Conductance

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It is the reciprocal of the resistance of the electrolytic solution and is defined as the current flowing through it when the applied potential difference is 1V.

If R is the electrical resistance offered by an electrolytic solution, V is the voltage applied and I is the current.

Conductance $= \dfrac{1}{\text{Resistance}}$ or $C = \dfrac{1}{R}$

Unit of conductance is inverse to ohm it represent as mho.

Then A/c Ohm's law

$V \propto I$

$V = IR$

$R = \dfrac{V}{I}$

Conductance $= \dfrac{1}{R} = \dfrac{I}{V} =$ Seimen (Ohm^{-1})

Conductor: Substances which allow electric current to flow through them are called conductors.

Examples- Metals, Aqueous solution of acids, bases and salts, fused salts and impure water etc.

Conductors are of two types:
   (i) Metallic conductors
   (ii) Electrolytic conductors or electrolytes.

   (i) Metallic conductors: The conductors which conduct electric current by movement of electrons without undergoing any chemical change are known as metallic conductors.
   Metals (Cu, Ag, Fe, Al etc), non metals (graphite) and various alloys and minerals are examples.

   (ii) Electrolytic conductors: Those substances whose water solution conducts the electric current and which are decomposed by the passage of current are called electrolytes. In this case, conduction takes place by movement of ions. Electrolytes also conduct electricity in fused state and undergo decomposition by passage the electric current.
   Substances whose aqueous solution does not conduct electric current are called non-electrolytes.
   They do not conduct electricity in the fused state. Solutions of cane sugar, glycerine, glucose, urea etc. are the examples of non electrolytes.

Strong electrolyte: Electrolytes which are completely ionized in aqueous solution or in their molten state; are called strong electrolyte.

Example- All salts, strong acid and strong base.

Weak electrolyte: Electrolytes which are not completely ionized in aqueous solution or in their molten state; are called weak electrolytes.

Examples: All carbonic acids (except sulphonic acid), CH_3COOH, HCN, NH_3, amine, etc.

Factors affecting electrolytic conduction:

(i) Nature of the electrolyte: The conductance of solution is depend on nature of electrolyte. Generally strong electrolyte ionized almost completely in the solution and hence conduct electricity to a large extend whereas weak electrolytes ionized to small extent.

(ii) Concentration of the solution: The conductance of solution increase with increase the dilution.

(iii) Temperature: Conductances increase with the increase the temperature because the all attraction force will be decrease.

(iv) Degree of ionization: Conductance of the solution increase with increase the degree of ionization.

(v) Interionic attractions: Mobility of ion decrease with increase the interionic attractions so conductance of electrolyte decrease.

(vi) Viscosity: Mobility of ion decreases with increase the viscosity so conductance of electrolyte decrease.

(vii) Solvation of ions: Movability of ion decrease with increase the solvation so conductance of electrolyte decrease.

- **Specific Conductance (simple called Conductivity)** $[\kappa]$:

The conductance of an electrolytic solution is directly proportional to the area of the electrodes (A) and inversely proportional to the distance (l) between the electrodes.

Conductance $\propto \frac{A}{l}$

Conductance = $K\frac{A}{l}$, **Where k → Specific conductance or conductivity.**

In short: Conductance of 1 cm^3 of the solution of the electrolyte.

Definition:- It is defined as the conductance of an electrolytic solution between two parallel electrodes each having an area of 1 sq. cm and separated by a distance of 1 cm.

The basic SI unit of conductivity

    → Seimen m^{-1} (SM^{-1})

    → Seimen cm^{-1} (scm^{-1})

(i)   Resistivity (ρ) = $R\frac{a}{l}$ = ohm$\frac{cm^2}{cm}$ = ohm cm or Ω cm.

(ii)   Specific conductance (κ) = $\frac{1}{\rho}$ = $\frac{1}{ohm\ cm}$ = ohm^{-1}cm^{-1} = Ω^{-1}cm^{-1} or S cm^{-1}

Equivalent Conductivity (Λ_{eq}):

   If one equivalent of electrolyte is dissolved in a solution, and the conductivity of two parallel electrode situated at 1 cm distance, is called equivalent conductivity. It is represented by Λ_{eq}.

$\Lambda_{eq} = \kappa \times V$

Where, κ = specific conductivity, V = volume of the solution in which 1 gm equivalent of the solute is dissolved. (V = 1/C)

$\Lambda_{eq} = \dfrac{1000K}{N}$ Where, N = Normality of solution.

Units of equivalent conductivity: cm^2 ohm^{-1} $equivalent^{-1}$

Molar Conductivity : (Λ_m)

   If one mole of an electrolyte is dissolved in a solution, than the conductivity of that solution between two parallel electrodes situated at 1 cm distance, is called molar conductivity. It is represented by (Λ_m)

   Mathematically, $\Lambda_m = \kappa \times V$ $\Lambda_m = \dfrac{1000K}{M}$

       Where M $\longrightarrow$ Conc. of the solution in mol/lit

   Unit = cm^2 $mole^{-1}$ ohm^{-1}

Cell constant:

   It is the distances between the two electrodes divided by area of the electrode.

G* $= \dfrac{l}{A} = R\kappa$

       Conductivity $=$ cell constant $\times$ conductance

Variation of Conductivity with concentration

   The conductivity of an electrolytic solution depends upon the following factors:

(1) Concentrations of ions.
(2) Speed of the ions (ionic mobility)
(3) Inter-ionic attraction or viscosity of the solvent.

   In general, greater the no. of ions in solution greater the electrical conductivity of the solution. But this is not always the case:

(1) For a strong electrolyte; the greater inter-ionic attraction at higher concentration retards the motion of ions and therefore conductivity decreases. By dilution the ions are far apart and therefore the inter-ionic attraction decreases due to which the conductivity increases.

- For strong electrolytes Λ increases slowly with dilution and can be represented by the equation
$$\Lambda_m = \Lambda_m^0 - AC^{1/2}$$
- The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte i.e charges on the cations and anion produced on the dissociation of the electrolyte in the solution.
  Example
  Thus $NaCl$, $CaCl_2$, $MgSO_4$ are known as 1-1, 2-1 and 2-2 electrolyte respectively.
(2) For a weak electrolyte; the degree of dissociation decreases with increase in concentration and therefore the conductivity of the solution also decreases.

  With dilution the equilibrium shifts to right and more ions are formed which results in an increase in conductivity. The dissociation of the weak electrolyte is complete at infinite dilution and the solution has maximum conductivity (e.g. Ammonium hydroxide, acetic acid)

(3) Degree of dissociation of a weak electrolyte $= \dfrac{\text{Conductivity at concentration,C}}{\text{Concductivity at infinite dilution}}$

$$\alpha = \frac{\lambda}{\lambda_0} = \frac{\text{Moles ionized}}{\text{Total moles}}$$

Kohlraush's Law of independent migration of ions:

The law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte. Thus, if $\lambda^{\circ}_{Na^+}$ and $\lambda^{\circ}_{Cl^-}$ are limiting molar conductivity of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:

$$\Lambda^0_{m(NaCl)} = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Cl^-}$$

In general, if an electrolyte on dissociation gives v_+ cations and v_- anions then its limiting molar conductivity is given by:

$$\Lambda^0_{m(NaCl)} = v_+\lambda^{\circ}_+ + v_-\lambda^{\circ}_-$$

Here, λ°_+ and λ°_- are the limiting molar conductivities of the cation and anion respectively.

The law is valid at any dilution but applied only at infinite dilution.

Uses of Kohlrausch's Law:

1. **Calculation of molar conductivity at infinite dilution for weak electrolytes:**

   As already mentioned, the molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally, firstly because the conductance of such a solution is low and secondly because the dissociation of such an electrolyte is not complete even at very high dilutions. The molar conductivity of such an electrolyte at infinite dilution can be calculated using Kohlrausch's law.

   Ex. $\lambda^{\circ}(CH_3COOH) = ? = \lambda^0_{CH_3COO^-} + \lambda^0_{H^+}$ ....(4)

Strong electrolyte

$$\lambda^\circ(CH_3COOK) = \lambda^0_{CH_3COO^-} + \lambda^0_{K^+} \qquad ....(a)$$

$$\lambda^\circ(HCl) = \lambda^0_{H^+} + \lambda^0_{Cl^-} \qquad ....(b)$$

$$\lambda^\circ(KCl) = \lambda^0_{K^+} + \lambda^0_{Cl^-} \qquad ....(3)$$

$$eq^n(a) + eq^n(b) - eq^n(3) = eq^n \qquad ....(4)$$

$$\lambda^\infty_{(CH_3COOK)} + \lambda^\infty_{(HCl)} - \lambda^\infty_{(KCl)} - \lambda^\infty_{(CH_3COOH)}$$

Ionic Mobility:

Ionic mobility of an ion is defined as its absolute velocity under a potential gradient 1 Vcm^{-1}

* Ionic Conductance:

Ionic Conductance of an ion is defined as the contribution made by it towards the equivalent conductance of the electrolyte at infinite dilution.

These are represented by λ_c & λ_a

$$\Rightarrow \lambda_\infty = \lambda_c + \lambda_a$$

$$\text{Where, } \lambda_c = \lambda_\infty - \lambda_a$$

$$\lambda_a = \lambda_\infty - \lambda_c$$

Faraday's Law of Electrolytes:

$$1 \text{ Mole} = 6.022 \times 10^{23} \text{ electron}$$

$$= 6.022 \times 10^{23} \times 1.6 \times 10^{-19} C$$

$$= 96487 \text{ C}$$

$$= 96500 \text{ C}$$

$$= 1 \text{ F}$$

1ˢᵗ Law:

This law states that the mass of a substance produced or consumed at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte.

Mathematically,

$$W \propto Q \qquad\qquad I = \frac{Q}{t}$$

Or, $\quad W \propto It$

Or, $\quad W = ZIt$

Where W $\rightarrow$ Mass of the substances produced or consumed at an electrode.

Q $\rightarrow$ quantity of charge passed

I $\rightarrow$ Current in ampere

t $\rightarrow$ Time in seonds

And Z $\rightarrow$ proportionality constant called electrochemical equivalent.

When t = 1 second and I = 1 ampere.

W = Z x 1 x 1

W = Z grams

∴ Electrochemical equivalent is defined as the mass of a substance produced or consumed by passing an electric current of 1 ampere through the electrolyte for 1 sec.

Electro-chemical equivalent(Z) = $\dfrac{equivalent\ wt.of\ element}{96500}$

Faraday Second Law of electrolysis:

It states that when same quantity of electricity passed through different electrolytes connected in series produces weight of the substances at respective cathodes that are proportional to their equivalent masses.

When same quantity of electricity is passed through two electrolytes then,

$$\frac{\text{Equivalent mass of A}}{\text{Equivalent mass of B}} = \frac{\text{Mass of A deposited}}{\text{Mass of B deposited}} \quad \text{or}$$

$$= \frac{W_A}{W_B} = \frac{E_A}{E_B}$$

$$\frac{\text{Equivalent mass of A}}{\text{Equivalent mass of B}} = \frac{\text{Electrochemical equivalent of A}}{\text{Electrochemical equivalent of B}}$$