have been stretched minus equilibrium distance (R_e) between the atoms *i.e.*, $x = R - R_e$. The factor k in equation $F = -kx$ is called force constant. So, if $x = 1$ cm, $k = -F$. Therefore, *force constant may be defined as the restoring force per unit displacement (or per cm) of a harmonic oscillator.* It is found to be related to the equilibrium vibrational frequency ω_e according to the equation,

$$\omega_e = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$$

where μ is the reduced mass of the system. To calculate k, the last equation can be rewritten as follows :

$$k = 4\pi^2 \omega_e^2 \mu = 4\pi^2 \omega_e^2 \frac{m_1 m_2}{m_1 + m_2} \qquad \left[\because \mu = \frac{m_1 m_2}{m_1 + m_2}\right]$$

where m_1 and m_2 are the masses of the oscillating atoms.

Thus, knowing vibration frequency ω_e and the masses of the atoms of the diatomic molecule, the force constant k can be calculated. Note that the unit of ω_e is in s^{-1}. It is found that force constant, increases almost directly with the multiplicity of the bond, as is clear from the following examples.

Bond	C—C	C=C	C≡C
Force constant (dyne/cm)	4.6×10^5	9.5×10^5	15.8×10^5

Thus, multiplicity of the bond can be predicted from the value of the force constant. For example, the force constant for C≡O in carbon monoxide is 18.6×10^5 dynes/cm, whereas the force constant for C=O in carbon dioxide is 15.2×10^5 dynes/cm. This result confirms that CO_2 has resonating structures containing both carbon, oxygen double and triple bonds. So, the struture of CO_2 can be depicted as :

$$O^{+}\text{—}C \equiv O^{-} \longleftrightarrow O = C = O \longleftrightarrow O^{-} \equiv C\text{—}O^{+}$$

(6) Determination of shape and symmetry of a molecule : Infrard spectroscopy has been proved very successful in deducing the shape or symmetry of molecules. For example, if NO_2 is linear, only two bands will be active in infrared spectrum and if bent then three bands will be found as in H_2O.

(7) In the study of reaction kinetics : The technique is helpful in the study of reaction kinetics as intermediate compounds can easily be detected and estimated, *e.g.*, progress of oxidation of a secondary alcohol to ketone is studied by getting infrared spectra of test portions at different times. In this case, we expect disappearance of O—H stretching ~ 2.8 μm (~ 3570 cm^{-1}) and appearance of C=O stretching ~ 5.8 μm (~ 1725 cm^{-1}).

(8) Calculation of moment of inertia and bond length : The value of B is given by

$$B = \frac{h}{8\pi^2 Ic}$$

$$\therefore \text{ Frequency separation, } \Delta\bar{\nu} = 2B = \frac{h}{4\pi^2 Ic}$$

Thus, knowing the frequency separation. the moment of inertia and hence the internuclear distance *i.e.*, bond length of a diatomic molecule can be calculated.

(9) Identification of functional groups : The functional groups present in a molecule can be detected with the help of different frequencies or wave numbers.

• 12.7. VIBRATIONAL SPECTRUM


Fig. 13. Vibratory motion of a diatomic molecule.

Using the concepts of quantum mechanics, it can be seen that if the vibratory motion of the nuclei of diatomic molecule (Fig. 13) is taken as equivalent to that of a **simple harmonic oscillator,** then the vibrational energy is obtained using quantum mechanics in the form of equation (1) *i.e.,*

$$E_v = \left(v + \frac{1}{2}\right)h\nu \qquad \ldots (1)$$

where, ν is the frequency of vibration and v is the vibrational quantum number with allowed values of 0, 1, 2, 3, etc.

Putting $\nu = \frac{c}{\lambda} = c\bar{\nu}_e$ or $c\omega_e$ where $\bar{\nu}_e$ or ω_e represents the equilibrium vibrational frequency in terms of wave numbers, equation (1) can be written as

$$E_v = \left(v + \frac{1}{2}\right)hc\omega_e \qquad \ldots (2)$$

Putting $v = 0, 1, 2, 3$ etc, in equation (2) it may be seen that the vibrational energy levels of a harmonc oscillator are equally spaced. These are shown diagrammatically in figure (13). For the lowest vibrational level, $v = 0$. Therefore, the energy for this level will be $E_0 = \frac{1}{2}hc\omega_e$.

The energy E_0 is called **zero point energy**. It means that even at *absolute zero when all translational and rotational motion cease in a crystal, the residual energy of vibration E_0 still remains, i.e., the vibrational motion still exists.*

• 12.8. RAMAN SPECTRUM

Prof. C.V. Raman of Calcutta University, observed in 1928 that when a substance (gaseous, liquid or solid) is irradiated with monochromatic light of a definite frequency ν, the light scattered at right angles to the incident light contained lines not only of the incident frequency, but also of lower frequency and sometimes of higher frequency as well. This effect is known as **Raman effect.** The Raman scattering had been predicted by the German physicist A. Smekal (1923). It was observed by C.V. Raman and K.S. Krishnan (1920). The lines with *lower frequency* are called **Stokes lines,** whereas lines with *higher frequency* are called **anti-Stokes lines.** Line with the same frequency as the incident light is called **Rayleigh line.** Raman further observed that the difference between the frequency of the incident light and that of a particular scattered line was constant depending only upon the nature of the substance being irradiated and was completely independent of the frequency of the incident light. If ν_i is the frequency of the incident light and ν_s, that of a particular scattered line, the difference, $\Delta\nu = \nu_i - \nu_s$ is called **Raman frequency** or **Raman shift.** Thus, the Raman frequencies observed for a particular substance are characteristic of that substance. The spectrum so observed is called **Raman spectrum** as shown in figure (14).

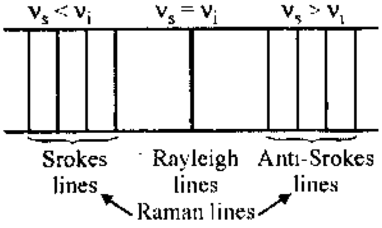


Fig. 14. A simplified repesentation of Raman spectrum.

[I] Rayleigh line : When the photon strikes the molecule, the energy is absorbed by the molecule and it gets excited to some higher energy level. In case it returns to the original level, it will emit the same energy as absorbed and thus we have scattering known as *Rayleigh scattering* and the line is known as Rayleigh line.

[II] Stokes lines : However, in most of the cases, the excited molecule does not return to the original level. It may return to a level higher than the original level, thereby emitting less energy than absorbed. This explains the occurrence of *Stokes lines*. Thus, a part of the energy of the incident photon remains absorbed by the molecule (so that molecule has higher energy than before).

[III] Anti-Stokes lines. The excited molecule may return to a level lower than the original level. Thus, more energy is emitted than absorbed. This explains the occurrence of *anti-Stokes lines.* In this case, the molecule has less energy than before.

The above different cases can be represented diagrammatically by figure (15).

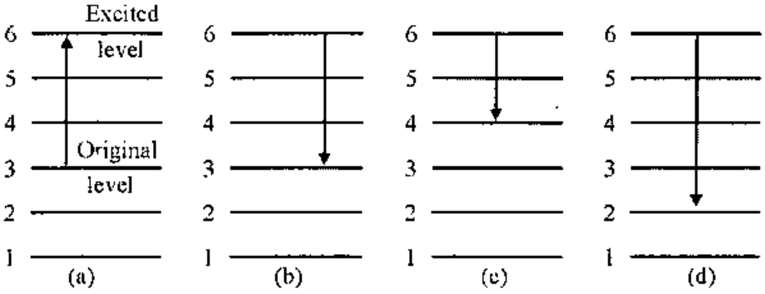


Fig. 15. (a) Energy absorbed by the molecule. (b) Rayleigh scattering. (c) Formation of Stokes lines (d) Formation of anti-Stokes lines.

[I] Experimental Raman Spectroscopy

The experimental set up for Raman scattering is shown in figure (16). Intense monochromatic radiations from a source consisting of a large spiral discharge tube with mercury electrodes is allowed to fall on the cell containing a gaseous or liquid sample. When the current discharge passes through the tube, mercury emits lines in its spectrum the most intense of which at 4358Å (*i.e.*, 435.8 nm) serves as the exciting line. The scattered light is observed at right angles to the direction of the incident radiation. The detector is either a photographic plate or a photomultiplier. The horn shape of the cell helps in reducing the direct reflection of the source from the back of the cell.

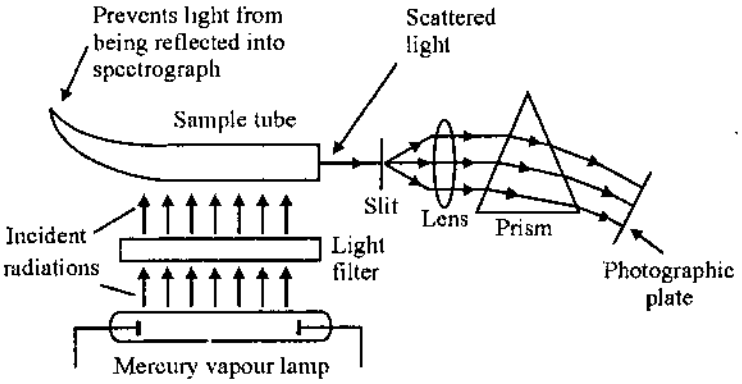


Fig. 16. The experimental set up for Raman spectroscopy.

The Raman spectra of gases are generally weaker than those of liquids. It is necessary to use very long discharge lamps and cells, the latter containing mirrors at both ends arranged so as to increase the effective path length of the cell. However, with the development of lasers, which are very powerful sources of monochromatic radiation, Raman spectroscopy has undergone radical changes.

[II] Applications of Raman Spectra

Raman spectroscopy, despite difficulties with sensitivity, has *several advantages* which make it an extremely important spectroscopic tool. It gives information about molecular vibrations that are inactive in the infrared region because of molecular symmetry. According to the ***'mutual exclusion rule'***, for centrosymmetric molecules (*i.e.*, molecules such as H_2, CO_2, C_2H_2, etc., that possess a centre of symmetry), the vibration which is active in infrared is inactive in Raman and the vibration which is inactive in infrared is active in Raman spectra. Raman spectroscopy, in fact, complements infrared spectroscopy. Thus, the stretching vibrations of homonuclear diatomic molecules (such as H_2, O_2, H_2, etc.) which are inactive in infrared (since they are not accompanied by a change in dipole moment which is already zero) are observed in Raman spectra. Also, the symmetric stretching vibration of CO_2, that is inactive in infrared, is active in Raman spectra.

Another example is that of planar dichloroethylene, $C_2H_2Cl_2$, which consists of *cis-* and *trans*-configurations in equilibrium. Only the *trans*-configuration has a centre of symmetry. Thus, the coincident frequencies observed in infrared and Raman spectra of the sample can be assigned to the *cis*-configuration. In this manner, the analysis of the mixture of the *cis-* and *trans*-isomers can be carried out.

Again, for CS_2 all the vibrations that are Raman-active are infrared-inactive and vice-versa, whereas for N_2O the vibrations are simultaneously Raman and infrared-active. From the spectral data we conclude that CS_2 has a centre of symmetry, whereas N_2O has no centre of symmetry. Thus, the CS_2 structure is of the type S—C—S, while the N_2O structure must be N—N—O rather than N—O—N.

Raman spectroscopy has another advantage in that it uses visible or ultraviolet radiation rather than infrared radiation. Hence, the walls of the sample cell and other units of the optical system can be made of glass or quartz rather than of special materials that are transparent to infrared radiations. Also, the experimentalist can work very conveniently with aqueous media since water is far more transparent in the visible and UV regions than in the infrared region. Thus, Raman spectroscopy can be utilized for the investigation of biological systems such as the polypeptides and the proteins in aqueous solution.

[III] Advantages of Raman Spectroscopy

Raman spectroscopy has a number of advantages over infrared spectroscopy which are discussed below :

(1) Raman spectra can be obtained not only for gases but even for liquids and solids, whereas infrared spectra for liquids and solids are quite diffused.

(2) Since Raman frequencies are independent of the frequency of the incident radiation, so by suitably adjusting the frequency of the incident radiation, Raman spectra can be obtained in the visible spectrum range where they can be easily observed rather than the more difficult infrared range.

(3) Raman spectra can be obtained even for molecules such as O_2, N_2, Cl_2 etc., which have no permanent dipole moment. Such a study is not possible by infrared spectroscopy.

[IV] P–Q–R Bands in Rotational-Vibrational Spectrum

The vibrational-rotational spectrum of a substance does not occur in the form of a single spectral line. However, a number of lines appear on either side of the expected position. Consider the equation,

$$\bar{\nu} = \omega \pm \frac{h}{4\pi^2 I_c} . J \text{ (where } I_c = \text{moment of inertia)}$$

The first term on the right hand side, *i.e.*, ω (fundamental frequency of the vibration) gives the origin of centre of the fundamental band due to one step change in vibrational transition. The second term, *i.e.*, $\pm \frac{h}{4\pi^2 I_c}$ gives the rotational fine structure becasue of rotational transition.

(i) If ***J* is positive** then a series of lines of higher frequency (shorter wavelengths) appear on the right side of the band origin. These lines are known as ***R*–branch** of the vibrational-rotational band.

(ii) If ***J* is negative,** then a series of lines of lower frequencies (longer wavelengths) appear on the left side of the band origin. These lines are known as ***P*-branch** of vibrational-rotational band. So, two lines appear, one on the right side and other on the left side of the origin for each possible value of *J*.

(iii) *J* may be close to zero, *i.e.*, in such a case, vibrational transition is not accompanied by any appreciable rotational changes. The moment of inertia in the final state must, however, be different from that in the initial state. This shows that there must be some small changes in rotational energy of these molecules. These changes give rise to a series of very closely spaced lines, known as ***Q*-branch** or ***Q*-band.** Such bands are generally observed in polyatomic moelcules.

• SUMMARY

- 1 micron (μ) = 1000 millimicron ($m\mu$) = 10^{-4} cm.
- $1 \text{ Å} = 0.1\ m\mu = 10^{-4}\ \mu = 10^{-8}$ cm.
- 1 nanometre (nm) = 1 $m\mu$ = $10^{-3}\ \mu$ = 10 Å
- 1 Hertz (Hz) = 1 cycle/second.
- In pure rotational spectrum, every two successive lines have a constant difference of wave number equal to $2B$. This is known as frequency separation or wave number separation, and $2B = h/4\pi^2 Ic$.
- The energy for the lowest vibrational level, *i.e.*, $v = 0$ is called zero point energy. It is given by, $E_0 = \frac{1}{2} hC\omega_e$.
- The difference in the frequency of incident and scattered light is known as Raman shift ($\Delta\nu$), *i.e.*, $\Delta\nu = \nu_i \sim \nu_s$.

• STUDENT ACTIVITY

1. Write the symbols used in spectroscopy.

2. Mention two applications of ultraviolet spectroscpy.

3. Describe the ranges used in infrared spectrum.

4. Define Rayleigh, Stokes and anti-Stokes lines.

• TEST YOURSELF

1. Explain the different regions of spectrum.
2. Mention the electromagnetic radiations.
3. Describe some important applications of ultra-violet spectroscopy.
4. Relate the units, micron, angstrom and nanometre.
5. Discuss the origin and theory of ultra-violet spectroscopy.
6. Derive an expression for rotational energy of a diatomic molecule.
7. Derive the expression for the frequency and wave number of lines in the rotational spectrum.
8. What are the selection rule for rotational and vibrational spectra ?
9. Describe the units used and range in infrared radiations.
10. Describe the molecular vibrations and origin of infrared spectrum.
11. Discuss the principle and different parts of an infrared spectrophotometer.
12. Mention some important applications of infrared spectroscopy.
13. Describe the expression for vibrational energy of a diatomic molecule taking it simple harmonic oscillator.
14. What is Raman spectrum ? How will you explain Rayleigh line, Stokes line and anti-Stokes lines in Raman spectrum ?
15. Describe the experimental technique of Raman spectroscopy.
16. Mention some important applications of Raman spectrum.
17. What are advantages of Raman spectroscopy over infrared spectroscopy ?
18. Write a note on P–Q–R bands in vibrational-rotational spectrum.
19. Identify the spectra which correspond to the following frequency/wavelength ?

    (a) 15,000 cm^{-1} (b) 50,000 cm^{-1}
20. What is Raman shift ?
21. What is zero point energy ?
22. Define fundamental frequency.
23. Arrange the energy required to produce rotational, vibrational and electronic transitions in increasing order.

24. State with reason which of the following molecules will show and not show rotational spectra? H_2, HCl, CH_4, CH_3Cl, CO, Cl_2 and O_2.

25. 1 Hertz is given by :

(a) 10^{-8} cm (b) 1 mμ (c) 1 cycle/second (d) 10 Å

26. Wave number separation is represented by :

(a) B (b) 2B (c) J (d) J (J + 1)

27. Fill in the blanks :

(i) H_2 will ……… rotational spectrum.

(ii) The region between 2000 and 4000 Å is known as ……… ultraviolet region.

(iii) In a diatomic molecule, the term $\frac{m_1 m_2}{m_1 + m_2}$ is called ……… mass.

ANSWERS

15. (a) Visible (ii) Ultraviolet **23.** Rotational < Vibrational < Electronic transitions

24. The condition for obtaining a pure rotational spectrum is that the molecule must have a permanent dipole moment so that it can interact with the electromagnetic radiation and absorb or emit a photon. Thus, *pure rotational spectrum is given only by polar molecules.* Consequently, homonuclear diatomic molecules (like H_2, N_2 etc.) and symmetrical linear molecules like CO_2 (or symmetrical molecules like C_6H_6) do not give rotational spectra. Thus, polar molecules like H_2O. NO, N_2O etc., give pure rotational spectra.

Out of the given molecules HCl, CH_3Cl and CO possess a permanent dipole moment and will give rotational spectra. H_2, CH_4, N_2 and O_2 being non-polar will not show rotational spectra.

25. (c) **26.** (b) **27.** (i) not show (ii) near (iii) reduced.

❑❑❑

U N I T

13

PHOTOCHEMISTRY

LEARNING OBJECTIVES

• 13.1. INTRODUCTION

Photochemistry is that branch of science which deals with the chemical processes that occur when a material system is illuminated by radiation from an external source. So, **photochemistry** *is the science of chemical effects of radiations whose wavelengths lie in the visible and ultraviolet regions, i.e., in the range* from 8,000Å to 2,000 Å. The chemical effects produced by the high energy radiations like X-rays, γ-rays etc. are studied under ***radiation chemistry.***

[I] Thermochemical Reactions and Photochemical Reactions

Ordinary chemical reactions are referred to as **thermal** or **dark** *reactions in order to distinguish* them from the photochemical reactions. All spontaneous chemical reactions are accompanied by a decrease in the free energy, whereas photochemical reactions take place with an increase of free energy, as a result of free energy supplied by light.

[II] Differences between Photochemical Reactions and Thermochemical Reactions

Photochemical reactions	Thermochemical reactions
1. These reactions involve absorption of light.	1. These reactions involve absorption or evolution of heat.
2. The presence of light is the primary requisite for the reaction to take place.	2. They can take place even in the dark.
3. Temperature has very little effect on the rate of photochemical reaction. Instead, the intensity of light has a marked effect on the rate of a photochemical reaction.	3. Temperature has significant effect on the rate of a thermochemical reaction.
4. The free energy change (ΔG) of a photochemical reaction may not be negative. A few examples of photochemical reactions for which ΔG is positive and still, they are spontaneous are synthesis of carbohydrates in plants and decomposition of HCl into H_2 and Cl_2.	4. The free energy change (ΔG) of a thermochemical reaction is always negative.

• 13.2. LAWS OF PHOTOCHEMISTRY

(1) Grotthus-Draper law : According to this law, *'Only those rays which are absorbed by the substance are effective in producing a chemical change'.*

This statement was based on theoretical data. All light radiations which are absorbed are not. however, effective in bringing about chemical reactions. Some of the light radiations are converted into heat and some other re-emitted as radiations of the same or lower frequency.

(2) Lambert's law : According to this law, ***'When a monochromatic beam of light passes through a homogeneous absorbing medium, equal fractions of incident radiations are absorbed by successive layers of equal thickness of the light absorbing substance'.*** In other words, ***'the rate of decrease of intensity with the thickness of absorbing medium is proportional to the intensity of the incident radiation'.***

Consider a thin layer of the medium of thickness dx and let I be the intensity of the radiation entering it, then mathematically, Lambert's law can be written as :

$$-\frac{dI}{dx} \approx I \quad \text{or} \quad \frac{dI}{dx} = -kI. \qquad \text{(where } k = \text{constant)}$$

The value of I can be calculated by integrating the above equation within proper limits. *i.e.*,

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_0^x k dx \quad \text{or} \quad \log_e \frac{I}{I_0} = -kx \quad \text{or} \quad \frac{I}{I_0} = e^{-kx} \quad \text{or } I = I_0 \,.\, e^{-kx}$$

where, I_0 is the intensity of the incident radiation, and k is a constant which depends upon the nature of the medium as well as on the wavelength of light employed.

(3) Beer's law : Beer (1852) showed that the absorption of light by solution depends upon the thickness (x) of the layer traversed and the molecular concentration (c), in that layer. According to this law, ***'The absorption of light remains constant when the concentration and the thickness of the absorbing layer are changed in an inverse ratio'.* In other words, *'the rate of decrease in intensity of radiation absorbed is proportional to the intensity of the incident radiation and also to the concentration of the solution.'***

Mathematically, $-\frac{dI}{dx} = \varepsilon c I$

where $c =$ concentration of the solution and ε is a constant.

On integration, $\log_e \frac{I}{I_0} = -\varepsilon c x$ ... (1)

or $\frac{I}{I_0} = e^{-\varepsilon c x}$ or $I = I_0\, e^{-\varepsilon c x}$.

This equation shows how the intensity of a monochromatic light falls from I_0 to I on passing through a thickness x of a solution of concentration, c.

Rewriting equation (1), we get

$$2.303 \log_{10} \frac{I}{I_0} = -\varepsilon c x \quad \text{or} \quad \log_{10} \frac{I}{I_0} = -\frac{\varepsilon}{2.303} \,.\, cx$$

or $$\log_{10} \frac{I}{I_0} = -\varepsilon' cx \quad \text{or} \quad \frac{I}{I_0} = 10^{-\varepsilon' cx}$$

or $$I = I_0 \,.\, 10^{-\varepsilon' cx}$$

where ε' is known as *molar extinction coefficient* of the absorbing medium, and is given by $\varepsilon' = 0.4343\ \varepsilon$. Now, it is known as molar **absorption coefficient** or **molar absorptivity** of the absorbing solution. The value of ε' depends upon the nature of the substance and the wavelength of the incident light. The quantity, $\log_e (I_0/I)$ is called the **optical density or absorbancy** (D) of the medium, *i.e.*,

$$D = \log_e \frac{I_0}{I} = \varepsilon'.c.x. \text{ (where } x = \text{ thickness of medium).}$$

(4) Law of photochemical equivalence or Stark- Einstein's law : Stark (1909) and Einstein (1912) gave the most important law of photochemistry, based on quantum theory. According to this law, ***'In a photochemical reaction, one quantum of active light (photon) is absorbed per molecule of the reacting substance which disappears'.***

Suppose the frequency of the absorbed light be ν. Then the corresponding quantum of energy absorbed per molecule will be $h\nu$, where h is Planck's constant. Therefore, the quantum of energy, E absorbed per mole of the reacting substance is given by.

$$E = Nh\nu \text{ erg mole}^{-1} \text{ (where } N = \text{Avogadro's number)}$$

$$= \frac{Nh\nu}{4.184 \times 10^7} \text{ cal mole}^{-1}.$$

$$\therefore \quad E = \frac{(6.023 \times 10^{23}) \times (6.626 \times 10^{-27}) \times \nu}{4.184 \times 10^7} \text{ cal mole}^{-1}$$

Now $\nu = c/\lambda$, where c is the velocty of light and λ is the wavelength of radiation absorbed.

$$\therefore \quad E = \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-27} \times 2.998 \times 10^{10}}{4.184 \times 10^7 \times \lambda}$$

$$= \frac{2.86}{\lambda} \text{ cal mole}^{-1}. \quad \ldots (2)$$

In equation (2), λ is expressed in cm, but *it is generally expressed in Angstrom unit*, Å (1Å = 10^{-8} cm). Thus,

$$E = \frac{2.86}{\lambda} \times 10^8 \text{ cal mole}^{-1} = \frac{2.86}{\lambda} \times 10^5 \text{ kcal mole}^{-1}$$

$$= \frac{11.97 \times 10^5}{\lambda} \text{ kJ mole}^{-1}.$$

Thus, it is clear, that the numerical value of E varies inversely with the wavelength of the light absorbed. Therefore, shorter the wavelength, the greater is the energy absorbed per mole. The quantity E, *i.e.*, energy absorbed per mole of the reacting substance is called **one einstein**, *i.e.*,

$$1 \text{ einstein} = \frac{2.86 \times 10^5}{\lambda} \text{ kcal mole}^{-1} = \frac{11.97 \times 10^5}{\lambda} \text{ kJ mole}^{-1}.$$

For violet light, $\lambda = 3750$ Å and $E = 76.2$ k cals. For red light, $\lambda = 7500$ Å and $E = 38.13$ k cals.

• 13.3. QUANTUM EFFICIENCY

[I] Definition of Quantum Efficiency

Quantum efficiency is defined as, *'the number of moles of the light absorbing substance that react chemically for each einstein of absorbed radiation'*, or *'the number of molecules reacting for each quantum of absorbed radiation'*. It is represented by ϕ. Mathematically,

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quantum of light absorbed during the same time}}$$

$$= \frac{\text{Number of moles or gram molecules reacting in a given time}}{\textit{Number of einsteins of light absorbed during the same time}}.$$

[II] Experimental Determination of Quantum Efficiency

The determination of quantam efficiency requires :

(a) The determination of the number of moles of the reacting substance that undergo chemical change in a given time.

(b) The number of einsteins of radiation absorbed by the light absorbing substance during that time.

The former factor can be determined by the usual analytical methods. However, the apparatus employed for determining the latter factor consists of the following units :

(i) Light source : Sunlight, arc light, mercury vapour lamp etc. are used for this purpose.

(ii) Monochromator *: Since the value of einstein depends upon* the value of einstein depends upon the wavelength of the incident light, it is necessary to use light of one wavelength of light falling within a narrow range of wavelengths. The line of desired wavelength is chosen by the use of properly chosen optical filters, which absorb the undesired wavelengths. Such device of using light of one wavelength, *i.e*, monochromatic light or light falling within a narrow range of wavelengths, is called a **monochromator**.

(iii) Reaction cell : The light from the monochromator enters a reaction cell which contains the reaction mixture. *The cell is generally made of glass or quartz with optical plane windows for* the free exit and entrance of light radiation.

(iv) Detector : A detector is used for determining the intensity of light coming from a reaction cell. The intensity of light is measured with the cell when empty and then with the reaction mixture.

The difference between the two readings will give the amount of energy absorbed by the reaction system under study.

The intensity of light can be measured by the following type of detectors :

(a) Chemical actinometers : When extreme accuracy is not desired, a chemical actinometer can be used to measure the intensity of light radiation. It generally consists of gas mixtures or solutions which are sensitive to light. When radiations fall upon these substances, a chemical reaction takes place and the extent of it gives a direct measure of energy absorbed.

The most frequently used actinometer is the uranyl oxalate actinometer. It consists of a 0.05 M solution of oxalic acid mixed with an equal volume of 0.01 M of uranyl nitrate or sulphate. On exposure to violet or ultraviolet light within wavelengths of 2540 Å and 4350 Å, oxalic acid gets decomposed, the uranyl ion (UO_2^{2+}) acting as a photosensitizer. The extent of the decomposition during a given period of time is determined by titration with standard $KMnO_4$ at the beginning and at the end of the exposure. The difference in the readings gives a measure of intensity of light absorbed.

$$UO_2^{2+} + h\nu \rightarrow (UO_2^{2+})^*$$

$$(UO_2^{2+})^* + (COOH)_2 \rightarrow CO_2 + CO + H_2O + (UO_2^{2+}).$$

(b) Thermopile : It consists of a series of unlike metals which are connected to a galvanometer. One end of it is coated with lamp black or platinum black and the other end is kept as such. The thermopile is kept in glass or quartz vessel. When light from a reaction cell is incident on the black surface, it gets heated up, resulting in a difference in temperatures of the black and the other cold end. So, a thermo-electric current flows in the circuit. The current produced is proportional to the intensity of light absorbed. Thermopiles are generally calibrated with standard light sources.

[III] Method for the Determination of Quantum Efficiency

First set up the apparatus as shown in figure (1). Then an empty cell or the cell filled with solvent (only in case of solutions), is placed in the path of the light beam and the light intensity is determined as such. Now fill the reaction vessel with the reaction mixture. Allow the light to pass through it for a known time. Then note the intensity of light after the reaction is over. The difference between the two readings will give the total energy absorbed by the reacting mixture in the given time. If the time is 1 second, the total energy absorbed divided by the volume of the reaction mixture gives the intensity of the radiation absorbed. Analyse the contents of the reaction mixture. Then determine the number of moles reacted in a given time. The value of ϕ is calculated as follows :

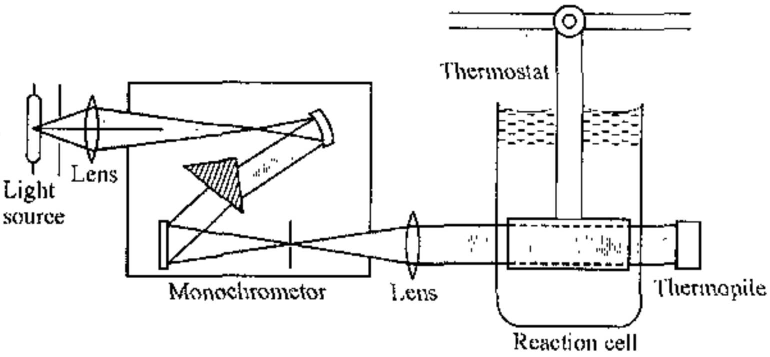


Fig. 1. An apparatus for photochemical experiments.

$$\phi = \frac{\text{No. of moles reacting in a given time}}{\text{No. of einsteins absorbed in the same time}}$$

[IV] Quantum Efficiencies of Some Photochemical Reactions

Some photochemical reactions with quantum yield or efficiency are mentioned in the following table.

S. No.	Photochemical Reaction	Wavelength (Angstroms)	Quantum Yield
1.	$SO_2 + Cl_2 \rightarrow SO_2Cl_2$	4,200	1
2.	$2HBr \rightarrow H_2 + Br_2$	2,070–2,540	2
3.	$H_2 + Cl_2 \rightarrow 2HCl$	2,000	10^5
4.	$H_2 + Br_2 \rightarrow 2HBr$	5,100	0.1

On the basis of values of quantum efficiencies, the different photochemical reactions can be divided into three categories :

(1) Those in which the quantum efficiency is a small integer, *e.g.*, 1, 2 or 3. Examples are combination of sulphur dioxide and chlorine and dissociation of hydrogen bromide, etc.

(2) Those in which the quantum efficiency is very high, *e.g.*, combination of hydrogen and chlorine etc.

(3) Those in which the quantum efficiency is very low, *e.g.*, combination of hydrogen and bromine etc.

In order to explain the above variations, Bodenstein pointed out that photochemical reactions involve two processes, *i.e.*,

(a) ***Primary process :*** In this process, the light quantum $h\nu$ is absorbed by a molecule A resulting in the formation of an excited molecule A^*. Thus,

$$A + h\nu \rightarrow A^*$$

The molecule which absorbs light may get dissociated giving atoms or free radicals.

(b) ***Secondary process :*** In this process, the excited atoms, molecules or free radicals produced in the primary process react further.

[V] Reasons for High and Low Quantum Efficiencies

(1) **Reasons for high quantum efficiency :** The reasons for high quantum efficiencies are :

(i) Sometimes, the atoms or free radicals initiate a series of chain reactions, *e.g.*, in the combination of H_2 and Cl_2 to give HCl and the quantum efficiency is of the order of 10^6 or even more.

(ii) The secondary reaction is exothermic, so that the heat of reaction may activate other molecules thereby causing them to react.

(iii) The activated molecules may not get deactivated before forming the products.

(2) **Reasons for low quantum efficiency :** The reasons for low quantum efficiencies are :

(i) Excited molecules may get deactivated before they form the products.

(ii) The primary photochemical process may get reversed as in the combination of H_2 and Br_2 to form HBr and the quantum efficiency is of the order of 0.01.

(iii) Collisions of excited molecules with non-excited molecules may cause the former to lose their energy.

(iv) The dissociated fragments may recombine to form the original molecule.

• 13.4. PHOTOSENSITIZATION

In order to bring about a photochemical reaction, it is necessary to have a certain minimum energy; the reactive system must be illuminated by light of corresponding wavelength, equal to or shorter than a certain maximum. *This maximum wavelength is called the* ***photochemical threshold.***

It is sometimes found that the substance used in the photochemical reaction may not absorb the light used. It is then necessary to introduce into the system a third substance capable of absorbing this wavelength. If this energy is sufficient to cause reaction and if the absorbing substance is not permanently transformed, then this phenomenon is known as **photosensitization.** Reactions brought about in this way are said to be **photosensitized** and the light absorbing but non-reacting substance is known as the **photosensitizer.** Since photosensitizer is not destroyed in the process, it is thus clear that only a very small amount may be effective.

Vogel (1873) discovered that photographic plates could be sensitized to green and red light, by treating them with certain dyestuffs. Atoms, such as those of mercury, xenon etc. are effective photosensitizers. Those reactions where halogen molecules are photosensitizers generally include decompositions and rearrangements. Chlorophyll sensitizes the photosynthesis of carbohydrates, zinc oxide sensitizes some photo-oxidations and reduction of organic compounds. Uranyl ion acts as a photosensitizer in the photochemical decomposition of oxalic acid.

$$UO_2^{2+} + h\nu \rightarrow (UO_2^{2+})^x$$

$$(UO_2^{2+})^x + HCOOC\text{—}COOH \rightarrow CO + CO_2 + H_2O + UO_2^{2+}$$

• 13.5. FLUORESCENCE

When a substance mostly vapour or liquid is irradiated by light, it itself begins to emit light and it stops emitting light or radiation as soon as the incident light is cut off. This phenomenon is called ***fluorescence.*** Such substances which emit radiations during the action of stimulating light are called ***fluorescent substances***. In fluorescence, it is essential for light to be absorbed before it is re-emitted. This distinguishes it from Tyndall, Rayleigh scattering and Raman effect. Fluorescence stops practically when the exciting light is shut off and this distinguishes it from phosphorescence, in which the emission continues for a short time even after the incident light is shut off.

According to Stokes (1852) the radiation emitted in fluorescence has a greater wavelength, *i.e.*, lower energy, than the exciting radiation, *i.e.*, the light originally absorbed. A few examples are known of anti-Stokes behaviour when the fluorescent radiation has a higher energy than the absorbed radiation.

[I] Resonance Fluorescence

An interesting case is known in which the atoms do not possess vibrational energy, they then exhibit what is known as ***resonance fluorescence,*** *i.e.*, the fluorescent light has the same frequency as that of the incident radiation. For example, if mercury vapour with atoms in the normal ($^1S_0$) state is exposed to ultraviolet light it will absorb resonance radiation of wavelength 2537 Å, and is converted into the excited state; *i.e.*, $^3P_1$.

$$Hg(^1S_0) + h\nu \longrightarrow Hg^*(^3P_1)$$

$$Hg^*(^3P_1) \longrightarrow Hg(^1S_0) + h\nu$$

If the pressure of the vapour is low, the collisions are not too frequent and the electrons in the excited atom will return to its normal level and emit the same radiation 2537 Å in a very short interval of time varying from 10^{-7} to 10^{-8} sec.

[II] Examples of Fluorescence

Fluorescence is exhibited by many substances. Among them are fluorite, CaF_2 (*the name fluorescence originates from it*), uranium glass, petroleum, solutions of dyestuffs as eosin, fluorescein, quinine sulphate, chlorophyll, vapours of sodium, iodine and acetone etc. Even simpler organic compounds as hydrocarbons (paraffins and olefines) have been found to fluoresce in ultraviolet region. Acetone absorbs 2700 Å corresponding to $C{=}O$ group and emits blue fluorescence and similar is the case with aldehydes and other ketones. Among inorganic substances there are only few instances such as uranium compounds and rare earths which show fluorescence.

[III] Applications of Fluorescence

Fluorescence had found many applications of practical and industrial uses *viz.*,

(1) ***In fluorescent tubes*** : In this, use is made of the fact that many inorganic solids also fluoresce. The modern tubular lights in which a mercury arc gives a large proportion of ultraviolet light is made in the tube coated internally with fluorescent salts giving visible light, with a distribution of intensity not far different from daylight.

(2) ***In fluorescent dyes and paints*** : Different types of dyes, paints and glasses exhibit characteristic fluorescent colours which make the substances nice to look at.

(3) ***In use of fluorescent microscope*** : It has been developed for biological purposes and it is based on the principle that almost all organic substances can be stimulated by visible or ultraviolet light.

(4) ***In television*** : It is based on the phenomenon of photoelectric effect. The cathode stream has to be made visible in cathode ray tube. This can be done by addition ZnS to which a little Ni is added to cut off the phosphorescence, otherwise the picture would be blurred.

(5) ***In analysis*** : The characteristic fluorescence of various substances when exposed to ultraviolet light provides a means of analysis. The intensity of fluorescence has been used for quantitative analysis. Concentration of riboflavin (Vit. B_2) in chloroform has been examined by this method. Again fluorescence produced by *X*-rays falling on a screen of barium platinocyanide or other material is the principle of the fluoroscope used in X-ray diagnosis.

• 13.6. PHOSPHORESCENCE

When a substance especially solid is irradiated by light, it begins to emit light, and when the light is shut off, the emission continues. The time interval for this emission may be from 10^{-2} second to hours or even days. This phenomenon is known as phosphorescence.

Phosphorescence is derived from the word phosphorous which glows in the dark, although it is not strictly phosphorescent. In fact, phosphorescence is best looked upon as slow fluorescence or phosphorescence of long duration.

[I] Characteristics of Phosphorescence

Some characteristics of phosphorescence are as follows :

(i) This phenomenon occurs even after the incident light is shut off.

(ii) This phenomenon is caused mainly by the ultraviolet and violet parts of the spectrum.

(iii) The time for which light is emitted from phosphorescent substances depends upon the nature of substance and sometimes on temperature changes.

(iv) Different colours may be obtained by mixing different phosphorescent substances.

(v) Phosphorescence is exhibited mainly by solids.

(vi) The magnetic and dielectric properties of phosphorescent substances are different before and after illumination.

[II] Examples of Phosphorescence

It is mostly observed in case of solids. In phosphorescence, the emission can only occur when the energy is taken from the surrounding medium according to Perrin. This leads to a delay in the electron jump by the action of the medium, which tries to keep the electron fixed in their neighbourhood in some sort of loose binding and this bond breaks with the help of thermal energy of the medium. The electron then returns with the accompaniment of phosphorescence and that is why phosphorescence does not occur in the gaseous state or in liquids. However, short after glow has been observed in denser medium, it has been seen to increase with the increase in the viscosity of the medium.

Phosphorescence is observed in solids because of greater difficulty in motion. It is found that if fluorescent substances are mixed by fusion with boric acid and are cooled, the masses which are formed then phosphoresce. The most common examples are of alkaline earth sulphides in which an addition of a trace of heavy metal enhances the phosphorescence.

• 13.7. DIFFERENCES AND SIMILARITIES BETWEEN FLUORESCENCE AND PHOSPHORESCENCE

[I] Similarities

(i) Both these phenomena are caused by UV and visible parts of the spectrum.

(ii) These are regarded as the secondary processes resulting from the primary process of absorption of a quantum of light (UV and visible) by an atom or molecule.

(iii) Both these phenomena are considerably affected by the substituents in molecule. Generally, electron-donating groups enhances and electron-withdrawing groups destroy the phosphorescence and fluorescence.

[II] Dissimilarities

S. No.	Fluorescence	Phosphorescence
1.	It is shown by gases, liquids and solids. No fluorescence will be observed in gases unless the pressure is low.	It is exhibited mainly by solids.
2.	It is instantaneous and starts within 10^{-6} to 10^{-4} second of absorption of UV or visible light. It stops as soon as incident light is cut off. Thus, life-time of fluorescence is very short.	Substances showing phosphorescence re-emit excess radiation within 10^{-4} to 20 sec or longer after the incident light absorption. Thus, life-time of phosphorescence is much longer than fluorescence. It does not stop as soon as the incident light is cut off.
3.	The extent of fluorescence depends upon the nature of the solvent and the presence of certain anions in solution. So, thiocyanate, bromide and *iodide anions show a marked quenching effect.*	The time for which the radiation is emitted from phosphorescent substance depends upon the nature of substance and sometimes on the *temperature changes.*
4.	Fluorimetry is comparatively simple and finds wider applications.	Phosphorescence is more complicated experimentally than fluorescence and, therefore, phosphorimetry finds limited applications.
5.	Fluorimetry is less sensitive than phosphorimetry.	Phosphorimetry is more sensitive than fluorimetry.
6.	Scattering problems are more severe in fluorimetry.	Scattering problems do not exist in phosphorimetry.

• 13.8. CHEMILUMINESCENCE

When a photochemical reaction occurs, light is absorbed. However, there are certain reactions in which light is produced. *The emission of light in chemical reactions at ordinary temperatures is* *known as chemiluminescence.* The chemiluminescence is just the reverse of a photochemical reaction. In order for a reaction to be chemiluminescent, it must furnish sufficient energy to raise at least one of the reactants or intermediates to an electronically excited state so that as it returns to the ground state, it emits energy in the form of radiation. A few examples of chemiluminescence are as follows :

(i) The oxidation of yellow phosphorus in oxygen or air to give P_2O_5 at ordinary temperature (– 10° to 40°C) is accompanied by the emission of visible greenish white luminescence.

(ii) The light emitted by glow worms is due to the oxidation of *luciferon* – a protein, by atmospheric oxygen in the catalytic presence of an enzyme called *luciferase.*

• SUMMARY

- **Lambert's law :** The rate of decrease of intensity with the thickness of absorbing medium is proportional to the intensity of the incident radiation.
- **Beer's law :** The rate of decrease of intensity of radiation absorbed is proportional to the intensity of incident radiation and also to the concentration of the solution.
- **Law of photochemical equivalence :** In a photochemical reaction, one quantum of active light (photon) is absorbed per molecule of the reacting substance which disappears.
- The number of molecules reacting for each quantum of absorbed radiation is called quantum efficiency of the reaction.
- $H_2 + Cl_2 \rightarrow 2HCl$ has very high and $H_2 + Br_2 \rightarrow 2HBr$ has low quantum efficiencies.
- The process in which light quantum (hv) is absorbed by the reacting molecule is called primary process. It occurs in the presence of light only.
- The process which follows the primary process is called a secondary process. It may occur in dark also.
- The process which does not occur in presence of light by itself, but occurs in the presence of a third substance (called photosensitizer) is called photosensitization.
- When a substance is irradiated by light, it itself begins to emit light and it stops emitting light or radiation as soon as the incident light is cut off. This phenomenon is known as **fluorescence.**
- When a substance is irradiated by light, it begins to emit light and when the light is shut off, the emission of light continues for sometime. This phenomenon is known as **phosphorescence.**

• STUDENT ACTIVITY

1. Mention two differences between photochemical reactions and thermochemical reactions.

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2. Define Beer's law.

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3. Define primary and secondary processes.

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4. Define fluorescence.

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• TEST YOURSELF

1. Write a short note on Stark-Einstein's law of photochemical equivalence.
2. Mention the reasons for low and high quantum efficiencies.
3. Describe the differences between photochemical and thermal reactions.

4. State and explain Beer's law.
5. Explan the term fluorescence smith two examples.
6. Explain the term phosphorescence.
7. Write a short note on photosensitization.
8. Mention three differences between fluorescence and phosphorescence.
9. Write a note on chemiluminescence.
10. Define Lambert's law.
11. Define photosensitizer with an example.
12. Name two phosphorescent substances.
13. Define an einstein.
14. Mention one reaction each in which the quantum efficiency is high and low.
15. What are photochemical reactions ?
16. The energy absorbed per mole of the reacting substance is known as :
    (a) erg (b) Hertz (c) einstein (d) joule
17. The quantum *efficiency for the reaction* $H_2 + Cl_2 \rightarrow 2HCl$ *is :*
    (a) One (b) Very high (c) Very low (d) Zero
18. **Fill in the blanks :**
    (*i*) *The process in which* light quantum is absorbed by the reacting substance is called .... process.
    (ii) The rate of decrease in intensity of radiation absorbed is dependent on intensity of incident radiation and concentration of the solution. This law is called .... law.

ANSWERS

16. (c) **17.** (b) **18.** (i) primary (ii) Beer's.

❑❑❑

UNIT

14

DILUTE SOLUTIONS AND COLLIGATIVE PROPERTIES

LEARNING OBJECTIVES

- Types of Physical Properties
- Osmosis and Osmotic Pressure
- Van't Hoff Theory of Dilute Solutions
- Isotonic solutions
- Raoult's Law of Lowering of Vapour Pressure
- Elevation of Boiling Point
- Depression in Freezing Point
- Abnormal Molecular Weights or Abnormal Solutes
- Van't Hoff Factor
  - ☐ Summary
  - ☐ Student Activity
  - ☐ Test Yourself

• 14.1. TYPES OF PHYSICAL PROPERTIES

The different classes of physical properties are as follows :

(i) Colligative property : It is the property which depends of the number of molecules only and not on their nature, *e.g.*, osmotic pressure, lowering of vapour pressure. depression of freezing point, elevation of boiling point.

(ii) Additive property : It is defined as the property which is the sum of the corresponding properties of all the atoms constituting the molecule, *e.g.*, molecular weight etc.

(iii) Constitutive property : It is defined as the property which depends upon the arrangement of atoms within the molecule, *i.e.*, upon the constitution of the molecule, *e.g.*. optical activity.

(iv) Additive and constitutive property : It is defined as the property which can not only be obtained by adding the corresponding properties of the constitutent atoms but also depends on the arrangement of atoms within the molecule, *e.g.*, parachor, rheochor, molecular refractivity, molecular viscosity etc.

• 14.2. OSMOSIS AND OSMOTIC PRESSURE

[I] Osmosis

Consider a solution of sugar contained in an inverted thistle funnel, the lower end of which is tied with a parchment paper. which acts as semi-permeable membrane. This funnel is then kept in a beaker containing water, as shown in figure (1). Water passes into the funnel through the membrane, whereby the level of the liquid in the funnel is risen appreciably. *The phenomenon of spontaneous flow of pure solvent (water) into a solution through a semi-permeable membrane is known as osmosis.*

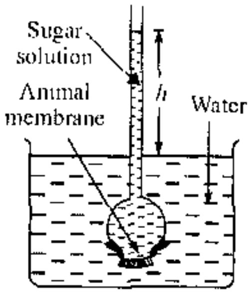

Fig. 1. Osmosis

Osmosis not only occurs between a pure solvent and a solution but also between two solutions of different concentrations.

So, **osmosis** may also be defined as, *'the spontaneous flow of solvent through a semi-permeable membrane from a solution of lower concentration to that of higher concentration'*. If two solutions are of equal concentrations, no osmosis will take place.

[II] Osmotic Pressure

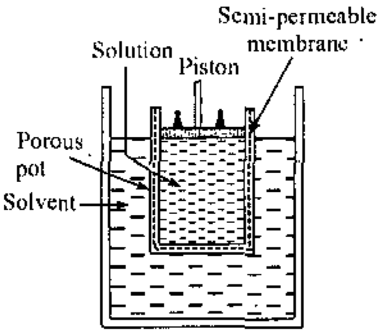

Fig. 2. Balancing of osmotic pressure.

Consider a solution of sugar contained in an inverted thistle funnel, the lower end of which is tied by a parchment paper, which acts as a semi-permeable membrane. This funnel is then kept in a beaker containing water as shown in figure (2). Water passes into the funnel through the membrane, whereby the level of the liquid in the funnel rises appreciably.

The flow of solvent through the membrane will continue till an equilibrium is established. At this stage, the hydrostatic pressure of the liquid column exactly balances the tendency of water to pass inside through the semi-permeable membrane. ***The hydrostatic pressure thus set up as a result of osmosis is a measure of osmotic pressure of the solution***. If the liquid rises to a height h in the tube of the funnel, then :

$$\text{Osmotic pressure of solution} = hdg,$$

where, d is the density of the solution and g is the acceleration due to gravity.

Osmotic pressure can also be defined as follows :

(i) Let the sugar solution be placed in a vessel, the walls of which are semi-permeable. It is tightly closed by a piston. This vessel is lowered into a larger vessel (*e.g.*, beaker) containing pure solvent (water), as shown in figure (2). The water on account of osmosis will have a tendency to flow into the smaller vessel through the semi-permeable membrane. This tendency can be checked by applying external pressure on the solution by placing increasing weights on the piston. By placing proper weights on the piston, the tendency of water to enter the smaller vessel through the membrane will be exactly balanced by its counter pressure from above.

So, **osmotic pressure** of a solution is defined as, ***'the excess pressure which must be applied to the solution in order to just prevent the flow of the solvent into it through a semi-permeable membrane'.***

(ii) In osmosis, the vapours of solvent permeate through a semi-permeable membrane in order to make the vapour pressures the same on both sides. As the vapour pressure of a liquid can be increased by applying pressure on it, osmosis may thus be stopped by applying some extra pressure on the solution or applying some negative pressure on the solvent. The vapour pressures on the two sides are thus equalised. So, ***osmotic pressure*** may be defined as, ***'the excess pressure which must be applied to the solution in order to increase its vapour pressure until it becomes equal to that of the solvent.'***

Alternately, ***osmotic pressure*** is also defined as, ***'the pressure withdrawn externally from the pure solvent in order to decrease its vapour pressure until it becomes equal to that of the solution.'***

[III] Measurement of Osmotic Pressure

Though a number of methods, *e.g.*, Pfeffer's method, de Vries plasmolytic method etc. are available for measuring the osmotic pressure of a solution, the methods mostly used for the purpose are due to (i) Morse and Frazer and (ii) Berkeley and Hartley.

Berkeley-Hartley's method : The apparatus (Fig. 3) consists of a porous pot on the walls of which is deposited a semi-permeable membrane of copper ferrocyanide. It is surrounded by a bronze

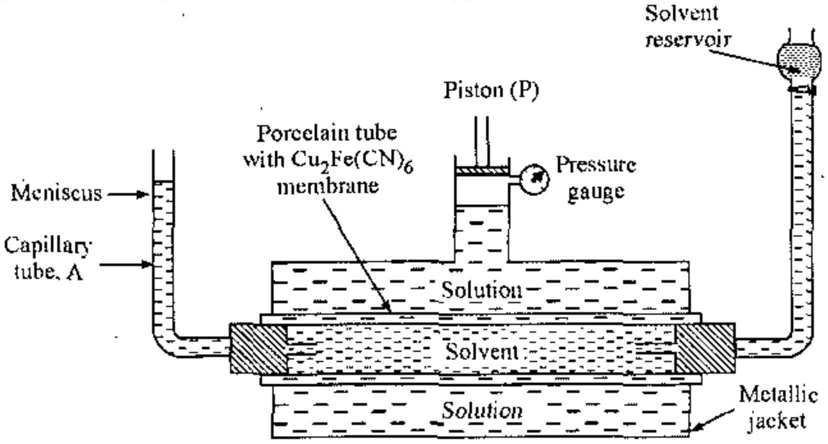

Fig. 3. Berkeley-Hartley's apparatus for measuring osmotic pressure

cylinder to which is fitted a piston, P. A pressure gauge is also attached to the piston to measure the osmotic pressure. The porous pot is fitted with a water reservoir on the right side and a capillary A on the left side. Water is placed in the porous pot, while the cylinder is filled with the solution whose osmotic pressure is to be determined. Water tends to pass from the porous pot into the solution through the semi-permeable membrane. This results in the lowering of the level of water in capillary A. Pressure is now applied externally by the piston so that the level of water in the capillary A remains stationary. The total applied pressure which is equal to the osmotic pressure of the solution can be read from the pressure gauge or by a manometer.

This method is an improved one in the sense that the equilibrium is established very quickly, strain on the membrane is not so much as in other methods and the concentration of the solution does not change during the measurements.

[IV] Effect of Temperature and Concentration on Osmotic Pressure

According to van't Hoff, osmotic pressure of a solution is due to the bombardment of solute particles on semi-permeable membrane. It will thus increase with the increase in the number of solute particles, *i.e.*, concentration of solution. Thus, osmotic pressure is directly proportional to concentration.

Furthermore, the bombardment of the solute particles on semi-permeable membrane depends upon their velocity and the latter in turn increases with temperature. Thus, osmotic pressure increases with increasing temperature, *i.e.*, they are directly proportional to each other.

[IV] Molecular Weight From Osmotic Pressure

According to van't Hoff, we have $PV = nRT$

where, $P =$ osmotic pressure; $V =$ volume of the solution, $n =$ number of moles of solute; $R =$ gas constant; $T =$ absolute temperature.

If w g of solute of molecular weight m be dissolved in the solution, then we have $n = w/m$

$$\therefore \qquad PV = \frac{w}{m} RT$$

Thus, the value of m can be calculated, provided the values of P, V, w and T are known.

Ex. 1. *Calculate the osmotic pressure of 5% solution of glucose ($C_6H_{12}O_6$) at 18°C.*

Solution. $T = (273 + 18) = 291$ K; $w = 5$, $V = 100$ c.c. $= 1/10$ litre,

m of glucose ($C_6H_{12}O_6$) $= 180$.

We know that,

$$P = \frac{w}{mV} \times RT$$

or

$$P = \frac{5}{180 \times 1/10} \times 0.0821 \times 291 = \mathbf{6.636\ atm.}$$

Ex. 2. *Calculate the osmotic pressure of M/10 solution of cane sugar at 27°C.*

Solution. Molecular weight of cane sugar ($C_{12}H_{22}O_{11}$) $= 342$.

For $M/10$ solution, it means that 1/10 g mole of cane sugar is dissolved in 1 litre of solution, *i.e.*, 342/10 g is dissolved in 1 litre.

$V = 1$ litre; $T = 27 + 273 = 300$ K; $m = 342$.

We know that,

$$P = \frac{w}{mV} \cdot RT = \frac{342 \times 0.0821 \times 300}{10 \times 342 \times 1} = \mathbf{2.463\ atmosphere.}$$

• 14.3. VAN'T HOFF THEORY OF DILUTE SOLUTIONS

van't Hoff observed the following similarities in the behaviour of dilute solutions and substances in the gaseous state. He showed that various laws which apply to gases, can also be applied to dilute solutions. This led him to formulate the following laws :

(1) Boyle-van't Hoff law (First law of osmotic pressure) : *The osmotic pressure (P) of a solution is inversely proportional to the volume (V) of the solution containing one mole of the solute at constant temperature or in other words, osmotic pressure of a solution is directly proportional to concentration (C) at constant temperature.* Thus,

$$P \propto \frac{1}{V} \propto C, \text{ at constant } T$$

This relationship is similar to the mathematical form of the Boyle's law for gases.

(2) Charles'-van't Hoff law (Second law of osmotic pressure) : *The osmotic pressure (P) of a solution at constant concentration is directly proportional to temperature (T) on the absolute scale.* Thus, $P \propto T$, at constant C

This relationship is similar to the mathematical form of the Charles' law for gases.

(3) Avogadro-van't Hoff hypothesis : *At a given temperature, solutions having equal molar concentrations of different solutes have the same osmotic pressure.*

This law is similar to Avogadro's law for gases.

(4) Simultaneous effect of concentration and temperature on osmotic pressure : Combining the first and second laws of osmotic pressure for a solution containing one mole of a solute, we obtain an expression :

$$P \propto \frac{T}{V}, \text{ if both } T \text{ and } V \text{ vary}$$

or
$$PV = KT \, (K = \text{constant}) \qquad \ldots (1)$$

van't Hoff obtained the value of K by substituting the values of P, V and T for sucrose solution. He observed that for a solution containing 10 g of sucrose (molecular weight = 342) per litre, the osmotic pressure was found to be 0.66 atmosphere, at 273K. Therefore,

$$K = \frac{PV}{T} = \frac{0.66 \times 34.2}{273} = 0.0821 \text{ lit atm/deg/mole}$$

The value of K is in good agreement with gas constant, R. So, substituting K by universal constant, R, in equation (1), we get,

$$PV = RT$$

In general, if n moles of a solute are dissolved in V litres then the above equation becomes,

$$PV = nRT$$

This equation is known as ***general solution equation.*** The above facts reveal that there exists an exact analogy between the dissolved state of a substance and its gaseous state. Thus, van't Hoff gave a law which can be stated as under :

'The osmotic pressure of a dilute solution is the same as the pressure, which the solute would exert if present as a gas at the same temperature, occupying the same volume as that of the solution, *i.e.,* ***gas laws are applicable to dilute solutions.'***

This is known as ***van't Hoff law of dilute solutions.***

• 14.4. ISOTONIC SOLUTIONS

Solutions which have the same osmotic pressures at the same temperature are said to be isotonic. When two solutions having the same osmotic pressures are brought in contact with each other through a semi-permeable membrane, there will thus be no transference of solvent from one solution to the other. Writing general solution equations for two solutions represented by subscripts 1 and 2, at the same temperature, we get.

$$P_1V_1 = n_1RT = \frac{w_1}{m_1} RT$$

$$P_2V_2 = n_2RT = \frac{w_2}{m_2} RT$$

$$\therefore \qquad P_1 = \frac{w_1}{m_1V_1} . RT \text{ and } P_2 = \frac{w_2}{m_2V_2} . RT$$

For isotonic solutions, $P_1 = P_2$

$$\because \qquad \frac{w_1}{m_1V_1} = \frac{w_2}{m_2V_2} \qquad \ldots (1)$$

Thus, according to van't Hoff theory of dilute solution, ***isotonic solutions have the same molar concentrations.***

The knowledge of isotonic solutions helps us in determining the molecular weight of a solute. If the molecular weight of one of the substances forming isotonic solutions is known, then that of the other can be calculated with the help of equation (1)*.

Ex. 1. *A 1.02% solution of glycerine is isotonic with 2% solution of glucose. What is the molecular weight of glycerine?*

Solution. For isotonic solution, we have

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*Of the two solutions separated by a s.p.m., if one is of lower O.P., it is said to be ***hypotonic*** relative to the second solution. If it has a higher O.P. than the second solution, it is said to be ***hypertonic*** relative to the second solution.

If red blood cells are put in distilled water (hypotonic solution), water passes into the cells and they swell. If red blood cells are placed in 1% NaCl solution (hypertonic solution), water comes out of the cells and they shrink.

$$\therefore \qquad \underset{\text{Glycerine}}{\frac{w_1}{m_1 V_1}} = \underset{\text{Glucose}}{\frac{w_2}{m_2 V_2}}$$

or $$\frac{1.02}{m_1 \times 0.1} = \frac{2}{180 \times 0.1} \qquad \text{[Mol. wt. of glucose } (C_6H_{12}O_6) = 180]$$

or $$m_1 = \frac{180 \times 0.1 \times 1.02}{2 \times 0.1} = \mathbf{91.8}$$

Ex. 2. *A solution containing 8.6 g/litre of urea (mol. wt. = 60) was found to be isotonic with a 5% solution of an organic solute. Calculate the molecular weight of the solute.*

Solution. For urea : $w_1 = 8.6; m_1 = 60; V_1 = 1$ litre

For unknown solute : $w_2 = 5; m_2 = ?; V_2 = 100$ c.c. $= 0.1$ litre

For isotonic solutions, we have

$$\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

or $$\frac{8.6}{60 \times 1} = \frac{5}{m_2 \times 0.1}$$

$$m_2 = \frac{60 \times 5 \times 1}{8.6 \times 0.1} = 348.83$$

• 14.5. RAOULT'S LAW OF RELATIVE LOWERING OF VAPOUR PRESSURE

[I] Relative Lowering of Vapour Pressure

It is a well known fact that when a non-volatile solute is dissolved in a liquid, the vapour pressure of the solution becomes smaller than the vapour pressure of the pure solvent. If p and p_s represent the vapour pressures of pure solvent and solution, respectively, then

$$\text{Lowering of vapour pressure} = p - p_s$$

$$\text{Relative lowering of vapour pressure} = \frac{p - p_s}{p}$$

So, relative lowering of vapour pressure is the ***ratio of lowering of vapour pressure and the vapour pressure of the pure solvent.***

[II] Mole Fraction of Solute

The mole fraction of solute is defined as the, *'**fraction of the total moles of the solute present in the solution,** i.e.,* ***ratio of moles of the solute to the total number of moles in solution.'***

If n_1 moles of a solute is dissolved in n_2 moles of a solvent, then the total number of moles in the solution will be $(n_1 + n_2)$.

$$\therefore \qquad \text{Mole fraction of solute} = \frac{n_1}{n_1 + n_2}$$

[III] Statement of Raoult's Law

According to Raoult's law, ***'relative lowering of vapour pressure is equal to the mole fraction of the solute.'*** Mathematically,

$$\frac{p - p_s}{p} = \frac{n_1}{n_1 + n_2} \qquad \ldots (1)$$

For dilute solutions, n_1 is very small as compared so n_2, so it can be neglected. Therefore, equation (1) becomes,

$$\frac{p - p_s}{p} = \frac{n_1}{n_2} \qquad \ldots (2)$$

Equation (2) is Raoult's law equation for dilute solutions.

[IV] Molecular Weight of Solute from Raoult's Law

If w_1 g of a solute of molecular weight m_1 be dissolved in w_2 g of a solvent of molecular weight m_2, then we can write :

$$n_1 = w_1/m_1, \text{ and } n_2 = w_2/m_2$$

Thus, equation (1) becomes :

$$\frac{p - p_s}{p} = \frac{w_1/m_1}{w_1/m_1 + w_2/m_2} \qquad \ldots (3)$$

For dilute solutions, equation (2) becomes :

$$\frac{p-p_s}{p} = \frac{w_1/m_1}{w_2/m_2} = \frac{w_1\, m_2}{w_2\, m_1} \qquad \ldots (4)$$

Thus, if lowering of vapour pressure produced by dissolving a known weight of solute in a known weight of solvent (known molecular weight) is determined, the molecular weight of solute can be calculated. The measurement of lowering of vapour pressure can be made by a number of methods, *e.g.*, static method (barometric method) etc., but the dynamic method by Walker and Ostwald gives the most accurate results.

Walker and Ostwald method : The apparatus is as shown in figure (4). It consists of two bulbs containing a weighed amount of the solution under study and are connected to the next two bulbs containing a weighed amount of the pure solvent. A weighed amount of anhydrous calcium chloride is taken in an accurately weighed U-tube. All the bulbs must be kept at the same temperature and air must be bubbled gradually to ensure that it gets saturated with the vapour in each bulb. Dry air is bubbled successively through the solution and solvent bulbs as well as U-tube.

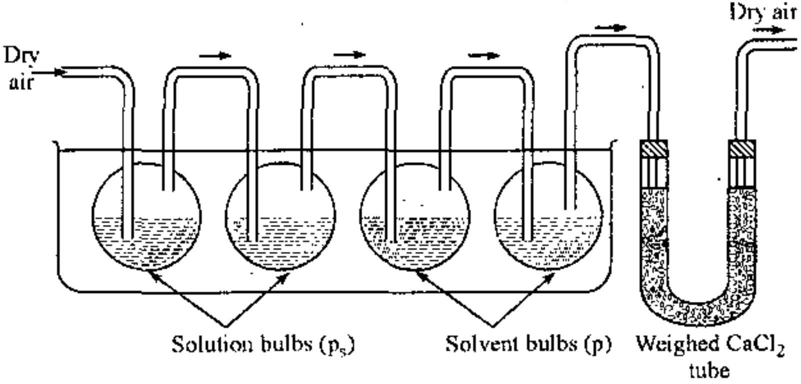

Fig. 4. Walker-Ostwald's apparatus

Dry air is first bubbled through the solution bulbs. The air as it passes through these bulbs takes up an amount of vapour which is proportional to the vapour pressure (p_s) of the solution at the experimental temperature. As the moist air, saturated upto vapour pressure p_s, passes through the solvent bulbs, it takes up further amount of vapour, which is proportional to the difference in vapour pressure of the pure solvent and the solution, *i.e.*, $p - p_s$. Thus, there will be a loss in the weight of bulbs containing solution and solvent. The air which has been saturated upto a pressure p is now passed through a U-tube containing anhydrous calcium chloride, which in turn absorbs all the water vapours. The calcium chloride tube is weighed at the end of the experiment. The increase in weight of U-tube should be equal to the total loss in the weight of solution and solvent bulbs, which in turn is proportional to p. Therefore,

Loss in weight of solution bulbs $\propto p_s$

Loss in weight of solvent bulbs $\propto p - p_s$

Loss in weight of solution bulbs + Loss in weight of solvent bulbs $\propto p_s + p - p_s \propto p$.

Gain in weight of $CaCl_2$ tube $\propto p$

$$\therefore \quad \frac{p-p_s}{p} = \frac{\text{Loss in weight of solvent bulbs}}{\text{Loss in weight of (solution + solvent) bulbs}} = \frac{\text{Loss in weight of solvent bulbs}}{\text{Gain in weight of } CaCl_2 \text{ tube}}$$

Thus, knowing the loss in weight of solution bulbs and solvent bulbs and gain in the weight of $CaCl_2$ tube, we can calculate the relative lowering of vapour pressure. Therefore, the molecular weight (m_1) of the non-volatile solute can be calculated from equation (4) as all the other values are known.

[V] Relation Between Osmotic Pressure and Lowering of Vapour Pressure

Consider a solution contained in an inverted thistle funnel at the end of which is tied a semi-permeable membrane (Fig. 5). The funnel is dipped in a chamber containing solution and the whole chamber is evacuated and is made air tight. The system in the figure cannot represent an equilibrium as the two liquids, *i.e.*, pure water and solution exert different vapour pressures and are in contact with the water vapours. As water vapours exert a higher vapour pressure (p), it will pass through the vapour phase into the solution, having vapour pressure, p_s. This process continues till the two vapour pressures become equal and a state of equilibrium is attained. Due to osmosis, the liquid rises in the tube to a certain height h. The rise in liquid level brings about dilution of the solution. This effect is, however, negligible and the vapour pressure of the solution still remains p_s. At equilibrium, the hydrostatic pressure due to liquid column is equal to the osmotic pressure of the solution. The mathematical derivation of the relation between lowering of vapour pressure (or relative lowering of vapour pressure) and osmotic pressure is carried out as follows:

Let p and p_s be the vapour pressures of the pure solvent and solution, respectively and let P be the osmotic pressure of the solution at temperature T of the experiment. The vapour pressure p_s of the solution is equal to the pressure of the vapour of the pure solvent outside the stem at the level of the surface of the solution in the stem, *i.e.*, B.

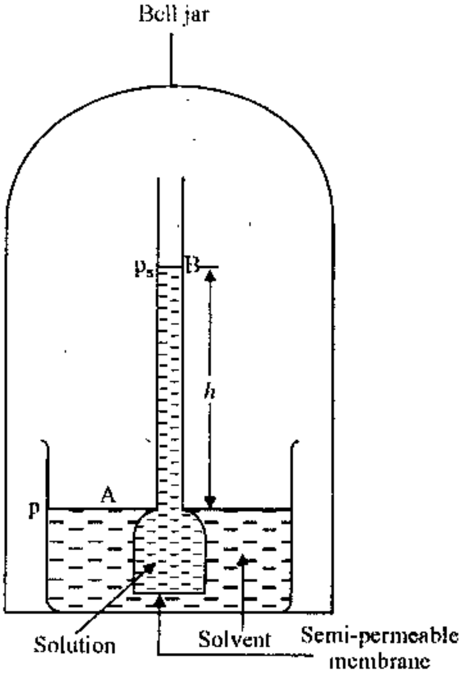

Fig. 5

$$\therefore \qquad p = p_s + hdg$$

$$\text{or} \qquad p - p_s = hdg \qquad \dots (1)$$

where, $h =$ height of the column of the solution from the surface of the solvent, $d =$ density of the vapour at the experimental temperature and $g =$ acceleration due to gravity. The osmotic pressure (P) of the solution is given by

$$P = h\rho g \qquad \dots (2)$$

where, $\rho =$ density of the solution and becomes the density of the solvent in the case of a dilute solution.

Dividing equation (1) by equation (2), we get

$$\frac{p - p_s}{P} = \frac{d}{\rho} \qquad \dots (3)$$

$$\text{But} \qquad d = M/V \qquad \dots (4)$$

where, $M =$ molecular weight of solvent and $V =$ molecular volume of vapours.

If the vapour is supposed to obey ideal gas laws, then $pV = RT$, *i.e.*,

$$V = \frac{RT}{p}$$

Then, from equation (4), $d = \dfrac{Mp}{RT}$

Substituting the value of d in equation (3), we get

$$\frac{p - p_s}{P} = \frac{Mp}{RT\rho}$$

$$\frac{p - p_s}{p} = \frac{MP}{RT\rho} \qquad \dots (6)$$

From equation (6), it is thus clear that the ***osmotic pressure is proportional to lowering of vapour pressure ($p - p_s$) or relative lowering of vapour pressure*** $\left(\dfrac{p - p_s}{p}\right)$.

[VI] Deduction of Raoult's Law

From van't Hoff theory of dilute solutions, we have

$$PV = n_1 RT$$

$$\text{or} \qquad P = \frac{n_1}{V} RT \qquad \dots (7)$$

where, $n_1 =$ number of moles of solute. $V =$ volume of the solvent, $P =$ osmotic pressure and $T =$ absolute temperature.

Since, $$V = \frac{Mn_2}{\rho}$$

where, n_2 = number of moles of solvent. Substituting the value of V in equation (7), we get

$$P = \frac{n_1RT\rho}{Mn_2}$$

Substituting this value of P in equation (6), we get

$$\frac{p - p_s}{p} = \frac{M}{RT\rho} \cdot \frac{n_1RT\rho}{Mn_2}$$

or $$\frac{p - p_s}{p} = \frac{n_1}{n_2}$$

This is the modified form of Raoult's law as applicable to dilute solutions, *i.e.*, when $n_1 << n_2$.

Ex. 1. *A current of dry air was passed through a series of bulbs containing a solution of 3.458g of a substance in 100 g of ethyl alcohol and then through a series of bulb containing pure alcohol. The loss in weight of the former and latter series of bulbs was 0.9675 g and 0.0255 g, respectively. Calculate the molecular weight of the substance.*

Solution. We know that,

$$\frac{p - p_s}{p} = \frac{\text{Loss in weight of solvent bulb}}{\text{Loss in weight of (solvent + solution) bulb}}$$

$$= \frac{0.0255}{0.9675 + 0.0255} = \frac{0.0255}{0.9930}$$

Therefore, $$\frac{0.0255}{0.9930} = \frac{w_1m_2}{w_2m_1} = \frac{3.458 \times 46}{100 \times m_1}$$ (Mol. wt. m_2, of ethyl alcohol = 46)

$$\therefore \quad m_1 = \frac{0.9930 \times 2.458 \times 46}{0.0255 \times 100} = \mathbf{61.94}$$

• 14.6. ELEVATION OF BOILING POINT

The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure. We know that the vapour pressure of a solution is always lower than that of the pure solvent. Thus, the presence of a non-volatile solute lowers the vapour pressure and to make it boil we have to increase the vapour pressure to the atmospheric pressure by raising the temperature. For a solution, this condition is obtained at a temperature higher than that for the pure solvent. Therefore, *a solution of a non-volatile solute always boils at a higher temperature than the*

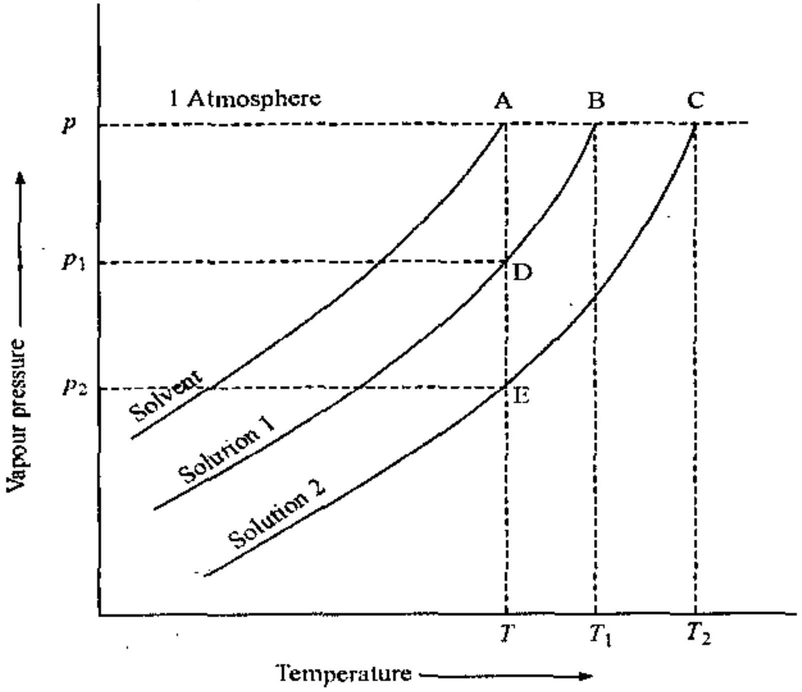

Fig. 6. Vapour pressure and temperature curves

pure solvent. The difference between the boiling point of a solution and the pure solvent is known as the ***elevation of boiling point*** **(ΔT).**

If we plot the vapour pressure of the pure solvent and two dilute solutions of different concentration (say 1 and 2) against temperature, a set of curves are obtained as shown in figure (6). If atmospheric pressure is represented by line pC, then boiling points of pure solvent, solution 1 and solution 2 will be T, T_1 and T_2, respectively.

For very dilute solutions, the curves are nearly parallel straight lines. The triangles ABD and ACE are similar. Thus,

$$\frac{AB}{AC} = \frac{AD}{AE}$$

or
$$\frac{T_1 - T}{T_2 - T} = \frac{p - p_1}{p - p_2}$$

where, p, p_1 and p_2 are the vapour pressures of pure solvent, solution 1 and solution 2, respectively.

If Δp and ΔT represent the respective lowering of vapour pressure and elevation of boiling point, then,

$$\frac{\Delta T_1}{\Delta T_2} = \frac{\Delta p_1}{\Delta p_2}$$

or
$$\Delta T \propto \Delta p$$

Thus, the ***elevation of boiling point is proportional to the lowering of vapour pressure.***

For dilute solutions, Raoult's law can be written as,

$$\frac{p - p_s}{p} = \frac{w_1 m_2}{w_2 m_1}$$

or
$$\Delta p = \frac{w_1 m_2}{w_2 m_1} \cdot p \qquad \ldots (1)$$

where, p = vapour pressure of pure solvent, p_s = vapour pressure of solution, w_1 = weight of solute of molecular weight m_1, w_2 = weight of solvent of molecular weight m_2.

For the same solvent, m is constant and p, the vapour pressure at the boiling point is also constant. So,

$$\Delta p = p m_2 \cdot \frac{w_1}{w_2 m_1} = \text{constant} \times \frac{w_1}{w_2 m_1}$$

$\therefore$
$$\Delta p \propto \frac{w_1}{w_2 m_1}$$

But we know that, $\Delta p \propto \Delta T$ so

$$\Delta T \propto \frac{w_1}{w_2 m_1}$$

or
$$\Delta T = k \cdot \frac{w_1}{w_2 m_1} \qquad \ldots (2)$$

where, k is a constant known as ***boiling point constant.***

If $w_1/m_1 = 1$ and $w_2 = 1$ g, then from equation (2)

$$k = \Delta T$$

So, ***boiling point constant*** is defined as *the elevation in boiling point produced by dissolving 1 mole of a solute in 1 g of a solvent.*

If $w_1/m_1 = 1$ and $w_2 = 100$ g, then from equation (2),

$$\frac{k}{100} = \Delta T$$

or K_{100} or $K = \Delta T$, where $k = 100\,K$ or $100\,K_{100}$

where, K or K_{100} is another constant, known as ***molecular elevation constant.*** It is defined as the *elevation in boiling point produced by dissolving 1 mole of a solute in 100 g of a solvent.*

Thus, replacing k by K in equation (2), we get

$$\Delta T = \frac{100\,K w_1}{w_2 m_1} \qquad \ldots (3)$$

If $w_1/m_1 = 1$ and $w_2 = 1000$ g, then from equation (2),

$$\frac{k}{1000} = \Delta T$$

or $$K_b = \Delta T, \text{ where } k = 1000K_b$$

where, K_b is a constant, known as ***molal elevation constant*** or ***ebullioscopic constant***. It is defined as, *the elevation in boiling point produced by dissolving 1 mole of a solute in 1000 g of a solvent.*

Replacing k by K_b in equation (2), we get,

$$\Delta T = \frac{1000\, K_b w_1}{w_2 m_1} \qquad \ldots (4)$$

Equations (2), (3) and (4) are different expressions connecting the elevation in boiling point and molecular weight of dissolved substance.

[I] Relation Between Molal Elevation Constant (K_b) and Latent Heat of Vaporisation (L_e)

van't Hoff showed that by thermodynamical reasoning, we can obtain the following expression:

$$K_b = \frac{RT^2}{1000L_e}$$

where, $T =$ boiling point of the solvent on the absolute scale, $R =$ gas constant and $L_e =$ latent heat of vaporisation per gram of solvent. As $R = 2$ calories,

$$K_b^* = \frac{0.002T^2}{L_e}$$

The unit of K_b is degree.

[II] Determination of Molecular Weight of a Non-Volatile Solute

Though a number of methods, *e.g.*, Beckmann's method. Cottrell's method etc. are available for determining the molecular weight of a non-volatile solute, the most convenient method generally employed in the laboratory is ***Landsberger's method.***

In Landsberger's method, the liquid is heated to its boiling point by passing the vapours of the pure boiling solvent into it. When the vapour is condensed, it gives out its latent heat of vaporisation which heats the liquid to its boiling point without any danger of super-heating.

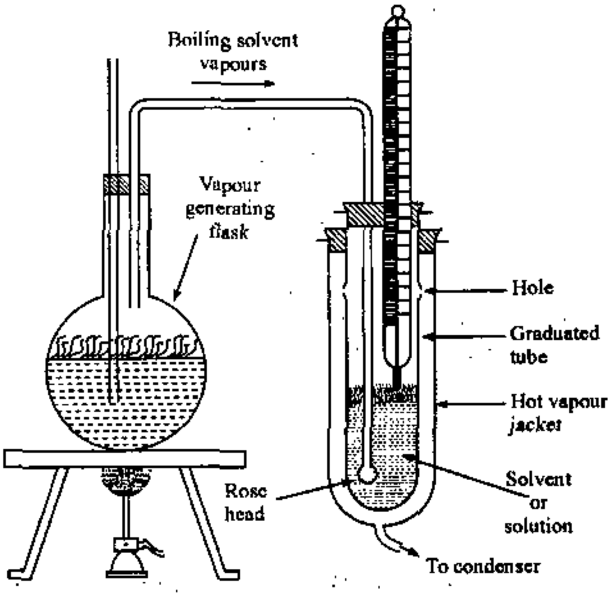

Fig. 7. Landsberger's apparatus.

The apparatus (Fig. 7) consists of a vapour generating flask in which solvent is taken and boiled. An inner boiling tube is taken and has a bulb with a hole in the side and is graduated in mL. It is fitted with an accurate thermometer (graduated to 0.01°) and a glass tube with a bulb blown at the end which has many holes in it. This bulb is known as *rose head*. It ensures uniform distribution of solvent vapours into the solvent. The inner tube is surrounded by an outer jacket which receives hot vapours from the inner tube through the hole. This jacket forms a protecting jacket and prevents loss of heat from the inner tube due to radiation and it further protects it from draughts of air.

In the actual experiment, about 7-8 ml of pure solvent is taken in the inner tube and vapours from vapour generating flask are passed into it. After sometime the liquid begins to boil. As soon as the temperature becomes constant, the thermometer reading is taken. This gives the boiling point

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*In case of water, $T = 100 + 273 = 373$ K; $L_e = 537$ calories and so

$$K_b = \frac{0.002 \times 373 \times 373}{537} = 0.518^\circ$$

(T) of the pure solvent. Now the supply of solvent vapour is cut off temporarily and a weighed amount (w_1) (say 0.5–1.0 g) of a non-volatile solute whose molecular weight is to be determined is added into the inner tube. The boiling point (T_1) of the solution is then taken as before. Immediately after the temperature is read off, the rose-head and thermometer are raised out of the solution and the volume of the solution noted.

The molecular weight (m_1) of the non-volatile solute is then calculated by the expression :

$$\Delta T = \frac{1000 K_b w_1}{w_2 m_1}$$

or

$$m_1 = \frac{1000 K_b w_1}{w_2 \, . \, \Delta T}$$

Knowing all the values of right hand side, we can easily calculate m_1.

Ex. 1. *(a) Calculate the value of K_b for water given that pure water boils at 100° C and latent heat of its vaporisation is 540 cal g^{-1} ($R = 2$ calories).*

Solution. Boiling point of water

$$(T) = 100°\text{C} = 100 + 273 = 373 \text{ K}$$

Latent heat of vaporisation of water (L_e) = 540 cal/g.

$$\therefore \qquad K_b = \frac{RT^2}{1000 L_e} = \frac{2 \times (373)^2}{1000 \times 540} = \mathbf{0.515°}$$

Ex. 2. *A solution containing 2.44 g of a solute dissolved in 75 g of water boiled at 100 413°C. Calculate the molecular weight of the solute. ($K_{1000} = 0.52°C$).*

Solution. $w_1 = 2.44$; $w_2 = 75$; $m_1 = ?$; $\Delta T = 100.413 - 100 = 0.413°$

$$\therefore \qquad \Delta T = \frac{1000 K_b w_1}{w_2 m_1}$$

or

$$m_1 = \frac{1000 K_b w_1}{w_2 \, . \, \Delta T} = \frac{1000 \times 0.52 \times 2.44}{75 \times 0.413} = \mathbf{40.96}$$

• 14.7. DEPRESSION IN FREEZING POINT

The freezing point of a liquid is that temperature at which the liquid form and its solid form remain in equilibrium. This is so when vapour pressures of both the forms are equal at the same temperature. Therefore, *freezing point of a liquid is that temperature at which the vapour pressures of the liquid and that of its solid form become equal.*

The lowering of vapour pressure due to dissolving of a solute causes the solution to freeze at a lower temperature, because at the freezing point of a liquid, its vapour pressure becomes equal to that of its solid form which separates out and is in equilibrium with its liquid phase. The solid form has a higher vapour pressure when it remains in equilibrium with the pure solvent at its freezing point. So, it may be concluded that the *freezing point of the solution is less than that of the pure solvent.* The difference between the freezing points of solvent and solution is called the *depression in freezing point* (ΔT).

On plotting a graph between the vapour pressure and temperature for a pure solvent, we get a curve AB (Fig. 8). There is a sharp break in the curve at B, below which the vapour pressure-temperature curve exhibits a sharp decrease in vapour pressure with a decrease in temperature. This indicates the existence of a solid along the part BB′ of the curve. At B, the liquid and solid phases co-exist and thus the temperature (T) corresponding to this point is the freezing point of the pure solvent. The vapour pressure- temperature curves for solutions 1 and 2 of different concentrations are as shown. Points F and C correspond to the freezing points of the solutions 1 and 2 which are T_1 and T_2, respectively.

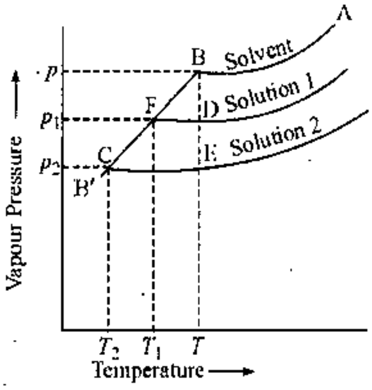

Fig. 8. Vapour pressure-temperature curves.

For very dilute solutions, the curves are nearly parallel straight lines. The triangles BFD and BCE are similar. Thus,

$$\frac{\text{FD}}{\text{CE}} = \frac{\text{BD}}{\text{BE}}$$

or
$$\frac{T-T_1}{T-T_2}=\frac{p-p_1}{p-p_2}$$

where, p, p_1 and p_2 are the vapour pressures of pure solvent, solution 1 and solution 2, respectively.

If Δp and ΔT represent the lowering of vapour pressure and depression in freezing point, respectively, then

$$\frac{\Delta T_1}{\Delta T_2}=\frac{\Delta p_1}{\Delta p_2}$$

or
$$\Delta T \propto \Delta p$$

Thus, the ***depression in freezing point is proportional to the lowering of vapour pressure.***

For dilute solutions, Raoult's law can be written as

$$\frac{p-p_s}{p}=\frac{w_1 m_2}{w_2 m_1}$$

or
$$\Delta p=\frac{w_1 m_2}{w_2 m_1}\cdot p \qquad \ldots (1)$$

where, $p =$ vapour pressure of the pure solvent, $p_s =$ vapour pressure of solution, $w_1 =$ weight *of solute of molecular weight* m_1, $w_2 =$ weight of solvent of molecular weight m_2.

For the same solvent, m_2 is constant and p, the vapour pressure at the freezing point is also constant. So,

$$\Delta p = pm_2\cdot\frac{w_1}{w_2\, m_1}=\text{constant}\times\frac{w_1}{w_2\, m_1}$$

∴
$$\Delta p \propto \frac{w_1}{w_2 m_1}$$

But we know that $\Delta p \propto \Delta T$

∴
$$\Delta T \propto \frac{w_1}{w_2 m_1}$$

or
$$\Delta T \propto \frac{kw_1}{w_2 m_1} \qquad \ldots (2)$$

where, k is a constant known as ***freezing point constant*** for the solvent.

If $w_1/m_1 = 1$ and $w_2 = 1$ g, then from equation (2), $k = \Delta T$

So, freezing point constant is defined as, the *depression in freezing point produced by dissolving 1 mole of solute in 1 g of a solvent.*

If $w_1/m_1 = 1$ and $w_2 = 100$ g, then from equation (2),

$$\Delta T=\frac{k}{100}=K \text{ or } K_{100}$$

or
$$k = 100K \text{ or } 100K_{100}$$

where, K or K_{100} is another constant, known as molecular depression constant. It is defined as, *the depression in freezing point produced by dissolving 1 mole of solute in 100 g of a solvent.*

Thus, replacing k by K in equation (2), we get

$$\Delta T=\frac{100\,Kw_1}{w_2 m_1} \qquad \ldots (3)$$

If $w_1/m_1 = 1$ and $w_2 = 1000$ g, then from equation (2),

$$\Delta T=\frac{k}{1000}=K_f \text{ or } K_{1000} \quad \text{where } k = 1000K_f = 1000K_{1000}$$

where, K_f (or K_{1000}) is a constant known as ***molal depression constant*** or ***cryoscopic constant.*** It is defined as, the *depression in freezing point produced by dissolving 1 mole of solute in 1000 g of a solvent.*

Thus, replacing k by K_f in equation (2), we get

$$\Delta T=\frac{1000K_f\, w_1}{w_2 m_1} \qquad \ldots (4)$$

Equations (2), (3) and (4) are different expressions connecting the depression in freezing point and molecular weight of a dissolved substance.

[I] Relation Between Molal Depression Constant (K_f) and Latent Heat of Fusion (L_f)

vant' Hoff showed that by thermodynamic reasoning, we can obtain the following expression:

$$K_f^* = \frac{RT^2}{1000L_f}$$

where, T = freezing point of the solvent on the absolute scale, R = gas constant, L_f = latent heat of fusion per gram of solvent. As $R = 2$ calories,

$$K_f = \frac{0.002\,T^2}{L_f}$$

[II] Determination of Molecular Weight of Non-Volatile Substance

Though a number of methods., *e.g.*, Rast's camphor method, Beckman's method etc. are available for determining the molecular weight of a non-volatile solute, the most convenient method generally and widely employed in the laboratory is *Beckmann's method.*

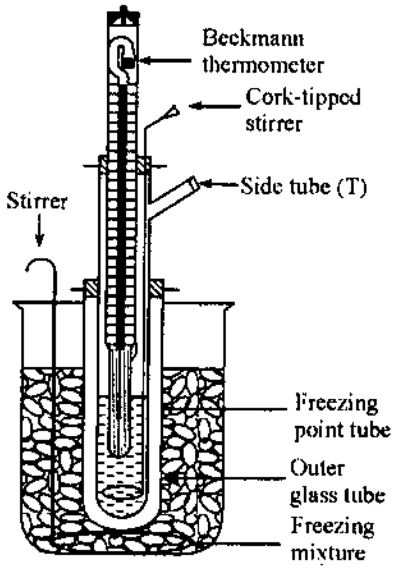

Fig. 9. Beckmann apparatus.

The apparatus as shown in figure (9) consists of an inner freezing point tube fitted with a Beckmann thermometer (it can read upto 0.01°) and a stirrer. This tube is fitted with a side tube (T) for introducing the solute. The freezing point tube is surrounded by an outer glass tube which serves as an air jacket and ensures a slow and uniform rate of cooling of liquid in the inner tube. The whole apparatus is enclosed in a glass jar containing freezing mixture and is provided with a stirrer.

In the actual experiment, 20g of the pure solvent (water) is taken in the inner freezing tube and stirred gently. The movement of the mercury thread in Beckmann thermometer is watched carefully. The temperature first falls below the freezing point of the solvent. It is then stirred and as the solvent starts solidifying, the temperature rises rapidly and finally becomes stationary. This temperature is noted. Let it be $T°$.

The freezing point tube is taken out of the freezing mixture and the solvent is melted. A weighed amount of the solute (w_1), whose molecular weight is to be determined is then added through the side tube. The experiment is repeated as before and freezing point of the solution is noted. Let it be $T_1°$. The depression in freezing point (ΔT) will then be $(T - T_1)°$.

The molecular weight (m_1) of the non-volatile solute is then calculated from the expression:

$$\Delta T = \frac{1000 K_f w_1}{w_2 m_1}$$

or

$$m_1 = \frac{1000\, K_f w_1}{w_2 \,.\, \Delta T}$$

Knowing all the values of right hand side, we can easily calculate m_1.

Ex. 1. *Calculate the molal depression constant of water, if the latent heat of fusion of ice at 0°C = 80 cal/g.*

Solution. Latent heat of fusion (L_f) = 80.0 cal/g

Freezing point of water (T) = 0°C = 0 + 273 = 273 K

$$\therefore \qquad K_f = \frac{RT^2}{1000L_f} = \frac{2 \times (273)^2}{1000 \times 80} = \mathbf{1.863°}$$

Ex. 2. 1.55 g of a substance dissolved in 40 g of benzene lowered the freezing point of benzene by 0.55°C. Calculate the molecular weight of the substance (K_f for benzene is 5.22° per 1000 g).

Solution. $w_1 = 1.55;\ w_2 = 40;\ \Delta T = 0.55;\ m_1 = ?$

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*For water : L_f = 80 calories and $T = 0 + 273 = 273$ K

Therefore, $K_f = \frac{0.002 \times 273 \times 273}{80} = 1.86°$

Now, $$m_1 = \frac{1000K_f \cdot w_1}{w_2 \Delta T} = \frac{1000 \times 5.22 \times 1.55}{40 \times 0.55} = 367.7$$

• 14.8. ABNORMAL MOLECULAR WEIGHTS OR ABNORMAL SOLUTES

It is seen that the molecular weights of certain substances, *e.g.*, NaCl, KNO_3 etc. in water when determined by any of the methods such as, osmotic pressure, lowering of vapour pressure, elevation in boiling point, depression in freezing point, are less than their normal molecular weights. However, molecular weights of certain substances (like benzoic acid in benzene) are greater than their normal molecular weights. The reason for this anomaly is that the substances either dissociate or associate in solution. The molecular weights thus obtained are far from normal. These are molecular weights known as ***abnormal molecular weights.*** Those solutes which give abnormal molecular weight are known as ***abnormal solutes***. This fact is explained as follows :

We know that the osmotic pressure (P) is directly proportional to concentration (C), which in turn is proportional to the number of particles. It is also established that the osmotic pressure is directly proportional to lowering of vapour pressure (Δp) and the latter is proportional to elevation of boiling point and depression in freezing point (ΔT). All these properties are in turn inversely proportional to molecular weight of the substance. Mathematically,

$$P \propto C \propto \text{No. of particles} \propto \Delta p \propto \Delta T \propto \frac{1}{\text{Mol. wt.}}$$

i.e., $$\text{Mol. wt} \propto \frac{1}{\text{Number of particles}}$$

In dissociation, the number of particles increases and so the observed molecular weight is less than the normal molecular weight. In association, the number of particles decreases and thus, the observed molecular weight is higher than the normal molecular weight. Thus,

$$\text{Normal mol. wt} \propto \frac{1}{\text{Normal number of particles}}$$

$$\text{Observed mol. wt.} \propto \frac{1}{\text{Number of particles after dissociation or association}}$$

$$\therefore \quad \frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{\text{No. of particles after dissociation or association}}{\text{Normal number of particles}}$$

• 14.9. VAN'T HOFF FACTOR

van't Hoff showed that all properties, *e.g.*, osmotic pressure (P), lowering of vapour pressure (Δp), elevation in boiling point (ΔT), depression in freezing point (ΔT) depend upon the concentration (C) of the solute, *i.e.*, on the number of particles of solute. These properties are known as ***colligative properties.**** For electrolytes, the number of particles increases and so the above colligative properties are all higher for solutions of electrolytes than for non-electrolytes of the same molecular concentration. The above colligative properties have a lower value for solutes which associate in solution. To account for this, van't Hoff introduced a factor known as vant Hoff factor (i). It is represented by,

$$i = \frac{P_{obs}}{P_{nor}} = \frac{\Delta p_{obs}}{\Delta p_{nor}} = \frac{\Delta T_{obs}}{\Delta T_{nor}}.$$

In general, $$i = \frac{\text{Observed colligative property of an electrolyte}}{\text{Normal colligative property of an electrolyte}}$$

Since these properties vary inversely as molecular weight of solutes, it follows that, van't Hoff factor,

$$i = \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}}$$

Ex. 1. *Calculate the osmotic pressure of N/10 NaCl solution which ionises to an extent of 80% at 27°C.*

Solution. Normal molecular weight of NaCl = 23 + 35.5 = 58.5

Normal osmotic pressure can be calculated as follows :

$$P = \frac{w}{mV} RT$$

$N/10$ solution of NaCl means 5.85 g of NaCl is dissolved in 1 litre. Therefore, $w = 5.85$; $V = 1$; $m = 58.5$; $T = 27 + 273 = 300$ K.

$$\therefore \qquad P = \frac{5.85 \times 0.0821 \times 300}{58.5 \times 1} = 2.463 \text{ atm.}$$

The degree of dissociation NaCl is represented as :

$$\begin{array}{cccl} NaCl & \rightleftharpoons Na^+ & + \; Cl & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ 1-\alpha & \alpha & \alpha & \text{(After dissociation)} \end{array}$$

where, $\alpha =$ degree of dissociation = 0.8

$$\text{Now,} \qquad \frac{\text{O.P. (observed)}}{\text{O.P. (normal)}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

$$\text{or} \qquad \frac{\text{O.P. (observed)}}{2.463} = \frac{1-\alpha+\alpha+\alpha}{1} = \frac{1+\alpha}{1} = \frac{1+0.8}{1} = \frac{1.8}{1}$$

$$\text{or} \qquad \text{Observed O.P.} = 2.463 \times 1.8 = \mathbf{4.433 \text{ atm.}}$$

Ex. 2. *The boiling point of an aqueous solution containing 5 g KCl per litre at 760 mm pressure is 100.065°C. Calculate the degree of dissociation ($K_b = 0.54$).*

Solution. Normal molecular weight of KCl = 39 + 35.5 = 74.5

$$\text{Observed molecular weight, } m = \frac{1000K_b}{w_2\Delta.T} = \frac{100 \times 0.54 \times 5}{1000 \times 0.065} = 41.53$$

KCl dissociates as :

$$\begin{array}{cccl} KCl & \rightleftharpoons K^+ & + \; Cl^- & \\ 1 & 0 & 0 & \text{(Before dissociation)} \\ (1-\alpha) & \alpha & \alpha & \text{(After dissociation)} \end{array}$$

where, $\alpha =$ degree of dissociation.

No. of particles after dissociation = $1 - \alpha + \alpha + \alpha = 1 + \alpha$

$$\therefore \qquad \frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

$$\text{or} \qquad \frac{74.5}{41.53} = \frac{1+\alpha}{1}$$

$$\text{or} \qquad \alpha = \frac{74.5}{41.53} - 1 = 1.793 - 1 = 0.793$$

$\therefore$ Degree of dissociation = **79.3%**

Ex. 3. *A 0.5% aqueous solution of potassium chloride is found to freeze at – 0.24°C. Calculate the van't Hoff factor of the solute at this concentration. K_f for water is 1.86° for 1000 g.*

Solution. The observed molecular weight (m_1) of KCl is given by,

$$m_1 = \frac{1000K_f w_1}{w_2 \Delta T}$$

Here, $w_1 = 0.5$; $w_2 = 100$; $\Delta T = (0 - 0.24) = 0.24$

$$\because \qquad m_1 = \frac{1000 \times 1.86 \times 0.5}{100 \times 0.24} = 38.75$$

Normal molecular weight of KCl = 39 + 35.5 = 74.5

$$\therefore \qquad \text{van't Hoff factor} = \frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{74.5}{38.75} = \mathbf{1.92}$$

• SUMMARY

- Colligative property is a physical property which depends only on the number of particles/molecules and not on their nature, *e.g.*, osmotic pressure, relative lowering of vapour pressure, elevation of b.pt., depression in f.pt. etc.
- The spontaneous flow of solvent through a semi-permeable membrane from a solution of lower concentration (or pure solvent) to that of higher concentration (or solution) is called osmosis.
- Osmotic pressure is the excess pressure which must be applied to the solution in order to just prevent the flow of the solvent into it through a semi-permeable membrane.
- Osmotic pressure is directly proportional to temperature and concentration of the solution.

- Solutions which have the same osmotic pressure at the same temperature are called isotonic solutions.
- **Raoult's law :** The relative lowering of vapour pressure is equal to the mole fraction of the solute.
- Osmotic pressure is proportional to lowering of vapour pressure, elevation of boiling point, depression in freezing point.
- **Molal elevation constant (K_b) :** It is elevation in boiling point produced by dissolving 1 mole of solute in 1000 gm (or 1 kg) of a solvent.
- **Molal depression constant (K_f) :** It is the depression in freezing point produced by dissolving 1 mole of solute in 1000 gm (or 1 kg) of a solvent.
- van't Hoff factor (i) $= \dfrac{\text{Normal molecular weight}}{\text{Observed molecular weight}} = \dfrac{\Delta P_{\text{obs}}}{\Delta P_{\text{nor}}} = \dfrac{\Delta T_{\text{obs}}}{\Delta T_{\text{nor}}}$

$$= \frac{\text{Observed colligative property of an electrolyte}}{\text{Normal colligative property of an electrolyte}}$$

$$= \frac{\text{Number of particles after dissociation or association}}{\text{Normal number of particles}}$$

• STUDENT ACTIVITY

1. Name four coligative properties.
2. Define osmotic pressure.
3. What are isotonic solutions ?
4. State and explain Raoult's law of lowering of vapour pressure.
5. Define molal elevation constant.
6. Describe the relation between molal depression constant and molar heat of fusion.
7. Explain van't Hoff factor.

• TEST YOURSELF

1. Discuss van't Hoff theory of dilute solutions.
2. Derive general solution equation for dilute solutions.
3. Define osmosis and osmotic pressure.
4. How osmotic pressure is helpful in determining the molecular weight of a non-volatile solute?
5. State and explain Raoult's law of lowering of vapour pressure. How is molecular weight of a non-volatile solute determined from the law ?
6. Write a short note on van't Hoff factor.

7. Write a short note on abnormal molecular weight.

8. Write a short note on isotonic solutions.

9. How will you determine the molecular weight of a solute from isotonic solutions ?

10. What do you understand by abnormal osmotic pressure ?

11. Derive a relation between osmotic pressure and lowering of vapour pressure.

12. Give the difference between diffusion and osmosis.

13. State and explain van't Hoff theory of dilute solutions.

14. What do you understand by mole fraction of a solution ?

15. Define molal elevation constant.

16. Define molal depression constant.

17. Define abnormal molecular weight.

18. What is the effect of concentration on osmotic pressure ?

19. How osmotic pressure of a solution is affected by temperature ?

20. Give one application of isotonic solutions.

21. Give the relation between molal elevation constant and latent heat of vaporisation.

22. Give the relation between molal depression constant and latent heat of fusion.

23. Define relative lowering of vapour pressure.

24. Calculate the molal depression constant for water.

25. Calculate the molal elevation constant for water.

26. A 1.46% solution of a compound has an osmotic pressure of 783 mm at 30°C. Calculate the molecular weight of the compound.

27. 6 gm of urea (mol. wt. 60) was dissolved in 180 gm of water at 27°C. Calculate the relative lowering of vapour pressure.

28. The latent heat of vaporisation of CS_2 is 85.9 cal and its boiling point 46.2°C. The solution of 0.938 gm of benzoic acid in 50 gm of CS_2 boiled at 47.387°C. Calculate the molecular weight of benzoic acid.

29. Calculate the freezing point of the solution produced by dissolving 8.42 gm of cane sugar (mol. wt. = 342) in 50 gm of water. Latent heat of fusion of ice is 80 cal gm^{-1}.

30. The solution of 1 gm of $AgNO_3$ in 50 gm of water freezes at –0.348°C. Calculate the degree of ionisation of $AgNO_3$. ($K_f = 1.86°$).

31. The vapour pressure of a solution is :
(a) Proportional to its total pressure
(b) Inversely proportional to concentration of solute
(c) Proportional to temperature of solution
(d) Proportional to absolute temperature of solution

32. The order of osmotic pressures of equal molecular concentrations of glucose, NaCl and $BaCl_2$ is :
(a) Glucose > NaCl > $BaCl_2$ (b) NaCl > $BaCl_2$ > Glucose
(c) $BaCl_2$ > NaCl > Glucose (d) Glucose > $BaCl_2$ > NaCl

33. In an aqueous solution 18 g glucose is present in 1000 g of solvent. It is :
(a) 1 molal (c) 2 molal (c) 0.5 molal (d) 0.1 molal

34. The cover of an egg is removed by means of dil. HCl and is then dipped in a saturated solution of salt. It will :
(a) Shrink (b) Expand
(c) Have no effect (d) First shrink and then expands

35. 1.25 g of a non-electrolyte dissolved in 20 g water freezes at 271.94 K. If $K_f = 1.86°$, then the molecular weight of solute is :
(a) 207.8 (b) 209.6 (c) 179.8 (d) 109.6

36. Assuming NaCl to be completely ionised the freezing point of 1 molal solution ($K_f = 1.86°$) is:
(a) – 1.86°C (b) – 3.72°C (c) + 1.86°C (d) + 3.72°C

37. The molal elevation constant of water is :
(a) 5.15° (b) 0.515° (c) $(0.515 \times 2)°$ (d) $(0.515 \times 3)°$

38. At 27°C the osmotic pressure of a solution containing 0.5 g/litre of a substance (mol. wt. = 150) is :
(a) 0.082 atm (b) 0.164 atm (c) 0.328 atm (d) 0.041 atm

39. The vant Hoff factors of glucose and NaCl are, respectively :
(a) 1, 1 (b) 2, 2 (c) 1, 2 (d) 2, 1

40. Fill in the blanks :

(i) $\frac{p-p_s}{p}$ is known as ....

(ii) Property which depends only on the number of particles is known as .... property.

(iii) The ratio $\frac{\Delta P_{\text{obs}}}{\Delta P_{\text{nor}}}$ is known as ....

(iv) Isotonic solutions have .... osmotic pressure at same temperature.

ANSWERS

24. 0.52° **25.** 1.86° **26.** 352.52 **27.** 0.01 **28.** 37.48 **29.** – 0.375° **30.** 59.04%
31. (b) **32.** (b) **33.** (d) **34.** (a) **35.** (d) **36.** (b) **37.** (b) **38.** (a) **39.** (c)
40. **(i)** relative lowering of vapour pressure **(ii)** colligative **(iii)** van't Hoff factor
(iv) same/equal.

❑❑❑

UNIT

15

PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

LEARNING OBJECTIVES

- Polar and Non-Polar Molecules
- Dipole Moment
- Magnetic Properties of Substances
  - ❑ Summary
  - ❑ Student Activity
  - ❑ Test Yourself

• 15.1. POLAR AND NON-POLAR MOLECULES

A molecule is composed of positively charged nuclei and negatively charged electrons in such a way that the molecule as a whole remains electrically neutral. The arrangement of these charged particles is different for different molecules. There are two possibilities:

(i) When the centre of gravity of the positive charges in a molecule is exactly at the same point as that of the negatively charged electrons in a molecule. Such a molecule is called a ***non-polar molecule***, *e.g.*, H_2, Cl_2. CO_2, CH_4, C_6H_6 etc.

(ii) When the centre of gravity of electrons in amolecule does not coincide with that of positive nuclei, the molecule is called a ***polar molecule***, *e.g.*, H_2O. NH_3, $CHCl_3$ etc. The molecule as a whole is neutral, so we have equal positive ($+q$) and negative ($-q$) charges separated by a certain distance (l) in a polar molecule. So, a polar molecule behaves like a small magnet and becomes dipolar. Therefore, it is called an ***electric dipole*** or simply a ***dipole*** (two poles). Sidgwick proposed that a dipole may be shown by an arrow with a crossed tail. The arrow (→) is placed parallel to the line of positive and negative charges and should be from positive end to negative end of the dipole, as shown in HCl molecule Fig. (1).

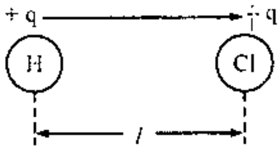


Fig. 1. Representation of dipole, where *l* is the bond length.

It can also be concluded that non-polar molecules do not have permanent dipoles, while polar molecules have permanent dipoles.

• 15.2. DIPOLE MOMENT

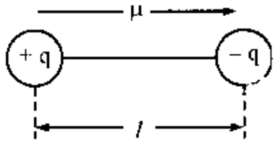


Fig. 2. Representation of dipole moment

The degree of polarity of a molecule can be expressed in terms of dipole moment. It is defined as, ***"the product of the magnitude of the charge (positive or negative) and distance between them (bond length)"***. If q is the charge at each end of the molecule and l is the distance between the positive and negative ends, the dipole moment ($\vec{\mu}$) is given by,

$$\vec{\mu} = q \times l$$

In a non-polar molecule, the distance l is zero as centres of gravity of positive and negative charges coincide, hence dipole moment is zero.

The dipole moment has a direction as well as a magnitude, *i.e.*, it is a vector quantity. It is frequently convenient to represent a dipole moment by an arrow showing the direction from the positive to the negative charge and the length of arrow represents the magnitude of dipole moment. Dipole moments being vectorial quantities, may be added vectorially.

The dipole moment arises due to the difference in the electronegativities of the two atoms held together by a chemical bond. In case of two or more bonds in a molecule, the net dipole moment will be the vector addition of dipole moments of chemical bonds. Each chemical bond has a definite dipole moment. The magnitude of dipole moment in a polar molecule depends on the difference in the electronegativities. The greater the difference in electronegativities, the greater is the dipole moment. Greater the dipole moment, greater is the degree of polarity of polar covalent bond between the two atoms.

[I] Unit of Dipole Moment

We know that, dipole moment (μ) = Electronic charge (q) × Bond length (l)

The charge is expressed in electrostatic unit (esu) and bond length in angstrom unit (1 Å = 10^{-8} cm). If an electron (charge = 4.8×10^{-10} esu), is assumed to be placed at a distance of 1 Å (= 10^{-8} cm), from an equal positive charge, then dipole moment (μ) of such a molecule is given by,

$$\mu = (4.8 \times 10^{-10} \text{ esu}) \times (10^{-8} \text{ cm}) = 4.8 \times 10^{-18} \text{ esu-cm}$$

The quantity 10^{-18} esu-cm is called one debye unit, denoted by D, *i.e.*, $1\ D = 10^{-18}$ esu-cm. So, $\mu = 4.8$ D. In S.I. system, the electronic charge,

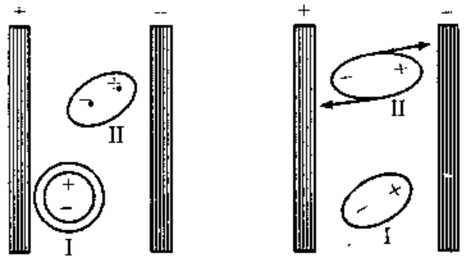
$$q = 1.602 \times 10^{-19} \text{ C} \quad \text{and} \quad l = 10^{-10} \text{ m, so,}$$

$$\mu = (1.602 \times 10^{19} \text{ C}) \times (10^{-10} \text{ m}) = 1.602 \times 10^{-29} \text{ Cm} = 4.8 \text{ D}$$

$$\therefore \qquad 1 \text{ D} = 3.336 \times 10^{-30} \text{ Cm}$$

[II] Electrical or Distortion Polarisation

Consider a non-polar molecule. When it is placed in an electric field between two charged poles, the latter will attract the electrons towards the positive pole, while the positive nuclei is attracted towards the negative pole. Thus, the positive and negative centres would no longer be coincident [Figure 3(a)]. Thus, *there will be an electrical distortion of the molecule to form an **electrical dipole.*** Such a distortion is termed ***distortion polarisation*** or ***electrical polarisation.***



(a) **(b)**

Fig. 3.

[III] Induced Dipole Moment

As soon as the electrical field applied to a non-polar molecule is withdrawn, the distortion also disappears. Thus, the distortion polarisation produced is, therefore, an ***induced polarisation*** and the moment that the induced dipole would acquire during the application of the field is known as ***induced dipole moment***, μ_i.

[IV] Polarisability

The induced dipole moment (μ_i) is directly proportional to the field strength, F. It is given by

$$\mu_i = \alpha \,.\, F$$

where the proportionality constant (α) is called the polarisability of the molecule. If $F = 1$, then $\alpha = \mu_i$. So, the ***polarisability of the molecule is a measure of the moment induced by a unit field.***

On the basis of electromagnetic theory, Clausius and Mosotti deduced the following relation between polarisability (α) and the dielectric constant (D) of the medium between two charged plates.

$$\frac{4}{3}\pi N\alpha = \frac{D-1}{D+2} \cdot \frac{M}{\rho} \qquad \ldots (1)$$

where N is Avogadro's number, M is molecular weight and ρ is the density of the substance.

[V] Molar Polarisation

The right hand side of equation (1) is termed ***molar polarisation.*** In a non-polar molecule, the polarisation is all induced. So, the induced molar polarisation (P_i) may be expressed as

$$P_i = \frac{4}{3}\pi N\alpha = \frac{D-1}{D+2} \cdot \frac{M}{\rho} \qquad \ldots (2)$$

P_i is the electrical distortion caused in one mole of a substance in a unit field. As N and α are independent of temperature, P_i will also be independent of temperature. Moreover, D is a dimensionless quantity and so the polarisation will be expressed in units of volume.

[VI] Permanent Dipole Moment

Each of the polar molecules has a positive and a negative end. In the absence of an electrical field, the molecules would be randomly oriented in all directions due to thermal effect. However, when such molecules are placed in an electric field between two charged plates, there will arise two effects. *Firstly*, the usual distortion of the positive and negative charges would occur giving rise to induced polarisation. *Secondly*, the field would tend to orient all the molecules in the direction of the field. If the molecules were stationary, these would be oriented at 180° to the direction of the field, the negative ends pointing towards the positive plate, as shown in figure 3 (*b*). This effect of the field on the molecules is called the ***orientation polarisation,*** P_0.

The molar polarisation, $\left[\frac{D-1}{D+2}\cdot\frac{M}{\rho}\right]$ which is measured from dielectric constant is the sum of two effects, *viz*., induced and orientation polarisations. The total molar polarisation is given by

$$P_t = P_i + P_0 \text{ and } P_t = \frac{D-1}{D+2}\cdot\frac{M}{\rho}$$

$$\therefore \quad \frac{D-1}{D+2}\cdot\frac{M}{\rho} = P_i + P_0$$

or

$$\frac{D-1}{D+2}\cdot\frac{M}{\rho} = \frac{4}{3}\pi N\alpha + P_0 \qquad \dots (3)$$

The molar orientation polarisation (P_0) of a substance having a dipole moment (μ) was given by Debye and is expressed as

$$P_0 = \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) \qquad \dots (4)$$

where k is Boltzmann's constant.

It is thus clear that in a non-polar molecule ($\mu = 0$), there is no orientation polarisation and moreover, the orientation polarisation is inversely proportional to temperature. So, from equations (3) and (4), we have

$$P_t = \frac{D-1}{D+2}\cdot\frac{M}{\rho} = \frac{4}{3}\pi N\alpha + \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) \qquad \dots (5)$$

Equation (5) is known as ***Debye equation.***

As the first term on the right hand side of equation (5) is constant and μ is also constant for a given substance, equation (5) may be written as

$$P_t = \frac{D-1}{D+2}\cdot\frac{M}{\rho} = a + \frac{b}{T} \qquad \dots (6)$$

where

$$a = \frac{4}{3}\pi N\alpha \quad \text{and} \quad b = \frac{4}{9}\cdot\frac{\pi N}{k}\mu^2$$

From equation (6), it is clear that the total molar polarisation varies linearly with $1/T$. It can be verified by plotting P_t against $1/T$ for several substances, as shown in figure (4). Figure (4) shows the linear plots for a gaseous non-polar molecule such as CH_4 ($\mu = 0$) and a gaseous polar molecule such as HCl with $\mu \neq 0$. For a non-polar molecule $\mu = 0$, so a plot of P_t and $1/T$ should give a straight line parallel to $1/T$ axis.

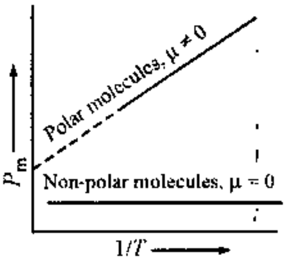


Fig. 4. Plot of P_t versus $1/T$ for gaseous polar and non-polar molecules.

[VII] Determination of Dipole Moment

A number of methods are available for determining the dipole moment. These are discussed as follows :

(1) Temperature method : By determining the dielectric constant directly, the total polarisation (P_t) of a substance is obtained, M and ρ being determined separately. As seen from equation (6), we have

$$P_t = a + \frac{b}{T}$$

If total polarisations P_1 and P_2 are determined at two temperatures T_1 and T_2, respectively then

$$P_1 = a + \frac{b}{T_1} \quad \text{and} \quad P_2 = a + \frac{b}{T_2}$$

$$\therefore \quad b = (P_1 - P_2)\left(\frac{T_1 T_2}{T_2 - T_1}\right)$$

The value of dipole moment, μ is easily calculated from that of b, *i.e.*,

$$b = \frac{4\pi N}{9k}\mu^2$$

or $$\mu = \sqrt{\left(\frac{9k}{4\pi N}\right) . b}$$

As $k = 1.3807 \times 10^{-16}$ erg K^{-1}, $\pi = 3.14$, $N = 6.023 \times 10^{23}$, we get

$$\mu = \sqrt{\left(\frac{9 \times 1.3807 \times 10^{-16} . b}{4 \times 3.14 \times 6.023 \times 10^{23}}\right)} = 0.0128 \times 10^{-18} . \sqrt{b} \text{ e.s.u.-cm.} \quad \ldots (7)$$

So, knowing b from equation (7), we can calculate the dipole moment easily.

(2) Ebert's method : Polar molecules in the gaseous state when subjected to an electric field will undergo both orientation and distortion polarisations. But when the same substance in the solid state is subjected to the same field, the orientation of molecules is not possible and only distortion polarisation will occur. Therefore, the total molar polarisation is given by

$$P_{\text{gas}} = P_i + P_0 \quad \text{and} \quad P_{\text{solid}} = P_i$$

$\therefore$ Orientation polarisation, $P_0 = P_{\text{gas}} - P_{\text{solid}}$

or $$\frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right) = P_{\text{gas}} - P_{\text{solid}}$$

or $$\mu = \sqrt{\left[\frac{9kT}{4\pi N}(P_{\text{gas}} - P_{\text{solid}})\right]} \quad \ldots (8)$$

As all the values of equation (8) are known, we can calculate the value of dipole moment.

[VIII] Applications of Dipole Moment

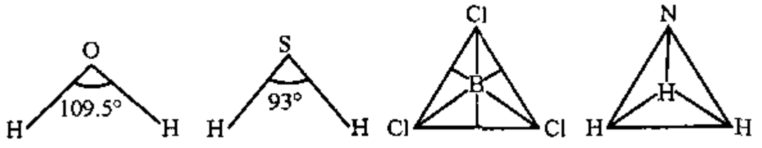
(1) In determining molecular structures of substances :

(a) Monoatomic molecules, like those of rare gases, have no dipole moment and are ***non-polar.***

(b) Diatomic molecules may be either polar or non-polar. Molecules of gases like O_2, N_2 etc. have $\mu = 0$, which indicates that the electron pairs bonding the constituent atoms exist at the same distance from the two atoms. But diatomic molecules of compounds have some dipole moment and so their structures are asymmetrical.

(c) Triatomic molecules may also be either polar or non-polar. The dipole moment of carbon dioxide is zero. So, it is a non-polar molecule, even though the C—O bonds are polar, as the shared electrons lie closer to the oxygen atom than to the carbon atom. This shows that CO_2 molecule is linear, as only in this way the dipole moment on one side of the molecule is cancelled by that on the other side and the net dipole moment is zero. So, it has the structure $O{=}C{=}O$. Similarly, carbon disulphide (CS_2) has a symmetrical linear structure, as its dipole moment is zero. It is non-polar and may be represented as $S{=}C{=}S$.

Water on the other hand, has an appreciable dipole moment ($\mu = 1.85D$). Thus, water cannot be linear. The two hydrogen atoms in a water molecule do not lie linearly on the two sides of the oxygen atom like H—O—H. Therefore, it should have an ***unsymmetrical*** or ***bent structure*** as represented by (fig. 5a). The dipole moment of each O—H bond is $1.60D$ and the angle between these two bonds should be 109°5′ to have the dipole moment of the molecules as $1.85D$. (The dipole moment of the molecule is given by, $\mu = 2m \cos \theta/2$, where m is the bond moment and θ is the angle between the two bonds). The dipole moment for a single H—S bond is nearly $0.8D$ and so the angle between the two bonds in the molecule of H_2S may be found to be 93°. Its structure is represented by figure 5(b).



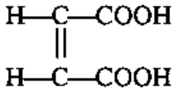
(a) (b) (c) (d)

Fig. 5. Structures of compounds

(b) Tetratomic molecules of the type BA_3 may be polar or non-polar. If it is non-polar *e.g.*, BCl_3 then all the atoms will lie in one plane and the angles between the different bonds are equal to one another as shown in figure 5(c). The chlorine atoms will be situated at the corners of an equilateral triangle and boron atom will be situated at the point of intersection of the three medians. Ammonia molecule has $\mu = 1.26D$ and its structure is as shown in figure 5(d). It is assigned a triangular pyramidal structure in which nitrogen atom lies at the apex of the pyramid and the hydrogen atoms lie at the three corners of the triangle, which forms the base of the pyramid.

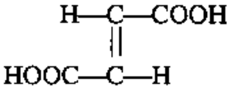
Molecules of PCl_3 or $AsCl_3$ also have triangular pyramidal structures, with P and As atoms at the apex.

(2) In distinguishing between cis and trans isomers : Dipole moment helps us in distinguishing between the cis and trans isomers of a compound. Consider for example, the case of maleic acid and fumaric acid. The cis form will have a dipole moment but in the trans form the effect produced in one half of the molecule is cancelled by that in the other half of the molecule.



$$\begin{array}{l} H-C-COOH \\ \quad\ \| \\ H-C-COOH \end{array}$$

Maleic acid
(cis form)



$$\begin{array}{r} H-C-COOH \\ \| \quad\quad\ \\ HOOC-C-H \end{array}$$

Fumaric acid
(trans form)

(3) In calculating the ionic character of a bond : Dipole moment helps us in determining the ionic character of a covalent bond. It has been seen that the H—Cl bond is 17% ionic in nature.

(4) In determining the polarity of a bond : Dipole moment gives us an indication of the polar character of a bond. The dipole moments of HF, HCl, HBr and HI are 1.92, 1.04, 0.78 and 0.83D, respectively. This shows that the polarity of the H—X bond decreases gradually as we move from fluorine to iodine (where, X = F, Cl, Br or I).

(5) In getting information regarding aromatic substitution : Dipole moments of the ortho, meta and para derivatives of benzene give us valuable information. The angles between the two substituents say nitro are 60°, 120° and 180°, respectively for the three dinitro benzenes. If both the substituents are the same, the dipole moment of para derivative should be zero. Its value will be maximum for the ortho derivative, while the dipole moment for the meta derivative will lie between that of para derivative and ortho derivative.

• 15.3. MAGNETIC PROPERTIES OF SUBSTANCES

The force F acting between two magnetic dipoles of pole strengths m_1 and m_2 separated by a distance r, is given by

$$F = \frac{1}{\mu} \cdot \frac{m_1 m_2}{r^2} \qquad \ldots (1)$$

where μ is a constant characteristic of the medium and is called ***magnetic permeability*** of the medium. It measures the tendency of the magnetic lines of force to pass through the medium, compared with their tendency to pass through vacuum for which $\mu = 1$. A substance is said to be **diamagnetic** when $\mu < 1$ and **paramagnetic** when $\mu > 1$. So, a diamagnetic substance is less permeable to the magnetic lines of force than a vacuum. The magnetic lines of force deflect towards a paramagnetic substance, whereas they deflect away from a diamagnetic substance.

The magnetic properties of matter are defined in terms of the magnetic field intensity vector, H and the magnetic induction or magnetic flux density, B. When a substance is placed in a magnetic field, the magnetic moment per unit volume, *i.e.*, magnetization, M is related to B and H by the expression,

$$B = \mu_0 (H + M) \qquad \ldots (2)$$

where μ_0 is the permeability of vacuum. Also, we have

$$B = \mu H \qquad \ldots (3)$$

From equations (2) and (3), we get

$$\begin{aligned} M &= H\,[(\mu/\mu^0) - 1] \\ &= H\,(\mu_r - 1) \qquad \ldots (4) \end{aligned}$$

where $\mu_r = \frac{\mu}{\mu_0}$ which is known as relative permeability of the medium. ($\mu_0 = 4\pi \times 10^{-7}\ JC^{-2}\ m^{-1}\ s^2$). Another term, **magnetic susceptibility,** is defined as

$$\chi = M/H = \mu_r - 1$$

Magnetic susceptibility is a dimensionless quantity. The **molar magnetic susceptibility,** is defined as

$$\chi_m = V_m \chi$$

where V_m is the molar volume.

Magnetic susceptibility and magnetic permeability are related to each other as

$$\chi = \frac{(\mu - 1)}{4\pi\rho}$$

where ρ is the desnity in g cm^{-3}.

In 1845, Faraday made a very important discovery that magnetism was a property which affected all bodies. In his experimental researches he found that the magnetic properties were not confined to a few elements like iron, nickel, cobalt etc. but that all substances and all forms of matter possess magnetic properties to some degree. He divided all the substances into three different types, *viz., paramagnetic, diamagnetic and ferromagnetic,* according to their behaviour in a magnetic field.

[I] Paramagnetism and Paramagnetic Substances

Those substances which are attracted by magnet and when placed in a magnetic field move from weaker to stronger parts of the field are called paramagnetic substances. This phenomenon is known as paramagnetism.

The susceptibility of a paramagnetic substance has a small positive value and is inversely proportional to the absolute temperature and thus obeys Curie's law. If a paramagnetic substance is kept in a magnetic field, the lines of force tend to accummulate it, as shown in figure (6).

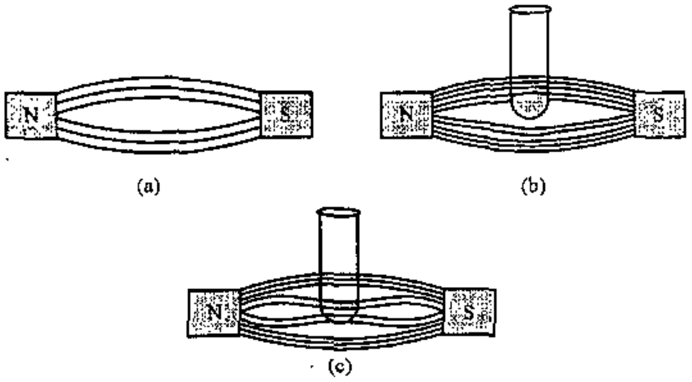


Fig. 6. Magnetic lines of force showing the effect of diamagnetic and paramagnetic substance on the magnetic field. (a) Vacuum (b) Diamagnetic (c) Paramagnetic.

Paramagnetic substances are much larger in number and consist of many metallic elements. Some gases and most of the salts and oxides of the elements belonging to different transitional series, *i.e.*, from Sc (21) to Cu (29), from Y (39) to Pd (46) and rare-earths Ce (58) to Yb (70), and also the elements belonging to the Pt and U-families are paramagnetic in nature.

[II] Diamagnetism and Diamagnetic Substances

Those substances which are repelled by magnet and when placed in a magnetic field move from stronger to weaker parts of the field are called diamagnetic substances. This phenomenon is known as diamagnetism.

The magnetic susceptibility of such substances has a small value and the value does not change with temperature. If a diamagnetic substance is kept in a magnetic field, the lines of forces tend to move away from the substance fig. (6). All other substances which are not paramagnetic are diamagnetic, *e.g.*, Zn, Cd, Hg, Sb, Bi etc.

[III] Ferromagnetism and Ferromagnetic Substances

Those substances which are attracted by magnet and can also be magnetised are called ferromagnetic substances. This phenomenon is known as ferromagnetism.

Ferromagnetic substances are rather few in number and consist of three elements Fe, Co, Ni: most of their alloys having a sufficient concentration of the metals, some of their compounds, *e.g.*, the oxides and sulphides of iron, the Heussler alloys (composition : Al 70%, Mn 20%, Cu 10% approx); as also some compounds of manganese and some ferrites of the type MeO, Me_2O_3 where Me is a metal of the iron group. Ferromagnetic substances show all the properties of paramagnetic substances to a much greater degree. The susceptibility has a positive value and the permeability is also very large. The susceptibility (κ) decreases as the temperature increases and obeys Curie's law.

i.e., $\kappa \propto \frac{1}{T}$

It is observed that as temperature is increased, the value of susceptibility drops suddenly at a particular temperature, known as ***Curie point*** or ***critical temperature***. At Curie point, the substance becomes paramagnetic. Curie points for cobalt and nickel are 1100°C and 400°C, respectively. It is also seen that above the Curie point, the susceptibility of a ferromagnetic substance is proportional to the difference of temperatures between the material and Curie point. This is known as ***Curie-Weiss law***.

• SUMMARY

- When the centre of gravity of electrons does not coincide with that of positive nuclei in a molecule, the molecule is said to be **polar**, *e.g.*, H_2O, NH_3 etc.
- When the centre of gravity of electrons exactly coincide with that of the positive charges in a molecule, the molecule is said to be **non-polar**, *e.g.*, H_2, N_2, CO_2, CH_4 etc.
- The product of the magnitude of the charge (positive or negative) and distance between them (bond length) is called dipole moment.
- The quantity 10^{-18} esu-cm is called one debye unit, denoted by D. However,
$$1D = 3.336 \times 10^{-30} \text{ cm.}$$
- The polarisability (α) of the molecule is a measure of the moment induced by a unit field.
- For vacuum, the magnetic permeability (μ) is unity. For diamagnetic substances, $\mu < 1$ and for paramagnetic substances, $\mu > 1$.
- Magnetic susceptibility is a dimensionless quantity.
- The substances which are attracted by magnets and when placed in a magnetic field move from weaker to stronger parts of the field are called paramagnetic substances and the phenomenon is known as paramagnetism.
- Those substances which are repelled by magnets and when placed in a magnetic field move from stronger to weaker parts of the field are called diamagnetic substances and the phenomenon is known as diamagnetism.
- Those substances which are attracted by magnets and can also be magnetised are called ferromagnetic substances and the phenomenon is known as ferromagnetism.

• STUDENT ACTIVITY

1. Define polar and non-polar molecules with examples.

2. What is distortion polarisation ?

3. Define dipole moment and mention its unit.

4. Write any one application of dipole moment.

5. What are diamagnetic and paramagnetic substances ?

• TEST YOURSELF

1. Explain the terms :

(i) Electrical polarisation	(ii) Induced dipole moment
(iii) Polarisability	(iv) Molar polarisation
(v) Paramagnetism	(vi) Diamagnetism
(vii) Ferromagnetism	(viii) Magnetic subsceptibility

2. How will you determine the dipole moment of a molecule ?

3. How dipole moment is used to determine the molecular structure of compounds ?

4. What are polar and non-polar molecules ? Explain with examples.

5. Define dipole moment and mention its unit.

6. Describe the applications of dipole moment.

7. Define paramagnetic and diamagnetic substances and give some examples.

8. How are magnetic substances classified ? Explain properties of these substances.

9. Bismuth is a :

(a) Paramagnetic substance
(b) Diamagnetic substance
(c) Ferromagnetic substance
(d) Antiferromagnetic substance

10. $CHCl_3$ is a :

(a) Polar molecule
(b) Non-polar molecule
(c) Normal molecule
(d) Complex molecule

11. Fill in the blanks :

(i) The measure of the moment induced by a unit field is called ....
(ii) Polarisation is expressed in units of ....
(iii) The dipole moment of boron trichloride molecule is nearly ....

ANSWERS

9. (b) **10.** (a) **11.** **(i)** polarisability **(ii)** volume **(iii)** zero.

❑❑❑