# Electrochemistry

(1)

Arrhenius theory of electrolytic dissociation :—

In 1887, a Sweedish Physicist S. Arrhenius gave a theory of electrolytic dissociation. The main postulates of ~~of~~ the ~~theory~~ theory are :—

① The molecules of an electrolyte (acids, bases, salts) in solution break up into two types of charged particles, called ions. The ions carrying positive charge are called cations. and the ions carrying negative charge are called anions.

⑪ The total charge carried by the cations are equal to the total charge carried by the anions, so that the solution is electrically neutral.

(iii) The ions are constantly ~~reunite~~ reuniting to form undisso-ciated or unionised molecule until an equilibrium is ~~formed~~. attained.
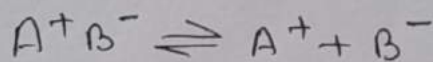
$$A^+B^- \rightleftharpoons A^+ + B^-$$

According to the law of chemical equilibrium.

$$K = \frac{[A^+][B^-]}{[A^+B^-]}$$

~~(b) The~~

(iv) The ions which are free to move are under the influence of electricity (electric field) and they are directed towards oppositely charged electrodes. Thus the (+) vely charged ions (cations) will move towards the negative electrode ~~(anode)~~ and negatively charged ions (anions)

will move towards positive electrodes. There The substances only. which can ionise in solution can conduct electricity. (They are called electrolytes.)

(V) The electrolytes having high degree of dissociation (or ionization) are called strong electrolytes, whereas the substances with low degree of dissociations are called weak electrolytes.

(VI) The properties of electrolytes are the properties of their ions. e.g the properties of acids and bases are the properties of H^+ or OH^- ions respectively.

(VII) These ions act like molecules The ions produced by the dissociation of an electrolyte behave like molecules towards Colligative properties. e.g. each NaCl molecule dissociates to give two ions viz. Na^+ and Cl^-. Hence the observed value of any Colligative property is double the expected value.

Limitations of Arrhenius Theory :—

Arrhenius theory suffers from some limitations. These are

(i) Arrhenius suggested that ionization of the electrolyte takes place when dissolved in water. However, X-ray studies have shown that many such electrolytes are already in the ionized state (e.g $Na^+ Cl^-$)

(ii) As an electrolyte can conduct electricity even in the molten state. ie the dissociation takes place even in the molten state. As such the function of water could not be explained by Arrhenius theory.

(iii) The Arrhenius theory fails to explain the behaviour of strong electrolytes, e.g.

(a) Ostwald's dilution law which is derived on the basis of Arrhenius theory, using the concept of ionic equilibrium, fails for the strong electrolytes, i.e a constant value of the dissociation constant K is not obtained.

(b) The degree of dissociation (α) of strong electrolytes calculated from conductance measurements $\left(\alpha = \lambda_c/\lambda_0\right)$ was found to be different from that calculated from colligative properties.

$\left[\text{Here } \lambda_c = \text{Equivalent conductance at concentration } c \atop \lambda_0 = \text{equivalent conductance at infinite dilution}\right]$.

(c) Strong electrolytes are completely dissociated even at moderate concentration., i.e $\alpha = 1$, at all concentrations. Hence Arrhenius view that conductance increases with dilution because the dissociation increases is not valid in case of strong electrolyte. The increase in conductance with dilution is, therefore, due to some other factors.

~~Equivalent and molar conductivity~~

Conductivity, equivalent and molar Conductivity :—

Conductivity is the measure of the ease at which an electric charge can pass through a material, or reciproca resistivity is called conductivity.

From ohm's law.
$$I = E/R.$$

I = Electric current (in ampere)
E = Potential difference (in volt)
R = Resistance (in ohms).

The resistance of any conductor varies directly as th length of the conductor (l) and inversely proportional a its area of cross section (a).

$R \propto l$; $R \propto \dfrac{1}{a}$

or $R \propto \dfrac{l}{a}$ $R = \rho \dfrac{l}{a}$ → eqⁿ No ① $\left[l/a = \text{Cell constant}\right]$

~~l = length of~~

When $l = 1cm$ and $a = 1, sq$ cm, then.

$$R = \rho$$

ρ is called the specific resistance or the resistivity of the

The reciprocal of resistivity is called the called the conductivity (specific conductance). It is denoted by χ (kapp

$$\chi = \frac{1}{\rho}.$$

From equation ①

$$R = \rho \frac{l}{a}.$$

$$\rho = R \times \frac{a}{l}$$

$$\frac{1}{\rho} = \frac{1}{R} \times \frac{l}{a}$$

$$K = \text{Conductance} \times \text{Cell constant}.$$

The unit of conductivity is $ohm^{-1} cm^{-1}$ or $S cm^{-1}$ ($S = $ Siemen

The SI unit of conductivity is $ohm^{-1} cm^{-1}$ or $\Omega^{-1} m^{-1}$ or $S m^{-1}$.

In case of an electrolyte the resistivity can be defined the resistance offered to of the electrolyte. all the ions present in 1 cm cu of solution or present in 1 ml of solution.

Equivalent Conductance :- Equivalent conductance is defined as the conducting power of all the ions produced by one gram equivalent of an electrolyte in a given solution.

or

Equivalent conductance is defined as the conductan of an electrolyte solution containing one gram equivalent of the electrolyte. It is denoted by Λ_{eq}.

$$\Lambda_{eq} = \chi \times V \rightarrow ①$$

Here $K = $ Specific conductance
$V = $ vol^m that contains one gm equivalent of the electrolyte.