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**SCHOOL OF SCIENCE AND HUMANITIES  
DEPARTMENT OF CHEMISTRY**

## **UNIT – 1 – Ionics – SCYA5303**

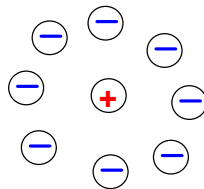
# DEBYE-HÜCKEL THEORY OF INTERIONIC ATTRACTION

## *Postulates of Debye-Hückel Theory*

- ✓ Strong electrolytes are assumed to be completely dissociated.
- ✓ The two ions present in the solution obey the Coulomb's law, i.e.

$$F = \frac{Q_1 Q_2}{r^2}$$

- ✓ Where  $Q_1$  and  $Q_2$  are the charges on the ions and  $r$  is the distance between them.
- ✓ An ion with specific charge is considered as point charge and, it is known as central ion.
- ✓ Due to its electrical character, the central ion is surrounded by a cloud of oppositely charged ion to form ionic atmosphere.
- ✓ The ionic atmosphere is assumed to be spherical symmetry (Fig. 1.1).



**Fig. 1.1: Ionic Atmosphere**

- ✓ The charge density of ionic atmosphere is the greatest in the immediate vicinity of its central ion and, it gradually decreases with increasing distance.
- ✓ The electrostatic interaction is assumed to be small in comparison with the energy of thermal movement.
- ✓ The electrostatic potential in the solution can be described by an equation known as the Poisson and Boltzmann equation.

## *Derivation of Debye-Hückel Theory of Ion-Ion Interaction*

The D-H theory is used to determine quantitatively the electric potential of central ion of ionic atmosphere in aqueous solution and the electric potential produced by surrounding distribution of ions in the ionic atmosphere.

The D-H theory of electrostatic interaction between mobile ions (unbound ions) in aqueous solution is based on the two concepts namely: Boltzmann Distribution Law and the Poisson Equation.

To derive D-H expression, the first step is to calculate the net charge density of ionic atmosphere using Boltzmann distribution law and the second step is to relate the electrostatic potential of each ion and its charge density using Poisson's equation.

## ***Boltzmann Distribution Law***

Debye and Hückel used Boltzmann distribution law of statistical mechanics for finding the average distribution charges around each ion and it is given by:

$$e^{\psi/KT}$$

where  $\psi$  is the electrostatic potential energy of ions in dilute solution (unbound ions) in which Coulombic force between ions is zero. These ions will have only their thermal movements in solution;  $K$  is the Boltzmann constant and  $T$  is the temperature.

Debye and Hückel calculated the electrical work done ( $W_{el}$ ) on the system from the electrostatic potential energy of interaction between each ion and average distribution of charges in the ionic atmosphere (point charge).

i.e. the electrical work done on a positive ion of valency  $Z_+$  and carrying an electronic charge  $\varepsilon$  to bring it to the ionic atmosphere is  $Z_+\varepsilon\psi$ . Similarly, the work done for bringing a negative ion is  $Z_-\varepsilon\psi$ .

For uni-univalent electrolyte, the values are equal to  $-\varepsilon\psi$  and  $+\varepsilon\psi$  for negative and positive ion respectively.

If  $n_+$  and  $n_-$  are the concentration (ions per unit volume,  $dV$ , ionic atmosphere) at the points ( $\psi = \psi$ ) and  $N$  (For uni-univalent electrolyte ( $N_+ = N_- = N$ ) is the concentration of ions at infinity distance where  $\psi = 0$ , we have:

$$n_+ = N\varepsilon e^{-\varepsilon\psi/KT} \quad n_- = N\varepsilon e^{+\varepsilon\psi/KT}$$

The net charge density ( $\rho$ ) of the point charge (ionic atmosphere) in dilute solution is given by:

$$\rho = [N\varepsilon e^{-\varepsilon\psi/KT} - N\varepsilon e^{+\varepsilon\psi/KT}]$$

$$\rho = N\varepsilon [e^{-\varepsilon\psi/KT} - e^{+\varepsilon\psi/KT}] \dots \dots (1)$$

### ***Poisson Equation***

The Poisson equation relates the electric potential ( $\psi$ ) of the unbound ion and its charge density ( $\rho$ ) at the ionic atmosphere is given by:

$$\nabla^2\psi = -\frac{4\pi}{D}\rho \quad \dots \dots (2)$$

Where  $D$  is the dielectric constant of the solvent and  $\nabla^2$  is the Laplacian operator.

### ***Linearized Combined Form of Poisson-Boltzmann Equation***

Substituting the charge density ( $\rho$ ) in Poisson equation (2), we get:

$$\nabla^2\psi = -\frac{4\pi}{D}[N\varepsilon (e^{-\varepsilon\psi/KT} - e^{+\varepsilon\psi/KT})]$$

$$\nabla^2 \psi = -\frac{4\pi}{D} \left[ \left( N \varepsilon e^{-\varepsilon \psi / KT} - N \varepsilon e^{+\varepsilon \psi / KT} \right) \right]$$

$$\nabla^2 \psi = -\frac{4\pi}{D} N \varepsilon \left[ -2 \sinh \left( \frac{\varepsilon \psi}{KT} \right) \right] \quad \because e^x - e^{-x} = 2 \sinh x$$

$$\nabla^2 \psi = \frac{8\pi \varepsilon^2 N}{KTD} \psi \quad \because \text{For a very small value of } x, \sinh x = x$$

$$\nabla^2 \psi = \kappa^2 \psi \quad \dots \dots (3)$$

$$\text{where } \kappa^2 = \frac{8\pi \varepsilon^2 N}{KTD} \quad (\text{or}) \quad \kappa = \left[ \frac{8\pi \varepsilon^2 N}{KTD} \right]^{1/2}$$

where  $\kappa$  is the D-H parameter.

Since  $N$  is the number or concentration of ions per unit volume in dilute solution (at infinite concentration), and it is known as its ionic strength. Hence,

$$N = I = \frac{1}{2} \sum m_i z_i^2$$

Therefore, the Debye Hückel parameter  $\kappa$  can be calculated as:

$$\therefore \kappa^2 = \left[ \frac{8\pi \varepsilon^2}{KTD} \right] \times \frac{1}{2} \sum m_i z_i^2 \quad (\text{or}) \quad \kappa^2 = \left[ \frac{8\pi \varepsilon^2}{KTD} \right] \times I$$

Therefore,  $\kappa^2$  is directly proportional to ionic strength.

Further, the reciprocal value of  $\kappa$  is known as Debye length and it is the radius of the ionic cloud.

$$(\text{or}) \quad \kappa^2 \propto \frac{I}{T} \quad (\text{or}) \quad \frac{1}{\kappa^2} = \frac{T}{I} \quad (\text{or}) \quad \frac{1}{\kappa} = \kappa^{-1} = \sqrt{\frac{T}{I}}$$

Since the ionic atmosphere is spherically symmetrical, the equation is independent of  $\theta$  and  $\Phi$ , is dependent only  $r$ , the equation (3) has the solution in terms of polar coordinate as:

$$\psi = \frac{ze}{\varepsilon r} e^{-\kappa r} \quad \dots \dots (4)$$

When the exponential term of equation (4) is expanded, we get:

$$\psi(r) = \frac{ze}{\varepsilon r} (1 - \kappa r) \quad \because [e^{-x} = 1 - x] \quad (\text{or}) \quad e^{-\kappa r} = 1 - \kappa r$$

$$\psi(r) = \frac{ze}{\varepsilon r} - \frac{zek}{\varepsilon} \quad \dots \dots (5)$$

Where,  $ze$  is the charge of the central ion.

The first term in equation (5) indicates the potential arising from the charge ( $ze$ ) of the central ion itself at a point of distance  $r$  while the 2<sup>nd</sup> term indicates the potential produced by surrounding distribution of ions in the ionic atmosphere.

## DEBYE-HÜCKEL LIMITING LAW

The Relation of Mean Ionic Activity Coefficient to the Ionic Strength of the Solution

The Debye and Hückel expression for a strong electrolyte of a dilute solution is given by:

$$\psi(r) = \frac{ze}{\epsilon r} - \frac{ze\kappa}{\epsilon}$$

In this expression the first term represents the electrostatic potential produced by the central ion itself and the second term represents the electric potential produced by the charge distribution in the ionic atmosphere.

The electrical work required to form an ionic atmosphere can be obtained by integrating the second term in Debye and Hückel equation from zero charge to full charge ( $ze$ ) as:

$$w_{el} = \int_0^{ze} \left(-\frac{\kappa}{\epsilon}\right) (ze) \quad \because \left[ \int x^n = \frac{x^{n+1}}{n+1} \right]$$

$$w_{el} = \left(-\frac{\kappa}{\epsilon}\right) \left[ \left( \frac{(ze)^2}{2} \right) \right]_0^{ze}$$

$$w_{el} = 0 - \frac{\kappa}{\epsilon} \left[ \frac{(ze)^2}{2} \right]$$

$$(or) \quad w_{el} = -\frac{z^2 e^2}{2\epsilon} \kappa \quad \dots\dots (6)$$

For dilute solutions, electrical work can also be written as:

$$w_{el} = KT \ln \gamma_i \quad \dots\dots (7)$$

where  $\gamma_i$  is the activity coefficient of the  $i^{\text{th}}$  ion in solution.

Comparing equations (6) and (7), we have:

$$KT \ln \gamma_i = -\frac{z^2 e^2}{2\epsilon} \kappa \quad \dots\dots (8)$$

$$\ln \gamma_i = -\frac{z^2 e^2}{2\epsilon KT} \kappa \quad \dots\dots (9)$$

$$\ln \gamma_i = -\frac{z^2 e^2}{2\epsilon KT} \sqrt{I} \quad \because \kappa^2 = I \quad (or) \quad \kappa = \sqrt{I}$$

$$(or) \log \gamma_i = -\frac{2.303e^2}{2\epsilon KT} |z_+ z_-| \sqrt{I} \quad \because z^2 = |z_+ z_-|$$

$$\log \gamma_i = -A |z_+ z_-| \sqrt{I} \dots \dots (10) \quad \text{where } A = \frac{2.303e^2}{2\epsilon KT}$$

By substituting the value of  $KT = 1.66 \times 10^{-20}$  at  $25^\circ\text{C}$  (298 K) in aqueous solution,  $\epsilon = 78.54$  and  $e = 1.609 \times 10^{-19}$ , we have the expression,

$$\log \gamma_i = -0.509 |z_+ z_-| \sqrt{I} \dots \dots (11)$$

The equations (10) and (11) are known as Debye-Hückel limiting law.

**Calculate the mean activity co-efficient ( $\gamma_{\pm}$ ) of (i) NaCl at a molality of 0.01 and (ii)  $\text{Na}_2\text{SO}_4$  at a molality of 0.001 in aqueous solution at  $25^\circ\text{C}$ .**

(i) In 0.01 molal NaCl solution, the molality of each ion = 0.01.

Hence,  $m_+ = 0.01$  and  $m_- = 0.01$ ; Also,  $z_+ = 1$  and  $z_- = 1$ .

The ionic strength is given by:

$$I = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

$$\therefore I = \frac{1}{2} (0.01 \times 1^2 + 0.01 \times 1^2) = 0.01$$

For uni-univalent electrolyte, the ionic strength is equal to its molality.

The mean activity co-efficient ( $\gamma_{\pm}$ ) is given by the equation:

$$\log \gamma_{\pm} = -A |z_+ z_-| \sqrt{I}$$

For water at  $25^\circ\text{C}$ , the constant  $A = 0.509$

$$\log \gamma_{\pm} = -0.509 (1 \times 1) \sqrt{0.01}$$

$$\log \gamma_{\pm} = -0.0509$$

$$\gamma_{\pm} = 0.889$$

(ii) In 0.001 molal  $\text{Na}_2\text{SO}_4$  solution,  $\text{Na}_2\text{SO}_4$  produces two  $\text{Na}^+$  ions and one  $\text{SO}_4^{2-}$  ions, and hence the molalities of the each ion would be:

$$m_+ = 2 \times 0.001 = 0.002 \text{ and } m_- = 1 \times 0.001 = 0.001; \text{ Also, } z_+ = 1 \text{ and } z_- = 2$$

The ionic strength is given by:

$$I = \frac{1}{2}(m_+ z_+^2 + m_- z_-^2)$$

$$\therefore I = \frac{1}{2}(0.002 \times 1^2 + 0.001 \times 2^2) = 0.003$$

The mean activity co-efficient ( $\gamma_{\pm}$ ) is given by the equation:

$$\log \gamma_{\pm} = -A|z_+ z_-| \sqrt{I}$$

For water at 25°C, the constant  $A = 0.509$

$$\log \gamma_{\pm} = -0.509(1 \times 2)\sqrt{0.003}$$

$$\log \gamma_{\pm} = -0.0558$$

$$\gamma_{\pm} = 0.879$$

## DEBYE-HÜCKEL-ONSAGER THEORY OF ELECTROLYTES

DHO theory assumes that strong electrolytes are completely ionized at all dilutions. It is observed that, there are three types of opposing forces which oppose the velocity (or mobility) of ions in solution in turn decreases its conductivity.

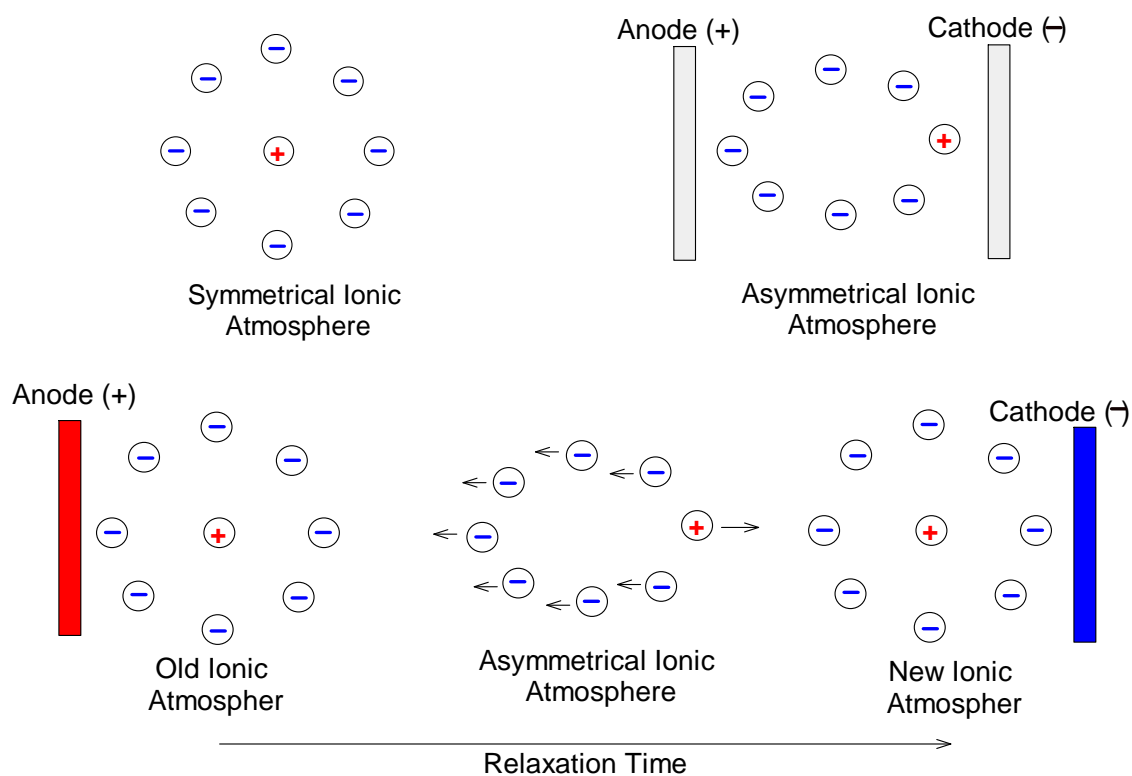
They are:

- 1) Relaxation Force (Asymmetric Effect)
- 2) Electrophoretic Force
- 3) Friction Force

### *Asymmetry Effect (Relaxation Effect)*

On account of electrostatic attraction, a central ion in solution is surrounded by opposite charge ions to form an ionic atmosphere, and it will have spherical (central) symmetry. But when an electric potential is applied, the central ion tends to move towards the oppositely charged electrode while the ionic cloud moves in the opposite direction of central ion. This effect creates an asymmetry in the ionic atmosphere (Fig. 1.2).

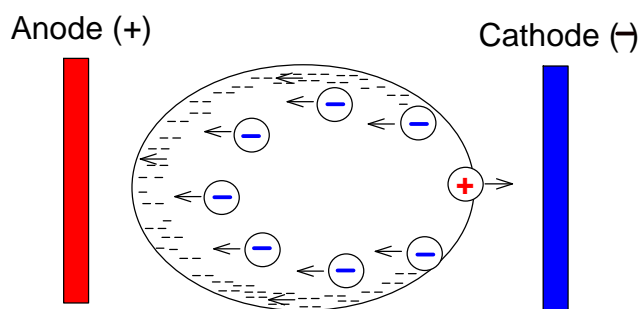
Because of asymmetric effect, the velocity (mobility) of central ion decreases in turn the conductance of the solution decreases. This effect is more in concentrated solution than in dilute solution. Note that the ionic atmosphere is repeatedly being destroyed and formed again. But the new ionic atmosphere is not formed at the same rate at which the old one disappears and the later takes more time to form is called relaxation time. So, the asymmetric effect is also known as relaxation effect and the opposing force for the decrease of conductance of the central ion is known as relaxation force.



**Fig. 1.2: Asymmetry Effect**

### ***Electrophoretic Effect***

This is another force that opposes the velocity of central ion and is responsible for lowering of its conductivity when an electric field is applied. The central positive ions move towards cathode whereas the negative ions move in the opposite direction towards anode.



**Fig. 1.3: Electrophoretic Effect**

The ions during their movement impart momentum of solvent molecules (water) since negative charge ions are in excess. Hence, the net momentum imparted to the solvent will have the direction of positive electrode. That is, the streaming of central ion occurs in a direction opposite to that of movement of solvent (water) molecules when an electric field is applied, and the phenomenon is known as electrophoretic effect (Fig. 1.3) and the force is known as electrophoretic force.



## DERIVATION OF DEBYE-HÜCKEL-ONSAGER EQUATION

### **Relaxation Force**

Asymmetry effect is the asymmetrical distribution of the ion cloud around a central ion which occurs from the finite relaxation time when a voltage is applied. It leads to a decrease in the mobility of ions. Onsager showed that the value of relaxation effect (force) as:

$$Relaxation\ Force = \left( \frac{\varepsilon^3 Z_i \kappa \omega V}{6DKT} \right)$$

$$where, \kappa = \left( \frac{4\pi\varepsilon^2 \sum c_i z_i^2}{DKT} \right)^{1/2} \text{ and } \omega = Z_+ Z_- \frac{2q}{1 + \sqrt{q}} \text{ and the value of } q \text{ is given by:}$$

$$q = \frac{Z_+ Z_-}{(Z_+ + Z_-)} \times \frac{(\lambda_+ + \lambda_-)}{(Z_+ \lambda_+ + Z_- \lambda_-)}$$

Where,  $\varepsilon \rightarrow$  Electronic charge;  $D \rightarrow$  Dielectric constant of medium;  $T \rightarrow$  Temperature;  $C_i \rightarrow$  Equivalent concentration of  $i^{th}$  ion;  $Z_i \rightarrow$  Valency of  $i^{th}$  ion;  $V \rightarrow$  Applied potential gradient;  $K \rightarrow$  Boltzmann constant

### **Electrophoretic Effect (Force)**

When an electromotive force is applied on an ionic atmosphere, the central ions moves in one direction and the oppositely charged ions present in their ionic atmosphere move in opposite direction.

The solvent molecules attached to ionic atmosphere also move in direction opposite to that of central ion. Thus, they cause friction due to which the mobility of the center ion is retarded. This effect is called electrophoretic effect.

On the of Stoke's law, Debye and Hückel calculated the following expression for the electrophoretic force on ion of  $i^{th}$  kind as:

$$Electrophoretic\ Force = \frac{\varepsilon K_i Z_i \kappa V}{6\pi\eta} \quad where, \kappa = \left( \frac{4\pi\varepsilon^2 \sum c_i z_i^2}{DKT} \right)^{1/2}$$

Where,  $\varepsilon \rightarrow$  Electronic charge;  $D \rightarrow$  Dielectric constant;  $T \rightarrow$  Temperature;  $c_i \rightarrow$  Concentration of  $i^{th}$  ion in gram equivalent;  $Z_i \rightarrow$  Valency of  $i^{th}$  ion;  $K_i \rightarrow$  Coefficient of frictional resistant of solvent opposing the motion of  $i^{th}$  kind ion;  $\eta \rightarrow$  Viscosity of the medium;  $V \rightarrow$  Applied potential gradient;  $K \rightarrow$  Boltzmann constant

### **Frictional Force**

Any moving ions experience resistive force by medium. If central ion is moving with uniform velocity, it experiences frictional force by the solvent of the solution (medium) in turn its velocity in the solution is decreased (or the conductivity of the solution is decreased).

That is, an ion with its ionic atmosphere travels in the solution, then the medium of the solution offers the frictional resistance. This force depends upon viscosity of the medium and its dielectric constant.

$$\text{Frictional Force} = u_i K_i$$

$u_i \rightarrow$  Steady velocity (or mobility) of  $i^{\text{th}}$  ion:  $K_i \rightarrow$  Coefficient of frictional resistant of solvent opposing the motion of  $i^{\text{th}}$  kind ion.

### **Derivation of Debye-Hückel-Onsager Equation**

Debye-Hückel theory explains the determination of electrical potentials of ionic atmosphere.

In 1927, Onsager explained the various factors which are responsible for opposing the velocity of central ion surrounded by the ionic atmosphere. The total electric force applied from external source on ionic atmosphere is equivalent to the sum of relaxation force, electrophoretic force and frictional force. The electromotive force applied from outside on center ion is equal to  $\varepsilon Z_i V$ , where  $\varepsilon$  is the electronic charge of ion of valency  $Z_i$  and  $V$  is the applied potential gradient.

Electromotive force applied on center ion = Sum of all opposing forces on center ion

$$\varepsilon Z_i V = \frac{\varepsilon^3 Z_i \kappa \omega V}{6DKT} + \frac{\varepsilon K_i Z_i \kappa V}{6\pi\eta} + u_i K_i$$

$$u_i K_i = \varepsilon Z_i V - \frac{\omega \varepsilon^3 Z_i \kappa V}{6DKT} - \frac{\varepsilon K_i Z_i \kappa V}{6\pi\eta}$$

$$u_i K_i = \varepsilon Z_i V - \left( \frac{\omega \varepsilon^3 Z_i \kappa V}{6DKT} + \frac{\varepsilon K_i Z_i \kappa V}{6\pi\eta} \right) \quad \dots (1)$$

Dividing throughout the equation (1) by  $K_i V$ , we get:

$$\frac{u_i K_i}{K_i V} = \frac{\varepsilon Z_i V}{K_i V} - \left( \frac{\omega \varepsilon^3 Z_i \kappa V}{6DKT} \times \frac{1}{K_i V} + \frac{\varepsilon K_i Z_i \kappa V}{6\pi\eta} \times \frac{1}{K_i V} \right)$$

$$\frac{u_i}{V} = \frac{\varepsilon Z_i}{K_i} - \left( \frac{\omega \varepsilon^3 Z_i \kappa}{6DKT} \times \frac{1}{K_i} + \frac{\varepsilon Z_i \kappa}{6\pi\eta} \right) \quad \dots (2)$$

Multiplying throughout the equation (2) by  $V$ , we get:

$$u_i = \frac{\varepsilon Z_i V}{K_i} - \left( \frac{\omega \varepsilon^3 Z_i \kappa V}{6DKT} \times \frac{1}{K_i} + \frac{\varepsilon Z_i \kappa V}{6\pi\eta} \right) \quad \dots (3)$$

If the potential gradient is taken as one volt per cm, then  $1 V = \frac{1}{300}$  electrostatic unit (esu) or electric potential.

Substituting potential gradient,  $V = \frac{1}{300}$  esu in equation 93), we have:

$$u_i = \frac{\varepsilon Z_i}{K_i} \times \frac{1}{300} - \left( \frac{\omega \varepsilon^3 Z_i \kappa}{6DKTK_i} \times \frac{1}{300} + \frac{\varepsilon Z_i \kappa}{6\pi\eta} \times \frac{1}{300} \right)$$

$$(or) \quad u_i = \frac{\varepsilon Z_i}{300K_i} - \left( \frac{\omega \varepsilon^2 Z_i}{6DKTK_i} + \frac{Z_i}{6\pi\eta} \right) \left( \frac{\varepsilon \kappa}{300} \right) \quad \dots (4)$$

Substituting the value of Debye-Hückel parameter,  $\kappa = \left( \frac{4\pi\varepsilon^2 \sum c_i Z_i^2}{DKT} \right)^{1/2}$ , we get:

$$u_i = \frac{\varepsilon Z_i}{300K_i} - \left( \frac{\omega \varepsilon^2 Z_i}{6DKTK_i} + \frac{Z_i}{6\pi\eta} \right) \left( \frac{\varepsilon}{300} \right) \left( \frac{4\pi\varepsilon^2 \sum c_i Z_i^2}{DKT} \right)^{1/2} \quad \dots (5)$$

At infinite dilution,  $\sum c_i Z_i^2 = 0$

Substituting  $\sum c_i Z_i^2 = 0$  in equation (6), the uniform velocity (or mobility) at infinite dilution ( $u_i^o$ ) will be:

$$u_i^o = \frac{\varepsilon Z_i}{300K_i} \quad \dots (6)$$

Replacing  $\frac{\varepsilon Z_i}{300K_i}$  by  $u_i^o$  in equation (5), we get:

$$u_i = u_i^o - \left( \frac{\omega \varepsilon^2 Z_i}{6DKTK_i} + \frac{Z_i}{6\pi\eta} \right) \left( \frac{\varepsilon}{300} \right) \left( \frac{4\pi\varepsilon^2 \sum c_i Z_i^2}{DKT} \right)^{1/2} \quad \dots (7)$$

According to Kohlrausch's law of independent migration of ions, the equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the contributions of the equivalent conductance of its constituent ions.

$$\lambda_o = \lambda_+ + \lambda_-$$

The equivalent conductance and ionic mobility are directly proportional to each other.

$$\lambda_+ = u_+ F \text{ and } \lambda_- = u_- F$$

Equivalent conductance ( $\lambda$ ) of any concentration is the product of mobility of ion ( $u$ ), 1 mol charge (or Faraday constant,  $F$ ) and degree of dissociation ( $\alpha$ ), and hence,

$$\lambda = \alpha u F \quad (or) \quad u_i = \frac{\lambda_i}{\alpha F} \quad \dots (8)$$

The equivalent conductance ( $\lambda^o$ ) at infinite dilution can also be defined for very dilute solution as:

$$\lambda_i^o = \alpha u_i^o F \quad (or) \quad u_i^o = \frac{\lambda_i^o}{\alpha F} \quad \dots (9)$$

Substituting  $u_i$  and  $u_i^o$  in the mobility equation (7), we get:

$$\frac{\lambda_i}{\alpha F} = \frac{\lambda_i^o}{\alpha F} - \left( \frac{\omega \varepsilon}{6DKT} \frac{\varepsilon Z_i}{K_i} + \frac{Z_i}{6\pi\eta} \right) \left( \frac{\varepsilon}{300} \right) \left( \frac{4\pi\varepsilon^2 \sum c_i Z_i^2}{DKT} \right)^{1/2} \dots (10)$$

From equation (6) and (9), uniform velocity (or mobility) at infinite dilution is:

$$\frac{\varepsilon Z_i}{300K_i} = \frac{\lambda_i^o}{\alpha F} \quad (\text{or}) \quad \frac{\varepsilon Z_i}{K_i} = \frac{300\lambda_i^o}{\alpha F}$$

Substituting the value of  $\frac{\varepsilon Z_i}{K_i}$  in equation (10), we get:

$$\frac{\lambda_i}{\alpha F} = \frac{\lambda_i^o}{\alpha F} - \left( \frac{\omega \varepsilon}{6DKT} \frac{300\lambda_i^o}{\alpha F} + \frac{Z_i}{6\pi\eta} \right) \left( \frac{\varepsilon}{300} \right) \left( \frac{4\pi\varepsilon^2 \sum c_i Z_i^2}{DKT} \right)^{1/2} \dots (11)$$

For complete dissociation in case of strong electrolyte,  $\alpha = 1$ .

$$\begin{aligned} \frac{\lambda_i}{F} &= \frac{\lambda_i^o}{F} - \left( \frac{\omega \varepsilon}{6DKT} \frac{300\lambda_i^o}{F} + \frac{Z_i}{6\pi\eta} \right) \left( \frac{\varepsilon}{300} \right) \left( \frac{4\pi\varepsilon^2 \sum c_i Z_i^2}{DKT} \right)^{1/2} \\ \lambda_i &= \lambda_i^o - \left( \frac{300\omega\varepsilon\lambda_i^o}{6DKT} + \frac{FZ_i}{6\pi\eta} \right) \left( \frac{\varepsilon}{300} \right) \left( \frac{4\pi\varepsilon^2}{DKT} \right)^{1/2} \left( \sum c_i Z_i^2 \right)^{1/2} \\ \lambda_i &= \lambda_i^o - \left( \frac{300\omega\varepsilon\lambda_i^o}{6DKT} + \frac{FZ_i}{6\pi\eta} \right) \left( \frac{\varepsilon}{300} \right) \left( \frac{4\pi\varepsilon^2}{DKT} \right)^{1/2} (c_+ Z_+^2 + c_- Z_-^2)^{1/2} \dots (12) \end{aligned}$$

$\because$  For uni-univalent electrolyte,  $\sum c_i Z_i^2 = c_+ Z_+^2 + c_- Z_-^2$

Substituting the value of constants in equation (12), we get:

$$\begin{aligned} \lambda_i &= \lambda_i^o - \left( \frac{9.90 \times 10^5 \omega \lambda_i^o}{(DT)^{3/2}} + \frac{29.15 Z_i}{\eta (DT)^{1/2}} \right) (c_+ Z_+^2 + c_- Z_-^2)^{1/2} \\ (\text{or}) \quad \lambda_i &= \lambda_i^o - \left( \frac{9.90 \times 10^5 \omega}{(DT)^{3/2}} \times \lambda_i^o + \frac{29.15 (Z_+ + Z_-)}{\eta (DT)^{1/2}} \right) \sqrt{(c_+ Z_+ Z_+ + c_- Z_- Z_-)} \\ \therefore \lambda_i &= \lambda_i^o - \left( \frac{9.90 \times 10^5 \omega}{(DT)^{3/2}} \times \lambda_i^o + \frac{29.15 (Z_+ + Z_-)}{\eta (DT)^{1/2}} \right) \sqrt{c(Z_+ + Z_-)} \end{aligned}$$

$\because \quad c \text{ (in gm - eq/L)} = c_i \times Z_i$

For uni-univalent ion,  $Z_+ = Z_- = 1$  and  $\omega = 2 - \sqrt{2}$

$$(\text{or}) \lambda = \lambda^o - \left( \frac{8.2 \times 10^5}{(DT)^{3/2}} \times \lambda_i^o + \frac{82.4}{\eta (DT)^{1/2}} \right) \sqrt{c} \quad \dots (13)$$

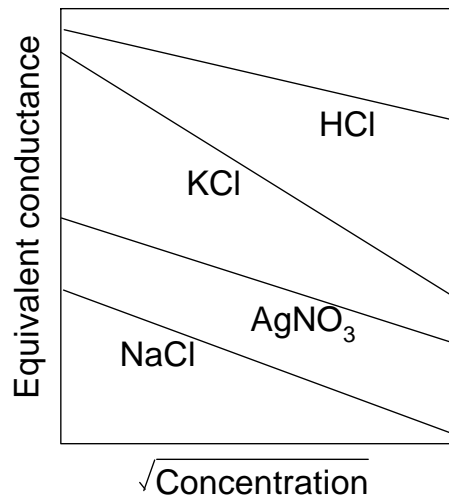
$$(\text{or}) \lambda = \lambda^o - (A + B\lambda_i^o) \sqrt{c} \quad \dots (14)$$

$$\text{where, } A = \frac{82.4}{\eta (DT)^{1/2}} \text{ and } B = \frac{8.2 \times 10^5}{(DT)^{3/2}}$$

The value of  $A$  and  $B$  for water at  $25^\circ\text{C}$  was found to be 60.2 and 0.224 respectively.

$$\therefore \lambda = \lambda^o - [60.2 + 0.224\lambda_i^o]\sqrt{c} \quad \dots (15)$$

*The above equation is the Debye Hückel Onsager equation for uni-univalent electrolyte dissolved in a solvent (water) at  $25^\circ\text{C}$ .*



**Fig. 1.4: Molar Conductance against  $\sqrt{c}$**

If the equation is correct, then by plotting molar conductance against  $\sqrt{c}$  would give a straight line of slope is equal to  $[60.2 + 0.224\lambda_i^o]$  and intercept is equal to  $\lambda_i^o$  (Fig. 1.4).

## **VARIATION OF CONDUCTANCE WITH APPLIED POTENTIAL**

### **Wein Effect (Conductance under High Potential Gradient)**

When the applied potential of 20,000 V/cm is applied, an ion will move at a speed of 1 m/s. That is the central ion will travel several times a thickness of the effective ionic atmosphere in the time of relaxation.

As a result, the moving central ion is practically free from the opposite charge of the ionic atmosphere (as there is no time for ions to build up ionic atmosphere to any extent). Under

these circumstances both asymmetric and electrophoretic effects will be greatly diminished at very high voltages.

Hence, the equivalent conductance at any appreciable concentrations will be greater under high potential than at low voltages.

### ***Debye-Falkenhagen Effect (Conductance under High AC Frequency)***

When a solution of a strong electrolyte is subjected to an AC potential of high frequency of  $10^7$ – $10^8$  s<sup>-1</sup>, the ionic atmosphere may not be established properly and maintain effectively.

Hence, the impeding effect (relaxation effect and electrophoretic effect) of ionic cloud on the movement of central ion is diminished partially or entirely.

Therefore, the conductance of a solution increases when the ionic cloud is exposed to AC electric field, in particular of high frequency.

## **CONCEPT OF ACTIVITY COEFFICIENT: MEAN ACTIVITY COEFFICIENT**

In 1908 G.N Lewis introduced the concept of activity and activity coefficient in order to explain the deviation of an electrolyte solution from ideal behavior.

When the solution is highly diluted, it means completely dissociated into ions, and all the ions are available for conductance. This solution is said to be ideal solution.

For ideal solution effective concentration (observed) is equal to actual concentration (theoretical). But the electrolyte which is not completely dissociated, in that case effective (observed) concentration is always less than actual (theoretical) concentration.

Lewis introduced the term activity and activity coefficient to explain the deviation from ideal behavior.

Activity refers to the ions which carry current in the solution. Activity coefficient is the ratio of effective concentration to the real concentration.

$$\text{Activity coefficient } (\gamma) = \frac{\text{Effective concentration } (a)}{\text{Actual concentration } (m)}$$

$$\text{(or) } a = m\gamma \quad \dots (1)$$

Consider an electrolyte  $A_xB_y \rightleftharpoons xA^+ + yB^-$

In this example, one mole of  $A_xB_y$  produces  $x$  moles of cations ( $A^+$ ) and  $y$  moles of anions ( $B^-$ ) in solution. Therefore, the activity of above electrolyte is defined as the product of activities of cations and anions.

$$a = (a_+)^x (a_-)^y \quad \dots (2)$$

But the activity of cation  $a_+ = m_+ \gamma_+$

where  $m_+$  is the concentration of cation and  $\gamma_+$  is activity coefficient of cation.

Similarly, the activity of anion  $a_- = m_- \gamma_-$

where  $m_-$  is the concentration of anion and  $\gamma_-$  is activity coefficient of anion.

As one mole of electrolyte produces  $x$  moles of cation, concentration of cation will be  $x$  times the concentration of electrolyte (i.e.  $m_+ = x \times m$  and  $m_- = y \times m$ ).

$$\therefore a_+ = xm\gamma_+$$

$$\text{Similarly } a_- = ym\gamma_- \quad \dots (3)$$

Let's put these values on equation (2), we get

$$a = (xm\gamma_+)^x (ym\gamma_-)^y$$

$$a = (x^x m^x \gamma_+^x) (y^y m^y \gamma_-^y)$$

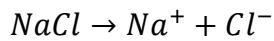
$$a = (x^x y^y) (m^x m^y) (\gamma_+^x \gamma_-^y)$$

$$a = (x^x y^y) (m^{x+y}) (\gamma_{\pm}^{x+y})$$

where  $\gamma_{\pm}$  is mean activity coefficient.

$$\text{Thus } a = x^x y^y m^{x+y} \gamma_{\pm}^{x+y} \quad \dots (4)$$

*Case 1:* For uni-univalent electrolyte e.g. HCl, NaCl, KCl etc.

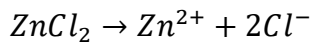


Here  $x=1$  and  $y=1$ . Therefore equation (4) becomes:

$$a = 1^1 1^1 m^{1+1} \gamma_{\pm}^{1+1}$$

$$a = m^2 \gamma_{\pm}^2 \quad \dots (5)$$

*Case 2:* For uni-bivalent electrolyte e.g.  $\text{Na}_2\text{CO}_3$ ,  $\text{ZnCl}_2$  etc.

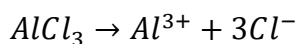


Here  $x=1$  and  $y=2$ . Therefore equation (4) becomes:

$$a = 1^1 2^2 m^{1+2} \gamma_{\pm}^{1+2}$$

$$a = 4m^3 \gamma_{\pm}^3 \quad \dots (6)$$

Case 3: For uni-trivalent electrolyte e.g.  $\text{AlCl}_3$



Here  $x=1$  and  $y=3$ . Therefore equation (4) becomes:

$$a = 1^1 3^3 m^{1+3} \gamma_{\pm}^{1+3}$$

$$a = 27m^4 \gamma_{\pm}^4 \quad \dots (7)$$

**Example 1:** Calculate the activity of  $\text{ZnCl}_2$  solution which is 0.5 molal. The mean molal ionic activity coefficient  $\gamma_{\pm} = 0.9$

**Solution:**  $\text{ZnCl}_2$  is uni-bivalent electrolyte.

Therefore, for  $x=1$  and  $y=2$ , the equation for activity becomes

$$a = 4m^3 \gamma_{\pm}^3$$

Let's substitute the values,

$$\therefore a = 4 \times (0.5)^3 \times (0.9)^3$$

$$a = 4 \times (0.125) \times (0.729)$$

$$a = 0.3645$$

## IONIC STRENGTH

Mathematically it is defined as “half of the sum of all the terms obtained by multiplying the molality of each ion by the square of its valency”. We have:

$$I = \frac{1}{2} (m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2 + \dots)$$

$$(or) I = \frac{1}{2} \sum_{i=1}^{i=n} m_i z_i^2$$

Where  $m_1, m_2, m_3 \dots$  are molalities and  $z_1, z_2, z_3 \dots$  are the valencies of the various ions present in the solution and  $i$  is 1 to  $n^{th}$  ion.

For example if a solution contains two ions namely  $K^+$  and  $\text{Cl}^-$ , the above equation contains only two terms, one for the cation and the other for the anion. Hence:

$$I = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2)$$

Where  $m_+$  and  $m_-$  are the molalities and  $z_+$  and  $z_-$  are the valencies of the cation and the anion respectively.



**Example 2:** Calculate the ionic strength of: (i) 0.15 molal KCl solution (ii) 0.25 molal  $K_2SO_4$  solution (iii) 0.2 molal  $BaCl_2$  solution and (iv) a solution which is 0.1 molal in KCl and 0.2 molal in  $K_2SO_4$ .

- (i) In 0.15 molal KCl solution, KCl dissociates to give one  $K^+$  ions and one  $Cl^-$  ions, and the molality of each ion = 0.15

Hence,  $m_+ = 0.15$  and  $m_- = 0.15$ ; Also,  $z_+ = 1$  and  $z_- = 1$

The ionic strength,

$$I = \frac{1}{2}(m_+z_+^2 + m_-z_-^2)$$

$$\therefore I = \frac{1}{2}(0.15 \times 1^2 + 0.15 \times 1^2) = 0.15$$

- (ii) In 0.25 molal  $K_2SO_4$  solution,  $K_2SO_4$  produces two  $K^+$  ions and one  $SO_4^{2-}$  ions, and hence the molalities of each ion would be;

$$m_+ = 2 \times 0.25 = 0.5 \text{ and } m_- = 1 \times 0.25 = 0.25; \text{ Also, } z_+ = 1 \text{ and } z_- = 2$$

The ionic strength is given by:

$$I = \frac{1}{2}(m_+z_+^2 + m_-z_-^2)$$

$$\therefore I = \frac{1}{2}(0.5 \times 1^2 + 0.25 \times 2^2) = 0.75$$

- (iii) In 0.2 molal  $BaCl_2$  solution,  $BaCl_2$  produces one  $Ba^{2+}$  ion and two  $Cl^-$  ions, and hence the molalities of each ion would be;

$$m_+ = 1 \times 0.2 = 0.2 \text{ and } m_- = 2 \times 0.2 = 0.4; \text{ Also, } z_+ = 2 \text{ and } z_- = 1$$

The ionic strength is given by:

$$I = \frac{1}{2}(m_+z_+^2 + m_-z_-^2)$$

$$\therefore I = \frac{1}{2}(0.2 \times 2^2 + 0.4 \times 1^2) = 0.6$$

- (iv) In a solution which is 0.1 molal in KCl and 0.2 molal in  $K_2SO_4$ :

The total molality of  $K^+$  ions  $m_1 = 1 \times 0.1 + 2 \times 0.2 = 0.5$

The molality of one  $Cl^-$  ion  $m_2 = 1 \times 0.1 = 0.1$  and

The molality of one  $SO_4^{2-}$   $m_3 = 1 \times 0.2 = 0.2$  and

Also,  $z_1 = 1$ ;  $z_2 = 1$  and  $z_3 = 2$

Hence the ionic strength,

$$I = \frac{1}{2}(m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2)$$

$$\therefore I = \frac{1}{2}(0.5 \times 1^2 + 0.1 \times 1^2 + 0.2 \times 2^2) = 0.7$$

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**SCHOOL OF SCIENCE AND HUMANITIES  
DEPARTMENT OF CHEMISTRY**

## **UNIT – 2 – Electrodeics and Electroanalytical Techniques – SCYA5303**

## THE STRUCTURE OF ELECTRICAL DOUBLE LAYER

The metal is made up of a lattice of positive ions and free electrons. When the metal is charged with an excess charge density, there is either an excess ( $q_M$  is negative) or a deficit ( $q_M$  is positive) of free electrons at the metal surface.

The excess charge density on the electrode surface is compensated by an accumulation of excess ions of the opposite charge in the solution. The amount of charge is a function of the electrode potential. This structure behaves essentially as a capacitor.

There are several theoretical models that describe the structure of the double layer. The three most commonly used ones are the Helmholtz model, the Gouy-Chapman model, and the Gouy-Chapman-Stern model.

***The Inner Helmholtz Plane (IHP), The Outer Helmholtz Plane (OHP) and a Diffuse Ionic Layer (Gouy Layer)***

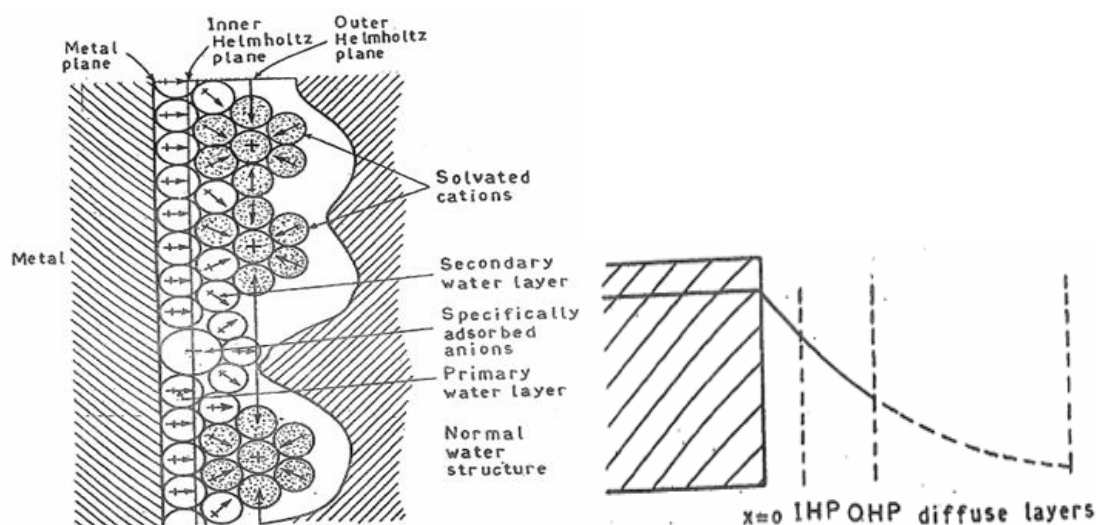
Helmholtz double layer is a dense layer of ions stuck to the electrode.

In this region, the potential varies linearly with distance. This dense layer is divided into inner and outer Helmholtz planes.

*The inner Helmholtz plane (IHP) is adjacent to the electrode surface and consists of completely oriented water dipoles and specifically adsorbed ions.*

*The outer Helmholtz plane (OHP) consists of largely of solvated ions (usually cations) at the closest distance approach from the electrode interface.*

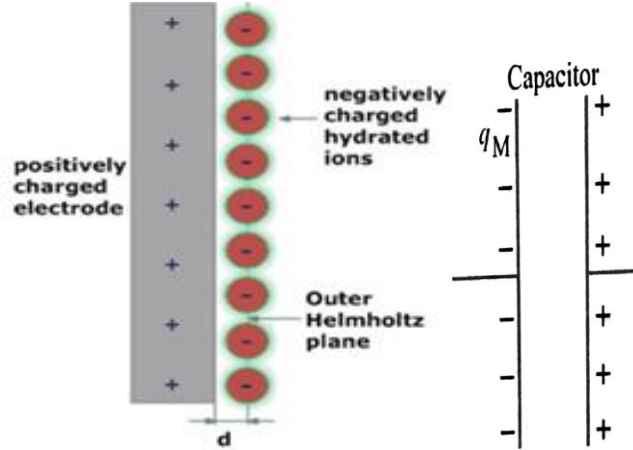
Finally, the disordering effect of thermal fluctuations and the ordering electrical forces tend to form a diffuse ionic layer (Gouy layer). The overall potential drop in the electrolyte side of the region is also shown in Fig. 2.1a and 2.1b.



**Fig. 2.1a: Electrode - Electrolyte Interface; 2.1b: Potential Distribution Across the Double Layer**

## HELMHOLTZ MODEL (or) HELMHOLTZ–PERRIN MODEL (or) PARALLEL PLATE CONDENSER MODEL

According to Helmholtz, the electrified interface consists of two sheets of charge, one on the electrode and the other in solution. Hence, it behaves like a parallel-plate condenser, since the charge densities on the two sheets are equal in magnitude but opposite in sign. The potential between these two layers of charge is a linear one (Fig. 2.2).



**Fig. 2.2: Helmholtz Model**

According to electrostatic theory of capacitors for the double layers, the potential difference  $V$  across a condenser of unit area is:

$$V = \left( \frac{d}{\epsilon_r \epsilon_0} \right) q_M \quad \dots (1)$$

$$dV = \left( \frac{d}{\epsilon_r \epsilon_0} \right) dq_M \quad \dots (2)$$

$$(or) \quad \left( \frac{dq_M}{dV} \right) = \left( \frac{\epsilon_r \epsilon_0}{d} \right) \quad \dots (3)$$

Where  $d$  is the distance between the plates,  $\epsilon_0$  is the permittivity of free space,  $\epsilon_r$  is the relative permittivity (dielectric constant) of the medium.

The capacitance of electrical capacitors is known as *integral capacitance*,  $K$  and is defined as the total charge  $q$  required to raise the potential difference  $V$  across the condenser by one volt. Mathematically it is given by:

$$K = \frac{q}{V} \quad \dots (4)$$

This is not necessarily be true for electrified interface, and hence it is convenient to define the capacitance as a *differential capacitance*,  $C$  as:

$$C = \left( \frac{dq_M}{dV} \right) \quad \dots (5)$$

Comparing equation (3) and (5), the *differential capacitance*,  $C$  of a parallel plate condenser is given as:

$$C = \left( \frac{\epsilon_r \epsilon_o}{d} \right) \quad \dots (6)$$

where  $d$  is the thickness of the double layer.

For  $\epsilon_o = 8.854 \times 10^{-12} \text{ F/m}$ ;  $\epsilon_r = 78.5$  and  $l = 0.3 \times 10^{-9} \text{ m}$ , we get:

$$C_H = 231.41 \text{ } \mu\text{Fcm}^{-2} \quad \dots (7)$$

### ***Limitations of Helmholtz Model***

- ✓ Helmholtz parallel plate condenser model predicts a constant capacity ( $C$ ) for the electrical double layer. It does not take into account the variation of the properties of double layer with concentration of electrolyte and temperature.
- ✓ Helmholtz model assumes a fixed layer of oppositely charged ions in solution. But in solution, due to thermal motion of liquid molecules such a rigid array of charges at an interface may not exist (the model neglects of interactions that occur away from the OHP).

## **GOUY-CHAPMAN MODEL**

According to Gouy-Chapman model, one layer is fixed on the electrode and the oppositely charged layer is diffused on the electrolyte [Fig. 2.3].

The solution side of the diffuse double layer is not near one molecule in thickness but extends to some distance into the liquid phase.

The distribution of positive and negative charges in this region is not uniform due to thermal agitation and the free movement of ions present in the solution.

The electrostatic attractions between opposite charges at the interface try to bring out orderliness while thermal agitation tends to bring disorderliness.

In this respect, the diffuse double layer theory is similar to the Dubye–Huckel concept of ionic atmosphere surrounding a given ion.

The distribution of ions in diffuse double layer is described by the Boltzmann distribution:

$$c_i = c_i^o \exp\left(\frac{-Z_i e \phi}{KT}\right) \quad \dots (1)$$

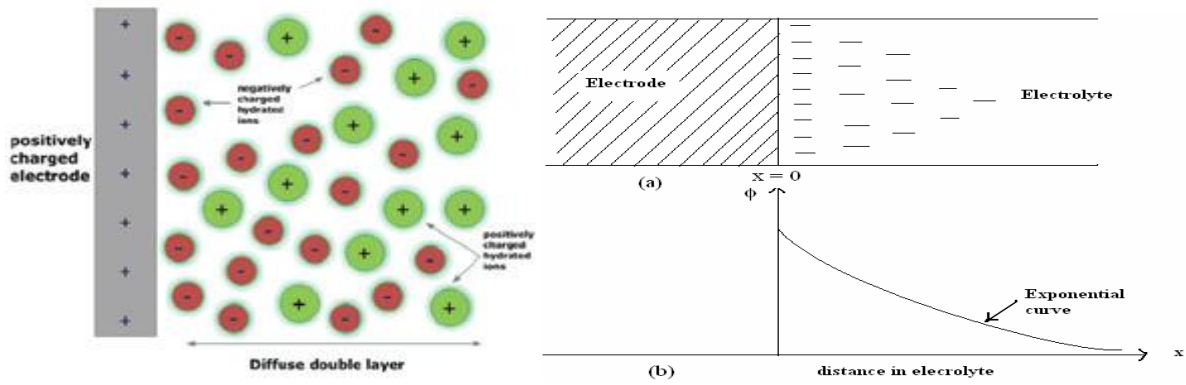
Where  $c_i^o$  is the concentration of  $i^{th}$  ion in the bulk,  $e$  is the unit electronic charge,  $Z_i$  is the valence of the ion,  $K$  is the Boltzmann constant and  $T$  is the absolute temperature.

The total charge density per unit volume for all ionic species is the sum over all ions:

$$\rho(x) = \sum_i c_i Z_i e \quad \dots (2)$$

Substituting  $c_i$  in equation (1), we get:

$$\rho(x) = \sum_i c_i^o Z_i e \exp\left(\frac{-Z_i e \phi}{KT}\right) \quad \dots (3)$$



**Fig. 2.3: Gouy – Chapman Model: (a) Schematic Charge Distribution (b) Potential Distribution in the Electrolyte**

According to Poisson equation in 1D which relates the electric potential with charge distribution as:

$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{e}{\epsilon_r \epsilon_0} \rho(x) \quad \dots (4)$$

where  $\phi$  is the electric potential,  $\rho$  is the charge density,  $x$  is the distance from the electrode.

Combining Equation (3) and (4) leads to the Poisson-Boltzmann equation:

$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{1}{\epsilon_r \epsilon_0} \sum_i c_i^o Z_i e \exp\left(\frac{-Z_i e \phi}{KT}\right) \quad \dots (5)$$

By using the property of derivatives, we have:

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{1}{2} \frac{\partial}{\partial \phi} \left( \frac{\partial \phi}{\partial x} \right)^2 \quad \dots (6)$$

Substituting  $\frac{\partial^2 \phi}{\partial x^2}$  in equation (5), we get:

$$\frac{1}{2} \frac{\partial}{\partial \phi} \left( \frac{\partial \phi}{\partial x} \right)^2 = -\frac{1}{\epsilon_r \epsilon_0} \sum_i c_i^o Z_i e \exp\left(\frac{-Z_i e \phi}{KT}\right) \quad \dots (7)$$

Rearranging and integrating equation (7) with respect to  $\phi$  on both the sides, we have:

$$\int \frac{d}{d\phi} \left( \frac{\partial \phi}{\partial x} \right)^2 = -\frac{2}{\varepsilon_r \varepsilon_o} \sum_i c_i^o Z_i \int \exp\left(\frac{-Z_i e \phi}{KT}\right) d\phi \quad \dots (8)$$

$$(or) \left( \frac{\partial \phi}{\partial x} \right)^2 = -\frac{2}{\varepsilon_r \varepsilon_o} \sum_i c_i^o Z_i \left[ \frac{\exp\left(\frac{-Z_i e}{KT}\right) \phi}{\frac{-Z_i e}{KT}} \right] + C \quad \dots (9)$$

$$\because \text{For definite integral, } \int e^{-mx} dx = \frac{e^{-mx}}{-m} + C$$

$$\left( \frac{\partial \phi}{\partial x} \right)^2 = -\frac{2e}{\varepsilon_r \varepsilon_o} \sum_i c_i^o Z_i \left( -\frac{KT}{Z_i e} \right) \times \exp\left(\frac{-Z_i e \phi}{KT}\right) + C \quad \dots (10)$$

$$(or) \left( \frac{\partial \phi}{\partial x} \right)^2 = \frac{2KT}{\varepsilon_r \varepsilon_o} \sum_i c_i^o \exp\left(\frac{-Z_i e \phi}{KT}\right) + C \quad \dots (11)$$

The integration constant in this expression can be evaluated if we define the potential in the solution at  $x = \alpha$  to zero. At the same limit,  $d\phi/dx$  also equals zero. In view of these conventions, Equation (11) becomes:

$$0 = \frac{2KT}{\varepsilon_r \varepsilon_o} \sum_i c_i^o + C \quad \dots (12) \quad [\because e^0 = 1]$$

$$C = -\frac{2KT}{\varepsilon_r \varepsilon_o} \sum_i c_i^o$$

Substituting the integration constant  $C$  in equation (11), we get:

$$\left( \frac{\partial \phi}{\partial x} \right)^2 = \frac{2KT}{\varepsilon_r \varepsilon_o} \sum_i c_i^o \exp\left(\frac{-Z_i e \phi}{KT}\right) - \frac{2KT}{\varepsilon_r \varepsilon_o} \sum_i c_i^o \quad \dots (13)$$

$$\left( \frac{\partial \phi}{\partial x} \right)^2 = \frac{2KT}{\varepsilon_r \varepsilon_o} \sum_i c_i^o \left[ \exp\left(\frac{-Z_i e \phi}{KT}\right) - 1 \right] \quad \dots (14)$$

This result may be integrated further if we restrict the electrolyte in solution to the symmetrical  $z : z$  type. In that case, equation (14) can be written as:

$$\left( \frac{\partial \phi}{\partial x} \right)^2 = \frac{2KT c_i}{\varepsilon_r \varepsilon_o} \left[ \exp\left(\frac{Z_i e \phi}{KT}\right) - 1 + \exp\left(\frac{-Z_i e \phi}{KT}\right) - 1 \right] \quad \dots (15)$$

$$(or) \left( \frac{\partial \phi}{\partial x} \right)^2 = \frac{2KT c_i}{\varepsilon_r \varepsilon_o} \left[ \exp\left(\frac{Z_i e \phi}{KT}\right) + \exp\left(\frac{-Z_i e \phi}{KT}\right) - 2 \right]$$

$$\text{But, } \left[ \exp\left(\frac{Z_i e \phi}{2KT}\right)^2 + \exp\left(\frac{-Z_i e \phi}{2KT}\right)^2 - 2 \exp\left(\frac{Z_i e \phi}{2KT}\right) \times \exp\left(\frac{-Z_i e \phi}{2KT}\right) \right] \quad \left[ \because \left(e^{\frac{x}{2}}\right)^2 = e^x \right]$$



$$(or) \quad \left(\frac{\partial \phi}{\partial x}\right)^2 = \frac{2KTc_i}{\epsilon_r \epsilon_o} \left[ \exp\left(\frac{Z_i e \phi}{2KT}\right) - \exp\left(\frac{-Z_i e \phi}{2KT}\right) \right]^2$$

$$\left(\frac{\partial \phi}{\partial x}\right) = \left(\frac{2KTc_i^o}{\epsilon_r \epsilon_o}\right)^{1/2} \left[ \exp\left(\frac{Z_i e \phi}{2KT}\right) - \exp\left(\frac{-Z_i e \phi}{2KT}\right) \right]^{2 \times \frac{1}{2}}$$

$$\frac{\partial \phi}{\partial x} = \left(\frac{2KTc_i^o}{\epsilon_r \epsilon_o}\right)^{1/2} 2 \sinh\left(\frac{Ze\phi}{2KT}\right) \quad \dots (16)$$

$$[\because e^x - e^{-x}] = 2 \sinh x$$

$$\frac{\partial \phi}{\partial x} = \left(\frac{2KTc_i^o}{\epsilon_r \epsilon_o}\right)^{1/2}$$

$$\frac{1}{2} \sinh\left(\frac{Ze\phi}{2KT}\right)$$

$$\frac{\partial \phi}{\partial x} = \left(\frac{8KTc_i^o}{\epsilon_r \epsilon_o}\right)^{1/2} \sinh\left(\frac{Ze\phi}{2KT}\right) \quad \dots (17)$$

The charge density of the diffuse layer is given as:

$$q_M = \epsilon_r \epsilon_o \left(\frac{\partial \phi}{\partial x}\right)_{x=0} \quad \dots (18)$$

$$q_M = \epsilon_r \epsilon_o \times \left(\frac{8KTc_i^o}{\epsilon_r \epsilon_o}\right)^{1/2} \sinh\left(\frac{Ze\phi}{2KT}\right)$$

$$q_M = (8KTc_i^o \epsilon_r \epsilon_o)^{1/2} \sinh\left(\frac{Ze\phi}{2KT}\right) \quad \dots (19)$$

By differentiating the equation with respect  $\phi$ , the differential capacitance is obtained as:

$$C_{GC} = \frac{dq_M}{d\phi_o}$$

$$C_{GC} = (8KTc_i^o \epsilon_r \epsilon_o)^{1/2} \frac{d}{d\phi_o} \left[ \sinh\left(\frac{Ze}{2KT} \phi\right) \right]$$

$$C_{GC} = (8KTc_i^o \epsilon_r \epsilon_o)^{1/2} \frac{Ze}{2KT} \left[ \cosh\left(\frac{Ze}{2KT} \phi\right) \right] \quad \because \frac{d}{dx} [\sinh(ax)] = a [\cosh(ax)]$$

$$C_{GC} = (8KTc_i^o \epsilon_r \epsilon_o)^{1/2} \left(\frac{Z^2 e^2}{4K^2 T^2}\right)^{1/2} \left[ \cosh\left(\frac{Ze}{2KT} \phi\right) \right]$$

$$C_{GC} = \left(\frac{2Z^2 e^2 c_i^o \epsilon_r \epsilon_o}{KT}\right)^{1/2} \cosh\left(\frac{Ze}{2KT} \phi\right) \quad \dots (20)$$

In order to assess the validity of the model, the following parameters  $\phi_o = 50$  mV,  $z = 1$ ,  $c_\infty = 0.1$  M are chosen, and the differential capacitance is determined as:

$$C_{GC} = 77.16 \mu F \text{ cm}^2$$

### Validity of Gouy–Chapman Model

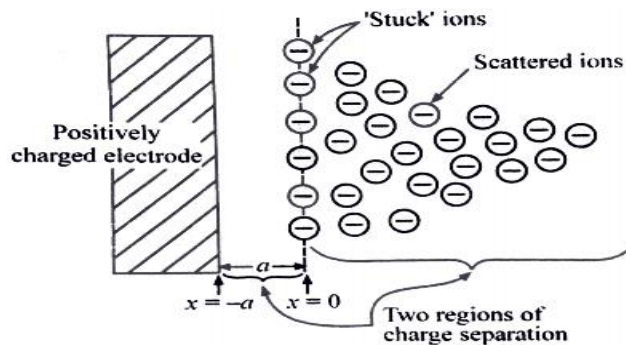
- ✓ The capacitance of the double layer varies with the potential, and it is not a constant.
- ✓ It predicts that the capacity of an interface should be hyperbolic cosine of the potential difference across it and this  $\cosh$  function gives inverted parabolas.
- ✓ Capacitance vs potential curves should be inverted parabolas.
- ✓ For very dilute solution, the experimental curves agree with a theory.
- ✓ But, at higher concentration and at potentials away from that of zero charge, Guoy–Chapman theory fails. The experimental and predicted shapes of the curve differ very much.
- ✓ In this model, ions are assumed as point charges and they are assumed to be very close to the metal surface. Hence the calculated capacitance values are found to be higher than the experimental values.

## STERN MODEL

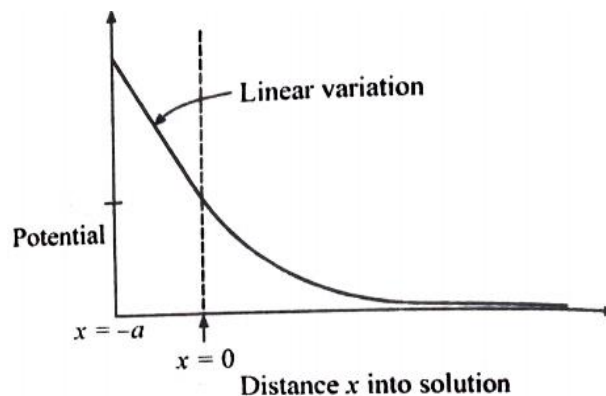
### Basic Assumptions in Stern Model

- ✓ Stern theory eliminates the point-charge approximation of the diffuse-layer theory.
- ✓ Stern theory divides the solution charge into two considerations.
- ✓ According to Stern model, a part of the charge  $q_S$  on the solution is immobilized close to the electrode in the OHP (the Helmholtz-Perrin charge,  $q_H$ ) and the remainder is diffusely spread out in the solution (the Gouy-Chapman charge,  $q_G$ ) [Fig. 24a].

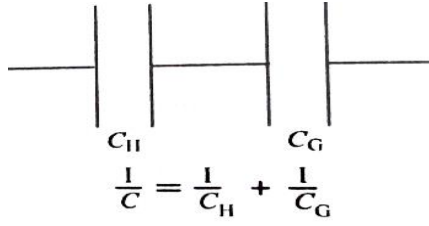
$$q_S = q_H + q_G \dots(1)$$



**Fig. 2.4: The Stern Model:**  
**2.4a: A layer of ions stuck to the electrode and the remainder scattered in cloud fashion**



**2.4b: The potential variation according to this model**



**2.4c:** The corresponding total differential capacity  $C$  is given by the Helmholtz and Gouy capacities in series.

### ***Variation of Potential***

When the charges are separated, potential drops result. The Stern model implies two potential drops [Fig. 24b and Fig. 24c]:

$$\partial(\varphi_M - \varphi_{bulk}) = \partial(\varphi_M - \varphi_H) + \partial(\varphi_H - \varphi_{bulk}) \quad \dots(2)$$

where  $\varphi_M$  and  $\varphi_H$  are the inner potentials at the metal and the Helmholtz planes, and  $\varphi_{bulk}$  is the potential in the bulk of the solution.

i.e. The equation (2) implies that Stern model has the potential-distance relations characteristics of Helmholtz-Perrin model and Gouy-Chapman model: a linear variation in the region from  $x = 0$  to the position of the OHP according to the Helmholtz-Perrin model, and an exponential drop in the region from OHP to the bulk solution according to Gouy-Chapman model.

### ***Differential Capacity of Stern Model***

The Stern model also implies that the separation of charges and potential regions produces a separation of differential capacities.

So, by differentiating the potential difference across the interface with respect to charge on the metal,  $q_M$ , we have:

$$\frac{\partial(\varphi_M - \varphi_{bulk})}{\partial q_M} = \frac{\partial(\varphi_M - \varphi_H)}{\partial q_M} = \frac{\partial(\varphi_H - \varphi_{bulk})}{\partial q_M} \quad \dots(3)$$

In the denominator of the last term, one can replace  $\partial q_M$  with  $\partial q_d$  because the total charge on the electrode is equal to the total diffuse charge. i.e.,

$$\frac{\partial(\varphi_M - \varphi_{bulk})}{\partial q_M} = \frac{\partial(\varphi_M - \varphi_H)}{\partial q_M} = \frac{\partial(\varphi_H - \varphi_{bulk})}{\partial q_d} \quad \dots(4)$$

When we examine each term in the equation, *each term represents the reciprocal of differential capacity*. Hence the above equation can be rewritten as:

$$\frac{1}{C} = \frac{1}{C_H} = \frac{1}{C_G} \quad \dots(5)$$

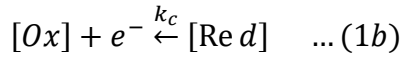
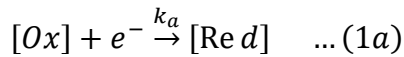
Where  $C$  is the total capacity of the interface,  $C_H$  is the Helmholtz-Perrin capacity and  $C_G$  is the Gouy-Chapman or diffuse charge capacity.

This capacity is identical to the expression for *the total capacity displayed by two capacitors in series*.

The conclusion therefore is that *an electrified interface has a total differential capacity* that is given by the Helmholtz and Gouy capacities in series.

## KINETICS OF ELECTRODE REACTIONS DERIVATION OF BUTLER-VOLMER EQUATION

Let us consider an electrode reaction in which a particular species is reduced by the transfer a single electron:



Where  $[Ox]$  and  $[Red]$  are the concentration of oxidized and reduced species respectively.

Let the rate of reduction and oxidation processes be  $k_c[Ox]$  and  $k_a[Red]$  respectively.

In a redox process, the magnitude of charge transfer per mole of the cathodic reaction brings a cathodic current ( $i_c$ ) and is given by:

$$i_c = nFk_c[Ox] \quad \dots \dots (2)$$

Where  $F$  is the Faraday constant.

An opposing anodic current density is arising from oxidation process is given by:

$$i_a = nFk_a[Red] \quad \dots \dots (3)$$

Where  $k_c$  and  $k_a$  are the corresponding rate constants.

Therefore, the net current density at the electrode is given by:

$$i = i_a - i_c \quad \dots \dots (4)$$

$$i = nFk_a[Red] - nFk_c[Ox] \quad \dots \dots (5)$$

According to Eyring Activated Complex Theory (ACT), the rate constant for the partial electrochemical reactions are given by:

$$k_c = \beta e^{\frac{-\alpha_c \eta F}{RT}} \text{ and } k_a = \beta e^{\frac{(1-\alpha_a) \eta F}{RT}}$$

Where  $\eta$  is the *over potential* ( $\eta = E - E_q$ ),  $\alpha_c$  and  $\alpha_a$  are cathodic and anodic charge transfer coefficients respectively and  $\beta$  is the some constant. Usually the  $\alpha$  values lies between 0 and 1.

Therefore, *the net current density equation (4)* at the electrode at any potential is given by:

$$i = \eta F \beta e^{\frac{(1-\alpha_a)\eta F}{RT}} [Red] - \eta F \beta e^{\frac{-\alpha_c \eta F}{RT}} [Ox] \quad \dots \dots (6)$$

For each ionic species at equilibrium, the rate of electron transfer in the cathodic direction is exactly balanced by the rate of electron transfer in the anodic direction. That is the two current densities at equilibrium potential are equal and is written as:

$$i_c = nF\beta [Ox] \text{ and } i_a = nF\beta [Red]$$

Since current density at equilibrium potential is known as exchange current density ( $I_o$ ) and it is given as:

$$I_o = i_c = i_a$$

Therefore, the equation (6) is simplified as:

$$i = I_o e^{\frac{(1-\alpha_a)\eta F}{RT}} - I_o e^{\frac{-\alpha_c \eta F}{RT}} \quad \dots \dots (7)$$

The expression (7) is known as Butler-Volmer equation.

## Tafel Equations

### Limiting Cases

**Case (1):** We know that  $e^x = 1 + x + \frac{x^2}{2!} + \dots$

Since  $x$  is very small, the first two terms can be considered for further derivation and higher orders can be neglected.

When the over potential  $\eta$  is very small, i.e.:  $\eta F/RT \ll 1$ , and hence we obtain:

$$i = I_o \left[ 1 + \frac{(1-\alpha)\eta F}{RT} \right] - I_o \left[ 1 - \frac{(\alpha\eta F)}{RT} \right] \dots \dots (8)$$

$$i = I_o + I_o \left[ \frac{\eta F}{RT} - \frac{\alpha\eta F}{RT} \right] - I_o + \frac{I_o \alpha \eta F}{RT}$$

$$i = I_o + I_o \left[ \frac{\eta F}{RT} - \frac{\alpha\eta F}{RT} \right] - I_o + \frac{I_o \alpha \eta F}{RT}$$

$$i = \frac{I_o \eta F}{RT} \quad \dots \dots (9)$$

$$\eta = \frac{i}{I_o} \left[ \frac{RT}{\alpha F} \right] \dots \dots (10)$$

The equation (10) shows that the current density is proportional to overpotential.

Case (2a): When  $\eta$  is large and positive, the first exponential is much higher than the second and hence it may be neglected and written as:

$$i = I_o \left[ e^{\frac{(1-\alpha)\eta F}{RT}} \right] \dots\dots (11)$$

Taking logarithm on both the sides, we get:

$$\log i = \log I_o + \frac{(1-\alpha)\eta F}{RT} \dots\dots (12)$$

Case (2b): When  $\eta$  is large and negative, the second exponential is much higher than the first and hence it may be neglected and written as:

$$i = I_o \left[ e^{-\frac{\alpha\eta F}{RT}} \right] \dots\dots (13)$$

Taking logarithm on both the sides, we get:

$$\log i = \log I_o - \frac{\alpha\eta F}{RT} \dots\dots (14)$$

The equations (12) and (14) are known as Tafel equations.

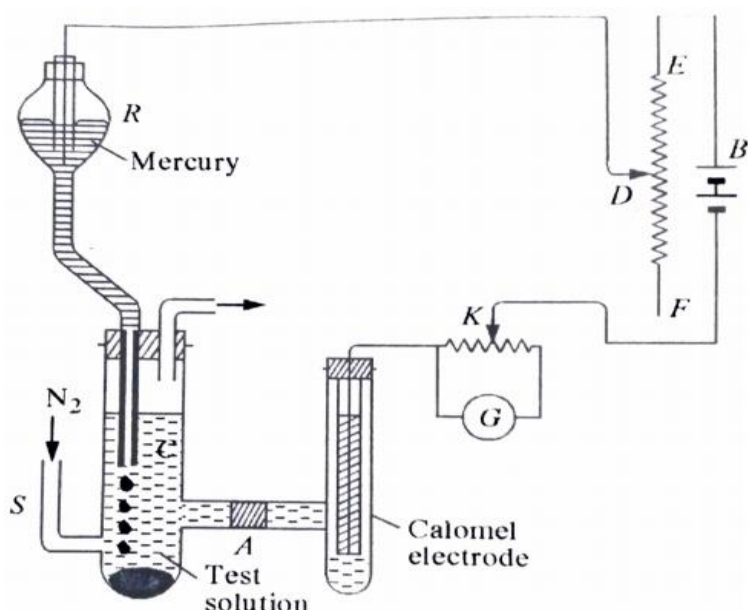
## POLAROGRAPHY

It deals with the study of current and potential relationship at a dropping mercury electrode (DME) in presence of reducible ionic species under certain controlled conditions.

A typical polarography cell consists of DME as cathode, a saturated calomel electrode (SCE) as anode and a solution containing reducible ions to be analysed [Fig. 2.5].

When potential is applied across the electrodes, three types of mass transfer / ion transfer takes place towards DME namely:

1. **Migration:** It is caused by the electrostatic attraction between electrode and the ionic species. It can be eliminated by using suitable supporting electrolyte such as 1M KCl, 1M KNO<sub>3</sub>. The electrolyte that does not take part any reaction but is only added to increase the conductivity is known as *supporting electrolyte*.
2. **Diffusion:** It refers to the movement of ionic species from bulk concentration  $C^o$  to the electrode surface.
3. **Convection:** It refers to the migration of ions due to stirring, vibration, temperature gradient. It can be eliminated by carrying out electrolysis under unstirred conditions.



**Fig. 2.5: Polarographic Cell**

- ✓ C is capillary tube;
- ✓ R is mercury reservoir;
- ✓ B is battery;
- ✓ EF is potentiometer wire;
- ✓ G is galvanometer (microammeter);
- ✓ A is calomel electrode;
- ✓ S is side tube;
- ✓ K is key (shunt) and
- ✓ D is sliding contact.

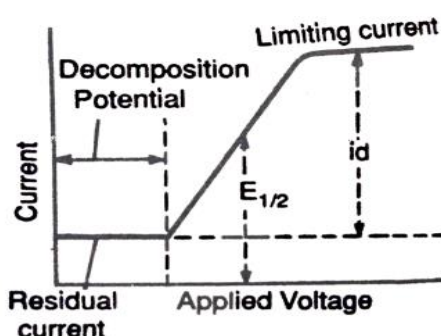
The Ilkovic equation describes the diffusion current density produced in polarographic cell and it is given by:

$$i_d = 607 \times n \times D^{1/2} \times m^{2/3} \times t^{1/6} \times C^o$$

Where,

- ✓  $i_d$  is the average diffusion current in microampere;
- ✓  $n$  is the number of electrons involved in electrode reaction;
- ✓  $D$  is the diffusion coefficient of electroactive species in  $\text{cm}^2 \text{s}^{-1}$ ;
- ✓  $m$  is the mass flow rate of mercury through the capillary in  $\text{mg s}^{-1}$ ;
- ✓  $t$  is the drop time in seconds;
- ✓  $C^o$  is the bulk concentration of the electroactive species in millimoles per litre and
- ✓ 607 is a combination numerical constant.

Polarographic data are obtained by measuring diffusion current as a function of the potential applied to the polarographic cell (electrolytic cell) [Fig. 2.6].



**Fig. 2.6: Diffusion Current versus Applied Voltage**

If the test solution contains a single electroactive species, the *current-voltage curve known as polarogram* is obtained.

In the polarogram, the limiting current (which is given by the height of the wave) *corresponds to the concentration of electroactive species*.

The potential at the centre of the rising part of wave is referred to as half wave potential and it is denoted as  $I_{1/2}$ . It can be *used to identify the particular species*.

#### ***Advantages of dropping mercury electrode (DME)***

- ✓ Its surface area is reproducible with a given capillary.
- ✓ The constant renewal of the electrode surface eliminates passivity or poisoning effects.
- ✓ The large hydrogen overpotential on mercury renders possible the deposition of substances difficult to reduce such as aluminium ion and manganese (II) ion.
- ✓ Mercury forms amalgams with many metals.
- ✓ The diffusion current attains a steady value immediately and is reproducible.
- ✓ The surface area of the electrode can be calculated from the weight of the drops. The dropping mercury electrode is therefore useful over the range + 0.3 to – 2.0 V vs. SCE.

#### ***Limitations of dropping mercury electrode (DME)***

- ✓ Above + 0.4 V mercury dissolves and gives an anodic wave due to oxidation to mercury (I) ion. At potentials more negative than – 1.8 V vs SCE visible hydrogen evolution occurs in acid solutions and at – 2.0 V the supporting electrolytes of alkali salts begin to discharge.

## **THE ILKOVIC EQUATION**

The diffusion current in polarography can be related to the concentration of reducible species by using the two Fick's laws of diffusion.

According to Fick's first law of diffusion, the number of moles of a substance that diffuse across the plane of unit area per unit time  $\left(\frac{dN}{Adt}\right)$  is proportional to the concentration gradient in the diffusion field.

$$\frac{dN}{Adt} = D \left( \frac{dc}{dx} \right) \quad \dots (1)$$

Where  $dN$  is the number of moles of the diffusible ions that diffuse across a cross-sectional plane in area  $A$  ( $\text{cm}^2$ ) in the time interval ( $dt$ ).

According to Fick's second law, the rate of change of concentration with time  $\left(\frac{dc}{dt}\right)$  as a result of diffusion of the substance across the plane is proportional to the differential of the concentration gradient.



$$\frac{dc}{dt} = D \left( \frac{\partial^2 c}{\partial x^2} \right) \quad \dots (2)$$

In both these laws, the proportionality constant  $D$ , is the diffusion coefficient of the diffusible ions.

The flow of current ( $i$ ) across a plane during electrolysis is given by:

$$i = n \times F \times \left( \frac{dN}{dt} \right)$$

$$i = nFDA \frac{dc}{dx} \quad \dots (3)$$

It is theoretically found that for linear diffusion to a flat surface:

$$\frac{dc}{dx} = \frac{C^o}{(D\pi t)^{\frac{1}{2}}} \quad \dots (4)$$

Where  $C^o$  is the concentration of ionic species in the bulk of the solution as  $t$  is time elapsed since the onset of electrolysis.

Substituting (4) in equation (3), we get:

$$i_d = nFAD \frac{C^o}{(D\pi t)^{\frac{1}{2}}}$$

$$i_d = nFAC^o \left( \frac{D}{\pi t} \right)^{\frac{1}{2}} \quad \dots (5)$$

The electrode that is employed in polarographic studies is the dropping mercury electrode (DME).

The DME is a spherical electrode of expanding radius and surface area. Its surface area changes with the age of the drop.

Ilkovic assumed linear diffusion for the current for DME.

He calculated surface area of the electrode-electrolyte boundary  $A_t$  at time  $t$  is given by:

$$\text{Drop volume at time, } t = \frac{4}{3} \pi r_t^3$$

$$\text{Drop mass at time, } t = \text{Volume} \times \text{Density}$$

$$\text{Drop mass at time, } t = \frac{4}{3} \pi r_t^3 \times \rho$$

Where  $\rho$  is the density of mercury and  $r_t$  is the drop radius at time  $t$ .

If  $m$  is the mass flow rate of mercury, then the drop mass at time  $t$  is equal to  $m \times t$ . Therefore,

$$\frac{4}{3}\pi r_t^3 \times \rho = m \times t$$

$$(or) r_t = \left[ \frac{3mt}{4\pi\rho} \right]^{\frac{1}{3}} \quad \dots (6)$$

The surface area of the mercury drop at time  $t$  is given by:

$$A_t = 4\pi r_t^2 \quad \dots (7)$$

Substituting  $r_t$  in equation (7), we get:

$$A_t = 4\pi \left[ \frac{3mt}{4\pi\rho} \right]^{\frac{2}{3}}$$

$$(or) A_t = \frac{4\pi \times 3^{\frac{2}{3}} \times m^{\frac{2}{3}} \times t^{\frac{2}{3}}}{4^{\frac{2}{3}} \times \pi^{\frac{2}{3}} \times \rho^{\frac{2}{3}}}$$

$$(or) A_t = 0.8515 \times m^{\frac{2}{3}} \times t^{\frac{2}{3}} \quad \dots (8)$$

Substituting the value of area  $A_t$  in equation (5), we get:

$$i_d = n \times F \times 0.8515 \times m^{\frac{2}{3}} \times t^{\frac{2}{3}} \times C^o \left( \frac{D}{\pi t} \right)^{\frac{1}{2}} \quad \dots (9)$$

$$(or) i_d = \frac{0.8515 \times n \times F \times C^o \times D^{\frac{1}{2}} \times m^{\frac{2}{3}} \times t^{\frac{2}{3}}}{(\pi t)^{\frac{1}{2}}} \quad \dots (10)$$

This equation on simplification by taking  $F = 96500$  C/mole, then,

$$i_d(\text{in microampere}) = 708 \times n \times m^{\frac{2}{3}} \times t^{\frac{1}{6}} \times C^o \times D^{\frac{1}{2}} \quad \dots (11)$$

If  $t$  is the drop time for DME, equation (11) gives the maximum value of the diffusion current for the DME for a particular potential is applied.

$$(or) i_d(\text{maximum}) = 708 \times n \times m^{\frac{2}{3}} \times t^{\frac{1}{6}} \times C^o \times D^{\frac{1}{2}} \quad \dots (12)$$

The average value of  $i_d$  during the life of a drop is estimated to be  $6/7^{\text{th}}$  of its maximum value at the time of drop fall, hence the equation (12) can be rewritten as:

$$(or) i_d(average) = 607 \times n \times m^{\frac{2}{3}} \times t^{\frac{1}{6}} \times C^o \times D^{\frac{1}{2}} \quad \dots (13)$$

Both the form of equations (12) and (13) are known as Ilkovic equation, which show that  $i_d$  is directly proportional to the bulk concentration  $C^o$  of the ions reducible at DME. Hence,

$$i_d = kC^o \quad \dots (14)$$

## HALF WAVE POTENTIAL

The potential at which the current is half of the diffusion current  $i_d$  known as half-wave potential ( $E_{1/2}$ ).

Let us consider, the redox half-cell reaction at the microelectrode (DME):



Where  $Ox$  stands for the electroactive species is being reduced and  $Red$  stands for the product.

So, the reversible half-cell potential of this system is given by the Nernst equation as:

$$E_{cathode} = E^o - \frac{0.0591}{n} \log \frac{[Red]_o}{[Ox]_o} \quad \dots (1)$$

Where the zero in the subscripts denotes the concentration of oxidant at DME electrode, cathode / solution interface.

Let  $E_{applied}$  be the potential applied between DME and the reference electrode, hence

$$E_{applied} = E_{cathode} + E_{anode} \quad \dots (2)$$

Since the anode is SCE, we can write equation as:

$$E_{applied} = \left[ E^o - \frac{0.0591}{n} \log \frac{[Red]_o}{[Ox]_o} \right] + E_{SCE} \quad \dots (3)$$

In beginning the electrolysis, this solution at the DME contains only the oxidised form of ions  $[Ox]_0$ .

When the potential is applied, the oxidant concentration starts to decrease around the electrode, and some of ions move towards the surface of DME from the bulk solution.

Hence the concentration gradient build up between bulk electrode surface and solution.

At the applied potential, the observed current ( $i$ ) is given by:

$$i = K\{[Ox] - [Ox]_0\}$$

$$i = K[Ox] - K[Ox]_0 \quad \dots (4)$$

Where  $K$  stands for the capillary characteristics and other constants of Ilkovic equation.

As soon as the current attains the limiting current, the concentration of  $[Ox]_0$  at the electrode surface becomes zero.

Therefore,

$$i_d = K[Ox] \quad \dots (5)$$

$$(or) [Ox] = \frac{i_d}{K}$$

Subtracting equation (5) from (4), we get:

$$i_d - i = K[Ox] - K[Ox] + K[Ox]_0$$

$$i_d - i = K[Ox]_0$$

$$[Ox]_0 = \frac{i_d - i}{K} \quad \dots (6)$$

Also, the concentration of the product  $[Red]_0$  at the electrode surface is directly proportional to current on current-potential curve.

$$i = K'[Red]_0$$

$$[Red]_0 = \frac{i}{K'} \quad \dots (7)$$

Substituting equations (6) and (7) in equation (3), we get:

$$E_{applied} = E_{SCE} + \left[ E^o - \frac{0.0591}{n} \log \frac{i/K'}{i_d - i/K} \right] \quad \frac{i/K'}{i_d - i/K} = \frac{i}{i_d - i} \times \frac{K}{K'}$$

$$(or) E_{applied} = E_{SCE} + E^o - \frac{0.0591}{n} \left[ \log \frac{K}{K'} + \log \frac{i}{i_d - i} \right]$$

$$(or) E_{applied} = E_{SCE} + E^o - \frac{0.0591}{n} \log \frac{K}{K'} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \quad \dots (8)$$

By definition,  $i = \frac{i_d}{2}$  when  $E_{applied} = E_{1/2}$

$$E_{1/2} = E_{SCE} + E^o - \frac{0.0591}{n} \log \frac{K}{K'} - \frac{0.0591}{n} \log \frac{\frac{i_d}{2}}{i_d - \frac{i_d}{2}}$$

$$E_{1/2} = E_{SCE} + E^o - \frac{0.0591}{n} \log \frac{K}{K'} \quad \dots (9)$$

Hence,  $E_{1/2}$  is constant which depends upon standard electrode potential of the redox system and independent of concentration of electroactive species.

Substituting equation (9) in (8), we get:

$$(or) E_{applied} = E_{1/2} - \frac{0.0591}{n} \log \frac{i}{i_d - i} \quad \dots (10)$$

Equation (10) is known as polarographic half wave potential.

In order to test the equation (10), a plot of  $E_{applied}$  versus  $\log \frac{i}{i_d - i}$  is made, which gives a straight line with slope is equal to  $-\frac{0.0591}{n}$ .

$E_{1/2}$  can also be determined, and it is the potential at which the term  $\log \frac{i}{i_d - i}$  becomes zero [Fig. 2.7].

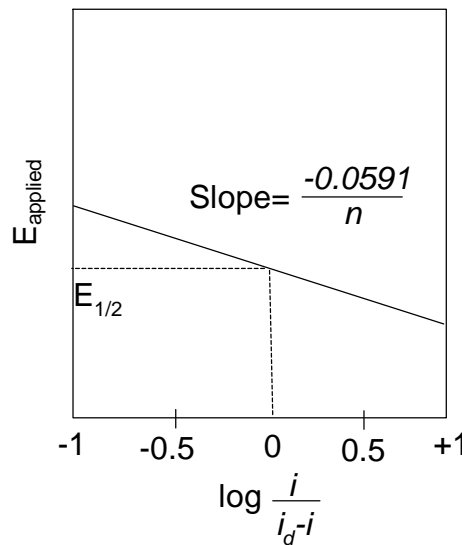


Fig. 2.7: Plot of  $E_{applied}$  versus  $\log \frac{i}{i_d - i}$

## CYCLIC VOLTAMMETRY FOR REDOX SYSTEM

Cyclic voltammetry (CV) is an electrochemical potentiodynamic technique in which the *current is measured* at the working electrode *during the potential scan from cathodic side to anodic side*.

### Instrumentation

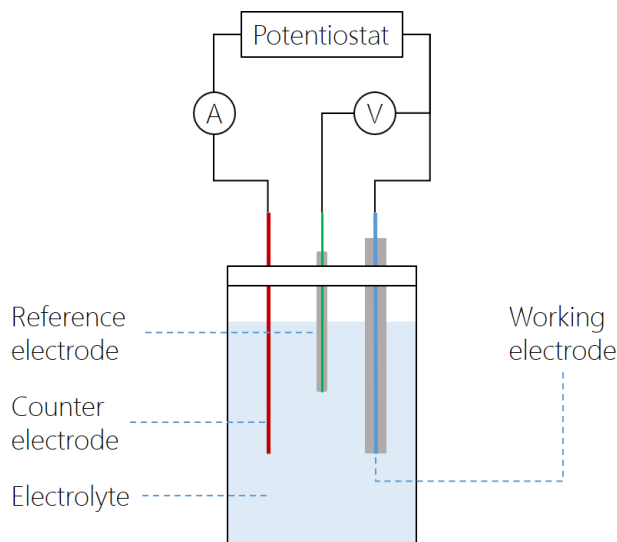
The CV consisting of a three-electrode cell system, a potentiostat and a data processor [Fig. 2.8]

The three-electrode cell system includes a working electrode, a reference electrode [*SCE* or *Ag / AgCl*], a counter electrode [*Pt* or graphite] and the electrolyte solution to be investigated.

The potentiostat is an electronic device which uses DC power supply. It is capable of impressing the potential linearly with time (*known as scan rate, usually expressed in mV/s*) with respect to reference electrode.

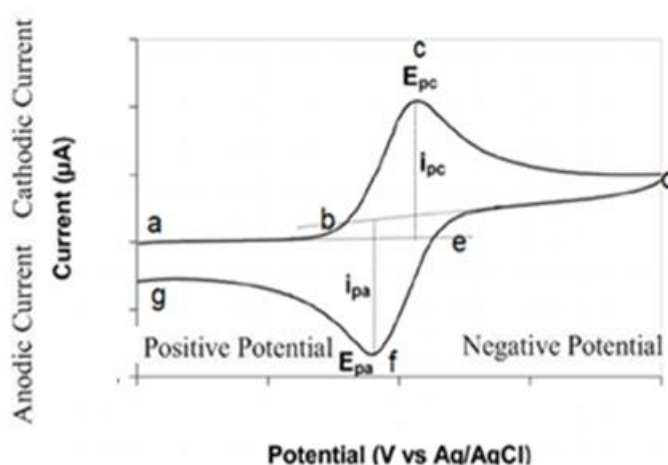
The potentiostat also has the voltage to current converter which helps to measure the resulting current utilized / produced at the working electrode using the counter electrode.

The data processor displays the resulting cyclic voltammogram.



**Fig. 2.8: Cyclic Voltammetry Cell Set-up**

### ***Cyclic Voltammogram of a Ferric-Ferrous Redox System / Principle and Working of Cyclic Voltammetry***



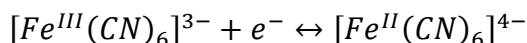
**Fig. 2.9: Cyclic Voltammogram for a Typical Redox System**

In cyclic voltammetry, *initially* the potential is impressed in the cathodic direction [forward scan] from the initial potential [OCP-open circuit potential] to switching potential. Then, the potential is reversed in the anodic direction [backward scan] from switching potential to the end potential [Fig. 2.9].

During the forward scan the electro-active species undergo reduction whereas during the backward scan the electroactive species undergo oxidation at the surface of working electrode.

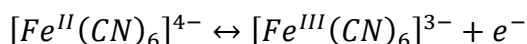
The current utilized by the reduction of ionic species,  $Fe^{3+}$  is measured at the surface of working electrode along the curve  $[a,b,c,d]$ , and is known as cathodic current,  $i_c$ .

The maximum current utilized by the ionic species at the surface of working electrode is known as  $i_{pc}$ , [cathodic peak current] and the corresponding potential is known as  $E_{pc}$ , cathodic peak potential.



When the potential is impressed in the reverse direction [backward scan] , the deposited electroactive species undergo oxidation in turn dissolve from the substrate and produces current along the curve  $[d,e,f,g]$ , and is known as anodic current,  $i_a$ .

The maximum current produced by the oxidation of electroactive substrate at the surface of working is known as  $i_{pa}$ , anodic peak current and the corresponding potential is known as  $E_{pa}$ , anodic peak potential.



### ***Applications of Cyclic Voltammetry***

Cyclic voltammetry provides considerable information:

- ✓ *on the thermodynamics of redox processes;*
- ✓ *on the kinetics of heterogeneous electron-transfer reactions; and*
- ✓ *on coupled chemical reactions or adsorption processes.*

## **AMPEROMETRIC TITRATIONS**

### ***Principle of Amperometric Titrations***

The amperometric titrations are also known as *polarographic titrations*. It is based on the principle of polarography, except that a constant electrode potential is applied to the working electrode (DME) with respect to SCE and the diffusion current,  $i_d$  of ionic species is measured at the working electrode as a function of the volume of the titrating solution.

According to Ilkovic equation ( $I_d = 607 \times n \times D^{1/2} \times m^{2/3} \times t^{1/6} \times C$ ), the diffusion current is directly proportional to the concentration of the electroactive species in the solution keeping all other factors of the equation constant.

*So, if some of the electroactive material in the solution is removed by interaction with some other reagent, the diffusion current will decrease proportionally.*

The end point is the intersection of two lines giving the change of current before and after the equivalence point.

### 1) Titration of Reducible Species ( $Pb^{2+}$ ) vs Non-reducible Species ( $SO_4^{2-}$ )

- Burette solution:  $SO_4^{2-}$
- Pipette solution:  $Pb^{2+}$
- Applied potential:  $-0.8\text{ V}$  with respect to SCE

When  $SO_4^{2-}$  solution is added into the reducible  $Pb^{2+}$  ions, the diffusion current of  $Pb^{2+}$  decreases due to its precipitation as  $PbSO_4$ . Once all the  $Pb^{2+}$  ions are precipitated, excess addition of  $SO_4^{2-}$  ions does not have any effect since the cation of the titrant is not reduced at this potential. Hence, the current now flowing is the residual current since the applied potential is constant.

If the measured current is plotted against the volume of titrant ( $H_2SO_4$  or  $Na_2SO_4$ ), an L shaped curve is obtained from which the end point is detected [Fig. 2.10].

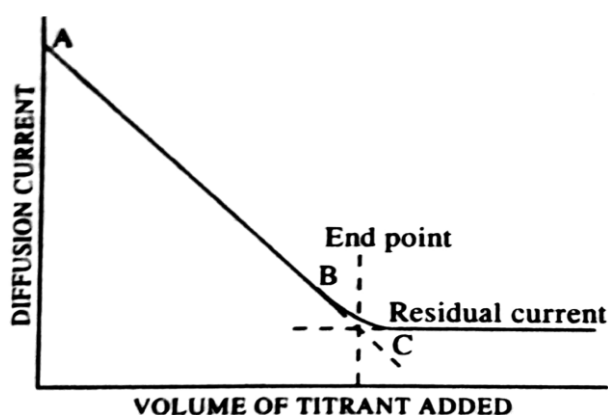


Fig. 2.10:  $Pb^{2+}$  vs  $SO_4^{2-}$  at constant potential of  $-0.8\text{ V}$  (vs SCE)

### 2) Titration of Non-reducible Species ( $Mg^{2+}$ ) vs Reducible Species (8HQ)

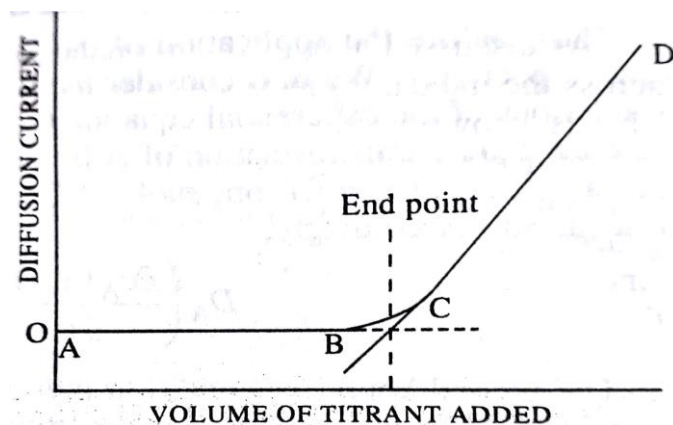
- Burette solution: 8-Hydroxy quinoline (8HQ)
- Pipette solution:  $Mg^{2+}$
- Applied potential:  $-1.6\text{ V}$  with respect to SCE

When a solution containing  $Mg^{2+}$  ion is titrated against with the reducible species such as 8-hydroxy quinoline (8HQ), 8HQ reacts with  $Mg^{2+}$  to form a greenish yellow magnesium hydroxyquinolate precipitate which does not give any diffusion current and hence, the current remains constant.

Once the reaction is completed, excess addition of 8HQ increases its concentration in solution which undergoes reduction at the working electrode in turn increases the diffusion current.

If the measured current is plotted against the volume of titrant (8HQ), a reverse L shaped curve is obtained from which the end point is detected [Fig. 2.11].





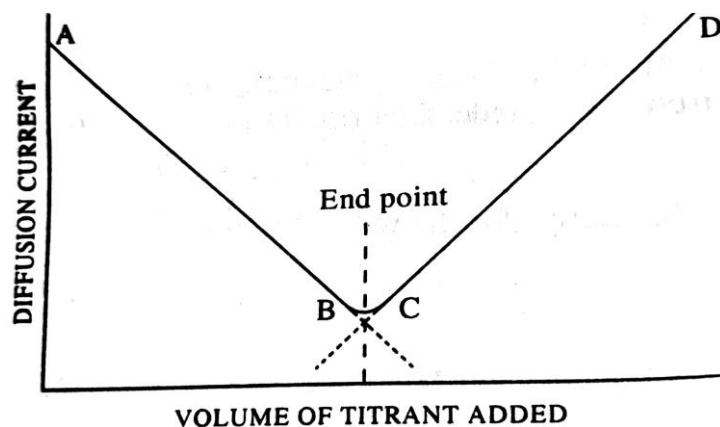
**Fig. 2.11:  $Mg^{2+}$  vs 8-Hydroxy quinoline at constant potential  $-1.6 V$  (vs SCE)**

### 3) Titration of Reducible Species ( $Cr_2O_7^{2-}$ ) vs Reducible Species ( $Pb^{2+}$ )

- Burette solution:  $Cr_2O_7^{2-}$
- Pipette solution:  $Pb^{2+}$
- Applied potential:  $-0.8 V$  with respect to SCE

When  $Cr_2O_7^{2-}$  ions are added into a solution containing reducible  $Pb^{2+}$  ions, the diffusion current of  $Pb^{2+}$  solution decreases due to formation of  $PbCr_2O_7$  crystals. Once all the  $Pb^{2+}$  are converted into crystals, excess addition of  $Cr_2O_7^{2-}$  ion increases its concentration in the solution, and starts to undergo reduction in turn increases the diffusion current.

If the measured current is plotted against the volume of titrant ( $Cr_2O_7^{2-}$ ), a V shaped curve is obtained from which the end point is detected [Fig. 2.12].



**Fig. 2.12:  $Pb^{2+}$  vs a standard solution of  $Cr_2O_7^{2-}$  at constant potential  $-0.8 V$  (vs SCE)**

#### Advantages of Amperometric Titrations

- ✓ Diffusion current is 20 times larger than DME which allows measuring the small concentration of ion (Micro-concentration of material can be determined).
- ✓ The rotating platinum electrode can be used at positive potential up to  $+0.9 V$  whereas DME can be used only  $+0.4$  to  $-2.0 V$ olts.

- ✓ The electrode is simple to construct.
- ✓ Steady diffusion state is reached quickly.

## ION SELECTIVE ELECTRODES (ISE)

*Ion selective electrodes have the ability to respond to the activity of a particular ion and develop a potential.* The glass electrode is a type of ISE that is sensitive to  $H^+$  ions. A number of such electrodes have been developed recently which are responsive to other ions like  $Na^+$ ,  $NH_4^+$ ,  $Ca^{2+}$ ,  $Cl^-$ ,  $F^-$ ,  $NO_3^-$  etc. The *membrane used in ion selective electrodes is sensitive to a particular chemical species.*

### **Basic Principle of ISE**

An ISE operates on the same principle as a pH electrode. In fact, a pH electrode is a type of ISE, which is sensitive to hydrogen ions. An ISE contains an internal reference solution and an internal reference electrode. The use of membrane is must in ISE. In ISE, the internal reference solution is sealed with an ion-selective membrane, which acts as ion sensor.

Generally, three different types of membranes are used in ISE and they are: i) glass membrane ii) solid-state crystal membrane and iii) liquid membrane.

The potential developed across ISE is measured on a millivolt scale with respect to an internal reference electrode (either a *calomel electrode* or a  $Ag/AgCl$  electrode). Based on the ion selective membranes used, the ISE are classified into three groups.

### **Glass Membrane Electrodes**

The selectivity of glass membranes depends on the composition of glass. Generally, they are based on  $Na_2O-Al_2O_3-SiO_2$  mixture. Those glass membranes rich in  $SiO_2$  but low in  $Al_2O_3$  are sensitive to proton ( $H^+$  ions) while those glass membranes rich in  $SiO_2$  with high content of  $Al_2O_3$  respond more strongly to alkaline metal ions [Fig. 2.13].

Two typical composition of glass membranes are:

- (i) 22%  $Na_2O$  + 6%  $Al_2O_3$  + 72%  $SiO_2$  – responds to  $H^+$  ions.
- (ii) 11%  $Na_2O$  + 18%  $Al_2O_3$  + 71%  $SiO_2$  – responds to  $Na^+$  ions.

The electrode potential of glass membrane electrode is given by the Nernst equation as:

$$E_G = E_G^0 + 0.0591 \log[H^+]$$

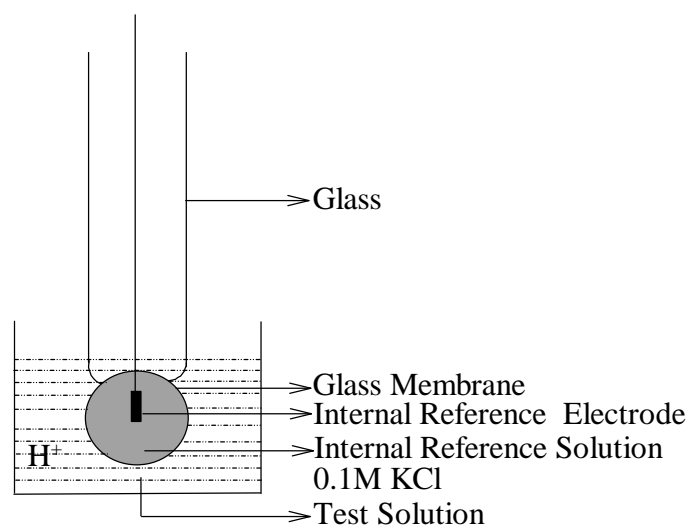
Therefore, the  $[H^+]$  can be measured by using the expression:

$$emf = E_{SCE} - E_G$$

$$emf = 0.2422 - E_G^0 - 0.0591 \log[H^+]$$

$$0.0591 \log[H^+] = 0.2422 - E_G^o - emf$$

$$\log[H^+] = \frac{0.2422 - E_G^o - emf}{0.0591}$$

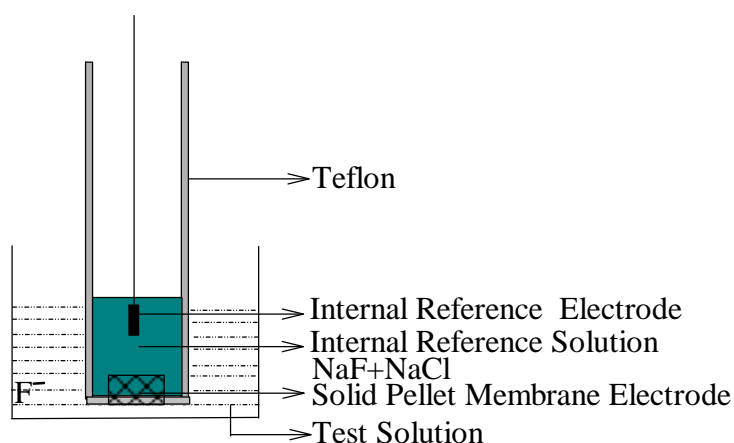


**Fig. 2.13: Glass Membrane Electrode**

### Solid State Membrane Electrodes

These electrodes are mainly anion responsive and several types are available for measuring the halide ion concentrations.

Materials used for solid state membrane include *lanthanum trifluoride ( $LaF_3$ ) crystal doped with europium difluoride ( $EuF_2$ ) for fluoride ions* and a pressed pellet of  $Ag_2S+AgCl$  for chloride ions.



**Fig. 2.14: Solid State Membrane Electrode**

A single crystal of  $LaF_3$  acts as sensing membrane in a fluoride electrode. However, it has very high electrical resistance. In order to minimize this,  $LaF_3$  crystal is usually doped with europium (II), which lowers the crystal resistance and facilitates ionic charge transport.

The electrode is usually manufactured with a *PTFE* body, and the doped  $LaF_3$  crystal is held in position with epoxy resin. The filling solution contains  $NaF + NaCl$  and the internal reference electrode is  $Ag/AgCl$ . This fluoride electrode can measure the fluoride ion activity as much less as  $10^{-6} M$  [Fig. 2.14].

A pressed pellet of polycrystalline  $Ag_2S + AgCl$  membrane is an example of chloride ion sensing electrode.

The electrode potential of solid-state membrane electrode is given by the Nernst equation as:

$$E_S = E_S^o + 0.0591 \log[F^-]$$

Therefore, the  $[F^-]$  can be measured by using the expression:

$$emf = E_{Ag/AgCl} - E_S$$

$$emf = 0.197 - E_S^o - 0.0591 \log[F^-]$$

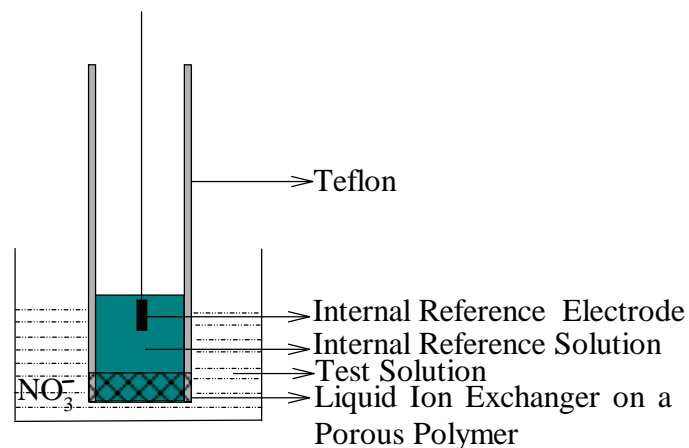
$$0.0591 \log[F^-] = 0.197 - E_S^o - emf$$

$$\log[F^-] = \frac{0.197 - E_S^o - emf}{0.0591}$$

## LIQUID MEMBRANE ELECTRODES

This type of electrodes is used for the measurement of calcium, nitrate, ammonium and other ions. In these electrodes, the active material is a large organic molecule capable of interacting specifically with an anion or a cation. The active organic molecules are adsorbed on the inert porous polymer support and used [Fig. 2.15].

- (i) *di-(n-decyl) phosphate* in PVC – responds to  $Ca^{2+}$  ions.
- (ii) *Tetra-dodecyl ammonium nitrate* in PVC – responds to  $NO_3^-$  ions.



**Fig. 2.15: Liquid Membrane Electrode**

The electrode potential of liquid membrane electrode is given by the Nernst equation as:

$$E_L = E_L^o + 0.0591 \log[NO_3^-]$$

Therefore, the  $[NO_3^-]$  can be measured by using the expression:

$$emf = E_{Ag/AgCl} - E_S$$

$$emf = 0.197 - E_L^o - 0.0591 \log[NO_3^-]$$

$$0.0591 \log[NO_3^-] = 0.197 - E_L^o - emf$$

$$\log[NO_3^-] = \frac{0.197 - E_L^o - emf}{0.0591}$$

### ***Applications of Ion Selective Membrane Electrodes***

- ✓ ISE are used in determining the concentrations of a number of cations such as  $H^+$ ,  $Na^+$ ,  $K^+$ ,  $Ag^+$ ,  $Li^+$ ,  $NH_4^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , etc.
- ✓ ISE can also be used for determining the concentration of anions like  $F^-$ ,  $CN^-$ ,  $S^{2-}$ , and other halide ions..
- ✓ Calcium ion electrode has important applications in physiological investigations because  $Ca^{2+}$  ion is known to influence bone formation, muscle contraction, cardiac expansion and contraction and nerve conduction.
- ✓ Also, calcium ion electrodes have been used to determine  $Ca^{2+}$  ion in boiler-feed water, soil, milk, seawater etc.
- ✓ ISE are used in determining the concentration of gas using gas sensing electrodes. The glass electrode is in contact with a very thin silicon rubber membrane ( $CO_2$  permeable) soaked in a dilute solution of  $NaHCO_3$  is an example of gas sensing electrode. When this electrode is dipped in the blood sample, it allows  $CO_2$  to permeate into the membrane.  $CO_2$  then reacts with  $NaHCO_3$  and alters the pH. This change in pH is then sensed by the glass electrode. Hence, the potential of the glass electrode gives a measure of  $CO_2$  in the blood sample.
- ✓ ISE provide a number of industrial uses such as predicting corrosion rates, degree of acidity, formation of complexes, extent of precipitation, solution conductivities etc.

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4. Allen J. Bard and Cynthia Zoski, "Electroanalytical Chemistry: A Series of Advances", 2011, Taylor & Francis Inc, Boca Roca, United States.



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## **UNIT – 3 – Crystal Structure – SCYA5303**

## CRYSTALLINE AND AMORPHOUS SOLIDS

### *Crystalline Solids*

- ✓ The solids in which atoms, ions or molecules are arranged in a definite regular pattern are known as crystalline solids.
- ✓ They are anisotropic. Their physical properties are different in different directions.
- ✓ They give regular cut when cut with a sharp-edged utensil.
- ✓ They are regarded as true solids.

### *Crystalline Solids*

- ✓ The solids in which atoms, ions or molecules are arranged in a random manner are known as amorphous solids.
- ✓ They are isotropic. Their physical properties are same in all directions.
- ✓ They give irregular cut when cut with a sharp-edged utensil.
- ✓ They are regarded as pseudo solids.

## TYPES OF CRYSTALLINE SOLIDS

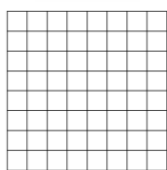
S. No.	Type	Properties	Examples
1.	Ionic Crystals	<ul style="list-style-type: none"><li>• Formed by the ionic bonds holding the oppositely charged ions together.</li><li>• Have high melting point.</li><li>• Brittle.</li><li>• Bad conductor of electricity.</li><li>• Soluble in polar solvents.</li></ul>	NaCl; ZnS; CaF <sub>2</sub>
2.	Covalent Crystals	<ul style="list-style-type: none"><li>• Formed by the mutual sharing of electrons binds the atoms together.</li><li>• Have high melting point.</li><li>• Hard.</li><li>• Bad conductor of electricity.</li><li>• Insoluble in polar solvents.</li></ul>	Diamond; SiC
	Metallic Crystals	<ul style="list-style-type: none"><li>• Formed by electrostatic force which holds Kernals and mobile electrons cloud together.</li><li>• Low to high melting point.</li><li>• Soft to very hard.</li><li>• Good conductor of electricity.</li><li>• Malleable and ductile.</li></ul>	Li; Fe; Cu

4.	Molecular Crystals	<ul style="list-style-type: none"> <li>Formed by Vanderwalls force (weak electrical attraction) which binds molecules together.</li> <li>Volatile.</li> <li>Soft.</li> <li>Bad conductor of electricity.</li> <li>Soluble in non-polar solvents.</li> </ul>	Ice; Solid I <sub>2</sub> ; Solid CO <sub>2</sub>
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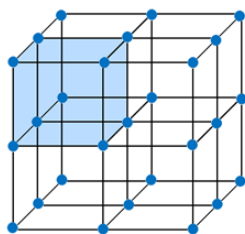
## UNIT CELL AND CRYSTAL LATTICE



**Fig. 3.1a: Unit cell**



**Fig. 3.1b: 2-D Crystal Lattice**



**Fig. 3.1c: 3-D Cubic Lattice with its Unit Cell**

**Unit Cell:** The fundamental building block of a crystal structure [Fig. 3.1].

**Space Lattice:** The ions, atoms or ions in any crystalline material are arranged in a regular three-dimension pattern. Such pattern of crystalline material is known as crystal lattice or space lattice [Fig. 3.1b and Fig. 3.1c].

**Lattice Parameters:** The magnitude of lengths along the direction of a unit cell (*lattice points*:  $a$ ;  $b$ ;  $c$ ) and the angle between three axes (*inter axial angles*:  $\alpha$ :  $\beta$ :  $\gamma$ ) are known as lattice parameters.

### Types of Unit Cell

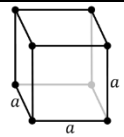
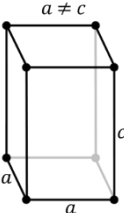
In general, there are four types of lattice arrangements used to describe the crystal systems.

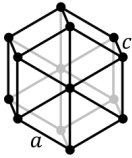
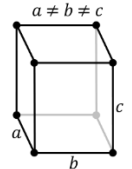
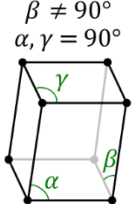
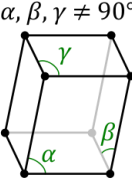
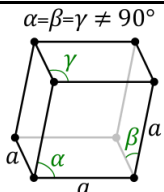
S. No.	Type of Unit Cell	Description of Unit Cell	Number of Atoms per Unit Cell
1.	Simple (or) Primitive Unit Cell ( $P$ )	In simple primitive unit cell, each atom at the corner is shared by eight more-unit cells and hence, the corner atoms contribute $1/8^{\text{th}}$ of the atom to one-unit cell.	$= 8 \times \frac{1}{8}$ $= 1 \text{ atom}$
2.	Face Centred Unit Cell ( $F$ )	In face centered unit cell, the atom at the face is shared by two-unit cells and hence, the face centred	$= \left( 6 \times \frac{1}{2} \right)$ $+ \left( 8 \times \frac{1}{8} \right)$



		<p>atom contributes <math>\frac{1}{2}</math> of the atom to one-unit cell.</p> <p>Further, each atom at the corner is shared by eight more-unit cells and hence, the corner atoms contributes <math>\frac{1}{8}</math><sup>th</sup> of the atom to one-unit cell.</p>	$= 3 + 1$ $= 4 \text{ atom}$
3.	Body Centred Unit Cell ( <i>I</i> )	<p>In face centered unit cell, the center atom belongs entirely to one-unit cell and hence, it contributes one atom to the unit cell.</p> <p>Further, each atom at the corner is shared by eight more-unit cells and hence, the corner atoms contributes <math>\frac{1}{8}</math><sup>th</sup> of the atom to one-unit cell.</p>	$= (1) + \left(8 \times \frac{1}{8}\right)$ $= 1 + 1$ $= 2 \text{ atom}$
4.	End Centered (or) Base Centred Unit Cell ( <i>R</i> )	<p>In end (or) base centered unit cell, each atom at the base is shared by two-unit cells and hence, it contributes <math>\frac{1}{2}</math> of the atom to one-unit cell.</p> <p>Further, each atom at the corner is shared by eight more-unit cells and hence, the corner atoms contributes <math>\frac{1}{8}</math><sup>th</sup> of the atom to one unit cell.</p>	$= \left(2 \times \frac{1}{2}\right)$ $+ \left(8 \times \frac{1}{8}\right)$ $= 1 + 1$ $= 2 \text{ atom}$

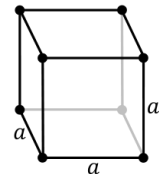
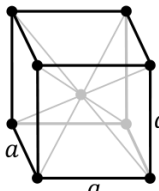
## CRYSTAL SYSTEMS

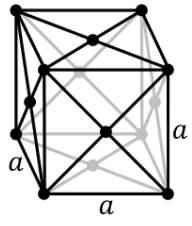
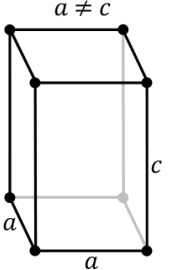
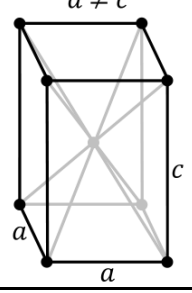
S. No.	Type	Structure Characteristics	Structure of Unit Cell Lattice
1.	Cubic System (or) Regular System Eg: NaCl; ZnS	It has equal intercepts ( $a=b=c$ ) and equal inter axial angles ( $\alpha=\beta=\gamma=90^\circ$ ) at right angle to each other.	
2.	Tetragonal System Eg: TiO <sub>2</sub>	It has two equal intercepts and the third one can be either shorter or longer than the other two ( $a=b \neq c$ ). Also, the three interfacial angles are at equal and right angle to each other ( $\alpha=\beta=\gamma=90^\circ$ ).	

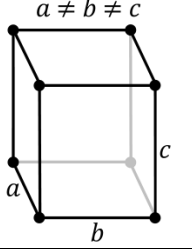
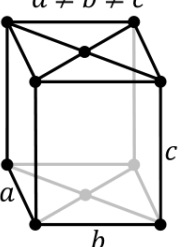
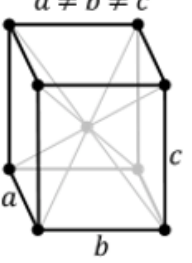
3.	Hexagonal System Eg: Graphite	It has two equal intercepts and the third one either shorter or longer ( $a=b \neq c$ ) and interfacial angles $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$ .	
4.	Orthorhombic System Eg: Rhombic Sulphur	It has intercepts not equal to each other ( $a \neq b \neq c$ ) but the three interfacial angles are at equal and right angle to each other ( $\alpha=\beta=\gamma=90^\circ$ ).	
5.	Monoclinic System Eg: Monoclinic Sulphur	It has intercepts not equal to each other ( $a \neq b \neq c$ ) and interfacial angles $\alpha=\gamma=90^\circ$ and $\beta \neq 90^\circ$ .	
6.	Triclinic System Eg: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	It has unequal intercepts ( $a \neq b \neq c$ ) and interfacial angles $\alpha=\beta=\gamma \neq 90^\circ$ .	
7.	Rhombohedral (Trigonal) System Eg: Calcite, $\text{CaCO}_3$	It has equal intercepts ( $a=b=c$ ) and equal inter axial angles ( $\alpha=\beta=\gamma=90^\circ$ ) but not at right angle.	

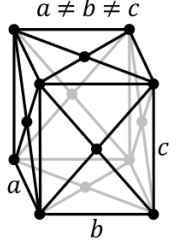
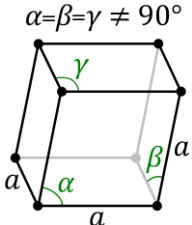
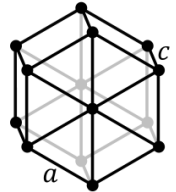
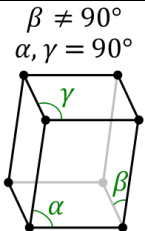
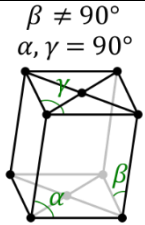
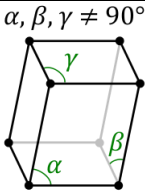
## BRAVAIS LATTICES

For a three-dimensional lattice called the space lattice, six parameters such as  $a$ ,  $b$ ,  $c$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$  are required to define a unit cell. There are fourteen distinguishable 3-dimensional space lattices that can be generated from seven crystal systems with the different types of unit cells.

S. No.	Crystal systems	Unit cell dimension and angles	Bravais Lattices
1.	Simple cubic lattice	It has equal intercepts ( $a=b=c$ ) and equal inter axial angles ( $\alpha=\beta=\gamma=90^\circ$ ) at right angle to each other. It has lattice points at all the eight corners of unit cell.	
2.	Body centered cubic lattice	It has equal intercepts ( $a=b=c$ ) and equal inter axial angles ( $\alpha=\beta=\gamma=90^\circ$ ) at right angle to each other. It has lattice points at all the eight corners and at the body centre.	

3.	Face centered cubic lattice	It has equal intercepts ( $a=b=c$ ) and equal inter axial angles ( $\alpha=\beta=\gamma=90^\circ$ ) at right angle to each other. It has lattice points at all the eight corners and at the six face centres of the unit cell.	
4.	Simple tetragonal lattice	It has two equal intercepts and the third one can be either shorter or longer than the other two ( $a=b\neq c$ ). Also, the three interfacial angles are at equal and right angle to each other ( $\alpha=\beta=\gamma=90^\circ$ ). It has lattice points at all the eight corners of the unit cell.	
5.	Body centered tetragonal lattice	It has two equal intercepts and the third one can be either shorter or longer than the other two ( $a=b\neq c$ ). Also the three interfacial angles are at equal and right angle to each other ( $\alpha=\beta=\gamma=90^\circ$ ). It has lattice points at all the eight corners and at the body centre of the unit cell.	

6.	Simple orthorhombic lattice	It has intercepts not equal to each other ( $a\neq b\neq c$ ) but the three interfacial angles are at equal and right angle to each other ( $\alpha=\beta=\gamma=90^\circ$ ). It has lattice points at all the eight corners of the unit cell.	
7.	End centred orthorhombic lattice	It has intercepts not equal to each other ( $a\neq b\neq c$ ) but the three interfacial angles are at equal and right angle to each other ( $\alpha=\beta=\gamma=90^\circ$ ). It has lattice points at all the eight corners and two at face centres opposite to each other of the unit cell.	
8.	Body centred orthorhombic lattice	It has intercepts not equal to each other ( $a\neq b\neq c$ ) but the three interfacial angles are at equal and right angle to each other ( $\alpha=\beta=\gamma=90^\circ$ ). It has lattice points at all the eight corners and at the body centre of the unit cell.	

9.	Face centred orthorhombic lattice	It has intercepts not equal to each other ( $a \neq b \neq c$ ) but the three interfacial angles are at equal and right angle to each other ( $\alpha = \beta = \gamma = 90^\circ$ ). It has lattice points at all the eight corners and at six face centres of the unit cell.	
10.	Simple rhombohedral (trigonal) lattice	It has equal intercepts ( $a = b = c$ ) and equal inter axial angles ( $\alpha = \beta = \gamma \neq 90^\circ$ ) but not at right angle. It has lattice points at all the eight corners of unit cell.	
11.	Simple hexagonal lattice	It has two equal intercepts and the third one either shorter or longer ( $a = b \neq c$ ) and interfacial angles $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ . It has lattice points at the twelve corners of hexagonal prism and two at the hexagonal face of the unit cell.	
12.	Simple monoclinic lattice	It has intercepts not equal to each other ( $a \neq b \neq c$ ) and interfacial angles $\alpha = \gamma = 90^\circ$ and $\beta \neq 90^\circ$ . It has lattice points at all the eight corners of the unit cell.	
13.	End centred monoclinic lattice	It has intercepts not equal to each other ( $a \neq b \neq c$ ) and interfacial angles $\alpha = \gamma = 90^\circ$ and $\beta \neq 90^\circ$ . It has lattice points at all the eight corners and two at face centres opposite to each other of the unit cell.	
14.	Simple triclinic lattice	It has unequal intercepts ( $a \neq b \neq c$ ) and interfacial angles $\alpha \neq \beta \neq \gamma \neq 90^\circ$ . It has lattice points at all the eight corners of unit cell.	

## MILLER INDICES

Miller Indices are mathematical notation used to represent crystal plane and its direction in the crystal structure.

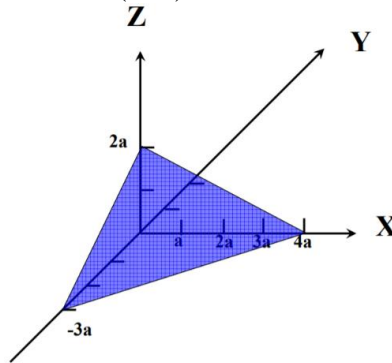
### Rules for Determining Miller Indices

- ✓ Identify the plane intercepts on the x, y, z axes.
- ✓ Rewrite the intercepts in fractional coordinates.

- ✓ Clear the fraction by taking the reciprocals of the fractional intercepts.
- ✓ Negative numbers/directions are denoted with a bar on top of the index (number)

### ***Illustration***

- ✓ Identify Intercepts on the x, y, z axes =  $4a, -3a, 2a$
- ✓ Divide by unit cell length in each direction x, y, z order =  $4, -3, 2$
- ✓ Invert the values =  $1/4, -1/3, 1/2$
- ✓ Multiply by a number (12 in this example) to give smallest whole number set =  $3, -4, 6$
- ✓ Place any minus signs over their index and write the whole number set in parenthesis without using commas, and other notations =  $(\bar{3}46)$

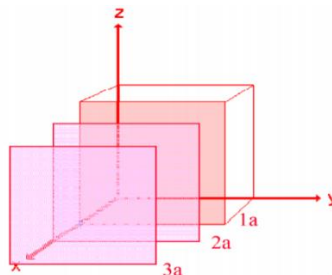


### ***Notation Summary used in Crystal Structure***

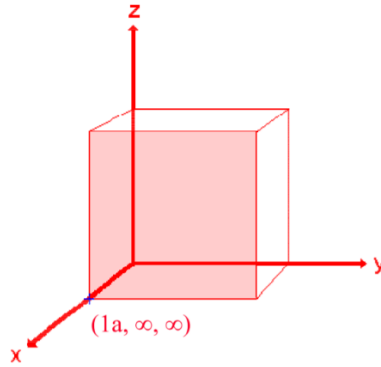
- ✓  $(h, k, l)$  represents a point – note exclusive use of commas for a point
- ✓  $[h\ k\ l]$  represents a direction
- ✓  $(h\ k\ l)$  represents a plane
- ✓  $\{h\ k\ l\}$  represents a family of planes

### ***Miller Indices for Planes: Illustration***

1. Consider the plane in pink, which is one of an infinite number of parallel planes, each one has a consistent distance (“a”) away from the origin.



2. The plane intersects the x-axis at point  $a$ . It runs parallel along y and z axes. Hence, this plane can be designated as  $(1a, \infty, \infty)$ . Miller Indices are the reciprocals of the intercepts of each crystal face. Hence, Miller Indices =  $(1/1, 1/\infty, 1/\infty) = (100)$ .



## Crystalline Planes and Miller Indices: Planes and Directions

Miller indices are mainly categorized into 3-groups They are:

1. One coordinate system (100)
2. Two coordinate system (110)
3. Three coordinate system (111)

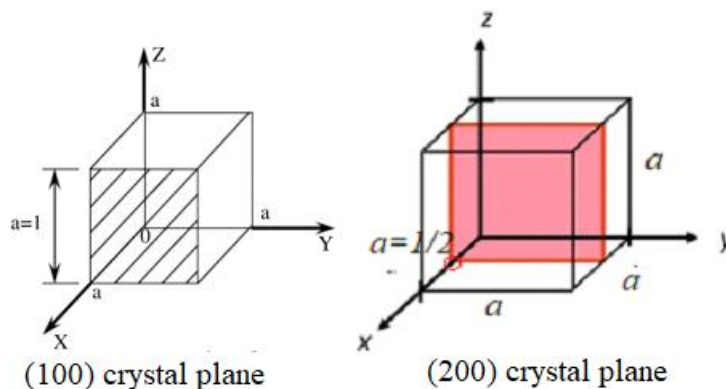
### 1. One Coordinate Systems

In one coordinate system, the plane will create intercept only in one axis, either it may be  $x$  or  $y$  or  $z$ , and the rest of the axes will be parallel.

The (100) will create intercept only on  $x$ -axis and the rest  $y$  and  $z$  will be parallel. In (010) plane, it will create intercept in  $y$ -axis and the rest will be parallel to  $x$  and  $z$ -axes. Similarly, in (001) plane, it will create intercept on  $z$ -axis and the rest will be parallel to  $x$  and  $y$  axes.

There are three more possibilities of planes in negative sides also, and hence a total of six members are there in (100) family. They are:  $\{(100)(010)(001)(\bar{1}00)(0\bar{1}0)(00\bar{1})\}$ .

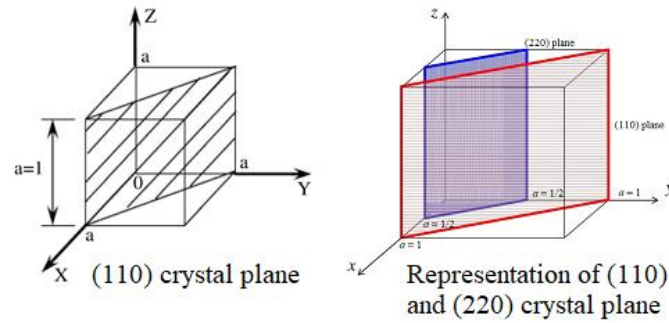
Similarly, the (200) will create intercept on  $x$ -axis as well as on  $y$ -axis, and it will be parallel to  $z$ -axis. The members of (200) family include:  $\{(200)(020)(002)(\bar{2}00)(0\bar{2}0)(00\bar{2})\}$ .



### 2. Two Coordinate Systems

In two coordinate system, the plane (110) will create intercepts on  $x$ -axis as well as on  $y$ -axis and the  $z$ -axis will be parallel to both the axes. The members of (110) family include:  $\{(110)(011)(101)(\bar{1}10)(1\bar{1}0)(10\bar{1})(\bar{1}\bar{1}0)(0\bar{1}\bar{1})(\bar{1}0\bar{1})\}$ .

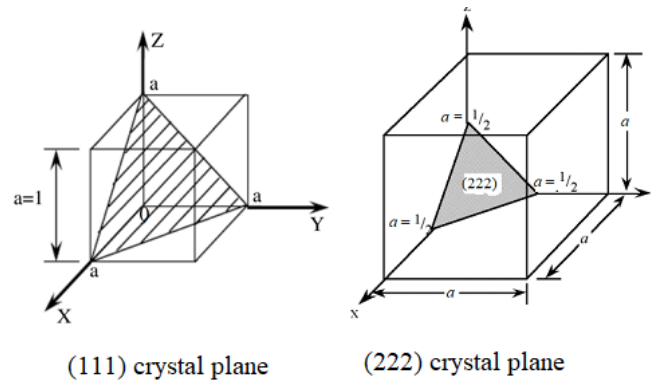
Similarly, it is possible to write the members of family (220) plane also.



### 3. Three Coordinate Systems

In three coordinate system, the plane (111) will create intercepts on all the three axes. The members of (111) family include:  $\{(111)(\bar{1}11)(11\bar{1})(\bar{1}\bar{1}1)(1\bar{1}\bar{1})(\bar{1}1\bar{1})\}$ .

Similarly, it is possible to write the members of family (222) plane also.



### Interplanar Spacing

If we consider the direction of planes, (100) and (200) are same. Similarly (110) and (220); (111) and (222) planes are same.

If we take the interplanar distance between these planes, all these pairs are different and hence, the distance between adjacent planes of Miller indices (hkl) can be determined by:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$

Where  $a = h$  length,  $b = k$  length and  $c = l$  length.

For a cubic crystal, we have:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

**Example 1: What are the Miller indices if the plane intersects the crystal axis (1)  $3a, 2b, c$  (2)  $-a, 1b, \infty$  (3)  $2a, b, 0$  (4)  $a, a, 0$ .**

Q. No.	Intercepts	Reciprocal	Clearing fractions	Miller Indices
1.	3, 2, 1	$\frac{1}{3}, \frac{1}{2}, \frac{1}{1}$	2, 3, 6	(236)
2.	-1, 1, $\infty$	$-\frac{1}{1}, \frac{1}{1}, \frac{1}{\infty}$	-1, 1, 0	$(\bar{1}10)$
3.	2, 1, 0	$\frac{1}{2}, \frac{1}{1}, \frac{1}{0}$	1, 2, 0	(120)
4.	1, 1, 0	$\frac{1}{1}, \frac{1}{1}, \frac{1}{0}$	1, 1, 0	(110)

**Example 2: Determine the Miller indices of a lattice having the coordinates (2,0,0), (0,3,0) and (0,0,1).**

Step 1: Find the intercept of the given lattice: (2,3,1)

Step 2: Take reciprocals:  $\frac{1}{2}, \frac{1}{3}, \frac{1}{1}$

Clear the fractions:  $6 \times \frac{1}{2}, 6 \times \frac{1}{3}, 6 \times \frac{1}{1} = 3, 2, 6$

Miller Indices of the given lattice: (326)

**Example 3: Determine the Miller indices of a plane that makes intercepts of  $4\text{\AA}$ ,  $3\text{\AA}$  and  $8\text{\AA}$  on coordinate axes of an orthorhombic lattice with the ratio of axial lengths  $a:b:c = 2:3:1$ .**

Parameters	x	y	z
Intercepts	$4\text{\AA}$	$3\text{\AA}$	$8\text{\AA}$
Lattice Parameters	2	3	1
Ratio	$\frac{4}{2} = 2$	$\frac{3}{3} = 1$	$\frac{8}{1} = 8$
Reciprocals	$\frac{1}{2}$	$\frac{1}{1}$	$\frac{1}{8}$
Clearing Fractions	$8 \times \frac{1}{2} = 4$	$8 \times \frac{1}{1} = 8$	$8 \times \frac{1}{8} = 1$
Miller Indices	(481)		

**Example 4: Potassium crystallizes in bcc lattice with unit cell length of  $5.34\text{\AA}$ . Calculate the distance of separation between the planes (110), (111), and (220).**

We know that, the interplanar distance for the given cubic unit cell is:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$



(1) For (110) plane:

$$d_{hkl} = \frac{5.34}{\sqrt{1^2 + 1^2 + 0^2}} = 3.77\text{\AA}$$

(2) For (111) plane:

$$d_{hkl} = \frac{5.34}{\sqrt{1^2 + 1^2 + 1^2}} = 3.08\text{\AA}$$

(3) For (110) plane:

$$d_{hkl} = \frac{5.34}{\sqrt{2^2 + 2^2 + 0^2}} = 1.88\text{\AA}$$

**Example 5: Calculate the separation between (123) planes in an orthorhombic lattice. Given  $a = 2\text{\AA}$ ,  $b = 2.5\text{\AA}$  and  $c = 1.8\text{\AA}$ .**

We know that, the interplanar distance for the given orthorhombic unit cell is:

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$$
$$d_{hkl} = \frac{1}{\sqrt{\frac{1^2}{2^2} + \frac{2^2}{2.5^2} + \frac{3^2}{1.8^2}}} = 0.52\text{\AA}$$

## LIMITING RADIUS RATIO

The ionic crystals are formed by strong electrostatic attraction between the anions and cations.

In general, in ionic crystals the cations are much smaller than the anions and hence, the cations always occupy the voids of the anions which tend to come as close to cations as possible.

*In ionic crystals, a stable configuration is formed when the ions are closely packed, such that each ion is surrounded by the other ion of opposite sign as possible, is known as its coordination number.*

Depending on the value of radius ratio, only certain configurations are possible in these crystals.

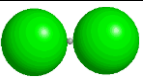
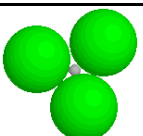
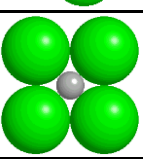
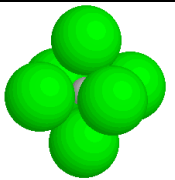
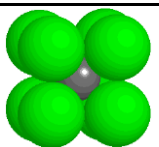
The radius ratio is defined as *the ratio of cations to that of anions*.

$$\text{Limiting Radius Ratio} = \frac{r_c}{r_a}$$

“The effect of radius ratio in determining the coordination number and shape of the ionic crystal is known as radius ratio effect”.

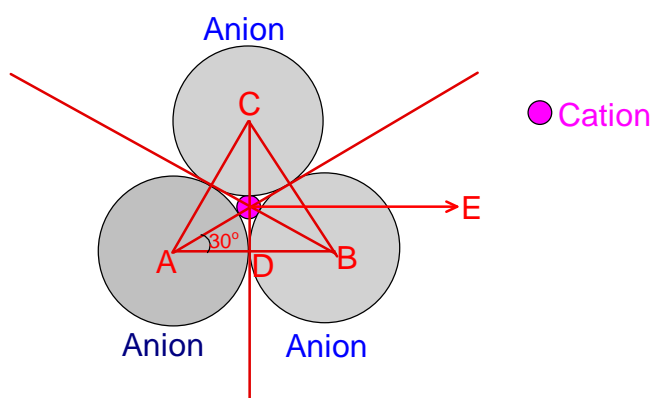
That is, on the basis of limiting radius ratio, we can say about coordination number and shape of the ionic crystal.

The table here summarizes the cation to anion radius ratios,  $r_c/r_a$ , for various coordination numbers and gives the name of the ionic crystal for each coordination number.

$r_c/r_a$	C.N.	Angle	Configuration	Image
$<0.155$	2	$180^\circ$	Linear	
$0.155-0.225$	3	$120^\circ$	Triangular	
$0.225-0.414$	4	$109.47^\circ$	Tetrahedral	
$0.414-0.732$	6	$90^\circ$	Octahedral	
$0.732-1.0$	8	$70.53^\circ$	Cubic	

### LIMITING RADIUS RATIO FOR TRIANGULAR CONFIGURATION

Let us consider three anions bonding with a cation. Here the cation occupies the voids created by three anions in turn creating trigonal structure.



$$\cos \theta = \frac{AD}{AE}$$

$$\cos 30 = \frac{AD}{AE}$$

$$\frac{\sqrt{3}}{2} = \frac{r_a}{r_a + r_c}$$

$$\frac{r_a + r_c}{r_a} = \frac{2}{\sqrt{3}}$$

$$1 + \frac{r_c}{r_a} = \frac{2}{\sqrt{3}}$$

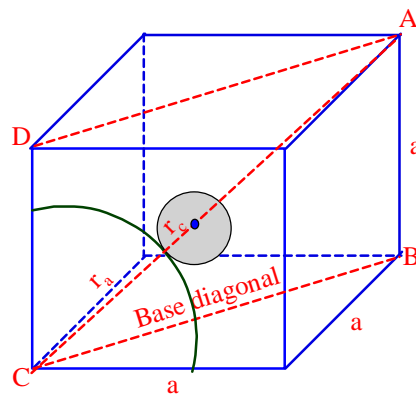
$$\frac{r_c}{r_a} = \frac{2}{\sqrt{3}} - 1 = 0.155$$

Since,  $\sqrt{3} = 1.732$

If the  $r_c/r_a$  ratio for CN = 3 is 0.155, a more stable configuration is possible with three anions bonding with a cation.

## LIMITING RADIUS RATIO FOR TETRAHEDRAL CONFIGURATION

Let us consider four anions bonding with a cation. Here the cation occupies the voids created by four anions in turn creating tetrahedral structure.



If the  $r_c/r_a$  ratio for CN = 4 is 0.225, a more stable configuration is possible with four anions bonding with a cation.

$$\text{Base diagonal, } BC = \sqrt{a^2 + a^2} = \sqrt{2a^2} = \sqrt{2} \ a$$

Since the two anions are touching each other,  $BC = 2r_a$  (where  $r_a$  is the radius of the anion)

$$\sqrt{2} \times a = 2r_a$$

$$a = \frac{2r_a}{\sqrt{2}}$$

$$\text{Body diagonal, } (AC)^2 = (BC)^2 + (AB)^2$$

$$AC = \sqrt{(\sqrt{2})^2 a^2 + a^2} = \sqrt{3} \ a$$

Also body diagonal ,  $AC = 2r_a + 2r_c$  (where  $r_c$  is the radius of the cation)

$$2r_a + 2r_c = \sqrt{3} a$$

$$2r_a + 2r_c = \sqrt{3} \times \frac{2r_a}{\sqrt{2}}$$

Dividing both the sides by  $2r_a$ , we get:

$$1 + \frac{r_c}{r_a} = \frac{\sqrt{3}}{\sqrt{2}}$$

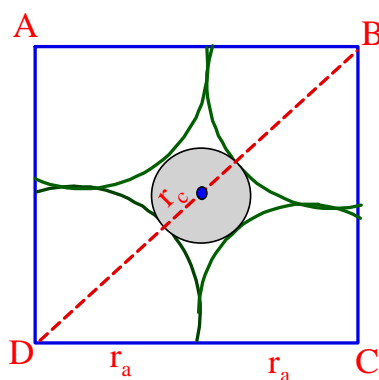
$$\frac{\sqrt{3}}{\sqrt{2}} = \frac{1.732}{1.414} = 1.2248$$

$$\frac{r_c}{r_a} = 1.2248 - 1 = 0.225$$

### LIMITING RADIUS RATIO FOR OCTAHEDRAL CONFIGURATION

In this arrangement four anions are in plane touching each other and two anions are above and below the center of four anions.

If the  $r_c/r_a$  ratio for CN = 6 is 0.414, a more stable configuration is possible with six anions bonding with a cation.



The configuration can also be viewed as six anions occupying the face centres of a cube and the cation occupying the body centre of the cube.

ABCD is a square in which  $CD = BC = 2r_a$  (where  $r_a$  is the radius of the anion).

$$(BD)^2 = (CD)^2 + (BC)^2$$

$$(BD)^2 = (2r_a)^2 + (2r_a)^2 = 8r_a^2$$

$$BD = \left(\sqrt{8r_a^2}\right) = 2\sqrt{2} r_a$$

Moreover  $BD = 2r_a + 2r_c$

$$2r_a + 2r_c = 2\sqrt{2} r_a$$

Dividing both sides by  $2r_a$ , we get:

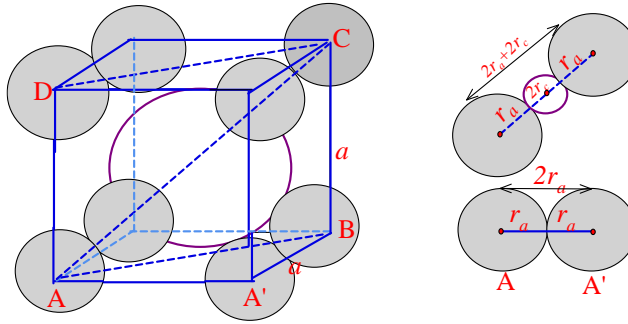
$$1 + \frac{r_c}{r_a} = \sqrt{2}$$

$$\frac{r_c}{r_a} = \sqrt{2} - 1 = 0.414$$

### LIMITING RADIUS RATIO FOR CUBIC CONFIGURATION

This configuration can be viewed as if eight anions are occupying at eight corners of a cube and are touching each other and the cation is occupying the body centre of the cube.

If the  $r_c/r_a$  ratio for CN = 8 is 0.732, a more stable configuration is possible with eight anions bonding with a cation.



Let the length of each side of a cube =  $a$  so the length of the face diagonal:

$$AB = \sqrt{a^2 + a^2}$$

Length of the body diagonal  $AC$  which contains the body center ion has length

$$= \sqrt{2a^2 + a^2} = \sqrt{3} a$$

Let  $r_c$  and  $r_a$  be the radius of cation and anion, respectively.

$$AC = 2r_a + 2r_c = \sqrt{3} a \text{ and } a = 2r_a$$

Divide both side by  $2r_a$

$$\frac{2r_a}{2r_a} + \frac{2r_c}{2r_a} = \sqrt{3} \times \frac{2r_a}{2r_a}$$

$$\frac{r_c}{r_a} = \sqrt{3} - 1 = 1.732 - 1 = 0.732$$

# METHODS OF CHARACTERIZING SOLIDS

## X-RAY DIFFRACTION METHOD

### *Principle*

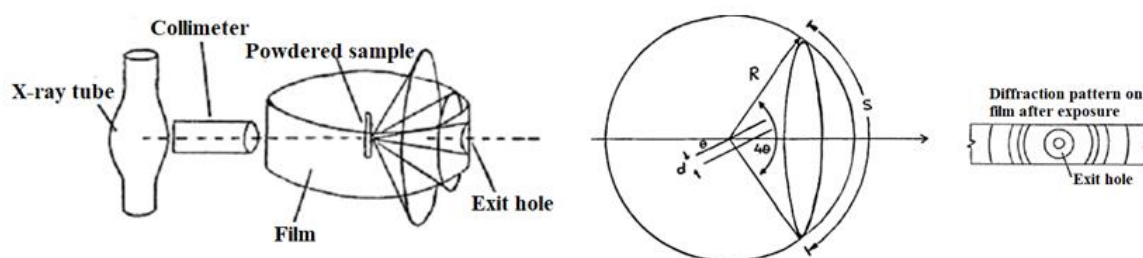
X-rays are shorter wavelength ( $10^{-8}$  cm) electromagnetic radiations with typical photon energies of 100eV–100keV. This wavelength range is comparable to inter-atomic distances and the size of atoms ( $10^{-8}$  cm), X-rays can be used for probing the structural arrangement of atoms and molecules of wide range of materials.

X-rays can be generated by using a device called an X-ray tube. It is an evacuated chamber consisting of tungsten filament as cathode and a metal target (Cu or Mo) as anode. When an electric current is passed through W-filament, it emits electrons. If a high potential is applied between the two electrodes, the electrons are accelerated (10-100eV), move with very high velocity and strike the metal target.

As a result, the core electron from the inner shell (K-shell) is knocked out, which creates an electron hole. Now an electron from the outer shell (L-shell) fills this hole and emits radiations in the form high energy X-rays. An X-ray tube with copper target can produce a strongest characteristic radiation of  $K_{\alpha 1}$  (due to ejection of an electron from 1s K-shell followed by filling the electron hole by 2s electron of L-shell) at a wavelength of about of  $1.54\text{\AA}$ . Similarly, an X-ray tube with molybdenum target can produce a strongest characteristic radiation of  $K_{\alpha 1}$  at a wavelength of about of  $0.71\text{\AA}$ . The X-ray tube can also emit X-ray radiations of  $K_{\alpha 2}$  (filling the electron hole of 1s K-shell by 2p electron of L-shell) and  $K_{\beta}$  (filling the electron hole of 1s K-shell by 3p electron of M-shell).

### *Experimental (Debye-Sherrer Powder Method)*

This method is used for characterizing the crystals with simple structure. By using this method, the interatomic distances with Miller indices and the edge length of a cubic crystal can be determined.



In Debye-Sherrer powder method, the sample in the form of very fine powder is placed in thin glass capillary tube and the sample is mounted at the centre of cylindrical camera known as Debye-Sherrer camera. This camera has hole for the incident X-ray and an opposite hole (exit hole) for the outgoing X-ray.

When a monochromatic X-ray is allowed to fall on the sample, the incident beam undergoes Bragg's reflection. The reflected X-rays will form a cone with Bragg's angle of  $2\theta$ . Each cone generates a pair of arcs on the photographic plate (film) and hence there will be several such pair of arcs and each one is corresponding to one set of (hkl) plane.

The Bragg's angle  $4\theta$  is related to the distances between the two arcs of a pair in a diffraction pattern is given as:

$$4\theta R = S \text{ (or) } 4\theta = \frac{S}{R}$$

Where  $R$  is the distance between sample and the film and  $S$  is the distance between two arcs.

### ***Characterization of Simple Cubic System by using X-ray Diffraction Pattern***

The relation between interplanar distance ( $d$ ) and interatomic distance ( $a$ ) with Miller indices ( $hkl$ ) for a cubic system is given by:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Substituting the value of  $d$  in Bragg's equation ( $n\lambda = 2d\sin\theta$ ), we get:

$$n\lambda = \frac{2a}{\sqrt{h^2 + k^2 + l^2}} \sin\theta$$

$$a = \frac{n\lambda}{2 \sin\theta} \sqrt{h^2 + k^2 + l^2}$$

There are three selection rules used for predicting the diffraction pattern of three types of lattices (SC, BCC, FCC) in a cubic system.

### ***Selection Rules***

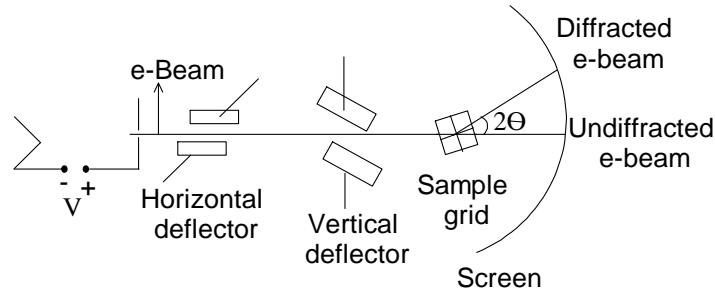
- ✓ If all the planes with  $(h+k+l)$  and  $(h^2+k^2+l^2)$  are odd / even and allow Bragg's reflection, indicate that the structure is of simple cubic / primitive.
- ✓ If the planes with  $(h+k+l)$  and  $(h^2+k^2+l^2)$  are even and allow Bragg's reflection, indicate that the structure is of BCC.
- ✓ If the planes with  $(h+k+l)$  and  $(h^2+k^2+l^2)$  are unmixed and allow Bragg's reflection, indicate that the structure is of FCC.

$(h+k+l)$	$(h^2+k^2+l^2)$	SC	BCC	FCC
1	1	(100)	-	-
2	2	(110)	(110)	-
3	3	(111)	-	(111)
2	4	(200)	(200)	-
3	5	(210)	-	-
4	6	(211)	(211)	-
6	12	(222)	(222)	(222)

# ELECTRON DIFFRACTION TECHNIQUE

## *Principle*

The electron diffraction technique is used for characterizing thin films, metal surfaces, gases etc. In electron diffraction method, electron gun is used to emit electrons. These electrons are accelerated by applying DC potential of 2–100kV between anode and cathode to form electron beam.



The beam will have kinetic energy equivalent to the change in electrical potential as:

$$\frac{1}{2}mv_a^2 = eV$$

Where,  $v_a$  is the final velocity of electrons after being accelerated through a potential  $V$ .

$$v_a^2 = \frac{2eV}{m}$$

$$v_a = \sqrt{\frac{2eV}{m}}$$

According to De-Broglie hypothesis, the wavelength of electron is given by:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

$$\lambda = \frac{h}{m\sqrt{\frac{2eV}{m}}} = \frac{h}{\sqrt{2eVm}}$$

$$\lambda = \frac{1.227}{\sqrt{V}}$$

Since the wavelength of electron is expressed in Å unit, this method can be used in crystallographic analysis for producing diffraction pattern. Electrons carry a negative charge and they can interact strongly with matter, and hence the electron beam is scattered by the nucleus as well as by the electrons in the atoms. As the electrons have mass, they are scattered much more efficiently by atoms than the X-rays.



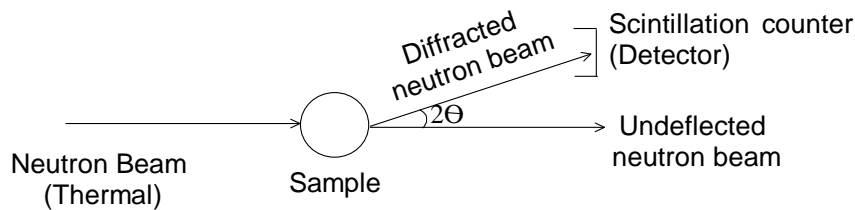
# NEUTRON DIFFRACTION TECHNIQUE

## Principle

Neutrons are generated in atomic fission from uranium. The neutrons have high velocity and can be slowed using the moderator, heavy water ( $D_2O$ ) so that thermal neutrons having a wavelength of about  $1 \text{ \AA}$  ( $100 \text{ pm}$ ) is produced. So, the velocity of these neutrons is not same. However, the root mean square velocity of neutrons is used to find the energy of thermal neutrons. During the interaction between thermal neutron and sample two types of diffraction occurs.

**Nuclear diffraction:** It is due to the interaction between neutrons and atomic nuclei.

**Magnetic diffraction:** It is due to the interaction between magnetic moment of neutrons and magnetic moment of atoms.



The velocity of thermal neutron is given by:

$$\frac{1}{2}mv_a^2 = \frac{3}{2}K_B T$$

$$v_a^2 = \frac{3K_B T}{m}; \quad v_a = \sqrt{\frac{3K_B T}{m}}$$

Where  $K_B$  is the Boltzmann constant and  $T$  is the temperature.

According to De-Broglie equation, the wavelength of neutron is given by:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

$$\lambda = \frac{h}{m\sqrt{\frac{3K_B T}{m}}} = \frac{h}{\sqrt{3K_B T m}}$$

In neutron diffraction method, a sample to be analyzed is placed in a beam of thermal neutrons to obtain a diffraction pattern that provides information of structure of materials. An important aspect of neutrons diffraction is their use in the investigation of magnetic structure of solids. This results from the facts that the neutrons possess magnetic moment. Because of their magnetic moment, the neutrons can interact with magnetic moment of scattering atom of solid. Hence it is useful in the structural studies of magnetic crystals such as anti-ferromagnetic crystals. In non-magnetic materials, the neutrons interact with the nuclei of the constituent atoms.

***Comparison of X-ray diffraction, Electron diffraction and Neutron diffraction***

<b>Diffraction Techniques</b>	<b>X-ray</b>	<b>Neutron</b>	<b>Electron</b>
Nature	Wave	Particle	Particle
Medium	Atmosphere	Atmosphere	High vacuum
Scattering by	Electron density	Nuclei and magnetic spin of electrons	Electrostatic potential
Wavelength range	1 – 10 Å	1 – 1.5 Å	0.02 – 0.05 Å
Wavelength selection	Variable	Variable	Variable
Applications	Crystal structure in simple cases; Phase purity: both qualitative and quantitative; Crystallinity; Unit cell size and shape.	Structural studies of magnetic crystals such as anti-ferromagnetic crystals; to determine ordered magnetic structures.	Structural studies of very thin films, metal surfaces, gases.

**References**

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DEPARTMENT OF CHEMISTRY**

## **UNIT – 4 – Crystal Defects and Non-stoichiometry – SCYA5303**

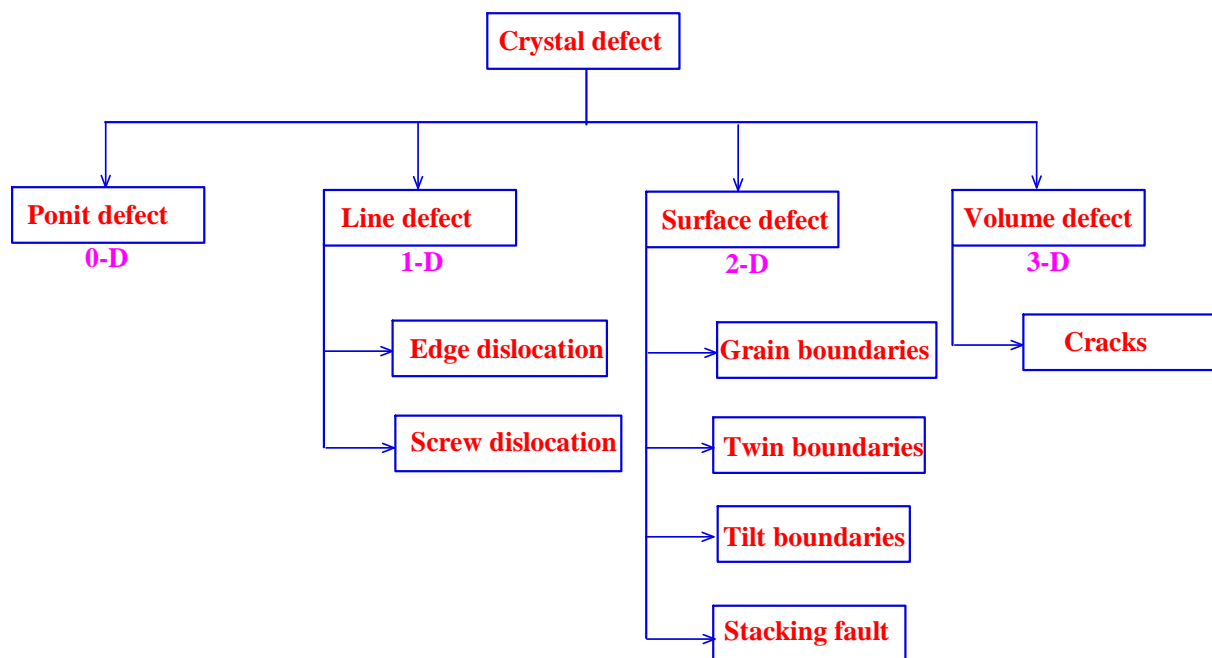
## INTRODUCTION: CRYSTAL DEFECTS

A crystal which has the same unit cell containing the same lattice points throughout the crystal is known as an ideal crystal. Ideal crystals exist only at absolute zero (0K) Temperature. At any temperature above 0 K, the crystals have some departure from complete ordered arrangement.

In actual practice it is very difficult to grow a perfect or an ideal crystal. Usually a solid consists of an aggregate of large number of small crystals. Single crystals are formed when the process of crystallization occurs at an extremely slow rate. Even these crystals are not free of defects.

The defects are irregularities in the arrangement of constituent particles. These irregularities are also called crystal defects.

The imperfection will not only change the properties of the crystals but also give rise to new properties. The defects can be broadly classified as point defects, line defects, surface defects and volume defects [Fig. 4.1].



*Fig. 4.1: Crystal Defects*

## TYPES OF DEFECTS: POINT DEFECTS

Point defects are broadly classified into two categories: 1. Stoichiometric defects 2. Non-stoichiometric defects [Fig. 4.2].

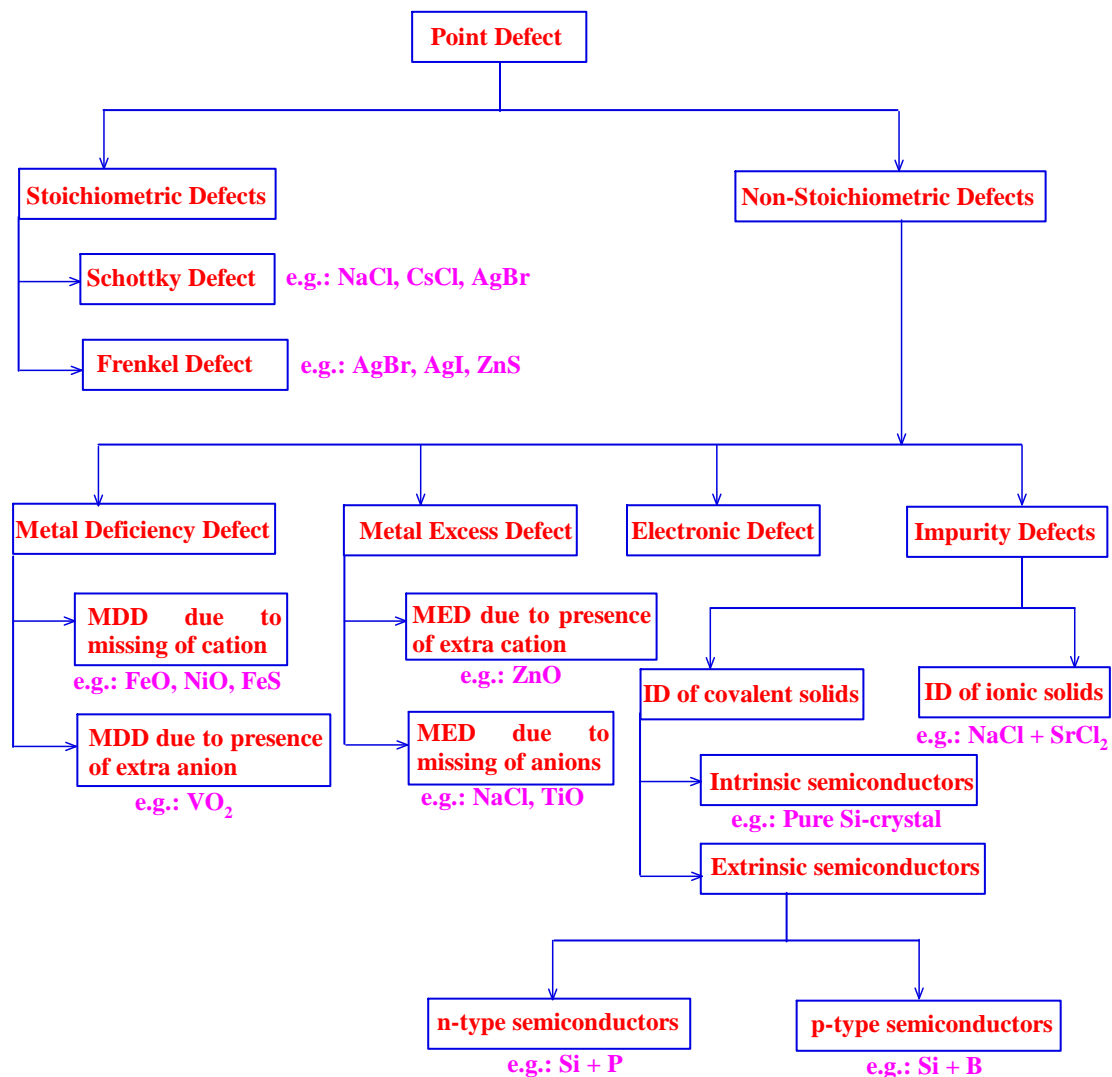
### *1. Stoichiometric Defects*

These are the point defects that do not disturb the stoichiometry of the solid. They are also called intrinsic or thermodynamic defects. Basically, these are of two types, namely, vacancy defects and interstitial defects.

(i) **Vacancy defect:** When some of the lattice sites are vacant, the crystal is said to have vacancy defect. The unoccupied position is called vacancies. This defect results in decrease in density of the substance. This type of defect may also develop when a substance is heated.

(ii) **Interstitial defect:** When some constituent particles (atoms or molecules) occupy interstitial sites (vacant places between the lattice sites), the crystal is said to have interstitial defect. This defect increases the density slightly.

It may be noted that vacancy and interstitial defects are shown by non-ionic solids. Since the ionic solids must always maintain electrical neutrality, they do not show simple vacancy or interstitial defects. However, they show these defects as Frenkel and Schottky defects



**Fig. 4.2: Point Defects**

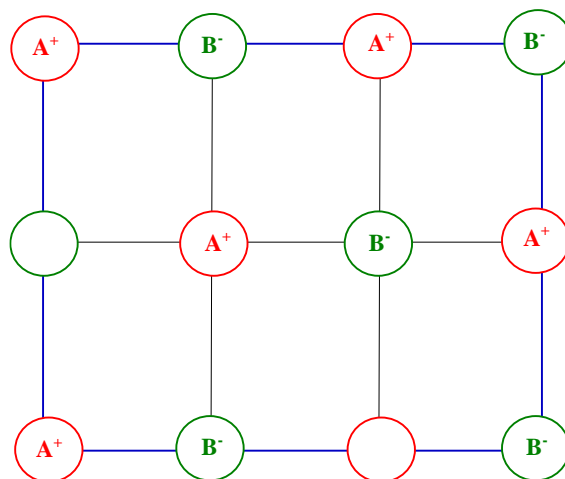
## 2. Nonstoichiometric Defects

The compounds in which the ratio of positive and negative ions present in the compound differs from ideal chemical formula of the compound are called nonstoichiometric compounds. The defects in these compounds are called non-stoichiometric defects.

## SCOTTKY DEFECTS AND FRENKEL DEFECTS

### 1. Schottky Defect or Vacancy Defect

Schottky defect was discovered by German scientist Schottky in 1930. It arises if some of the ions are missing from their normal lattice sites [Fig. 4.3]. This is basically a vacancy defect in ionic solids. The lattice sites which are unoccupied are called lattice vacancies or holes.



**Fig. 4.3: Schottky Defect**

Since the crystal has to remain electrically neutral, equal number of cations and anions are missing.

It is generally shown by ionic solids having high co-ordination number and cations and anions of similar sizes. For example, NaCl, KCl, KBr, CsCl and AgBr which are ionic solids, show Schottky defects.

In this type of defect, equal number of cations and anions are missing from their positions, however, the crystal remains neutral.

In this type of defect, density of crystal decreases.

### 2. Frenkel Defect or Interstitial Defect

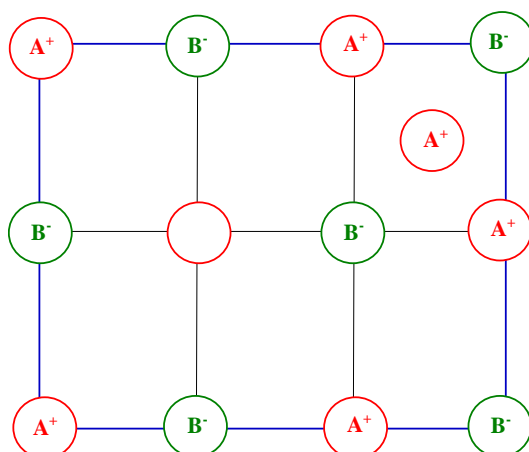
This defect was discovered by a Russian scientist Frenkel in 1926. In this type of defect, a particular ion (specifically cation), because of its small size, moves from its lattice position into interstitial position [Fig. 4.4].

In this type of defect, density of crystal remains constant. Further, the crystal remains electrically neutral because the number of cations and anions remains the same.

Frenkel defect is generally shown when the co-ordination number is low and the size of anion is much larger than the size of cation.

These defects can be in AgCl, AgBr, AgI and ZnS because of the small size of  $\text{Ag}^+$  and  $\text{Zn}^{2+}$  ions. It may be noted that AgBr shows both, Frenkel as well as Schottky defects.

It may be noted that AgBr shows both, Frenkel as well as Schottky defects.



**Fig. 4.4: Frenkel Defect**

**Table 4.1: Comparison Between Schottky and Frenkel Defects**

S No.	Schottky defect	Frenkel defect
1.	It is produced because of missing ions from their normal crystal sites.	It is produced when some ions are displaced from their normal sites and occupy interstitial sites.
2.	The presence of Schottky defect lowers the density of the crystal.	It does not affect the density of the crystal.
3.	It is generally shown by ionic solids having high co-ordination number and cations and anions of similar sizes. Examples: NaCl, CsCl.	It is generally present in ionic solids having low co-ordination number and larger anions than cations. Examples: AgCl, ZnS.

## THERMODYNAMICS OF SCHOTTKY DEFECT FORMATION

The change of an ideal crystal to a defect crystal with vacant lattice sites will be accompanied by a change in free energy at constant volume and temperature is given by:

$$\Delta G = \Delta H - T\Delta S \quad \dots (1)$$

where  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  are the respective changes in free energy, enthalpy and entropy.

Further, neglecting the entropy by the vibration of the atoms, the entropy of the defect structure will be essentially its configurational entropy ( $\Delta S_{conf.} = \Delta S$ ).

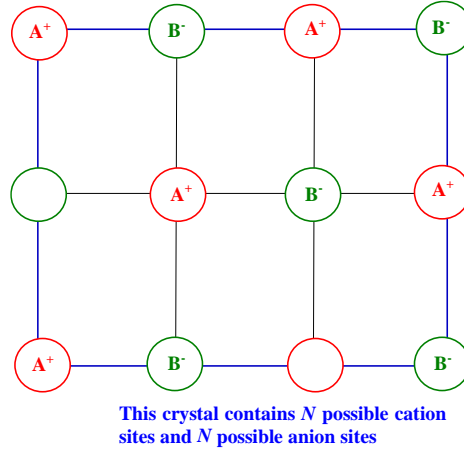
At equilibrium, the overall change in free energy of the crystal due to the defect formation is zero. So, we can write:

$$\left( \frac{\partial(\Delta G)}{\partial n} \right)_{T,V} = 0 \quad \dots (2)$$

Let us calculate the equilibrium concentration of Schottky defects in an ionic crystal of stoichiometry  $AB$ .

Let  $\Delta H_s$  the enthalpy required to form one mole of Schottky defects in the crystal  $AB$ .

This means that this is the energy needed to produce one cation and one anion vacancy in  $AB$  [Fig. 4.5].



**Fig. 4.5: Schottky Defect Formation**

If the number of Schottky defects is  $n_s$  per unit volume at  $T$  K, then there are  $n_s$  cation vacancies and  $n_s$  anion vacancies in a crystal containing  $N$  possible cation sites and  $N$  possible anion sites, then the Boltzmann formula tells us the entropy of such system as:

$$\Delta S = k \ln W \quad \dots (3)$$

where  $W$  is the number of ways of distributing  $n_s$  defects over  $N$  possible sites at random, and  $k$  is the Boltzmann constant ( $1.38 \times 10^{-23}$  J/K).

If the available total cationic site is  $N$  and the number of cation vacancies is  $n_s$ , then the number of occupied cationic sites will be  $(N - n_s)$ .

The number of ways in which  $n_s$  cation vacancies and  $(N - n_s)$  cationic sites can be arranged in  $N$  available cationic sites is:

$$w_c = \frac{N!}{(N - n_s)! n_s!} \quad \dots (4)$$

The number of ways in which  $n_s$  anion vacancies and  $(N - n_s)$  anionic sites can be distributed among in  $N$  available anionic sites is:

$$w_a = \frac{N!}{(N - n_s)! n_s!} \quad \dots (5)$$

The total number of ways of distributing these defects,  $W$ , is:

$$W = w_c \times w_a \quad \dots (6)$$



Therefore, the change in entropy due to introducing defects into a perfect crystal:

$$\Delta S = k \ln W = k \ln \left( \frac{N!}{(N - n_s)! n_s!} \right)^2 = 2k \ln \left( \frac{N!}{(N - n_s)! n_s!} \right)$$

$$\Delta S = 2k \ln \left( \frac{N!}{(N - n_s)! n_s!} \right) \dots (7)$$

Applying Stirling's approximation, we have:

$$\Delta S = 2k[N \ln N - (N - n_s) \ln (N - n_s) - n_s \ln n_s]$$

If the enthalpy change for the formation of a single defect is  $\Delta H$ , and assume that the enthalpy change for the formation of  $n_s$  defects is  $n_s \Delta H$ , then the Gibbs free energy change is given by:

$$\Delta G = n_s \Delta H_s - 2kT[N \ln N - (N - n_s) \ln (N - n_s) - n_s \ln n_s]$$

At equilibrium, Gibbs free energy of the system must be a minimum with respect to changes in the number of defects  $\left(\frac{d\Delta G}{dn_s}\right)$ , and hence we have:

$$\Delta H_s - 2kT[N \ln N - (N - n_s) \ln (N - n_s) - n_s \ln n_s] = 0 \dots (8)$$

Since,  $N \ln N$  is considered as a constant term, so its differential becomes zero. So, the differentiation of  $d(N \ln N)$  is 0 and  $d(N \ln N)$  is  $(\ln N + 1)$ .

So, by differentiating equation (8) with respect to  $n_s$ , then we have:

$$\Delta H_s - 2kT[-\{[\ln (N - n_s) + 1](-1)\} - (\ln n_s + 1)] = 0$$

$$\Delta H_s - 2kT[\ln (N - n_s) - \ln n_s] = 0$$

$$\Delta H_s = 2kT \left[ \ln \left( \frac{(N - n_s)}{n_s} \right) \right]$$

$$\frac{\Delta H_s}{2kT} = \left[ \ln \left( \frac{(N - n_s)}{n_s} \right) \right] \dots (9)$$

Taking exponentials on both the sides, we get:

$$\exp \left( \frac{\Delta H_s}{2kT} \right) = \frac{(N - n_s)}{n_s}$$

$$n_s = (N - n_s) \exp \left( \frac{-\Delta H_s}{2kT} \right) \dots (10)$$

Since  $N \gg n_s$ , approximately  $N - n_s$  can be taken as  $N$ .

$$n_s \approx N \exp\left(\frac{-\Delta H_s}{2kT}\right) \quad \dots (11)$$

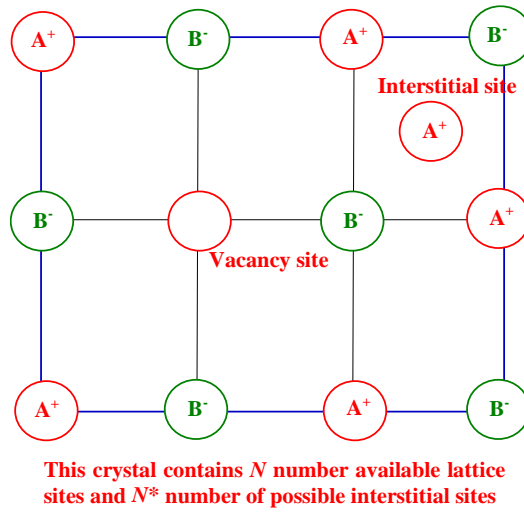
In molar quantities,

$$\frac{n_s}{N} \approx \exp\left(\frac{-\Delta H_s}{2RT}\right) \quad \dots (12)$$

$\Delta H_s$  is the enthalpy required to form one mole of Schottky defects.

## THERMODYNAMICS OF FRENKEL DEFECT FORMATION

A crystal with Frenkel defects will have equal number of vacancies and interstitials [Fig. 4.6].



**Fig. 4.6: Frenkel Defect Formation**

Let the number of Frenkel defects be  $n_f$ .

If  $N$  is the total number of available lattice sites, then there will be  $(N - n_f)$  occupied sites.

The number of ways in which  $n_f$  vacancies and  $(N - n_f)$  occupied sites can be distributed among in  $N$  available lattice sites gives the probability as:

$$w = \frac{N!}{(N - n_f)! n_f!}$$

Let the total number of interstitial sites be  $N^*$ .

The number of ways in which  $n_f$  interstitial atoms and  $(N^* - n_f)$  unoccupied interstitial sites can arrange gives the probability as:

$$w^* = \frac{N^*!}{(N^* - n_f)! n_f!}$$

In this case, total configurational probability  $W = w \times w^*$ .

$$\Delta S = k \left[ \ln \frac{N!}{(N - n_f)! n_f!} + \ln \frac{N^*!}{(N^* - n_f)! n_f!} \right]$$

Applying Stirling's approximation, we have:

$$\Delta S = k \left\{ [N \ln N - (N - n_f) \ln (N - n_f) - n_f \ln n_f] + [N^* \ln N^* - (N^* - n_f) \ln (N^* - n_f) - n_f \ln n_f] \right\}$$

If the enthalpy change for the formation of a single defect is  $\Delta H$ , and assume that the enthalpy change for the formation of  $n_f$  defects is  $n_f \Delta H$ , then the Gibbs free energy change is given by:

$$\Delta G = n_f \Delta H_f - kT \left\{ [N \ln N - (N - n_f) \ln (N - n_f) - n_f \ln n_f] + [N^* \ln N^* - (N^* - n_f) \ln (N^* - n_f) - n_f \ln n_f] \right\}$$

At equilibrium, Gibbs free energy of the system must be a minimum with respect to changes in the number of defects  $\left(\frac{d\Delta G}{dn_f}\right)$ , and hence we have:

$$n_f \Delta H_f - kT \left\{ [N \ln N - (N - n_f) \ln (N - n_f) - n_f \ln n_f] + [N^* \ln N^* - (N^* - n_f) \ln (N^* - n_f) - n_f \ln n_f] \right\} = 0$$

Since,  $N \ln N$  and  $N^* \ln N^*$  are constants, so their differential become zero. Differentiation of:  $\ln x$  is  $1/x$  and  $x \ln x$  is  $(1 + \ln x)$ , the we have:

$$\Delta H_f - kT \left[ -\{[\ln (N - n_f) + 1](-1)\} - (\ln n_f + 1) \right] - kT \left[ -\{[\ln (N^* - n_f) + 1](-1)\} - (\ln n_f + 1) \right] = 0$$

$$\Delta H_s - kT [\ln (N - n_f) - \ln n_f] - kT [\ln (N^* - n_f) - \ln n_f] = 0$$

$$\Delta H_f = kT \left[ \ln \left( \frac{(N - n_f)}{n_f} \right) \right] + kT \left[ \ln \left( \frac{(N^* - n_f)}{n_f} \right) \right]$$

$$\frac{\Delta H_f}{kT} = \left[ \ln \left( \frac{(N - n_f)}{n_f} \right) + \ln \left( \frac{(N^* - n_f)}{n_f} \right) \right]$$

$$\frac{\Delta H_s}{kT} = \ln \left[ \frac{(N - n_f)(N^* - n_f)}{n_f^2} \right]$$

Taking exponentials on both the sides, we get:

$$\exp \left( \frac{\Delta H_f}{kT} \right) = \left[ \frac{(N - n_f)(N^* - n_f)}{n_f^2} \right]$$

$$n_f^2 = \left[ \frac{(N - n_f)(N^* - n_f)}{\exp\left(\frac{\Delta H_f}{kT}\right)} \right]$$

$$n_f^2 = NN^* \exp\left(\frac{-\Delta H_f}{kT}\right)$$

$$n_f = \frac{1}{2} \sqrt{NN^*} \exp\left(\frac{-\Delta H_f}{kT}\right)$$

where  $\Delta H_f$  is the energy needed to form a mole of Frenkel defects.

## VACANCIES AND INTERSTITIALS IN NON-STOICHIOMETRIC CRYSTALS

The compounds in which the ratio of positive and negative ions present in the compound differs from ideal chemical formula of the compound are called nonstoichiometric compounds. The defects in these compounds are called non-stoichiometric defects. However, in these crystals, the electrical neutrality of the crystal is maintained.

Non-Stoichiometric behaviour is the most commonly found for transition metal compounds. It is also found for some lanthanides and actinides.

There are of two types non-stoichiometric crystals depending upon whether positive ions are in excess or negative ions are in excess. These are also known as metal excess defects and metal deficiency defects, respectively.

### EXTRINSIC DEFECTS: METAL EXCESS DEFECTS

In these defects, the positive ions are in excess. These may arise due to the following two ways:

1. Anionic vacancies
2. Excess cations occupying interstitial sites

#### *1. Anionic Vacancies*

In this case, negative ions may be missing from their lattice sites leaving holes in which the electrons remain entrapped to maintain the electrical neutrality [Fig. 4.7].

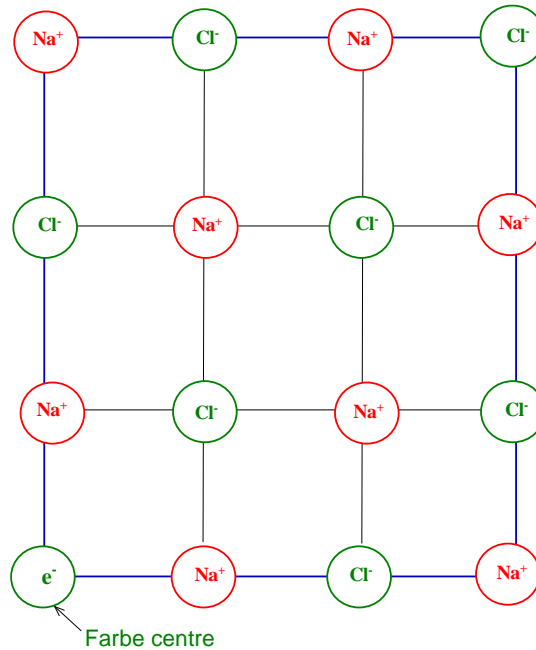
Consequently, there is an excess of positive (metal) ions all though the crystal as a whole is electrically neutral. This type of defect is observed in those crystals which are likely to form Schottky defects.

*Example:* When NaCl crystal is heated in the presence of Na-vapours, then excess of Na-ions are deposited around the crystal.

Due to the force of attraction of sodium ion, some of the  $\text{Cl}^-$  ions come out of the lattice and thereby leaving a vacancy is called anionic vacancy. This anionic vacancy is occupied by the electron liberated from Na-atom ( $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$ )

The electron trapped in anionic vacancy is called Farbe Centre (F Centre). Farbe (German word) = Colour. When such solids containing Farbe centres are irradiated with light, then electrons are excited and crystal becomes photoconducting.

Since, the conductivity is due to electron, this is n-type semiconductor.



**Fig. 4.7: Metal Excess Defect: Anionic Vacancies**

Solids containing Farbe centres are paramagnetic in nature since electrons in Farbe centres are unpaired.

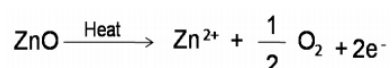
In the case of defected NaCl, the colour is yellow. Similarly, Potassium in KCl makes the crystal appear violet, while the excess of lithium ion in LiCl makes the crystal appear pink.

## 2. Excess Cations Occupying Interstitial Sites

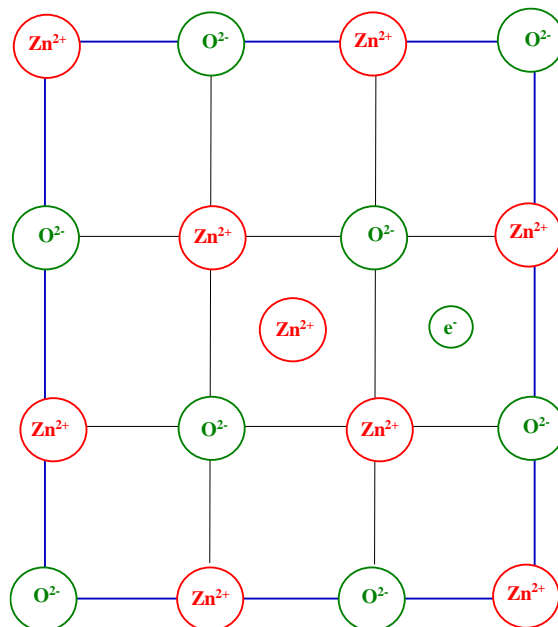
In this case, there are extra positive ions occupying interstitial sites to maintain electrical neutrality [Fig. 4.8].

The defect may be visualized as the loss of metal atoms which leave their electrons behind. The excess metal ions occupy interstitial positions. This type of defect is found in crystals which are likely to develop Frenkel defect.

*Example:* The common example is zinc oxide ( $\text{ZnO}$ ) which is white in colour at room temperature. On heating, it loses oxygen reversibly at high temperature and turns yellow in colour.



The excess  $\text{Zn}^{2+}$  ions are trapped in interstitial sites and equal numbers of electrons are trapped in the neighbouring interstitial sites to balance the electrical charge. This electron give rise to enhanced electrical conductivity.



**Fig. 4.8: Metal Excess Defect: Excess Cations Occupying Interstitial Sites**

### ***Consequences of Metal Excess Defects***

- ✓ The crystals with metal excess defect conduct electricity due to presence of free electrons. However, the conductivity is very low because the number of free electrons is very small.
- ✓ Because of low conductivity as compared to conductivity of metals, these are called semiconductors. These compounds are also called n-type semiconductors.
- ✓ The crystals with metal excess defects are generally coloured. For e.g. non-stoichiometric sodium chloride is yellow, non-stoichiometric potassium chloride is violet.

## **EXTRINSIC DEFECTS: METAL DEFICIENCY DEFECTS**

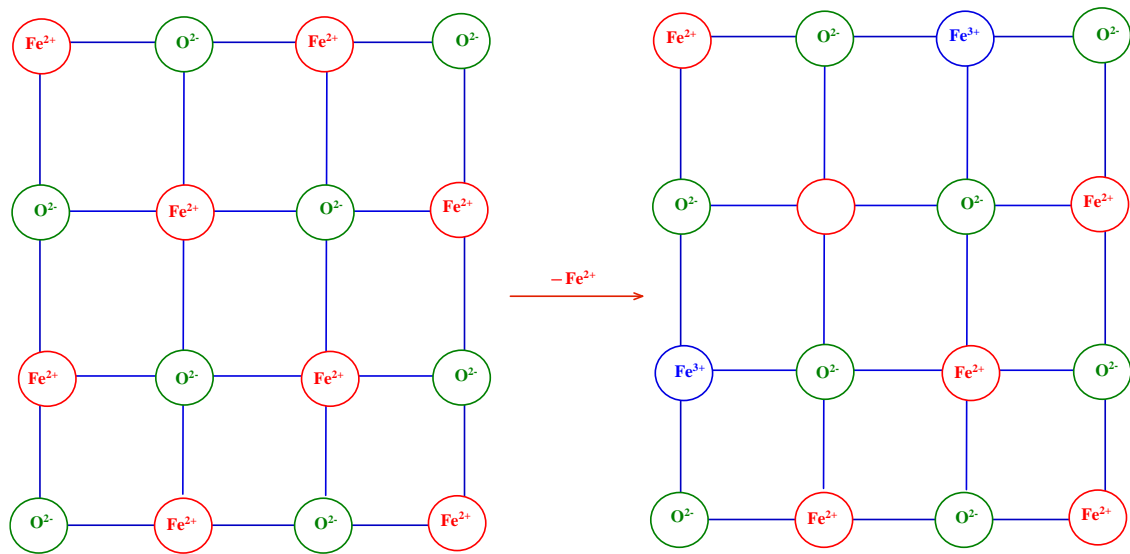
These defects occur when the crystal contains lesser number of positive ions than negative ions. These defects can arise due to the following two reasons:

1. Cation vacancies
2. Excess anions occupying interstitial sites

### ***1. Cation Vacancies***

In this case, the positive ions may be missing from their lattice sites [Fig. 4.9]. The extra negative charge may be balanced by some nearby metal ion acquiring two positive charges instead of one.

This type of defect is possible in metals which show variable oxidation state. The common example of compounds having this defect are ferrous oxide, ferrous sulphide and nickel oxide.



**Fig. 4.9: Metal Deficiency Defect: Cationic Vacancies**

In the case of iron pyrites ( $\text{FeS}$ ), two out of three ferrous ions in a lattice may be converted into  $\text{Fe}^{3+}$  state and the third  $\text{Fe}^{2+}$  ion may be missing from its lattice site. Therefore, the crystal contains  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions. This gives rise to exchange of electrons from one  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  ion in which  $\text{Fe}^{2+}$  changes to  $\text{Fe}^{3+}$  and  $\text{Fe}^{3+}$  changes to  $\text{Fe}^{2+}$  ion.

As a result, the crystal has metallic lustre. Because of the natural colour of iron pyrites and metallic lustre, some samples of minerals shine like gold and have been nick-named as fool's gold.

Similarly,  $\text{FeO}$  is mostly found with a composition of  $\text{Fe}_{0.95}\text{O}$ . It may actually range from  $\text{Fe}_{0.93}\text{O}$  to  $\text{Fe}_{0.96}\text{O}$ . In crystals of  $\text{FeO}$ , some  $\text{Fe}^{2+}$  are missing and the loss of positive charge is compensated by the presence of required number of  $\text{Fe}^{3+}$  ions. Moreover, since there is exchange of electrons, the substances become conductors.

## 2. Excess Anions Occupying Interstitial Sites

In this case, there are extra anions occupying interstitial sites to maintain electrical neutrality [Fig. 4.10]. The defect may be visualized as the excess oxide ions (produced by the oxidation of metal oxide) occupy interstitial positions. This type of defect is found in crystals which are likely to develop Frenkel defect.

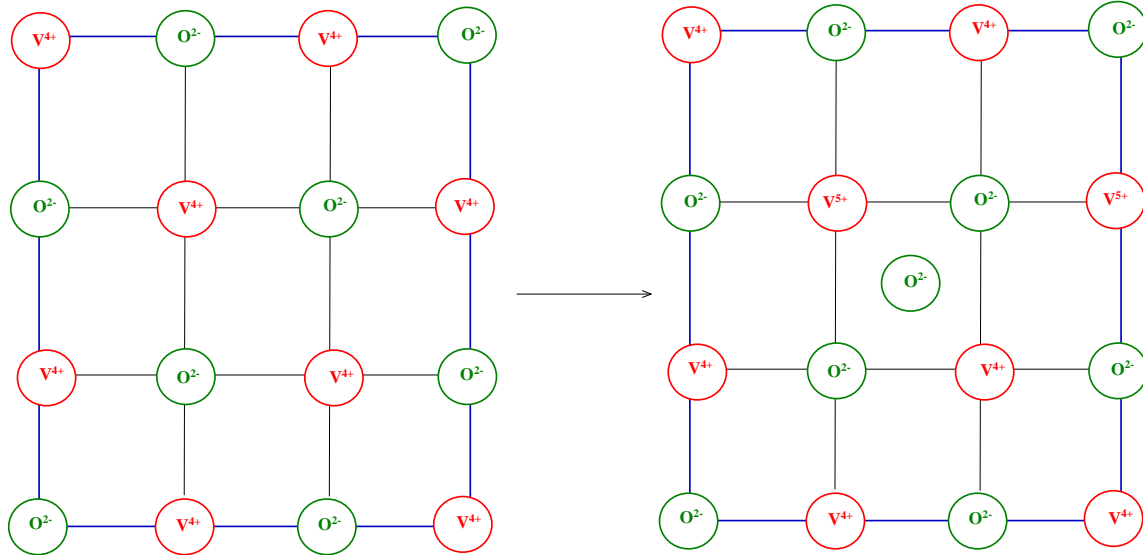
This type of defect is not found in practice as it is difficult to accommodate large anions into the interstitial positions.

*Example:* The common example is vanadium oxide ( $\text{VO}_2$ ).

In this case, the charge is balanced by increase in oxidation state of nearby cation ( $\text{V}^{4+}$  to  $\text{V}^{5+}$ ). Due to its self-oxidation, it produces an extra oxide anion. This excess  $\text{O}^{2-}$  ion is trapped in

interstitial sites and equal numbers of negative charges are balanced by the oxidation of  $V^{4+}$  to  $V^{5+}$  state.

Further, the migration  $V^{5+}$  ions in the crystal lattice with respect to the interstitial oxide ion makes the substance p-type semiconductor and gives rise to enhanced electrical conductivity.



**Fig. 4.10: Metal Deficiency Defect: Excess Anions Occupying Interstitial Sites**

### ***Consequences of Metal Deficiency Defects***

We have seen that in metal deficiency defects, one of the cation  $A^+$  is changed into  $A^{2+}$  cation. This type of conversion takes place through the movement of an electron from  $A^+$  to  $A^{2+}$ . Such type of movement of positive hole and makes the crystal showing metal deficiency defects behaves semiconductors.

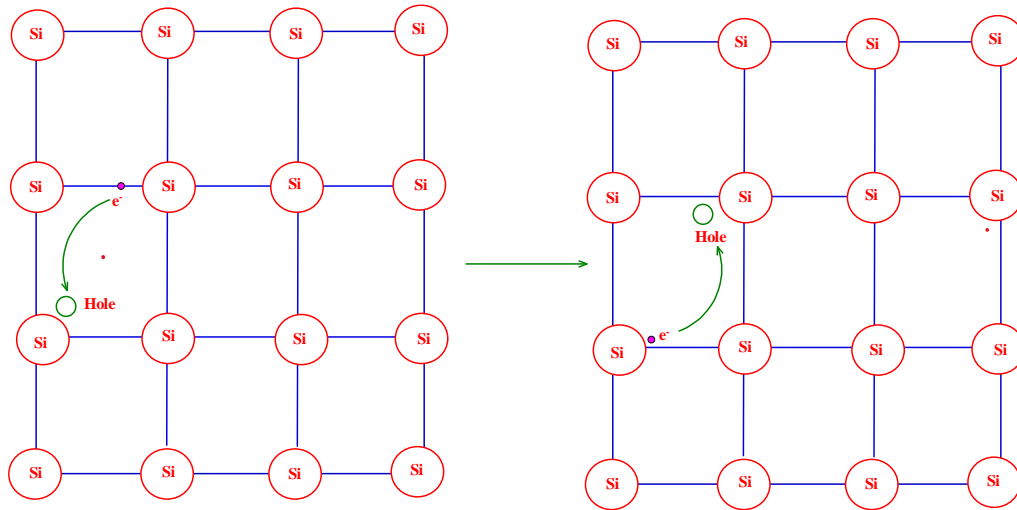
1. Intrinsic Defects: Electronic Defects
2. Extrinsic Defects: Impurity Defects in Ionic Solids

## **INTRINSIC DEFECTS: ELECTRONIC DEFECTS**

Pure silicon crystal has bonding electrons but as temperature increases, some of bonding electrons are excited and thereby creating a hole.

The adjacent electron moves into this hole and the hole moves in a direction opposite to that of the electron, and hence the hole-electron motion causes electronic imperfections [Fig. 4.11].





**Fig. 4.11: Intrinsic Defects: Electronic Defects**

## EXTRINSIC DEFECTS: IMPURITY DEFECTS (*n*-TYPE AND *p*-TYPE SEMICONDUCTORS)

Some atoms of pure crystals displaced by the atoms of either a greater number of valence electrons (example: *As*) or a smaller number of valence electrons (example: *Ga*) than that of silicon. Crystal remains neutral and density also remains the same.

Based on the impurity added, we have two types of extrinsic semiconductors:

*i) n-type semiconductors:* Silicon semiconductor doped with  $V^{\text{th}}$  group elements (pentavalent impurities) like *As*, *Sb*, *P* is known as *n*-type semiconductors.

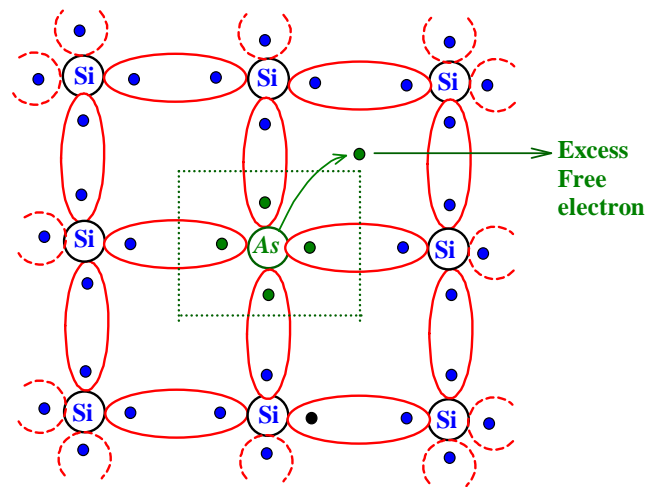
The process of adding impure metal atom directly into a pure semiconductor is known as doping and the added impure metal atom is known as dopant.

The arsenic metal atom is an example of pentavalent impurity. When an arsenic atom is added into a silicon crystal, it replaces one of the silicon atoms and thereby forming four covalent bonds with nearby four silicon atoms [Fig. 4.11]. Further, the fifth electron of arsenic atom remains totally free and can move independently in the crystal lattice in turn can act as charge carrier when subjected to an electric field and is responsible for maximum conductance of semiconductor.

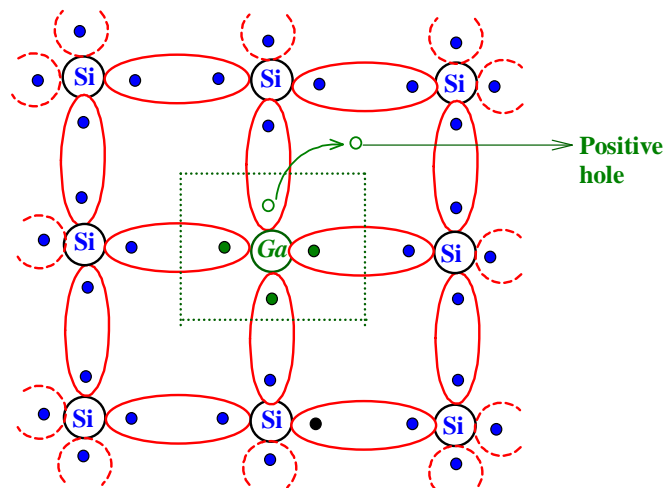
*ii) p-type semiconductors:* Silicon semiconductor doped with  $\text{III}^{\text{rd}}$  group elements (trivalent impurities) like *Ga*, *Al*, *B* is known as *p*-type semiconductors. The gallium metal atom is an example of trivalent impurity.

When a gallium atom is added into a silicon crystal, it replaces one of the silicon atoms and thereby forming three covalent bonds with nearby three silicon atoms. Since gallium is an electron deficient atom, it creates a positive hole with respect to the fourth silicon atom in the crystal lattice [Fig. 4.12].

Further, this positive hole of gallium atom can move independently in the crystal lattice in turn can act as charge carrier when subjected to an electric field and is responsible for maximum conductance of semiconductor.



*Fig. 4.11: Extrinsic Defects: n-Type Semiconductor*

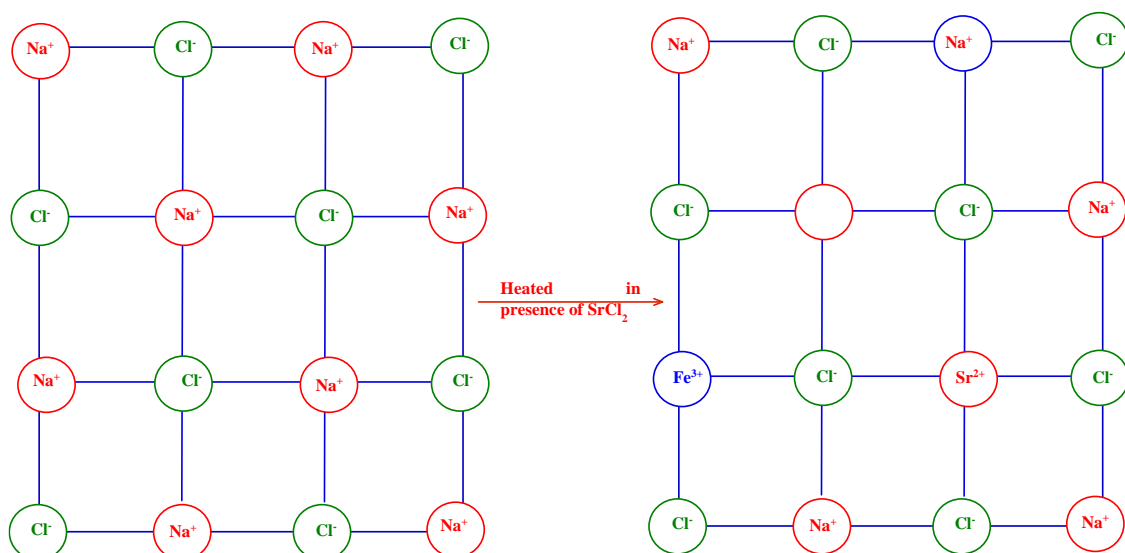


*Fig. 4.12: Extrinsic Defects: p-Type Semiconductor*

## EXTRINSIC DEFECTS: IMPURITY DEFECTS IN IONIC SOLIDS

Impurity defects is an extrinsic defect which occurs when a foreign particle (atom or ion) is introduced in the crystal lattice.

The impurity particle can occupy the interstitials of the crystal lattice. If molten NaCl containing a little amount of  $\text{SrCl}_2$  is crystallised, some of the sites of  $\text{Na}^+$  ions are occupied by  $\text{Sr}^{2+}$  [Fig. 4.13].



**Fig. 4.13: Extrinsic Defects: Impurity Defects in Ionic Solids**

Each  $\text{Sr}^{2+}$  replaces two  $\text{Na}^+$  ions to maintain electrical neutrality. It occupies the site of one  $\text{Na}^+$  ion and the other site remains vacant. The cationic vacancies thus produced are equal in number to the number of  $\text{Sr}^{2+}$  ions.

Another example is the solid solution of  $\text{CdCl}_2$  and  $\text{AgCl}$ . At absolute zero temperature, all the crystals have systematic arrangement of constituent particles, but as the temperature rises above zero Kelvin, some deviation from systematic arrangement takes place.

## SOLID ELECTROLYTES: FAST-ION CONDUCTORS

### INTRODUCTION TO FAST ION CONDUCTORS

#### 1. Ionic Conductivity

In most ionic solids, ions are trapped on their lattice sites. They vibrate continuously at infrared frequencies but rarely have enough thermal energy to escape from their lattice sites. If they are able to escape and move into adjacent lattice sites, we have the makings of ionic conduction, also referred to as ionic migration, hopping or diffusion.

Ionic conduction is easier at higher temperatures and especially if crystal defects are involved.

In defect-free solids, there are no atom vacancies and interstitial sites are completely empty.

For ionic conduction to occur, a minimum requirement is that either some sites are vacant and adjacent ions can hop into the vacancies, leaving their own sites vacant, or there are some ions in interstitial sites which can hop into adjacent interstitial sites.

At higher temperatures, ions have greater thermal energy and vibrate more vigorously; also, defect concentrations are higher.

For example, the conductivity of  $\text{NaCl}$  at  $\sim 800^\circ\text{C}$ , just below its melting point, is  $\sim 10^{-3} \text{ S cm}^{-1}$ , whereas at room temperature, pure  $\text{NaCl}$  is an insulator with a conductivity much less than  $10^{-12} \text{ S cm}^{-1}$ .

In contrast to most ionic solids, there exists a small group of solids called solid electrolytes, fast ion conductors and superionic conductors, in which one set of ions can move quite easily.

Such materials often have special crystal structures with open tunnels or layers through which the mobile ions may move.

The conductivity values, e.g.  $10^{-3} \text{ S cm}^{-1}$  for  $\text{Na}^+$  ion migration in  $\beta$ -alumina at  $25^\circ\text{C}$ , are comparable to those observed in strong liquid electrolytes.

**Table 4.2: Properties of Metals and Solid Electrolytes**

S. No.	Properties	Metals	Solid Electrolytes
1.	Conductivity range	$10 - 10^5 \text{ S/cm}$	$10^{-3} - 10 \text{ S/cm}$
2.	Charge carriers	Electrons	Ions
3.	Temperature effect	Conductivity increases linearly as the temperature decreases	Conductivity decreases exponentially as the temperature decreases

**Table 4.3: Ionic Conductivity versus Electronic Conductivity**

S. No.	Conductor	Material	Electrical Conductivity, S/m
1.	Ionic	Ionic crystals	$<10^{-16} - 10^{-2}$
		Solid electrolytes	$10^{-1} - 10^3$
		Strong (liquid) electrolytes	$10^{-1} - 10^3$
2.	Electronic	Metals	$10^3 - 10^7$
		Semiconductors	$10^{-3} - 10^4$
		Insulators	$<10^{-10}$

## 2. General Characteristics of Solid Electrolytes

1. These have a rigid framework structure within which one set of ions forms a mobile sublattice.
2. Conductivities as high as  $1 \text{ S cm}^{-1}$ , similar to those of strong liquid electrolytes, occur.
3. Solid electrolytes are intermediate between typical ionic solids, in which all ions are fixed on their lattice sites, and liquid electrolytes, in which all ions are mobile.
4. The structural requirements for high ionic conductivity are (i) there must be available empty sites for ions to hop into and (ii) the energy barrier for ions to hop between sites is small ( $\sim 0.1 - 0.9 \text{ eV}$ ).
5. High levels of ionic conduction are rare but modest amounts are common, especially in non-stoichiometric or doped materials.

## TYPES OF FAST ION CONDUCTORS

### 1. Silver Ion Conductors

#### (i) *AgI Fast Ion Conductors*

*AgI* undergoes a phase transition at 146°C and the high-temperature form,  $\alpha$ -*AgI*, has exceptionally high conductivity,  $\sim 1 \text{ S cm}^{-1}$ , which is four orders of magnitude larger than that of  $\beta$ -*AgI* at room temperature. The activation energy for conduction in  $\alpha$ -*AgI* is only 0.05 eV and its structure is so suited for easy motion of  $\text{Ag}^+$  that the ionic conductivity actually decreases slightly on melting at 555°C.

#### (ii) *RbAg<sub>4</sub>I<sub>5</sub> Fast Ion Conductors*

In order to stabilize the highly conducting  $\alpha$ -*AgI* phase at lower temperatures, various anionic and cationic substitutions were tried.

The most successful involves partial replacement of Ag by Rb in  $\text{RbAg}_4\text{I}_5$ , which has the highest ionic conductivity at room temperature of any known crystalline substance,  $0.25 \text{ S cm}^{-1}$ . Its activation energy for conduction is 0.07 eV. The amount of electronic conductivity in  $\text{RbAg}_4\text{I}_5$  is negligibly small,  $\sim 10^{-9} \text{ S cm}^{-1}$  at 25°C.

### 2. Sodium Ion Conductors

#### (i) *Sodium $\beta$ -alumina ( $\text{NaAl}_{11}\text{O}_{17}$ ) Fast Ion Conductors*

$\beta$ -alumina is a series of compounds that exhibit fast ion conducting properties.

Parent compound is sodium  $\beta$ -alumina,  $\text{NaAl}_{11}\text{O}_{17}$ . General formula is  $\text{M}_2\text{O} \cdot n\text{X}_2\text{O}_3$ , where  $n$  can range from 5 to 11 and M is a monovalent cation (alkali metal)<sup>+</sup>,  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{NH}_4^+$ , and X is a trivalent cation  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ , or  $\text{Fe}^{3+}$ . High conductivity of the compound is related to the crystal structure.  $\beta$ -alumina has electronic conductivity of  $\approx 10^{-1} \text{ S cm}^{-1}$  at 300°C,  $\approx 10^{-8} \text{ S cm}^{-1}$  at  $-180^\circ\text{C}$  with an activation energy of  $0.16 \pm 0.01 \text{ eV}$ .

#### (ii) *NASICON Fast Ion Conductors*

The name Nasicon, taken from Na Superionic Conductor, refers to a non-stoichiometric material with a framework built of  $\text{ZrO}_6$  octahedra and  $(\text{Si,P})\text{O}_4$  tetrahedra which encloses a 3D network of interconnected pathways in which  $\text{Na}^+$  ions reside.

The Na sites are only partially occupied and easy 3D migration of  $\text{Na}^+$  ions is possible. The stoichiometry, and hence the Na content, are controlled by adjusting the P:Si ratio to give the general formula,  $\text{Na}_{1+x}\text{Zr}_2\text{P}_3-x\text{Si}_x\text{O}_{12}$ , which is a solid solution in the system  $\text{NaZr}_2(\text{PO}_4)_3 - \text{Na}_4\text{Zr}_2(\text{SiO}_4)_3$ . The  $\text{Na}^+$  ion conductivity of the Nasicon solid solutions depends greatly on composition  $x$  and has a maximum conductivity at  $x = 2$  which is comparable to that of  $\beta''$ -alumina at higher temperatures,  $> \sim 150^\circ\text{C}$ .

At lower temperatures, the structure undergoes a phase transition on cooling from rhombohedral to monoclinic symmetry, which has the effect of reducing the mobility of  $\text{Na}^+$  ions and the conductivity at room temperature is only  $1 \times 10^{-4} \text{ S cm}^{-1}$ .

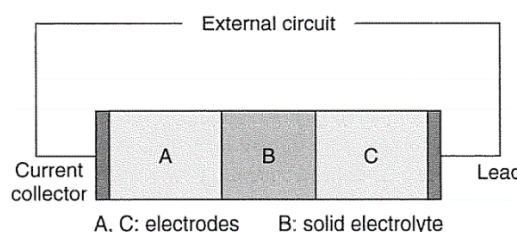
### 3. Oxide Fast Ion Conductors

Oxide ion conductors have important applications in O<sub>2</sub> sensors, pumps and solid oxide fuel cells, SOFCs. The best-known oxide ion conductor is yttria-stabilised zirconia, YSZ.

The high-temperature, cubic polymorph of zirconia has the fluorite crystal structure and may be stabilised to room temperature by formation of solid solutions with CaO, Y<sub>2</sub>O<sub>3</sub>, etc. Such ‘stabilised zirconias’ are good O<sup>2-</sup> ion conductors at high temperatures, mainly because the mechanism of solid solution formation involves the creation of vacant O<sup>2-</sup> sites in order to preserve electroneutrality.

Typical conductivities in stabilised zirconias are in the range 10<sup>-1</sup>–10<sup>-2</sup> S cm<sup>-1</sup> at 800°C with activation energy for conduction in the range 0.8–1.3 eV. At lower temperatures, their conductivities are much lower than those of the good Na<sup>+</sup> and Ag<sup>+</sup> ion solid electrolytes.

## APPLICATIONS OF SOLID ELECTROLYTES IN BATTERIES



**Fig. 4.14: Representation of a Battery**

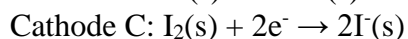
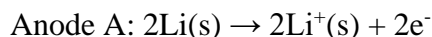
### 1. Lithium-Iodine Battery

LiI has relatively low ionic conductivity, but was used in heart pacemaker batteries in the early 1970's, where a low current, small, long lasting, and generate no gases during discharge.

A    B    C  
Li / LiI / I<sub>2</sub> (P2VP)

where the cathode is a , poly-2-vinyl-pyridine polymer embedded with iodine.

Electrode reactions are:



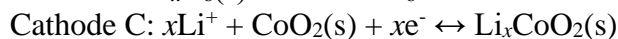
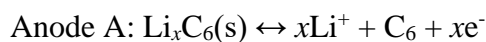
LiI contains intrinsic Schottky defects and the small Li<sup>+</sup> cations are able to pass through the solid electrolyte, while the electrons travel through the circuit to perform work.

### 2. Lithium-Ion Batteries

Driving reaction is that of Li with CoO<sub>2</sub> to form an intercalation compound, Li<sub>x</sub>CoO<sub>2</sub> and anode is Li in graphitic carbon.

A                      B                      C  
 Li<sub>x</sub>C / Li<sup>+</sup> electrolyte / LiCoO<sub>2</sub>

Electrode reactions are:

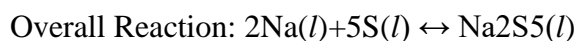
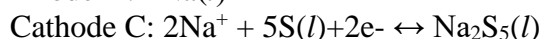
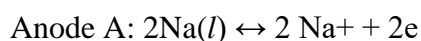


### 3. Sodium Batteries

Na<sup>+</sup> conduction has been used in a high-temperature secondary battery, the sodium sulfur battery. It uses NASICON and β-alumina as the electrolyte. It has an energy density of 110 Wh/kg, with lightweight Na and energetic reaction. Electrolyte separates molten sulfur/molten sodium

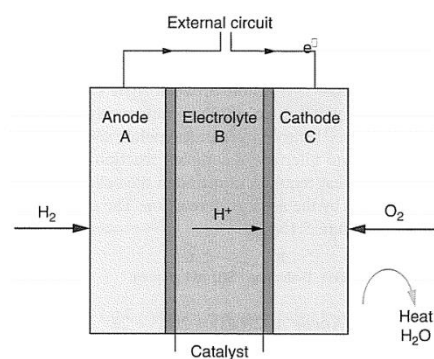
A                      B                      C  
 Na(l) / β-alumina / S(l), C (graphite)

Electrode reactions are:



Reaction is completed when low polysulfides are formed, terminating with Na<sub>2</sub>S<sub>3</sub>.

## APPLICATIONS OF SOLID ELECTROLYTES IN FUEL CELLS



**Fig. 4.14: Representation of a Fuel cell**

### 1. Proton Exchange Membrane Fuel Cell

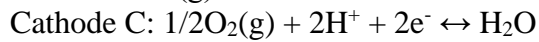
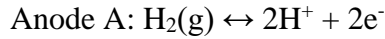
Proton Exchange membrane Fuel cells operate at ~80°C. Electrolyte is a conducting polymer membrane (Nafion), which is a sulfonated fluoropolymer. The strongly acidic –SO<sub>2</sub>OH group allows movement of H<sup>+</sup>, but not e<sup>-</sup>.

Output voltage is ~1V at 80°C with a current flow of 0.5A/cm<sup>2</sup>. A membrane of 1 m<sup>2</sup> provides about 1 kW. Cells are placed together to form a stack. Large fuel cells are produced and can

power banks, hospitals (250 kW). Medium cells (7 kW) can power a house and heat hot water. Fuel cells powered the Space Shuttle.

A	B	C
H <sub>2</sub> (g)/C, Pt/Polymer exchange Membrane, Nafion / C, Pt/O <sub>2</sub> (g)		

Electrode reactions are:

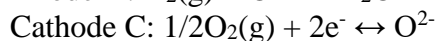
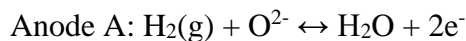


## 2. Solid Oxide Fuel Cell (SOFC)

SOFC's employ a ceramic oxide (ceria- or yttria-doped zirconia, Y<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub>), which becomes O<sup>2-</sup> conducting at very high temperature (800-1000°C) and requires heating, but at this temperature reforming and H<sup>+</sup> production can take place internally without Pt.

A	B	C
H <sub>2</sub> (g)/electrode/solid oxide electrolyte / electrode/O <sub>2</sub> (g)		

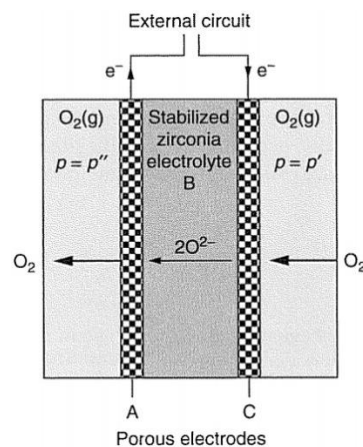
Electrode reactions are:



The solid oxide electrolyte can withstand the extreme conditions of H<sub>2</sub> at the anode at 800°C. (many oxides would be reduced). Cathode materials must be able to conduct both oxide ions and electrons, and must similar thermal expansion coefficients as the electrolyte.

## APPLICATIONS OF SOLID ELECTROLYTES IN SENSORS: OXYGEN SENSOR

Calcium Stabilized Zirconia (CSZ) is used in O<sub>2</sub> detection, in oxygen meters and oxygen sensors.



**Fig. 4.15: Representation of an Oxygen Sensor**



Gas pressures tend to equalize, and if  $p' > p''$  oxygen ions pass through the stabilized zirconia. A potential difference (because the ions are charged) is formed, indicating the oxygen is present (in the sensor) and a measurement of the potential gives the oxygen pressure difference (in the oxygen meter).

Oxygen gas is reduced to  $O^{2-}$  at the right-hand electrode (C).

The oxide ions are able to pass through the doped zirconia and are oxidized to oxygen gas at the left-hand electrode (A).

Electrode reactions are:

Anode A:  $2O^{2-} \leftrightarrow O_2 (p'') + 4e^-$

Cathode C:  $O_2 (p') + 4e^- \leftrightarrow 2O^{2-}$

Overall:  $O_2 (p') \leftrightarrow O_2 (p'')$

Under standard conditions, the change in Gibb's Free energy is related to the standard emf of the cell:  $\Delta G^\circ = -nE^\circ F$

Applying the Nernst equation to the cell reaction in an oxygen meter:

$$E = E^\circ - \frac{2.303RT}{4F} \log \left\{ \frac{p''}{p'} \right\}$$

$E^\circ$  is zero, since under standard conditions the oxygen pressure is equal.

Typically, the pressure of the oxygen on one side of the cell ( $p''$ ) is set to be a known reference pressure, usually either pure oxygen at 1 atm or atmospheric oxygen pressure (~0.21 atm).

$$E = E^\circ - \frac{2.303RT}{4F} \log \left\{ \frac{p'}{p_{ref}} \right\}$$

All of the quantities in the equation are known or can be measured, enabling a direct measure of the unknown oxygen pressure  $p'$ .

In order for an oxygen sensor or meter to operate, there must not be any electronic conduction through the electrolyte.

Oxygen meters find use in detection of waste gases in chimneys, exhaust pipes, etc.

Sensors for other gases operate using different electrolytes in the detection of  $H_2$ ,  $F_2$ ,  $Cl_2$ ,  $CO_2$ ,  $SO_x$ ,  $NO_x$ .

## SUPERCONDUCTORS: INTRODUCTION

**Definition:** Metals/ alloys, which conduct electricity with zero resistance when cooled below to its critical (threshold) temperature are known as super conductors.

### Examples

S. No.	Superconductor	Critical Temperature
1.	He	4 K
2.	Hg	4.2 K
3.	Pb	7.2 K
4.	Alloy of Pu, Ga and Co	18.5 K
5.	Alloy of Cu, Ba, Ce, and Tl	125 K

### Properties

- ✓ They possess greater resistivity than other elements at room temperature
- ✓ On adding impurity to super conducting element, the critical temperature can be lowered
- ✓ In superconducting state, all electromagnetic effects disappear
- ✓ Superconductors can exhibit Meissner effect

## HIGH TEMPERATURE SUPERCONDUCTORS (HTSC)

High Temperature Superconductors (HTSC) are superconductors which show superconductivity at unusual high temperature. Generally, superconductors having  $T_c$  more than 35 K ( $-238^\circ\text{C}$ ) are categorized as HTSCs.

## CUPRATE SUPERCONDUCTORS (COPPER BASED SUPERCONDUCTORS)

Cuprates are one class of superconductors which comes under the category of high temperature superconductors (HTSCs).

**Example:** Yttrium barium cuprate ( $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ) ( $T_c = 90 \text{ K}$ ;  $-183^\circ\text{C}$ ). Since, its critical temperature is 90 K, which is liquid nitrogen's boiling point, meaning that it is feasible to use liquid nitrogen to cool to such temperatures.

The constituents of this material yttrium, barium and copper are in 1:2:3 molar stoichiometric ratio and hence, they are called as 1:2:3 superconductors.

### Synthesis of 1:2:3 Superconductor by Solid State Ceramic Method

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , a 1:2:3 super conductor can be synthesized by solid state ceramic method. This method involves the following steps:

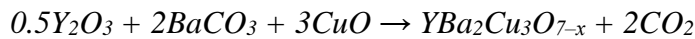
- ✓ Preparation of homogeneous mixture of three oxides ( $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$ ) in the required molar ratio.
- ✓ Heating them to obtain oxygen deficient superconductor in a muffle furnace.

- ✓ *Annealing the product to room temperature to retain its composition, structure and superconducting properties.*

High purity samples of  $Y_2O_3$ ,  $BaCO_3$  and  $CuO$  are taken in 0.5:2:3 molar proportions, mixed thoroughly till an intimate mixture in the form of pellet is obtained. This is pressed into a pellet is placed in a platinum crucible and heated to about  $950^\circ C$  for about 2-3 days in a muffle furnace.

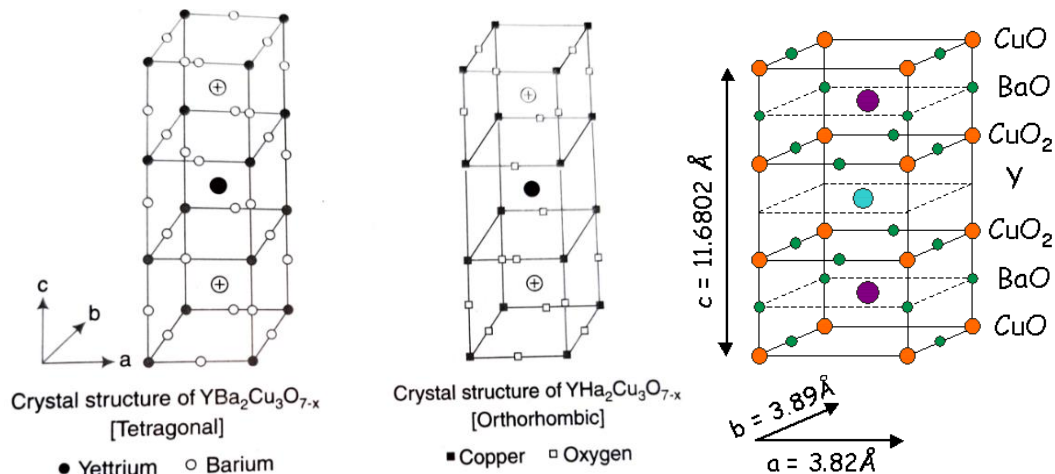
The yttrium barium cuprate, thus obtained is annealed to room temperature inside the furnace to retain its composition, structure and superconducting properties.

The solid-state reaction which occurs during heating process is:



### ***The Crystal Structure of $YBa_2Cu_3O_{7-x}$ (1:2:3) Super Conductor***

The crystal structure of  $YBa_2Cu_3O_{7-x}$  (1:2:3) is shown in the figure 4.16.



***Fig. 4.16: Crystal Structure of Cuprate Superconductor***

The unit cell of  $YBa_2Cu_3O_7$  is made up of three perovskite unit cells.

In this type, barium atoms are occupied at the A-lattices of perovskites (type-A) in the top and bottom units while yttrium atom is at the centre of B-type lattice (at the middle perovskite unit cell).

Hence, Y and Ba are stacked in the sequence [BaYBa] along the c-axis. All corner sites of the unit cell are occupied by Cu and there are four possible crystallographic sites for oxygen.

Cuprate superconductors contain copper oxides in both the oxidation states +3 and +2. For example,  $YBa_2Cu_3O_7$  is described as  $Y^{3+}(Ba^{2+})_2(Cu^{3+})(Cu^{2+})_2(O^{2-})_7$ .

If the unit cell of  $YBa_2Cu_3O_7$  is stoichiometric, then this unit cell should contain seven oxygen atoms.

In order to obtain non-stoichiometric oxygen deficient  $[O_{7-x}]$  unit cell of 1:2:3 compound, the four oxygen atoms from the vertical edges of the central perovskite cell and two each from the Cu–O horizontal layers edges are removed.

These oxygen deficient vacant sites are believed to be responsible for the distortion of the tetragonal unit cell to orthorhombic structure causing superconductivity. That is, the conductivity of cuprates is attributed to the electrons present inside the weakly coupled  $CuO_2$ .

## IRON SUPERCONDUCTORS (IRON BASED SUPERCONDUCTORS)

Another class of HTSCs are iron based superconductors.

The first iron-based high-temperature superconductor is the fluorine doped lanthanum Oxide iron arsenide ( $LaFeAsO_{1-x}F_x$ ) superconducts at 26 K ( $-247^\circ C$ ).

The undoped  $LaFeAsO$ , which is the parent compound to the superconductor, is a member of the large  $LnTmPnO$  family.

$Ln \rightarrow$  represents a 4f rare earth element;

$Tm \rightarrow$  transition metal element with more than half filled 3d shell which consists Mn, Fe, Co, Ni;

$Pn \rightarrow$  pnictogen element. Pnictogens are the group 15 elements of the periodic table. This group consists of nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), bismuth (Bi).

These iron superconductors are also referred to as “Oxypnictide”. Oxypnictide are class of materials including oxygen, a pnictogen. Iron arsenide superconductors can be divided into different classes.  $LaFeAsO_{1-x}F_x$  belongs to 1111 class and  $Ba_{1-x}K_xFe_2As_2$  was the first representative of the 122 family, where *the numbers simply represent the corresponding compositions*.

### Synthesis of Fluorine Doped $LaFeAsO$ by Solid State Metathesis Route

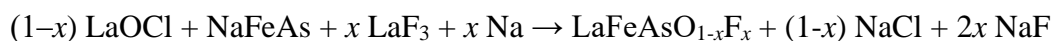
The process uses  $LaOCl$  and  $NaFeAs$  as *precursors*.

The synthesis of 1111 compounds of the La-Fe-As-O system can be done by heating the *precursors*  $LaOCl$  and  $NaFeAs$  in a molar ratio of 1:1 via the metathesis route.

In this process, the mixture is heated to about  $750^\circ C$  for 48 h, followed by heating to  $950^\circ C$  for about 96 h. Then the mixture is cooled down and well homogenized between each step so that the amount of desired product is increased with each reaction step. The resulting product is the formation of a binary mixture consisting of lanthanum oxide and iron arsenide ( $LaO$  and  $FeAs$ ).

For the synthesis of the  $LaFeAsO_{1-x}F_x$  ( $x = 0.05, 0.10, 0.15$ ) series, stoichiometric amounts of  $LaOCl$ ,  $NaFeAs$ ,  $LaF_3$  and elemental Na is allowed to react in the one-step synthesis mentioned above.

The solid-state reaction which occurs during the process is:

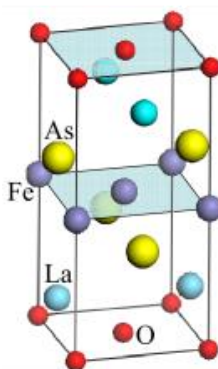


The reaction mixtures of the whole series ( $x = 0-0.15$ ) are heated in vessel setup: alumina crucibles enclosed by silica tubes. To remove the co-products formed (salts NaCl and NaF), the obtained mixtures is washed with water (three times) and ethanol, followed by drying the product under high vacuum.

### ***The Crystal Structure of Undoped LaFeAsO Superconductor***

The crystalline material LaOFeAs is composed of a stack of alternating LaO and FeAs layers. The FeAs layer is sandwiched between LaO layers.

It is noted that, these two layers are positively and negatively charged respectively, and that the La–O chemical bond in the *LaO layer* is ionic whereas the *Fe–As* has a predominantly covalent nature.



***Fig. 4.17: Crystal Structure of Iron Superconductor***

Thus, the chemical formula may be expressed as  $(\text{La}^{+3}\text{O}^{-2})^{+1} (\text{FeAs})^{-1}$ . The *charge carriers* can be increased by the substitution of the  $\text{O}^{2-}$  ion by  $\text{F}^{-}$  ion.

Doping of the system with fluorine suppresses both the magnetic order and the structural distortion (structural transition from tetragonal to monoclinic) favours superconductivity.

## **APPLICATIONS OF HIGH TEMPERATURE SUPERCONDUCTORS**

### ***1. Magnetic Resonance Imaging (MRI)***

MRI is a non-intrusive medical imaging technique that creates a two-dimensional picture of say tumors and other abnormalities within the body or brain. MRI required a magnetic field to be set up for recording images. Although normal electromagnets can be used for this purpose, because of resistance they would dissipate a great deal of heat and have large power requirements. Superconducting magnets on the other hand have almost no power requirements apart from operating the cooling. Once electrical current flows in the superconducting wire, the power supply can be switched off because the wires can be formed into a loop and the current will persist indefinitely as long as the temperature is kept below the transition temperature of the superconductor.

### ***2. Magnetic Levitation***

Because of the diamagnetic nature of HTSCs, any magnetic field in contact with HTSCs will get repelled and this phenomenon could be used in creating vehicles that move using the

principle of levitation rather than motors driving them, which is a highly inefficient system. People already have developed such trains, which are also called Maglev trains. Though they have not been made for production of commercial use, people have shown that such trains are indeed possible and they carry massive scope for future, as Maglev trains have a very high efficiency because of the fact that the train never touches the track, and the losses due to friction are zero.

### **3. *Superconducting Transmission System***

Since HTSCs show zero resistance below critical temperature, the transmission system made from the wires made from a HTSCs material can greatly reduce the ohmic losses because of the current and this can lead to increase in efficiency, and decrease in the total power consumption. In fact, people have already such transmission wires and are using it for small scale power transfer, because of the fact that it is economically not feasible to do so for larger lengths.

### **4. *Non-intrusive Diagnosis using SQUIDS***

Detecting heart and brain diseases at early stages has always been a challenge in medical domain. In order to diagnose such disease people used to go with intrusive tests, which are harmful and expensive. Superconducting quantum interference device (SQUID) made using a superconductors material can be used as an agent to diagnose such disease using non-invasive techniques. SQUID is incredibly sensitive to small magnetic fields so that it can detect the magnetic fields from the heart  $10^{-10}$  Tesla and even the brain  $10^{-13}$  Tesla. As a result, SQUIDS are used in non-intrusive medical diagnostics of the brain.

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**SCHOOL OF SCIENCE AND HUMANITIES  
DEPARTMENT OF CHEMISTRY**

## **UNIT – 5 – Preparative Methods of Solids – SCYA5303**

## SOLID STATE REACTIONS

Solids do not react together at room temperature. It is necessary to heat them to much higher temperature (1000 – 1500°C) so that the reaction can occur at appreciable rate. Hence both thermodynamic and kinetic factors are important in solid state reactions.

### Spinel

Spinel have the general formula  $AB_2O_4$

1.  $MAl_2O_4$  Aluminate Spinel,  $M = Mg, Ni$
2.  $MFe_2O_4$  Ferrite spinel,  $M = Zn, Co, Ni, Mn$
3.  $MCr_2O_4$  Chromite spinel,  $M = Zn, Co, Ni, Mn, Mg, Cu$

Several commercially important magnetic oxides have the spinel structure. The parent spinel is  $MgAl_2O_4$ . It has *ccp* oxide ions with  $Mg^{2+}$ ,  $Al^{3+}$  in tetrahedral and octahedral interstices, respectively.

Many oxides, sulphides and halides have the spinel structure and different charge combinations are possible.

### Precursors

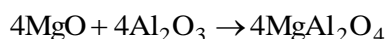
S. No.	Name of Spinel	Precursors	Reaction Temperature
1.	$MgAl_2O_4$ , Aluminate spinel	$MgCO_3 + Al_2O_3$	1400 – 1600°C
2.	$ZnFe_2O_4$ , Ferrite spinel	$Zn(COO)_2 + Fe_2[(COO)_2]_3$	1000°C
3.	$MnCr_2O_4$ , Chromite spinel	$Mn(CrO_4) + C_5H_5N$	1100°C

## WAGNER REACTION MECHANISM FOR PREPARING MAGNESIUM ALUMINATE SPINEL

The precursors used for preparing  $MgAl_2O_4$  are  $MgCO_3$  and  $Al_2O_3$ .

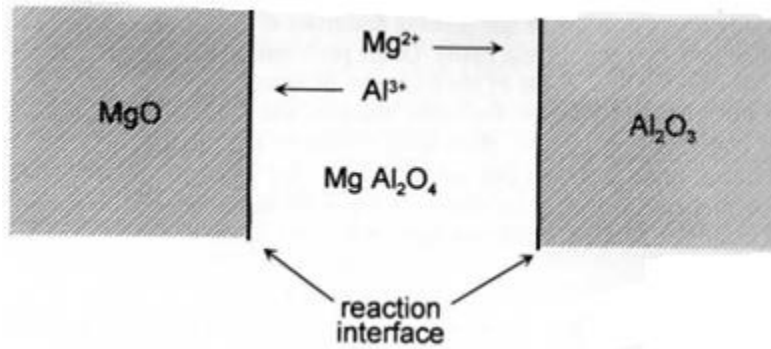
When these precursors are heated to about 1500°C, initially  $MgCO_3$  decomposes to give  $MgO$  at about 650-700°C, and at very high temperature, the reaction between  $MgO$  and  $Al_2O_3$  gives magnesium aluminate spinel  $MgAl_2O_4$ .

During this process,  $Mg^{2+}$  in  $MgO$  and  $Al^{3+}$  in  $Al_2O_3$  gain sufficient thermal energy and enable them to interchange and reorganize with oxide ions to form  $MgAl_2O_4$  spinel **at the interface of  $MgO$  and  $Al_2O_3$  crystal**.



In order for further reaction to occur (the  $MgAl_2O_4$  interface to grow thicker), counter diffusion of  $Mg^{2+}$  and  $Al^{3+}$  ions must occur through product layer and this mechanism is known as Wagner reaction mechanism.





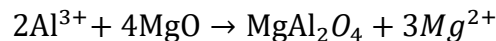
**Fig. 5.1: Wagner Reaction Mechanism for Preparing Magnesium Aluminite Spinel**

For the growth of  $\text{MgAl}_2\text{O}_4$  at the interface of  $\text{MgO}$  and  $\text{MgAl}_2\text{O}_4$ , the  $\text{Al}^{3+}$  ion must diffuse towards left hand side through the product layer.

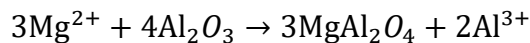
Further, for the growth of  $\text{MgAl}_2\text{O}_4$  at the interface of  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$ , the  $\text{Mg}^{2+}$  ion must diffuse towards right hand side through the product layer.

The reaction that occurs at the two interfaces may be written as:

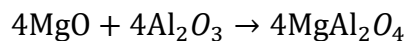
- a) At the interface of  $\text{Mg} / \text{MgAl}_2\text{O}_4$



- b) At the interface of  $\text{MgAl}_2\text{O}_4 / \text{Al}_2\text{O}_3$



- c) Overall reaction is:



The reaction (b) gives three times spinel product than the reaction (a) and hence the right-hand side interface should grow three times that of left-hand interface [Fig. 5.1].

## **CHEMICAL PRECURSOR METHOD FOR PREPARING $\text{BaTiO}_3$ CRYSTAL ( $\text{ABO}_3$ PEROVSKITE CRYSTAL)**

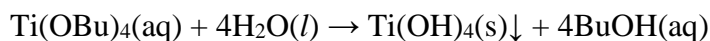
Barium titanate,  $\text{BaTiO}_3$ , is a ferroelectric material widely used in modern electronic industry for fabricating capacitor because it has high dielectric constant and is capable of creating and storing electrical charges (dipoles). For fabricating modern electronic circuits, it is important to have a product of controlled grain size and the chemical precursor method is one way to achieve this.

### **Chemical Precursor Method for the Synthesis of $\text{BaTiO}_3$**

The precursors used in this method for preparing  $\text{BaTiO}_3$  are: Tetra butoxy titanium, barium chloride and an excess of oxalic acid.

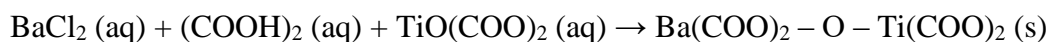
### ***Step 1: Preparation of titanium oxo oxalate***

The first step in the preparation of BaTiO<sub>3</sub> is to prepare an oxo-oxalate of titanium. When an aqueous solution of oxalic acid solution is added to titanium butoxide, which initially hydrolyses to give a precipitate of titanium hydroxide, in turn redissolves in the excess oxalic acid to form titanium oxo oxalate.

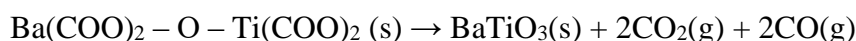


### ***Step 2: Synthesis of barium titanate***

When barium chloride solution is added slowly in to titanium oxo oxalate solution in presence of excess oxalic acid, barium titanyl oxalate precipitate is obtained.



This precipitate contains barium and titanium in the correct ratio and is easily decomposed by heating to give ABO<sub>3</sub> type of crystal, barium titanate. The temperature used for this final heating is 920 K.



## **SOL-GEL METHOD FOR THE PREPARATION OF SILICA AEROGEL**

The precipitation methods always have the disadvantage that the stoichiometry of the precipitate(s) may not be exact if one or more ions are left in solution. The sol-gel method overcomes this limitation, because the reactants never precipitate out.

First, a concentrated solution or colloidal suspension of the reactants, the ‘sol’, is prepared, which is then concentrated or matured to form the ‘gel’. This homogeneous gel is then heat-treated to form the product.

The porous crystalline solids are classified into microporous materials (pore dia: <2 nm) and mesoporous materials (pore dia: 2-50 nm).

Such porous materials find applications in optoelectronics for fabricating optical fibres, in membrane technology for water purification, to use as thermal insulators in furnaces, used as catalysts for various catalytic reactions.

### **Preparation of Silica Aerogel**

Optical fibres need to be free of impurities such as transition metal ions and conventional methods of preparing silica glasses are inadequate.

The sol-gel process is one way of forming fibres of sufficient purity. These processes use volatile compounds of silicon which are more easily purified, for example by fractional distillation than silica.

It is possible to produce silica fibres using a liquid silicon alkoxide  $\text{Si}(\text{OR})_4$ , where R is methyl, ethyl, or propyl, is hydrolysed by mixing with water.

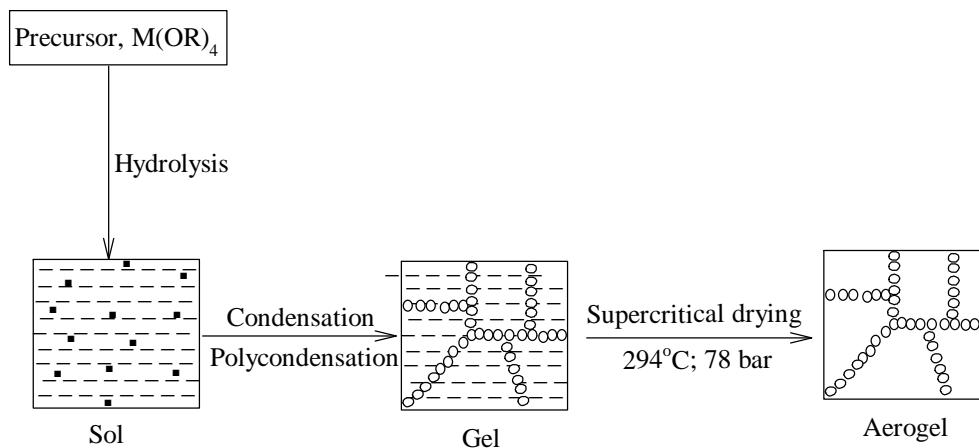
### ***Precursors for Preparing Silica Aerogel***

The precursors used in sol-gel process for the synthesis of nanoporous materials are metal alkoxides,  $\text{M}(\text{OR})_4$ . They readily react with water to form gels.

- ✓ Tetra methoxy silane (TMOS),  $[\text{Si}(\text{OCH}_3)_4]$
- ✓ Tetra ethoxy silane (TEOS),  $[\text{Si}(\text{OC}_2\text{H}_5)_4]$
- ✓ Tetra butoxy titanate,  $[\text{Ti}(\text{OC}_4\text{H}_9)_4]$

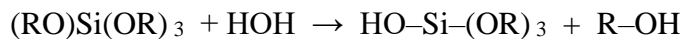
### ***Process***

The process consists of four main steps: (i) Hydrolysis of precursors (ii) Condensation followed by polycondensation (iii) Gelation (iv) Super critical drying.

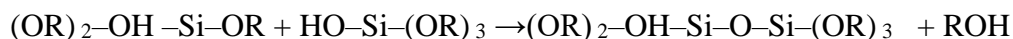
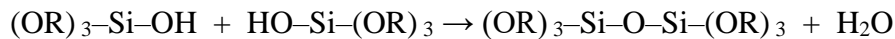


***Fig. 5.2: Sol-Gel Method for the Preparation of Silica Aerogel***

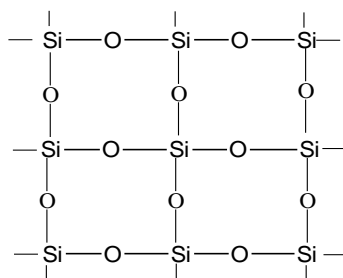
***Hydrolysis:*** It occurs through the addition of water and to form silanol,  $(\text{Si}-\text{OH})$  particles.



***Condensation:*** The self-condensation of silanol groups produces siloxane linkages,  $(\text{Si}-\text{O}-\text{Si})$  filled with byproducts of water and alcohol.



***Polycondensation:*** The condensation process continues to form poly condensed silica gel with  $\text{Si}-\text{O}-\text{Si}$  linkages.



**Super Critical Drying:** The gels are subjected to super critical drying in an autoclave. The critical pressure and critical temperature used are 78 bar and 294°C respectively in order to remove liquid from silica gel to form the network structure of silica aerogel.

## **SELF PROPAGATING HIGH TEMPERATURE SYNTHESIS (or) COMBUSTION SYNTHESIS**

Combustion synthesis is used for preparing refractory materials including borides, nitrides, oxides, hydrides, silicides, intermetallics, ceramics etc.

Some important products such materials and their applications include:

- ✓ Hydrides (e.g.,  $\text{MgH}_2$ ) for hydrogen storage.
- ✓ Borides (e.g.,  $\text{TiB}_2$ ) for abrasives and cutting tools.
- ✓ Carbides (e.g.,  $\text{SiC}$  and  $\text{TiC}$ ) for abrasives and cutting tools.
- ✓ Nitrides (e.g.,  $\text{Si}_3\text{N}_4$ ) for high strength, heat resistant ceramics.
- ✓ Oxides (e.g., cuprates) for high temperature superconductors.
- ✓ Silicides (e.g.,  $\text{MoSi}_2$ ) for high temperature heating elements.

### **Process**

Combustion synthesis is also known as self-propagating high temperature synthesis. It uses highly exothermic ( $\Delta H < -170 \text{ kJ mol}^{-1}$ ) and even explosive reaction to maintain a self-propagating high reaction temperature.

It is used to prepare many refractory material including borides, nitrides, high temperature oxides, silicides, intermetallics and ceramics.

In order to carry out combustion synthesis the reactants in powdered form ( $0.1\text{-}1\mu\text{m}$ ) is mixed together and prepared in the form of pellets. These pellets are ignited at high temperature in presence of an appropriate gas or metals using a laser or electrical coil or heat resistive coil. Once ignited the reaction propagates as a wave through the pellets and the reaction temperature varies from 1500-3000°C.

Self-ignition can sometimes be achieved by ball milling. The reaction times are very short since the products are produced immediately after the combustion.

The typical examples for combustion reaction are:

1.  $\text{MoO}_3 + 2\text{SiO}_2 + 7\text{Mg} \rightarrow \text{MoSi}_2 + 7\text{MgO}$
2.  $\text{WO}_3 + \text{C} + 2\text{Al} \rightarrow \text{WC} + \text{Al}_2\text{O}_3$
3.  $\text{TiO}_2 + \text{B}_2\text{O}_3 + 5\text{Mg} \rightarrow \text{TiB}_2 + 5\text{MgO}$
4.  $2\text{Ta} \xrightarrow{\text{N}_2 \text{ atmosphere}} \text{Ta}_2\text{N} \xrightarrow{\text{N}_2 \text{ atmosphere}} \text{TaN}$

## ION EXCHANGE REACTIONS

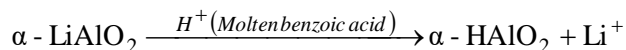
Metal oxides having layer structures are tunnel packed can undergo ion exchange reaction in aqueous solution or in molten salt media at relatively lower temperatures. It is accompanied by minimal reorganization of this structure of the parent solid to accumulated incoming ion.

### 1. Ion exchange of Lithium Aluminium ( $\text{LiAlO}_2$ ) with protons ( $\text{H}^+$ ions)

$\text{LiAlO}_2$  crystallizes in three different structure namely  $\alpha$ ,  $\beta$ ,  $\gamma$  of which only  $\alpha$ - $\text{LiAlO}_2$  adopts rock salt super structure.

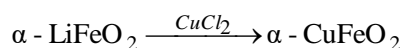
So,  $\alpha$ - $\text{LiAlO}_2$  having rock salt super structure can exchange its  $\text{Li}^+$  ions with  $\text{H}^+$  in molten benzoic acid.

The  $\beta$  and  $\gamma$  forms of  $\text{LiAlO}_2$ , where both Li and Al are tetrahedrally coordinated, and hence do not exhibit a similar ion exchange process.



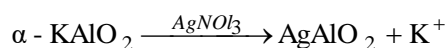
### 2. Ion exchange of Lithium Ferroate with Cu ion

When  $\alpha$ - $\text{LiFeO}_2$  is converted to  $\text{CuFeO}_2$  by exchange with molten  $\text{CuCl}$ , the structure changes from  $\alpha$ - $\text{LiFeO}_2$  to octahedral delafossite to provide a linear anion coordination for  $\text{Cu}^+$  ion.



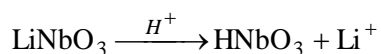
### 3. Ion exchange of Potassium Aluminate with Ag ion

When  $\text{KAlO}_2$  is transformed to  $\text{AgAlO}_2$  by ion-exchange, there is a structure change from cristobalite to ordered wurtzite. The change probably occurs to provide a tetrahedral coordination for  $\text{Ag}^+$ .



### 4. Ion exchange of Lithium Niobate with hot aqueous acid

The conversion of  $\text{LiNbO}_3$  to  $\text{HNbO}_3$  by the treatment with hot aqueous acid involves the exchange of  $\text{Li}^+$  by protons, which is accompanied by a topotactic transformation of the rhombohedral  $\text{LiNbO}_3$  structure into the cubic perovskite structure of  $\text{HNbO}_3$ .



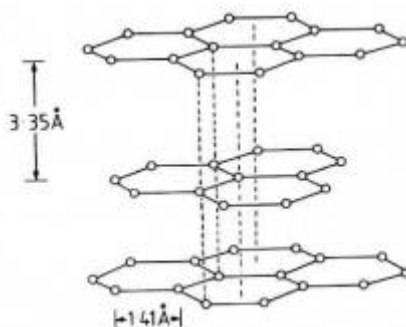
# INTERCALATION AND DE-INTERCALATION REACTIONS (PREPARATION OF INTERCALATIVE COMPOUNDS)

## 1. Preparation of Graphite Intercalative Compounds

The process of inserting atoms, molecules, and ions as compounds in to the host structure is known as intercalation.

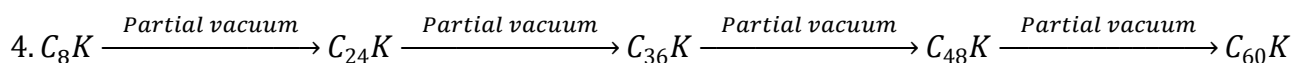
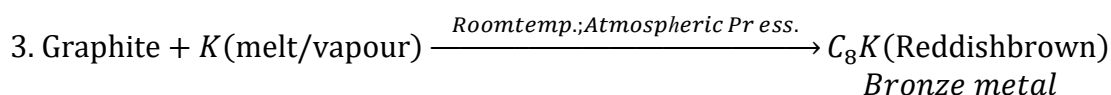
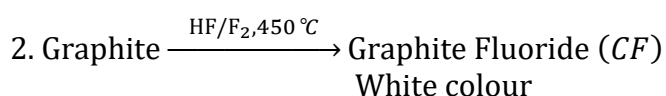
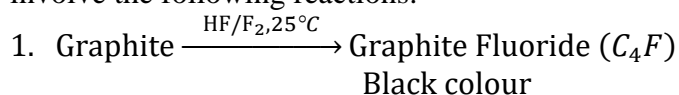
Graphite has a layered structure in which each carbon atom in the hexagonal layer is bonded to three other carbon atoms by strong covalent bond forces but the different layers are held by weak Vander Waal's force of attraction.

Typical intercalation reactions can occur on graphitic structure with the anions like fluoride, alkali atoms like potassium and the compounds like ferric chloride ( $\text{FeCl}_3$ ). During intercalation, the atoms, ions or molecules are inserted between the two layers graphitic structures (Fig. 5.3).



**Fig. 5.3: The Structure of Graphite**

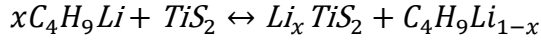
The intercalation reactions of HF, K melt and ferric chloride into the host graphite structures involve the following reactions:



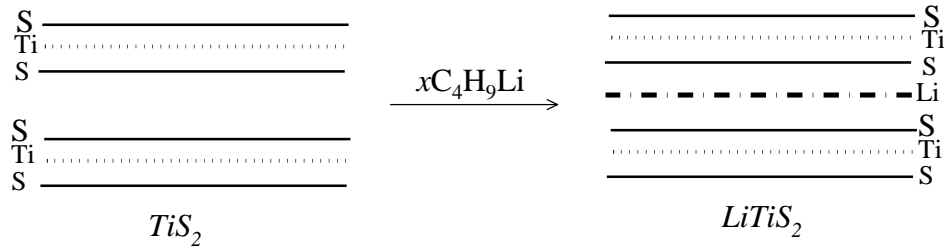
## 2. Preparation of Chalcogenides Based Intercalative Compounds

### (i) Chemical Reagent Method

Lithium ions can be inserted between the  $\text{TiS}_2$  (Fig. 5.4) by using  $n$ -butyl lithium as the source of lithium ion, and the process is known as intercalation.



During intercalation, the inserted ions are shuttled back to the host structure titanium disulphide.

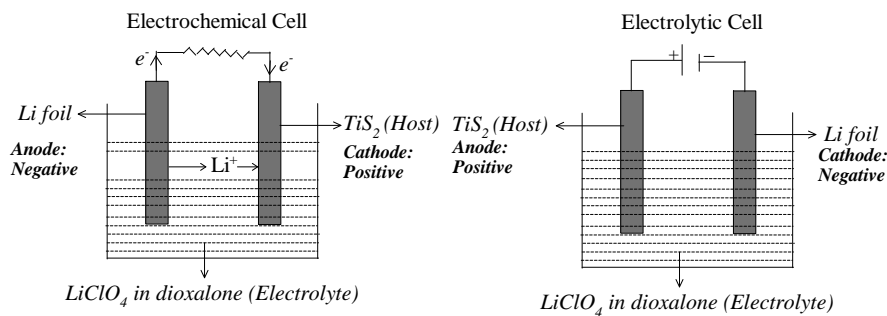
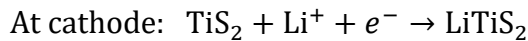


**Fig. 5.4: The Structure of Graphite**

### (ii) Electrochemical Method

In this method Li-foil is used as anode,  $\text{TiS}_2$  host bonded with Teflon as cathode and  $\text{LiClO}_4$  dissolved in dioxane is used as electrolyte (Fig. 5.5).

When anode and cathode are interconnected by an external insulated wire the electrons flow from anode to cathode, in which lithium foil liberates lithium ions with the liberation of electrons. The lithium ions migrate through the electrolyte and get inserted between the layers of titanium disulphide structure, and the process is known as intercalation.



**Fig. 5.5: Schematic Representation of Li/TiS<sub>2</sub> Cell**

The process of removing the inserted ions from the host structure is known as de-intercalation reaction. During the reaction, the inserted ions are shuttled back to the lithium foil. The passing of direct current into the  $\text{Li/TiS}_2$  cell is the driving force for de-insertion reactions so that the following reactions take place.

At the negative electrode oxidation takes place:  $\text{LiTiS}_2 \rightarrow \text{TiS}_2 + \text{Li}^+ + e^-$

At the positive electrode, reduction takes place:  $\text{Li}^+ + e^- \rightarrow \text{Li}$

## METHODS OF SINGLE CRYSTAL GROWTH

### HYDROTHERMAL THERMAL METHOD OF SINGLE CRYSTAL GROWTH

#### *Definition and Principle*

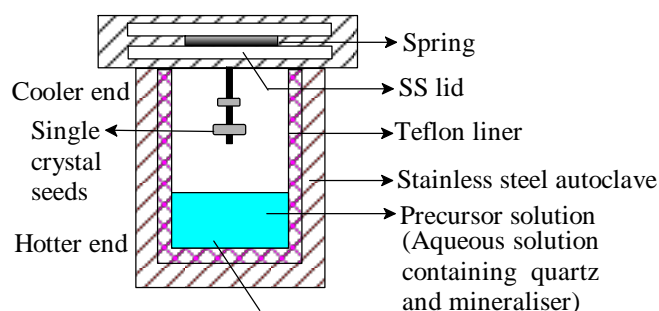
Hydrothermal synthesis (also called as thermal hydrolysis or hydrothermal hydrolysis) involves the processing of aqueous solution of metal salts in an autoclave at elevated temperatures (typically 100 – 500°C) and pressures of 0.1 – 2 kbar (Fig. 5.6). This method can be used for the synthesis of single crystal in bulk new phase compound and magnetic crystalline particle.

In hydrothermal process, water is mixed with metal precursors and the solution mixture is placed in an autoclave and maintained at relatively high temperatures and pressures to carry out the single crystal growth in bulk size.

Under these super critical conditions:

- ✓ Solubility of most ionic species increases.
- ✓ Viscosity of water decreases and exhibits greater mobility.
- ✓ The increase of mobility allows Ostwald ripening to continue at a faster rate increasing the uniformity of the precipitate.

Size and morphological control in hydrothermal reactions is achieved by controlling the conditions of time and temperature.



**Fig. 5.6: An Autoclave for Hydrothermal Synthesis**

#### *(i) Synthesis of Quartz Single Crystal*

The first industrial process to use hydrothermal method of synthesis was the production of quartz crystals for use as oscillators in radios.

Quartz,  $\text{SiO}_2$ , can be used to generate a high frequency alternating current via the piezoelectric effect. For the single crystal growth in hydrothermal method, a suitable mineralizer is used. Any compound that added to the aqueous solution of precursors to speed up the crystal growth is known as mineralizer. For growing a quartz single crystal NaOH is used as mineralizer.

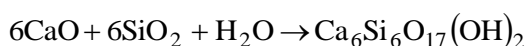


When the autoclave is heated at 360°C and 1.7 kbar, the silica is dissolved in 0.1 molar NaOH solution and is transported into the autoclave of the cooler part where it gets supersaturated, crystallizes out and grow as single crystal in kilogram size on seed crystal. The alkaline solution returns to the hotter region where it can dissolve more silica.

### ***(ii) Preparation of Calcium Silicate Hydrate (CSH) New Phase***

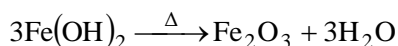
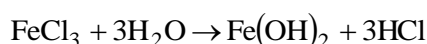
An example of calcium silicate hydrate is xonolite. The presence of xonolite single crystal in cement when used in making concrete structure is capable of developing very high compressive strength within 72 hours duration.

To prepare CSH single crystal, lime and silica are heated at temperature at 500°C and pressure 0.1 – 2 kbar.



### ***(iii) Synthesis of Ferric Oxide Magnetic Single Crystalline Solids***

Magnetic  $\alpha\text{-Fe}_2\text{O}_3$  single crystal can be prepared by using aqueous solution of  $\text{FeCl}_3$  in a stainless-steel autoclave and subjected for hydrolysis followed by heating to a temperature of 300°C with a pressure of 0.1 kbar.



## **CZOCHELSKI CRYSTAL GROWTH TECHNIQUE**

This technique is used for preparing single crystal silicon, which is used in electronic industries for making diodes and transistors.

To prepare single crystal silicon, the precursor used is electronic grade silicon (EGS, purity 99.9999%). The EGS can be obtained from metallurgical grade silicon (MGS, purity, 99.8%).

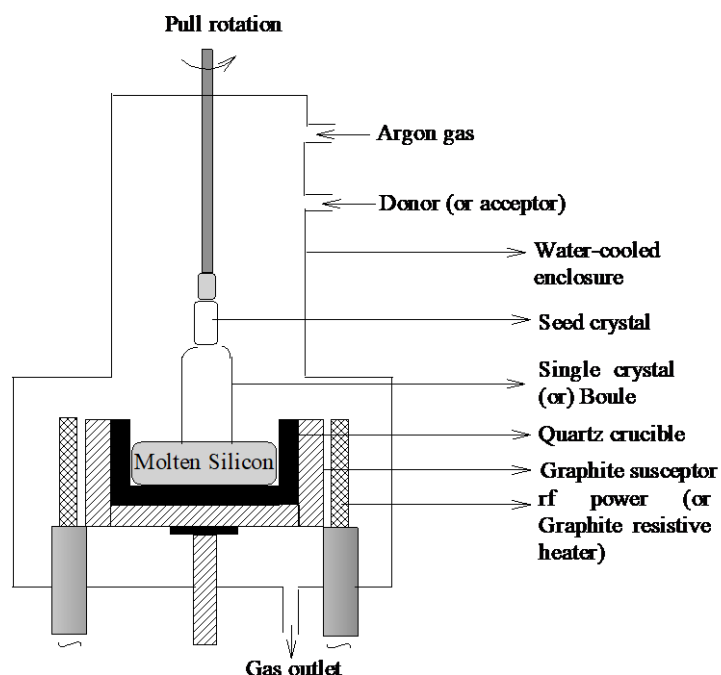
So, in the first step of preparation of EGS, the MGS is dissolved in HCl to obtain trichlorosilane.

Since trichlorosilane is a low boiling liquid (33.1°C), it is fractionally distilled under reduced pressure in presence of hydrogen atmosphere. This process produces EGS.



### ***Principle***

In Czochralski process, electronic grade silicon is placed in a rotating quartz crucible and melted at 1415°C. Then a single crystal silicon seed rod is inserted in to the melt and gradually pulled out to grow single crystal ingot (boule). After slicing the silicon vapours is used for integrated circuits for micro fabrication.



### ***Process***

Czochralski process is carried out in an inert chamber filled with argon gas to avoid the contamination. In Czochralski process, electronic grade silicon (EGS) is placed in rotating quartz crucible and melted at  $1415^{\circ}\text{C}$  by using electric resistant rf coil. Now the rotating single crystal seed rod is submerged in molten silicon.

When the seed rod is about to melt, it is gradually pulled out to grow ultra-pure single crystal silicon ingot of definite diameter and length.

The diameter of the silicon ingot is decided by the temperature of the melt and pull rate. In order to grow extrinsic semiconductor suitable dopants are added in to the melt.

### **References**

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