

Unit - 1

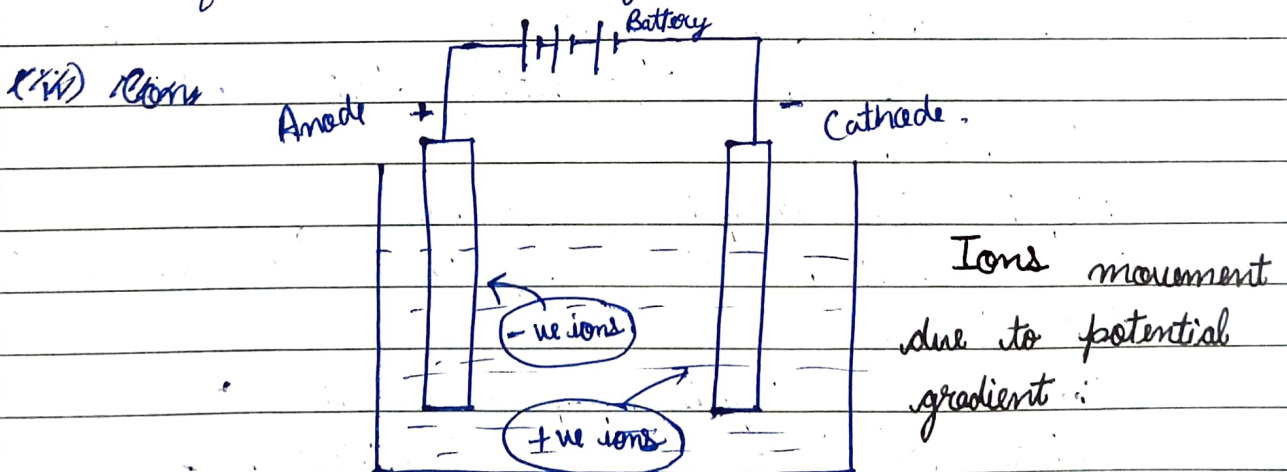
ION TRANSPORT IN SOLUTION

- => The movement of charged particles (ions) in a liquid medium (solution).
- => In a solution, ions can be positively charged (cations) or negatively charged (anions).
- => The movement of these ions can occur through different mechanisms:-

(i) Migration

(The movement of ions due to electric field).

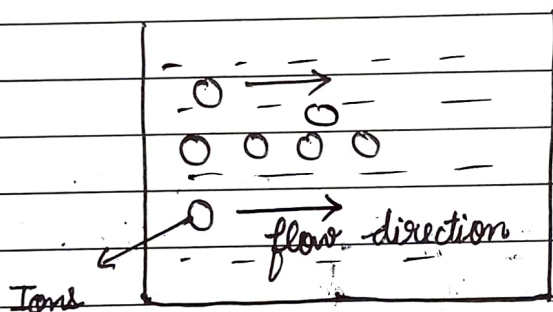
- => When an electric field is applied to solution, ions migrate towards the oppositely charged electrode.
- => Cations (+ve ions) move towards the cathode (-ve electrode).
- => Anions (-ve ions) move towards the Anode (+ve electrode).
- => The Migration rate depends on the strength of the electric field, the ion's charge and its size.



(ii) Convection

It is the bulk movement of ions within a solution due to

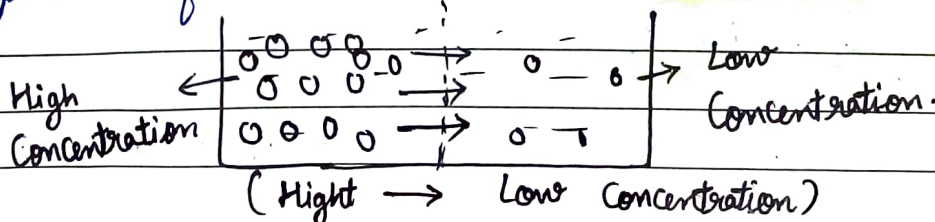
- fluid flow.
- ⇒ When a solution is stirred to fluid flow, ions are carried along with the moving fluid.
- ⇒ This movement help the ions for mixing and transporting larger distances as compare to diffusion.
- ⇒ It is important in natural systems, such as in the movement of ions in oceans and rivers.
- ⇒ In laboratory stirring is applied for mixing the ions in solution.



Ions movement with Solvent flow.

(iii) Diffusion

- ⇒ Ions moves from regions of higher concentration to regions of lower concentration, until equilibrium is reached.
- ⇒ Diffusion is the primary mechanism of ion transport in the absence of an applied electric field or fluid flow.
- ⇒ The Rate of diffusion depends on the concentration gradient, the ion's diffusion coefficient, and the properties of the solvent.



Debye - HUCKEL THEORY

It describes the behaviour of ions in dilute electrolyte solutions.

It is given by Peter Debye and Erich Hückel in 20th Century.

⇒ This theory helps to understand the effects of ion-ion interactions, conductivity and activity coefficients of electrolyte solutions.

The Debye-Huckel equation which relates the activity coefficient (γ) of an ion to its concentration (C) in a solution. The equation is given by:-

$$\log \gamma_{\pm} = -A \pm \frac{\sqrt{C}}{\sqrt{T}}$$

where $\gamma_{\pm}$ = it is the activity coefficient of the ion.

$A \pm$ = it is the Debye-Huckel Constant, related to the strength of the ion-ion interactions.

C is the concentration of the ion in mol/L.

T is the temperature in Kelvin.

In Debye-Huckel equation:

The activity coefficient (γ) is directly proportional to concentration. if concentration increases the activity coefficient increases.

The activity coefficient (γ) also depends on temperature and solvent properties.

This theory is useful in understanding and predicting the behavior of electrolyte solutions at low to moderate concentrations.

~~Debye Huckel theory~~

Debye - Huckel limiting law :-

- * It describes the behaviour of dilute electrolyte solutions.

Law :-

It states that the mean activity coefficient $\gamma_{\pm}$ of an ion in an electrolyte solution is inversely proportional to the square root of the ionic strength (I) of the solution.

Mathematical Expression :-

$$\gamma_{\pm} = 1 - \frac{AZ}{\sqrt{I}}$$

where, $\gamma_{\pm}$ = Mean Activity Coefficient of an ion.

A = Constant

Z = Valence of the ion

I = Ionic strength of the solution.

- * If the Activity Coefficient decreases the ionic strength will increase.

- * Debye - Huckel limiting law is only valid for very dilute electrolyte solutions.

Electrical double layer and Multi layer

Electrical double layer:-

* The electrical double layer is formed at the interface between an electrode and an electrolyte.

* It consists of two layers:-

→ The inner layer known as the Helmholtz layer

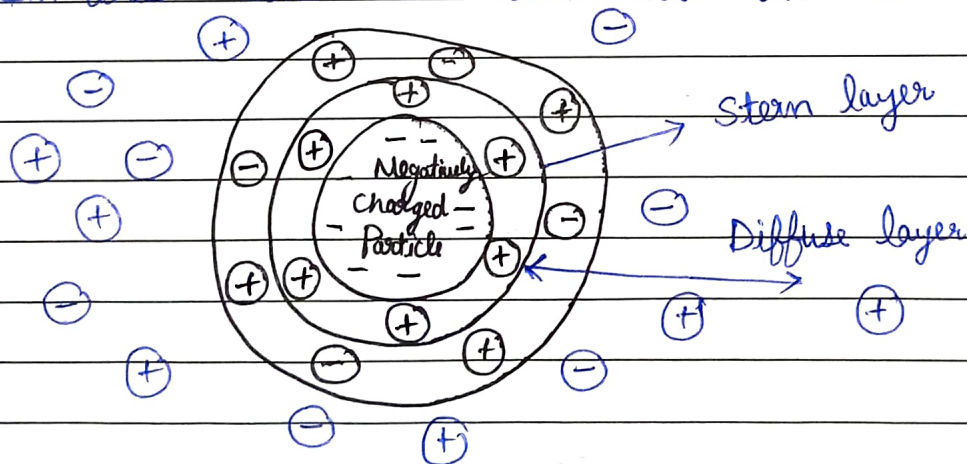
→ The outer layer called diffuse layer.

* Helmholtz layer:- (Stern layer).

In this ions are tightly bound to the electrode surface.

Diffuse layer:-

In this ions are distributed in the electrolyte.



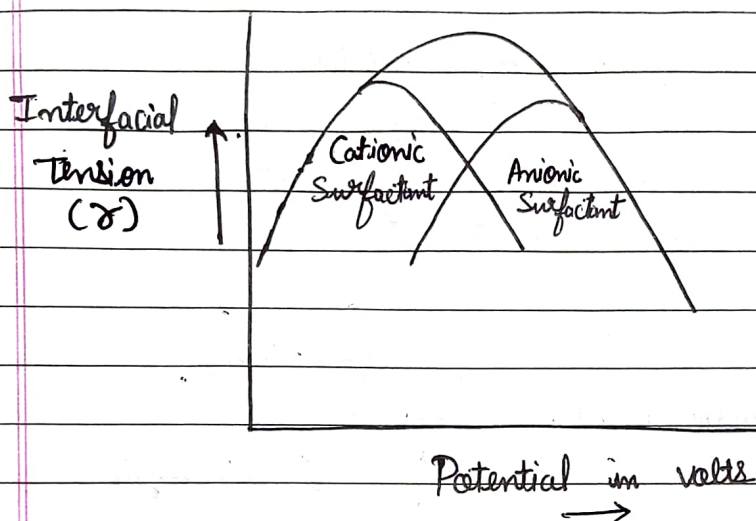
Multiple layer:-

* This layer forms when additional layers of ions form on the primary double layer.

* It takes place in specific conditions

Electrocapiillary curve:-

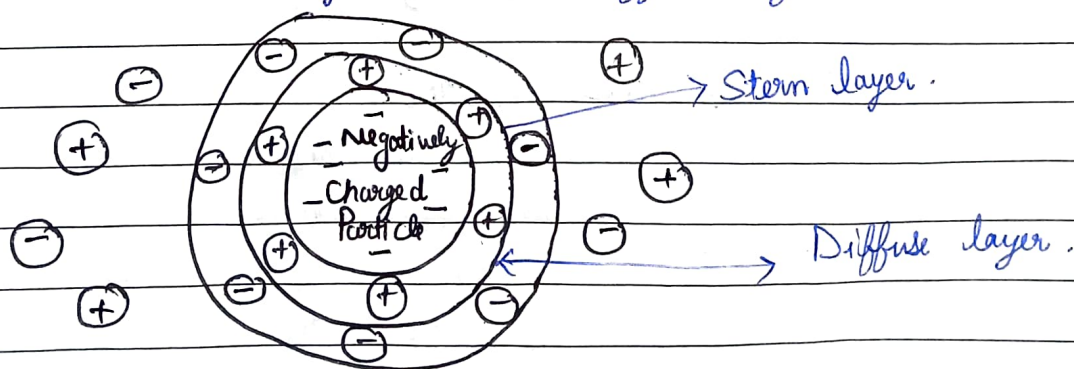
- * It is a plot of the interfacial tension (γ) between an electrode and an electrolyte solution.
- * The Electrocapiillary curve (ECC) is used to study the structure and properties of electrochemical double layer (EDL)



EDL (Electrochemical double layer).

It consists of two layers:-

- The inner layer known as the Helmholtz layer (Stern layer).
- The outer layer called diffuse layer.

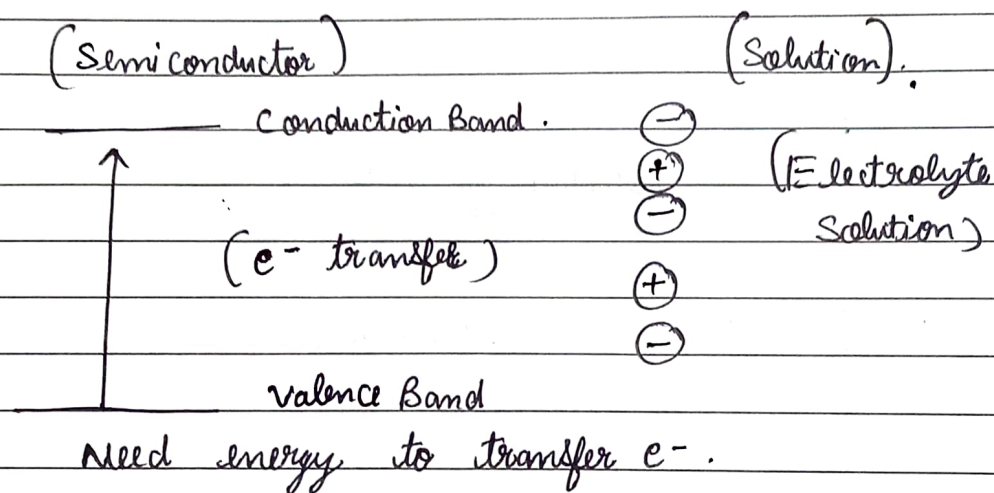


Electrocapiillary curve used to study a variety of phenomena:-

- The adsorption of ions onto the electrode surface.
- The structure of Electrochemical double layer.
- The kinetics of electrode reactions.
- It is also used to determine Zero-Point Potential (ZPP) of an electrode.

Garrett - Brattain Space Charge model

* The Garrett-Brattain Space Charge model is a model of the electrical double layer at a semiconductor electrolyte interfaces.



* It was developed by Garrett and Brattain in 1950.

Function of this model:-

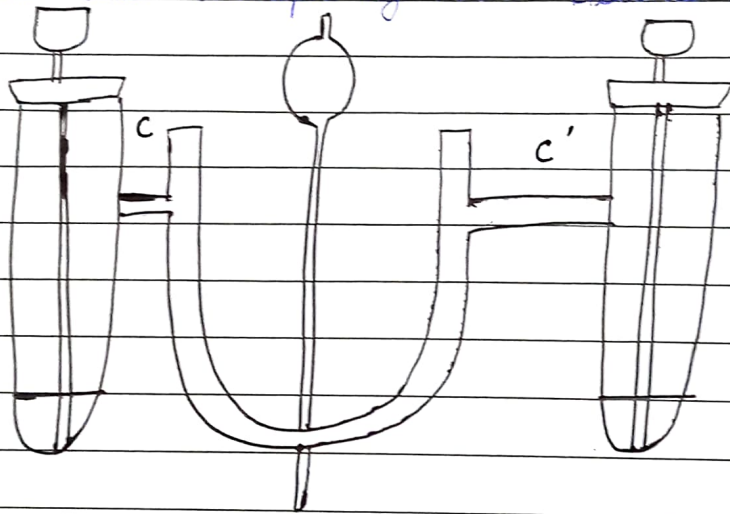
- * The e⁻ transfer from valence band to conduction band in semiconductor.
- * The charge on semiconductor creates electric field that goes into the liquid (solution) around it.
- * This field pulls the ions with different charge creating a layer of extra charge on the surface.

Garrett-Brattain model uses:-

- * The Potential Difference across the electrical double layer.
- * The Capacitance of the electrical double layer.
- * The Current-voltage characteristic of a semiconductor electrode.

Tiselius method of Separation of proteins :-

- * The Tiselius method, also known as free solution electrophoresis.
- * It is a technique used to separate the proteins based substance on their different electric charges.
- * It was developed by Arne Tiselius in ~~the~~ 1930s.



Function of this Method:-

- * In the Tiselius method, a mixture of proteins is placed in a U-shaped tube filled with an electrolyte solution.
- * An electric field is applied across the tube, causing the proteins to migrate towards the electrode with the opposite charge.
- * The proteins move at different speeds depending on their electric charge and size.

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- * As the proteins move, they form ~~distinct~~ ^{distinct} fix boundaries that can be observed visually or by measuring the refractive index of the solution.

Limitations of Tiselius method :-

- * It is a slow process compare to methods for protein detection.
- * It is difficult to scale & develop for industrial application.

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Debye-Huckel onsager equation.

This theory explains the determination of electrical Potentials of ionic atmosphere.

Mathematical expression for Debye-Huckel onsager equation is:-

Λ_c

$$\Lambda_c = \Lambda_0 - \left[\frac{82.4}{(DT)^{1/2} \eta} + \frac{8.2 \times 10^5}{(DT)^{3/2}} \Lambda^0 \right] \sqrt{C}.$$

Where

D = Dielectric Constant of water

T = Temperature in Kelvin Scale

Λ_c = Equivalent Conductance at Conc. 'C'

Λ_0 = equivalent Conductance at almost Zero Conc. or infinite dilution.

η = viscosity co-efficient of solvent.

In short form of this equation is:-

$$\Lambda_c = \Lambda_0 - b\sqrt{C}.$$

Where, b is Constant and depends on the nature of the solvent and temperature.

Application of onsager equation:-

* Determine the ionic dissociation of electrolytes.

- * Study the behavior of electrolytes of solution
- * used to study the conduction of electrolytes.

Limitations of the equation: