Kohlrausch law of independent migration of ions:-

The limiting molar conductivity of an electrolyte can be represented as the sum of individual contributions of cations & anions of that electrolyte.

If $\lambda^\circ_{Na^+}$ and $\lambda^\circ_{Cl^-}$ are limiting molar conductivities of sodium and chlorine ions respectively then the limiting molar conductivity of the sodium chloride is given by following equation

$$\lambda^\circ_{NaCl} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$$

In general if an electrolyte on dissociation gives n^+ cations and n^- anions then its limiting molar conductivity can be given as follows:

$$\boxed{\lambda^\circ_m = n^+\lambda^\circ_+ + n^-\lambda^\circ_-}$$

(Q) Represent the limiting molar conductivity of cryolite (an ore of aluminium).

soln :- $Na_3(AlF_6)$ ← cryolite

$$\lambda^\circ_m = 3\lambda^\circ_{Na^+} + \lambda^\circ_{(AlF_6)^{3-}}$$

Notes # Weak electrolytes :→ Weak electrolytes like acetic acid have lower degree of dissociation at higher concentrations and change in λ_m with dilution is due to the increase in the degree of dissociation [α]. In such cases λ_m increases steeply on

dilution, especially near lower concentration. At infinite dilution (when $C \to 0$) electrolytes dissociate completely [i.e., $\alpha = 1$]. At any concentration C if α is the degree of dissociation then it can be represented as follows

$$\alpha = \frac{\lambda_m}{\lambda_m^\circ}$$

And using the value of concentration C and degree of dissociation α the dissociation constant of weak electrolyte like Acetic acid can be calculated as follows

$$K = \frac{C\alpha^2}{1-\alpha}$$

$$= \frac{C\left(\frac{\lambda_m}{\lambda_m^\circ}\right)^2}{1-\frac{\lambda_m}{\lambda_m^\circ}} = \frac{C\frac{\lambda_m^2}{\lambda_m^{\circ 2}}}{\frac{\lambda_m^\circ - \lambda_m}{\lambda_m^\circ}}$$

$$K = \frac{C\lambda_m^2}{\lambda_m^\circ(\lambda_m^\circ - \lambda_m)}$$