The ratio of equivalent conductance at dilution V (λ_V) to the equivalent conductance at infinite dilution (λ_∞) gives the degree of dissociation, *i.e.*,

$$\alpha = \frac{\lambda_V}{\lambda_\infty} = \frac{\lambda_C}{\lambda_0}$$

CLASSIFICATION OF ELECTROLYTES

- Electrolytes have been classified into two types on the basis of their conductance.
  - **Strong electrolytes :** Those electrolytes which possess a high value of equivalent conductance even at high concentrations (*i.e.*, when the dilution is not very large) and whose equivalent conductance increases gradually with dilution and then becomes constant are called strong electrolytes. Examples are mineral acids (HCl, H_2SO_4, HNO_3), alkalies (NaOH, KOH), alkaline earth metal hydroxides [*e.g.*, $Ca(OH)_2$, $Ba(OH)_2$], and salts (*i.e.*, NaCl, KCl, etc.).
  - **Weak electrolytes :** Those electrolytes which possess a low value of equivalent conductance at ordinary concentration and whose equivalent conductance increases rapidly with dilution but does not approach a constant value are called weak electrolytes. Examples are organic acids (*e.g.*, CH_3COOH) and weak bases (*e.g.*, NH_4OH).

KOHLRAUSCH'S LAW

Kohlrausch's Law of Independent Migration of Ions

- According to this law "the equivalent conductance of an electrolyte at infinite dilution is the sum of two values, one depending upon the cation and the other upon the anion."

  Mathematically, $\lambda_\infty = \lambda_c + \lambda_a$

  Where, λ_c and λ_a are the equivalent conductivities (ionic conductances) of the cation and anion respectively. The law is valid at any dilution but is applied only at infinite dilution.

Ionic Conductance and Ionic Mobility

- **Ionic mobility** of an ion is defined as its absolute velocity (*i.e.* the distance travelled in cm/sec) under a potential gradient of one volt per cm.

  $\lambda_c \propto u_c$ and $\lambda_a \propto u_a$

  or $\lambda_c = ku_c$ and $\lambda_a = ku_a$

  where, u_c and u_a are the ionic mobilities of the cation and anion respectively and k is a proportionality constant.

  Ionic conductance is expressed in $ohm^{-1}\ cm^2$ while ionic mobility is expressed in cm^{-1}.

Applications of Kohlraush's law

- This law is useful
  - **In the calculation of molar conductivity at infinite dilution ($\Lambda°$) for weak electrolytes *e.g.***

    $\Lambda°_{CH_3COOH} = \Lambda°_{CH_3COONa} + \Lambda°_{HCl} - \Lambda°_{NaCl}$
  - **In the calculation of degree of dissociation of weak electrolyte *i.e.***

    As explained earlier that the degree of dissociation of a weak electrolytes at dilution V may be given as

$$\alpha = \frac{\Lambda°_V}{\Lambda°_\infty} = \frac{\text{Equivalent conductivity at dilution } V}{\text{Equivalent conductivity at infinite dilution}}$$

  - **In the calculation of solubility of a sparingly soluble salt.** Substances like AgCl, $BaSO_4$, $CaCO_3$, Ag_2CrO_4 are generally insoluble but they do have a very small but definite solubility in water. The solubility of such sparingly soluble salt is obtained by determining the specific conductivity (κ) of a saturated salt solution.

$$\Lambda_V = \Lambda°_\infty = \kappa.V \quad \text{...(i)}$$

$$\therefore \quad \Lambda°_\infty = \frac{(\kappa)\times 1000}{\text{molarity}}, \text{ Solubility} = \frac{(\kappa)\times 1000}{\Lambda_{eq}}$$

Illustration 3

Calculate the molar conductivity for NH_4OH. Given that molar conductivity for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 523.28, 280.0 and 129.8 $ohm^{-1}\ cm\ mol^{-1}$ respectively.

Soln.:

Given $\Lambda°_{Ba(OH)_2} = \lambda°_{Ba^{2+}} + 2\lambda°_{OH^-} = 523.28$ ...(i)

$\Lambda°_{BaCl_2} = \lambda°_{Ba^{2+}} + 2\lambda°_{Cl^-} = 280.00$ ...(ii)

$\Lambda°_{NH_4Cl} = \lambda°_{NH_4^+} + \lambda°_{Cl^-} = 129.80$ ...(iii)

we have to calculate $\Lambda°_{NH_4OH} = \lambda°_{NH_4^+} + \lambda°_{OH^-} = ?$

multiply eqn. (iii) by 2 and then subtract it from eqn. (ii)

$\lambda°_{Ba^{2+}} + 2\lambda°_{Cl^-} - 2\lambda°_{NH_4^+} - 2\lambda°_{Cl^-}$

$\lambda°_{Ba^{2+}} - 2\lambda°_{NH_4^+} = 280 - 2 \times 129.80 = 20.4$ ...(iv)

Now subtract (iv) from (i)

$\lambda°_{Ba^{2+}} + 2\lambda°_{OH^-} - \lambda°_{Ba^{2+}} + 2\lambda°_{NH_4^+}$

$2\lambda°_{NH_4^+} + 2\lambda°_{OH^-} = 523.28 - 20.4 = 502.88$

$$\therefore \quad \Lambda°_{NH_4OH} = \frac{502.88}{2} = 251.44\ ohm^{-1}\ cm^2\ mol^{-1}$$

ELECTROCHEMICAL CELLS

- Electrochemical cell is a single arrangement of two electrodes and an electrolyte for producing electric current due to chemical action within the cell or for producing chemical action due to production of electricity.

Electrochemical Cell

To convert chemical energy into electrical energy, *e.g.* galvanic cell, dry cell, lead storage batteries	To convert electrical energy into chemical energy. *e.g.* electrolytic cell used for purification of metals.

Galvanic Cell

- A typical galvanic cell is made up of two half cells, one containing a zinc electrode dipped in zinc sulphate solution and other half cell contains copper electrode dipped in copper sulphate solution.