Electrochemistry

Electrochemistry is a branch of chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reactions - i.e how chemical energy produced in a redox reaction can be converted into electrical energy or how electrical energy can be used to bring about a redox reaction which is otherwise non-spontaneous.

(B) **Conductance**

The ease with which electricity flow through a solution is called conductance (C) of the solution. It is defined as the reciprocal of the resistance (R) of the solution.

i.e. $C = \frac{1}{R}$

It is expressed in unit ohm^{-1} (or Ω^{-1}). In S.I system the unit of conductance is siemen (S).

Specific conductance (K)

The resistance of any conductor varies directly as its length (l) and inversely as its cross-sectional area (a)

i.e $R \propto l$

and $R \propto \frac{1}{a}$

So, $R \propto \frac{l}{a}$

or $R = \rho \frac{l}{a}$ ——— ①

where ρ is a constant depending upon the nature of the material and is called specific resistance of material.

If $l = 1m$ and $a = 1m^2$

$R = \rho \times \frac{1}{1^2}$

$\rho = R$

Thus specific resistance is defined as resistance of a specimen 1 m in length and $1 m^2$ cross-sectional area. In other word, it is the resistence of one metre of one metre cube of the material.

The reciprocal of specific resistance is called specific conductance. It is denoted by K, i.e.

$$K = \frac{1}{\rho} \quad \text{——— (2)}$$

From equation (1) $\rho = \frac{a}{l} R$

putting the value of ρ in equation (2) we get-

$$K = \frac{1}{\frac{a}{l} R} = \frac{l}{a} \cdot \frac{1}{R}$$

$$\boxed{K = \frac{l}{a} \cdot \frac{1}{R}}$$

or. $\boxed{K = \frac{l}{a} \times C}$ { C = conductance, R = Resistance }

$$\therefore K = \frac{l}{a} \times C$$

S.I. unit of $K = \frac{m}{m^2} \times S = S\,m^{-1}$

Equivalent Conductance (Λ_E)

The conductivity power of all the ions produced by one gram equivalent of an electrolyte in a given solution is called equivalent conductance (Λ_E).

$$\Lambda_E = K \times \frac{1000}{C}$$

where K = specific conductance

C = concentration of solution which contains one gram equivalent of electrolyte dissolved per litre of the solution i.e. Normality of solution.

Relation between equivalent conductance and specific conductance

The equivalent conductance of an electrolyte solution is not found directly and it is expressed in terms of specific conductance. In order to co-relate the equivalent conductance and specific conductance, we consider a rectangular metallic vessel with two opposite sides exactly 1 cm apart. If now 1 c.c solution is placed in this vessel, the area of opposite faces of the cube covered by solution will be 1 sq. cm. The measured conductance of the solution will be its specific conductance. If 1 c.c of the solution is placed in the above vessel containing 1 gram equivalent of electrolyte then by definition, then by definition, the measured conductance will also be equal to the equivalent conductance.

$$\Lambda_E = K$$

Now, if 9 c.c of pure solvent are added so that the total volume occupied by solution is 10 c.c, the measured conductance is still equivalent conductance because 10 c.c of diluted solution still contains 1 gram equivalent of the electrolyte. But by definition of the specific conductance, the measured conductance of the diluted solution will be ten times of the specific conductance.

Thus, $$\Lambda_E = K \times 10$$

Similarly if solution is diluted 100 times its volume, the measured conductance still be equivalent conductance but will be 100 times the specific conductance.

$$\Lambda_E = K \times 100$$

In general if the solution contains one gram equivalent of electrolyte dissolved in V c.c of the solution, then,

$$\Lambda_E = K \times V$$

If c gram equivalent of electrolytes are dissolved per $1000 cm^3$ of solution, then volume of the solution containing one gram equivalent of electrolyte will be 1000/c. Thus,

$$\boxed{\Lambda_E = K \times V = K \times \frac{1000}{c}}$$

Here concentration of solution in normality

unit of equivalent conductance (Λ_E)

$$\Lambda_E = K \times \frac{1000}{C}$$

unit of Λ_E = $ohm^{-1}\ cm^{-1} \times \frac{cm^3}{g\text{-}equiv} = ohm^{-1}\ cm^2\ g\text{-}equiv^{-1}$.

$= S\ m^2\ g\text{-}equiv^{-1}$ (S.I unit).

Molar conductance (Λ_m)

The conductivity power of all the ions produced by one mole of electrolyte in a given solution is known as molar conductance. It is denoted by Λ_m.

$$\Lambda_m = K \times \frac{1000}{C}$$

c = concentration of solution in molarity

K = specific conductance.

unit of Λ_m

$$\Lambda_m = K \times \frac{1000}{C}$$

unit of Λ_m = $ohm^{-1}\ cm^{-1}\ \frac{cm^3}{mol} = ohm^{-1}\ cm^2\ mol^{-1}$

$= S\ m^2\ mol^{-1}$ (S.I unit).

Effect of dilution on specific conductance and molar conductance (or equivalent conductance)

The conductance of solution is due to the presence of ions in solution. Since, on dilution the degree of dissociation of electrolyte is increased and more and more ions are produced in solution.

Molar conductance of an electrolyte increase with increase in dilution. This is attributed to increase in degree of dissociation of the electrolyte. Since increase in the number of ions on dilution of solution is much less than increase in volume of solution. Therefore, the number of ions per unit volume (e.g. per c.c) decreases. Thus, specific conductance decreases on dilution of solution but equivalent conductance or molar conductance increases with dilution of solution.

Q1 Specific conductance of a decimolar solution of potassium chloride at 18°C is 1.12 $S\,m^{-1}$. The resistance of a conductivity cell containing the solution at 18°C was found to be 55 ohm. What is the cell constant?

Ans — 61.6 m^{-1}

Q The resistance of 0.01 M solution of an electrolyte was found to be 210 ohm at 25°C. Calculate the molar conductance of solution at 25°C. Cell constant = 0.88 cm^{-1}

Ans.