TOPICS

- Conductance of electrolytic solution
- Specific conductance, Equivalent conductance, Molar conductance
- Kohlrausch's law

Electrolytes

- Substances whose solution in water conducts electric current.
- Conduction takes place by the movement of ions.
- Examples are salts, acids and bases.

- Substances whose aqueous solution does not conduct electricity are called **non electrolytes.**
- Examples are solutions of cane sugar, glucose, urea etc.

Types of Electrolytes:

- Strong electrolyte are highly ionized in the solution.

➢ Examples are HCl, H_2SO_4, NaOH, KOH etc

- Weak electrolytes are only feebly ionized in the solution.

➢ Examples are H_2CO_3, CH_3COOH, NH_4OH etc

Specific Conductivity

Conductivity (or **specific conductance**) of an electrolyte solution is a **measure** of its ability to conduct electricity.

Specific conductance, $\kappa = \frac{1}{\rho}$

But $\rho = \frac{a}{\ell}R$

$\therefore K = \frac{\ell}{a.R}$

$K = \left(\frac{\ell}{a}\right)$ x Conductance

l/a is known as cell constant

The SI unit of Specific Conductance is Sm^{-1}

Molar Conductance

- It is defined as the conducting power of all the ions produced by 1 mole of an electrolyte in the given solution.
- It is represented as **μ**.

$$\mu = K \times V$$

K= specific conduction of the solution

V= volume in cc containing 1mole of the electrolyte

If M is the molarity of the solution then-

$$\mu = K \times 1000/M$$

- SI unit is Siemen metre square per mol.

Equivalent Conductance

- It is defined as the conducting power of all the ions produced by 1 gram of an electrolyte in the given solution.
- Equivalent conductance is represented by λ

Mathematically, $\lambda = k \times V$

K= specific conduction of the solution

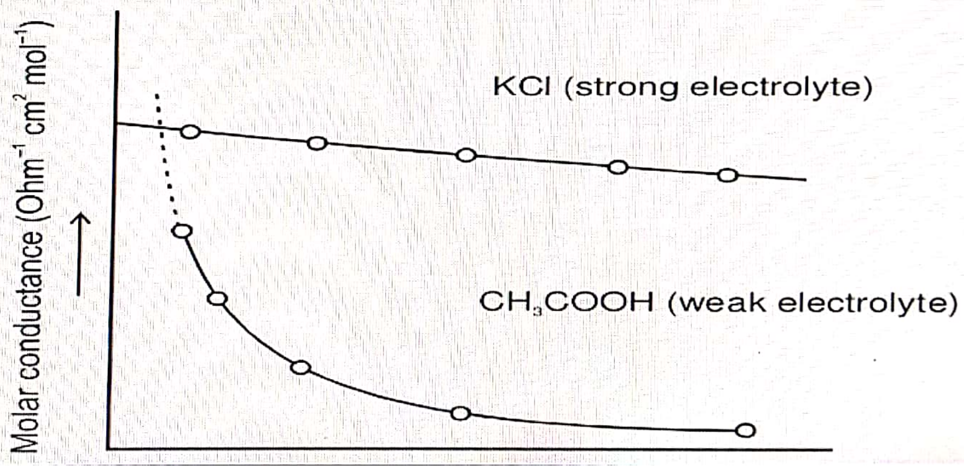
V= volume in cc containing 1 gram equivalent of the electrolyte

If N is the normality then-

$$\lambda = k \times \frac{1000}{Normality}$$

Effect of Dilution on Conductivity

- Specific conductivity decreases on dilution.
- Equivalent and molar conductance both increase with dilution and reaches a maximum value.
- The conductance of all electrolytes increases with temperature



Relation between equivalent conductivity and molar conductivity

$$\mu = \text{valency factor(or n - factor)} \times \lambda$$

i.e.

Molar conductivity = n- factor x equivalent conductivity

Kohlrausch's Law

"Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte."

$$\lambda_{\infty} = \lambda_a + \lambda_c$$

Where λ_a and λ_c are known as ionic conductance of anion and cation at infinite dilution respectively.

Kohlrausch's Law

Statement: "At time infinite dilution, the molar conductance of an electrolyte can be expressed as the sum of the contributions from its individual ions"

i.e. $\Lambda^{\infty}_{m} = v_{+}\lambda^{\infty}_{+} + v_{-}\lambda^{\infty}_{-}$

where, v_{+} and v_{-} are the number of cations and anions per formula unit of electrolyte respectively and, λ^{∞}_{+} and λ^{∞}_{-} are the molar conductivities of the cation and anion at infinite dilution respectively.

For e.g. The molar conductivity of HCl at infinite dilution can be expressed as,

$\Lambda^{\infty}_{HCl} = v_{H^+}\lambda^{\infty}_{H^+} + v_{Cl-}\lambda^{\infty}_{Cl-}$; For HCl, $v_{H^+} = 1$ and $v_{Cl-} = 1$.

So, $\Lambda^{\infty}_{HCl} = (1 \times \lambda^{\infty}_{H+}) + (1 \times \lambda^{\infty}_{H-})$; Hence,

$$\Lambda^{\infty}_{HCl} = \lambda^{\infty}_{H+} + \lambda^{\infty}_{Cl-}$$

Kohlrausch's law of independent migration of ions

- High accuracy in dilute solutions, molar conductivity is composed of individual contributions of ions.
- Limiting conductivity of anions and cations are additive, the conductivity of a solution of a salt is equal to the sum of conductivity contributions from the cation and anion

$$\Lambda^0_m = v_+ \Lambda^0_+ + v_- \Lambda^0_-$$

Applications of Kohlrausch's law

- **Determination of Λ^{∞}_{m} for weak electrolytes:**

  The molar conductivity of a weak electrolyte at infinite dilution (Λ^{∞}_{m}) cannot be determined by extrapolation method. However, Λ^{∞}_{m} values for weak electrolytes can be determined by using the Kohlrausch's equation.

  $$\Lambda^{\infty}_{CH3COOH} = \Lambda^{\infty}_{CH3COONa} + \Lambda^{\infty}_{HCl} - \Lambda^{\infty}_{NaCl}$$

- **Determination of the degree of ionization of a weak electrolyte:**

  The Kohlrausch's law can be used for determining the degree of ionization of a weak electrolyte at any concentration. If λ^{c}_{m} is the molar conductivity of a weak electrolyte at any concentration C and, λ^{c}_{m} is the molar conductivity of a electrolyte at infinite dilution. Then, the degree of ionization is given by, $\alpha = \Lambda^{c}_{m} = \Lambda^{\infty}_{m} = \Lambda^{c}_{m}/(v_{+}\lambda^{\infty}_{+} + v_{-}\lambda^{\infty}_{-})$

Thus, knowing the value of Λ^{c}_{m}, and Λ^{∞}_{m} (From the Kohlrausch's equation), the degree of ionization at any concentration can be determined.