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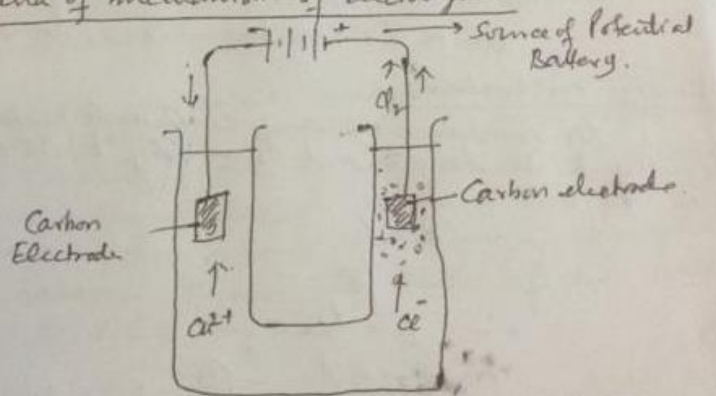
Electrolytic Conductance

A substance which allows an electric current to flow through it is called conductor while the one which does not allow any electric current to flow through is called an insulator.

Metallic Conduction	Electrolytic conduction.
Metals are the best conductors	
1 It occurs due to flow of electrons.	1. It occurs due to movement of ions in solution or a fused electrolyte.
2. No change in the chemical properties of the conductors occurs.	2. It involves chemical reaction which takes place at electrodes.
3. It does not involve the transfer of any matter.	3. It involves transfer of matter in the form of ions.
4. It shows an increase in resistance as temperature is increased.	4. It shows a decrease in resistance as the temperature is increased.

Phenomena of mechanism of electrolysis.



Electrolytic cell : electrolysis of $CuCl_2$

Cathode

Reduction of ions, complexes or molecules to lower oxidation state
Deposition of metals on the electrode after the discharge.

Anode.

Oxidation of ions, complexes or molecules to species in a higher oxidation state.
Ionization of the electrode material to form soluble ions or complexes.

Electrolytic conductance.

Conductance. When current is passed through a solution of an electrolytic conductor, the current flows through it is proportional to the applied ~~conductor~~, potential difference E.

Acording to ohm's law

$$I = \frac{E}{R} \quad -①$$

I = current in ampere
R = Resistance in ohm

However, instead of resistance the terms conductance (L) is used in electrochemistry. It is reciprocal of electrical ~~con~~ resistance.

$$L = \frac{1}{R} \quad -②.$$

It is expressed in ohm^{-1} denoted as Ω^{-1} (Omega inverse). Units of conductance is S (Siemen) Ω^{-1} is S.

Specific conductance.

The resistance of any conductor is proportional directly to its length and inversely to its cross-sectional area i.e.

$$R \propto l.$$

$$\propto \frac{1}{a}.$$

$$\therefore R \propto l/a$$

$$\text{or } R = \rho \frac{l}{a} \quad -③$$

When ρ (rho) is the constant of proportionality and is called resistivity or specific resistance.

The reciprocal of specific resistance i.e. $1/\rho$ is called specific conductance.

$$k = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{a}. \quad -④$$

$$= \frac{l}{a} \times \text{conductance}$$

$$\text{or } k = \frac{l}{a} \times L$$

$l = 1cm$ $\quad a = 1cm^2$ $\quad k = L$

Thus the specific conductance may be defined as the conductance of a solution in cell in which the electrodes are a unit distance apart and have unit area.

Unit

$$k = \frac{1}{a} \times L$$

$$= \frac{\text{meter}}{\text{meter}^2} \times \text{Siemen}$$

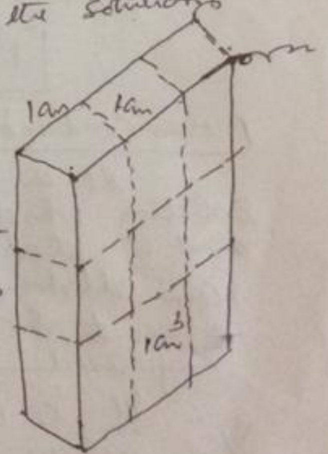
$$K = Sm^{-1} \quad (\text{SI unit})$$

$$K = ohm^{-1} cm^{-1} \quad (\text{CGS})$$

Equivalent conductance

Although the specific conductance is a property of the conducting medium in dealing with solutions of electrolyte a quantity of greater significance is the equivalent conductance.

The equivalent conductance of an electrolyte is defined as the conductance of a volume of solution containing one g equivalent of dissolved substance when placed between two parallel electrodes 1 cm apart and large enough to contain between them the whole of the solution. This is denoted by λ.



To understand the meaning of the equivalent conductance imagine a rectangular container with two opposite sides made of a metallic conductor and forming electrodes exactly 1 cm apart. Consider 1cm³ solution containing 1 g equivalent of an electrolyte is placed in the container.

According to definition

Specific conductivity (k) = Conductance of 1cm³ of solution containing 1gm equivalent of electrolyte.

If the solution is diluted to say 9 cm³, the conductance of the solution will be nine times the specific conductance as there will be now nine cubes. But even now, solution contains 1g equivalent of the electrolyte between the electrodes, the conductance measured will be equivalent conductance.

$$\lambda = 9 \times k$$

Hence in general

$$\lambda = V \times k$$ where V = volume of the solution containing 1g equivalent of the electrolyte.

If c is the concentration in g equivalent / l, then the concentration per cm³ is c/1000, and the volume containing one equivalent of the solute is 1000/c.

$$\therefore \quad \lambda = \frac{1000k}{c} \quad \text{---} \ (5)$$

unit

$$\lambda = \frac{k\,(S cm^{-1})}{c\,(eq\ cm^{-3})}$$

$$= S\ cm^2\ eq^{-1} \ (CGS)$$

In SI system the unit is $S\ m^2\ eq^{-1}$

$$\boxed{1\ S m^2 eq^{-1} = 10^4\ S\ cm^2\ eq^{-1}}$$

Molar Conductance.

It is the conductance of that volume of solution which contains one mole of the solute and is placed between two parallel electrodes of 1cm distance apart and having sufficient area to hold whole of the solution. It is represented by λ.

If c is the concentration in moles/litre, the molar conductivity Λ is

$$\Lambda = \frac{1000k}{c}$$

unit

$$\lambda = \frac{1000k}{c} = \frac{(S cm^{-1}) \times cm^3 \times 1000}{mol}$$

$$= S cm^2 mol^{-1} \ (CGS)$$

$= 10^4 \times S\,m^2\,mol^{-1}$ (SI)

Relation between equivalent conductance and molar conductance.

$$\text{Equivalent conductance} = \frac{\text{Molar Conductance}}{\text{Number of individual charge that are being carried}}$$

$$\lambda = \frac{\Lambda}{z}$$

Thus in a solution of NaCl, each ion carries a unit charge in each direction $z = 1$. Therefore, the equivalent conductance of NaCl is the same as its molar conductance. In $MgSO_4$ on the other hand, each ion transports two units charge,

$$\lambda_{MgSO_4} = \frac{\Lambda_{MgSO_4}}{2}.$$