

* Equivalent Conductance -

Specific Conductance

- κ is suitable for metallic conductance but in the case of electrolytic conductance another quantity is much greater significance known as equivalent conductance.

It is defined as the conducting power of all the ions produced by 1 gm equivalent of an electrolyte in a given solution.

It is denoted by ' Λ '.

Unit -

$$\text{ohm}^{-1} \text{cm}^2 \quad \text{OR} \quad \Omega^{-1} \text{cm}^2$$

Equivalent conductance increases with increasing dilution.

* Relationship between Λ and κ -

Equivalent conductance is related to specific conductance by the relation -

$$\Lambda = \kappa \times \phi$$

where,

Λ = Equivalent conductance

κ = Specific conductance.

ϕ = Volume of the solution in C.Cs

Containing 1 gm equivalent of the electrolyte.

* Theory of strong electrolyte -

Various ~~theor~~ theories

were put forward ~~for~~ in the case of strong electrolyte. But the accepted theory is that of Debye and Huckel. This theory was later developed by Onsager on the basis of inter ionic concept.

* Debye Huckel Theory -

The failure of Ostwald's dilution law in case of strong electrolytes has been explained satisfactorily both qualitatively and quantitatively by Debye-Huckel (1923). This theory is based upon the following assumptions -

(1) All strong electrolytes are completely ionised in all dilutions i.e. their degree of ionisation is 100%.

(2) The ratio of $\lambda_v / \lambda_\infty$ for strong electrolytes does not represent the degree of ionization, ~~is due to~~ but it is only a conductivity ratio.

(3) The increase in conductivity (λ_v) of a strong electrolyte solution on dilution, is due to increase in the mobility of ions.

(4) The two ions present in the solution obey the Coulomb's law i.e.

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

where, Q_1 and Q_2 are the charge on the ions and r is the distance between them.

(5) Each ion is surrounded by an ionic atmosphere of oppositely charged ions. To this atmosphere, solvent molecules are then attached. Thus, a +ve ion is surrounded by -ve ions and vice versa. ~~This ionic atmosphere may be assumed to be formed as~~

* Debye - Huckel Onsager's Eqⁿ -

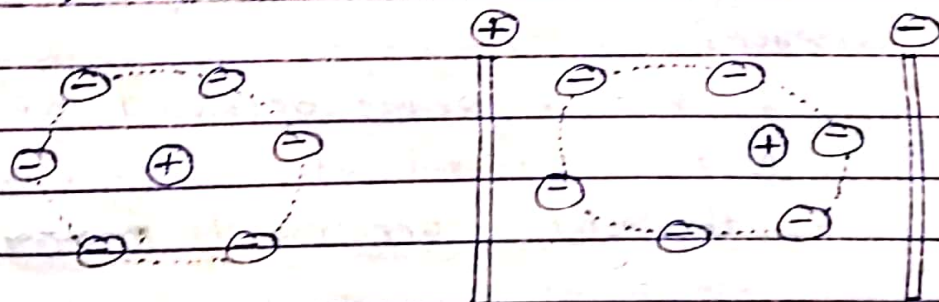
In the case of strong electrolyte ~~there~~^{following} reasons assigned for the decrease in the ionic mobility. i.e. the value of λ_v is much less than λ_{∞} .

The ~~three~~^{following} reasons are -

(1) - Relaxation effect -

Due to inter ionic forces each ion has a tendency to be surrounded by ions of opposite charge called the ionic atmosphere.

Let us suppose a -ve ion surrounded by the ionic atmosphere of +ve ions. when E.M.F. is applied, the -ve ions move towards anode where by the ionic atmosphere of +ve ions is left behind to disperse while a new ionic atmosphere is under formation in front of it. But the new ionic atmosphere is not formed at the same rate at which the old disperse and the latter takes more time called 'the relaxation time.'



Symmetric ionic atmosphere

Asymmetric ionic atmosphere.

Thus, the rate of moving ion there will be always an excess of ions of opposite sign. The ion therefore will always be dragged back. The ~~the~~ effect of decreasing the mobility of ion is known as

Relaxation effect. or Asymmetric factor.

Onsager shown that the value of relaxation force may be given by -

$$\text{Relaxation force} = \frac{\epsilon^3 \sum_i Z_i K}{6 D k T} w V.$$

where. ϵ , $\sum_i Z_i K$ and K have there usual effect.

(2). Electrophoretic Effect -

The solvent molecule attached to ionic atmosphere move in direction opposite to that of central ion. Thus they causes friction due to which, the mobility of the central ion is retarded. This effect is called Electrophoretic effect.

Debye - Huckel calculated the following expression for the electrophoretic force on an ion of i th kind -

$$\text{Electrophoretic force} = \frac{K V K_i}{6 \pi \eta} \cdot \epsilon Z_i$$

where,

η = viscosity coefficient of the medium.

K_i = Co-efficient of fractional resistance of the solvent opposing the ~~medium~~ motion of i th kind.