Now, $\Lambda_m \alpha$ number of ion present in solution
or
Amt. of electrolyte dissociated

$\Lambda_m^0 \alpha$ max. number of ion present in solution
or
Initial amt of electrolyte

$$\Rightarrow \frac{\Lambda_m}{\Lambda_m^0} = \frac{\text{Amt. of electrolyte dissociated}}{\text{Initial amt. of electrolyte}} = \alpha$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} \text{ or } \alpha = \frac{\Lambda_{eq}}{\Lambda_{eq}^0}$$

(iii) To calculate dissociation constant of weak electrolyte :-

| | $MX \rightleftharpoons$ | $M^+(aq)$ + | $X^-(aq)$ |
|---|---|---|---|
| I.C | $C$ | $0$ | $0$ |
| E.C | $C - C\alpha$ | $C\alpha$ | $C\alpha$ |

$$K_a = \frac{[M^+][X^-]}{[MX]}; \quad K_a = \frac{C^2\alpha^2}{C(1-\alpha)}; \quad K_a = \frac{C\alpha^2}{1-\alpha}$$

$$K_a = \frac{C\left(\frac{\Lambda_m}{\Lambda_m^0}\right)^2}{\left(1 - \frac{\Lambda_m}{\Lambda_m^0}\right)} \quad \Rightarrow \quad K_a = \frac{\left(\frac{C\Lambda_m^2}{\Lambda_m^{02}}\right)}{\left(\frac{\Lambda_m^0 - \Lambda_m}{\Lambda_m^0}\right)}$$

$$\Rightarrow K_a = \frac{C\Lambda_m^2}{\Lambda_m^0(\Lambda_m^0 - \Lambda_m)}$$

Alternative method of obtaining $\Lambda_m^0$ for weak electrolyte

$$K = \frac{c\Lambda^2}{\Lambda^0(\Lambda^0 - \Lambda)}$$

$$K\Lambda^0(\Lambda^0 - \Lambda) = c\Lambda^2$$

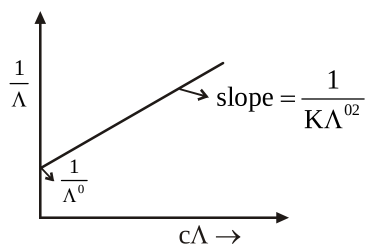
$$K\Lambda^{02} - K\Lambda\Lambda^0 = c\Lambda^2$$

Divide the ecpression by $K\Lambda^{02}\Lambda$

$$\frac{K\Lambda^{02}}{K\Lambda^{02}\Lambda} - \frac{K\Lambda\Lambda^0}{K\Lambda^{02}\Lambda} = \frac{c\Lambda^2}{K\Lambda^{02}\Lambda}$$

$$\frac{1}{\Lambda} - \frac{1}{\Lambda^0} = \frac{c\Lambda}{K\Lambda^{02}}$$

$$\frac{1}{\Lambda} - \frac{1}{\Lambda^0} + \frac{c\Lambda}{K\Lambda^{02}}$$




Plot of $\frac{1}{\Lambda}$ vs $c\Lambda$

(iv) To calculate the solubility of sparingly soluble salt :-

**Solubility :-** Amount of salt dissolved in IL of solvent ($molL^{-1}$)
For sparingly solube salt, amount of salt dissolved in 1L is so small that it form infintely diluted solution.

$$\Lambda_m = \frac{\kappa \times 1000}{M}, \text{ for sparingle soluble salt}$$

$$\Lambda_m^0 = \frac{\kappa \times 1000}{S}$$

**Problem:** The molar conductivity of acetic acid at infinite dilution is 390.7 and for 0.01 M acetic acid is $3.907\ S\,cm^2 mol^{-1}$. Calculate pH of solution

**Soln.**

| | $CH_3COOH \rightleftharpoons$ | $CH_3COO^-$ + | $H^+$ |
|---|---|---|---|
| Initial conc. | 0.01 | 0 | 0 |
| At equilibrium | $0.01 - 0.01\ \alpha$ | $0.01\ \alpha$ | $0.01\alpha$ |

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{3.907}{390.7} = 0.01$$

$$\left[H^+\right] = 0.01\alpha = 10^{-4}$$

$$pH = -\log\left[H^+\right] = 4$$

**Problem:** The specific conductance of saturated solution of AgCl and that of water is $0.32 \times 10^{-5}$ and $4 \times 10^{-7}\ S\,dm^{-1}$. The ionic conductance of $Ag^+$ and $Cl^-$ at infinite dilution is 0.525 and $0.75\ S\,dm^2 mol^{-1}$. The solubility of AgCl is ________ mol $L^{-1}$.

**Soln.** $\Lambda_m^0 = \frac{\kappa_{AgCl}}{\text{Solubility}}$

$$\kappa_{solution} = \kappa_{AgCl} + \kappa_{H_2O}$$

$$\kappa_{AgCl} = 0.32 \times 10^{-5} - 4 \times 10^{-7} = (32 - 4) \times 10^{-7} = 28 \times 10^{-7}$$

$$\text{Solubility} = \frac{\kappa_{AgCl}}{\Lambda_m^0} = \frac{28 \times 10^{-7}}{(0.525 + 0.75)} = 21.96 \times 10^{-7}\ mol\ L^{-1}$$

**Problem:** From the following molar conductivities at infinite dilution

$$\Lambda_m^0\left[Ba(OH)_2\right] = 457.6\Omega^{-1}cm^2mol^{-1}$$

$$\Lambda_m^0\left(BaCl_2\right) = 240.6\Omega^{-1}cm^2mol^{-1}$$

$$\Lambda_m^0\left(NH_4Cl\right) = 129.8\Omega^{-1}cm^2mol^{-1}$$

Calculate $\Lambda_m^0$ for $NH_4OH$.

**Soln.**

$$\Lambda_m^0\left[Ba(OH)_2\right] = \lambda^0_{Ba^{2+}} + 2\lambda^0_{OH^-} = 457.6 \quad \text{... (1)}$$

$$\Lambda_m^0\left(BaCl_2\right) = \lambda^0_{Ba^{2+}} + 2\lambda^0_{Cl^-} = 240.6 \quad \text{... (2)}$$

$$\Lambda_m^0\left(NH_4Cl\right) = \lambda^0_{NH_4^+} + \lambda^0_{Cl^-} = 129.8 \quad \text{... (3)}$$

$$\Lambda_m^0\left(NH_4OH\right) = \lambda^0_{NH_4^+} + \lambda^0_{OH^-}\ ;\ \text{eq } 3 + \frac{1}{2}\text{eq } 1 - \frac{1}{2}\text{eq } 2$$

$$\Rightarrow \Lambda_m^0\left(NH_4OH\right) = \Lambda_m^0\left(NH_4Cl\right) + \frac{1}{2}\Lambda_m^0\left[Ba(OH)_2\right] - \frac{1}{2}\Lambda_m^0\left(BaCl_2\right)$$

$$= 129.8 + \frac{1}{2}(457.6) - \frac{1}{2}(240.6) = 238.3\Omega^{-1}cm^2mol^{-1}$$