ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

Arrhenius (1887) put forward the theory of electrolytic dissociation, as a more explicit form of one he had proposed in 1883, which forms the basis of the modern treatment of electrolytes.

Postulates of Arrhenius theory

In aqueous solution, the molecules of an electrolyte undergo spontaneous dissociation to form positive and negative ions.

The assumption made was that when an acid, base or salt is dissolved in water, a considerable portion becomes spontaneously dissociated into positive and negative ions. The Arrhenius assumption was based on degree of ionization, so it valid on weak electrolytes (incomplete ionization) but it failure with respect to strong electrolytes (complete ionization in either strong and weak electrolytes).

The decreasing of equivalent conductance at high concentration as Arrhenius suggest belong to decreasing of degree of ionization of electrolyte. The Arrhenius interpretation concentrate about number of ions and he ignore the mobility of ions. The Arrhenius suggestion are only apply on weak electrolytes because the strong electrolytes are completely dissociate at high concentration.

Degree of ionization (α)

= Number of dissociate d molecules / Total number of moelcules of electrolyte before dissociation

At moderate concentrations, there exists an equilibrium between the ions and undissociated molecules, such as, NaOH? Na⁺ + OH⁻; KCl? K⁺ + Cl⁻

This equilibrium state is called ionic equilibrium.

Each ion behaves osmotically as a molecule.

Factors affecting degree of ionization

1- At normal dilution, value of α is nearly 1 for strong electrolytes, while it is very less than 1 for weak electrolytes.
2- Higher the dielectric constant of a solvent more is its ionizing power. Water is the most powerful ionizing solvent as its dielectric constant is highest.

3- \( \alpha \propto \frac{1}{\text{Con. of solution}} \propto \frac{1}{\text{wt.of solution}} \)

\( \propto \) Dilution of solution \( \propto \) Amount of solvent

4- Degree of ionization of an electrolyte in solution increases with rise in temperature.

5- Presence of common ion: The degree of ionization of an electrolyte decreases in the presence of a strong electrolyte having a common ion.

**Onsager Equation of Electrical Conductivity**

Debye-Hückel at 1923 later Onsagar at 1926 studied the behavior of ions in electrolytic solution. Their conclusions were: as a result of attractive forces between opposites ions, there is an aggregation around an ion by opposite ions besides to solvent molecules. Any ion is seem as a center of sphere which a rounded by opposites ions and solvent molecules. The ion in centre called **central ion** while the rounded ions and solvent molecules called **ion-atmosphere**. The net charge in ion atmosphere is equal of that for central ion but in opposite charge.

The ion atmosphere is symmetrical at normal conditions(absence of applied voltage). When the voltage is apply, there are two effects are caused:

**1-Asymmetry effect**

The passing of current in solution causes deformation of ionic atmosphere(asymmetric). The central ion move toward an electrode while the ionic atmosphere to move in reverse direction(opposite direction). which causes the charge density to be high in one terminal of ionic atmosphere(+ or -) ,thus the later similar to polar molecule which follow by electrical attraction and retardation of ionic atmosphere movement. The ionic atmosphere return to original state after short
time(symmetry). The time between asymmetry and symmetry states called "**relaxation time**". This effect causes the decreasing of equivalent force.

The asymmetric effect is represented as follows:

\[ B = 8.2 \times 10^5 \Lambda \eta / (DT)^{3/2} \]

where \( D \) is the dielectric constant, \( \eta \) is the viscosity in poises, and \( T \) is the absolute temperature (°K). The Onsager equation of electrical conductivity was derived by L. Onsager. A secondary effect arises from the fact that as an ion migrates through the solution, its counter-ion cloud does not keep up with it. Instead, new counter-ions are
2-Electrophoretic effect

The ionic atmosphere involves both solvent molecules and electrolyte ions. The movement of central ion in opposite direction of ionic atmosphere causes withdrawing of solvent molecules in reverse movement of central ion atmosphere. A new retardation force of central ion is rise as a result of friction between central ion and solvent molecules. This force called *electrophoretic effect* which causes decreasing of equivalent conductance. The electrophoretic effect represents as following:

\[ A = \frac{82.4}{(DT)^{1/2}} \eta \]

where \( D \) is the dielectric constant, \( \eta \) is the viscosity in poises, and \( T \) is the absolute temperature (°K).
The Onsager equation of electrical conductivity assumes the form

\[ \Lambda = \Lambda_0 - (A + B \Lambda_0)C^{1/2} \]

And

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

Here \( \Lambda \) is the equivalent electrical conductivity, \( \Lambda_0 \) is the equivalent electrical conductivity for infinite dilution, \( C \) is the concentration in moles per liter, and