$$\log \gamma_\pm = -0.0558$$

$$\gamma_\pm = 0.879$$

9.21. DETERMINATION OF ACTIVITY COEFFICIENTS OF ELECTROLYTES

The mean activity coefficients of various electrolyte can be determined experimentally by a number of methods. Some of them are:

(i)   Solubility method

(ii)   Vapour pressure method

(iii)   Freezing point method

(iv)   Electromotive force method

(v)   Equilibrium constant method.

It is important to note that activity coefficient of a single ion cannot be determined experimentally, because it is impossible to isolate an ion in free state. Hence only mean activity coefficients of various electrolytes, are usually determined. We shall discuss here some of these methods.

(i) Solubility Method:

This method is particularly used for sparingly soluble salts. When a solution is saturated with a salt there is an equilibrium between the excess solid and the ions in the solution. To consider a simple case, such as that of sparingly soluble salt silver chloride in contact with its saturated solution, the equilibrium may be represented by

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$
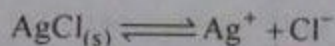
Where Ag^+ and Cl^- ions refer to the hydrated ions in the solution. The corresponding equilibrium constant is given as

$$K = \frac{a_{Ag^+} \times a_{Cl^-}}{a_{AgCl}} \tag{9.87}$$

Since the silver chloride is present in the solid state, its activity is taken as unity by convention.

$$K.(a_{AgCl}) = (a_{Ag^+})(a_{Cl^-}) \qquad \therefore a_{AgCl} = 1$$

$$K_S = (a_{Ag^+})(a_{Cl^-}) \tag{9.88}$$

Where the constant, K_S is known the solubility product constant of the silver chloride.

In general for any electrolyte having the general formula AB(s), in contact with its saturated solution, the equilibrium between the solid and the ions in solution is

$$AB_{(s)} \rightleftharpoons A^+ + B^-$$

and the solubility product constant is given by

$$K_s = (a_{A^+})(a_{B^-}) \tag{9.89}$$

This expression is the basis of the solubility product principle which states that when a solution is saturated with a given salt, the product of the activities (or concentrations) of its constituent ion, raised to the appropriate powers, must be constant, irrespective of the nature of other electrolytes present in the solution.

If the activity of each ion is written as the product of its concentration in gram ions per liter and the corresponding activity coefficient, then the expression for the solubility product of $AB_{(s)}$ becomes.

$$K_s = \gamma_+ [A^+] \gamma_- [B^-]$$

$$K_s = \gamma_+ \gamma_- [A^+][B^-]$$

$$K_s = \gamma_\pm^2 [A^+][B^-]$$

Taking logarithms on both sides we get (on rearranging)

$$\log K_s = \log \gamma_\pm^2 + \log [A^+][B^-]$$

$$\log K_s = 2\log \gamma_\pm + \log [A^+][B^-]$$

$$\log [A^+][B^-] = \log K_s - 2\log \gamma_\pm$$

The solubility 'S' of such a salt is equal to the moles per liter of the salt that dissolves, if no species of electrolyte $AB_{(s)}$ other than A^+ and B^- exist in solution.

$$[A^+] = [B^-] = S$$

Thus $\log S.S = \log K_s - 2\log \gamma_\pm$

$$\log S^2 = \log K_s - 2\log \gamma_\pm$$

$$2\log S = \log K_s - 2\log \gamma_\pm$$

$$\log S = \frac{1}{2}\log K_s - \log \gamma_\pm \tag{9.90}$$

Since K_s is solubility product, and is constant at a given temperature, so variation of mean activity coefficient i.e. $\gamma_\pm$, can be related with the solubility of that compound at a given temperature. In order to find the utility of last equation, now consider the data that are obtained when a sparingly soluble salt is dissolved in solutions that contain various amounts of neutral or non-reacting electrolyte, that do not contain the ions A^+ or B^-. Debye-Huckel theory again suggests that at low ionic strength.

$$-\log \gamma_{\pm} = 0.5091\, z_i^2 \sqrt{\mu}$$

$$-\log \gamma_{\pm} \propto \sqrt{\mu}$$

Hence we write the previous equation.

$$\log S = \frac{1}{2}\log K_S + 0.5091\, z_i^2 \sqrt{\mu}$$
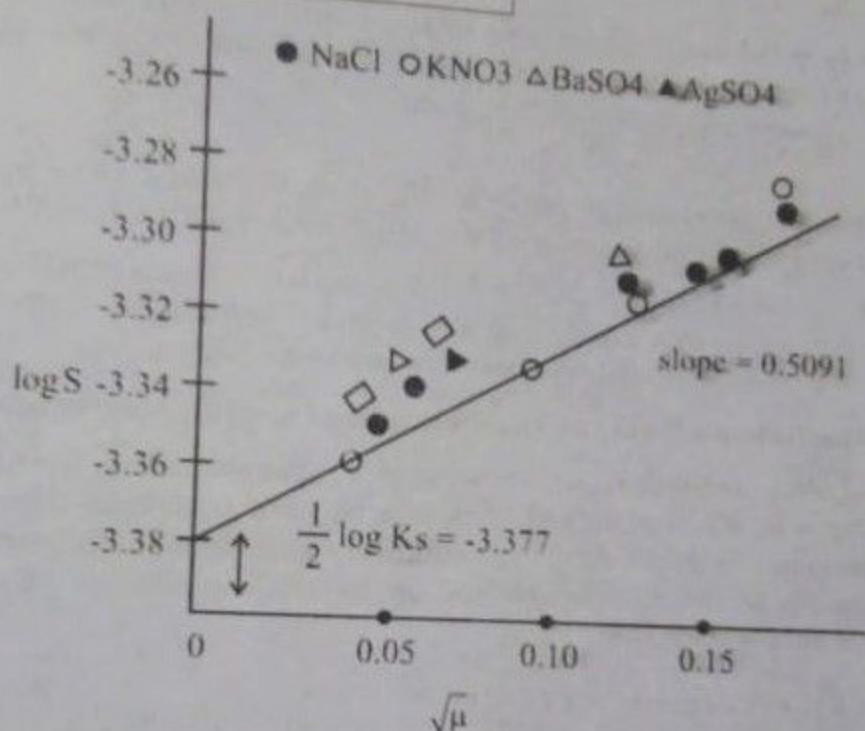
(9.91)

Fig. 9.8 Calculation of K_s by extra-polation method

If "log S" is plotted against $\sqrt{\mu}$ by using a complicated but experimentally convenient salt $[Co(NH_3)_4\, C_2O_4][Co(NH_3)_2\,(NO_2)_2\, C_2O_4]$, a straight line is obtained, which supports Deby-Huckel predictions of linear relation and straight line has been drawn with predicted slope of 0.5091

The Fig 9.8 shows the effect of added salts on the solubility of a salt $[Co(NH_3)_4\, C_2O_4][Co(NH_3)_2\,(NO_2)_2\, C_2O_4]$ containing a singly charged cation and a singly charged anion. For this particular set of data that the linear relation is rather rough and that support for Debye-Huckel theory is given but is not very convincing here. It is just such difficulties that the theory frequently encounters particularly in solutions other than those of extremely low ionic strength.

An extrapolation can be made in Fig 9.8 with/ without D.H.T and one obtains for the L.H.S of equation (9.91) at zero ionic strength, the value −3.377. Again the limit of zero ionic strength corresponds to the complete absence of ionic interactions. Therefore,

$$\gamma_{\pm} = 1 \qquad \text{and} \qquad \log \gamma_{\pm} = 0$$

$$\frac{1}{2} \log K_s = -3.377$$

$$\log K_s = -6.754$$

$$K_s = \text{Antilog} \, (-6.754)$$

$$K_s = 1.76 \times 10^{-7}$$

With this value one is again able to learn equation 9.91 around to give an expression for the activity coefficient of the singly soluble salt at any concentration.

$$\boxed{\log \gamma_\pm = -3.377 - \log S} \tag{9.92}$$

The solubility data, used to construct Fig-(9.8) can therefore be made to give $\gamma_\pm$ for the dissolved salt in all the solutions studied. Although, the D.H.T was used to aid in the extrapolation to obtain "K_s" in Fig 9.8, it should be recognized that these results do not depend on this theory and are valid for any aqueous solution at this temperature, for which the solubility of the salt can be measured.

(ii) Activity Coefficients from the Dissociation of a weak electrolyte

Other studies of chemical equilibria besides those that make use of oxidation-reduction reactions in electrochemical cells, can be used to deduce thermodynamic properties of non-ideal systems. Acid-base equilibria provide many illustrations. The traditional example is the equilibrium set up by the dissociation of acetic acid, CH₃COOH, here abbreviated HAc.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
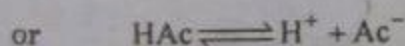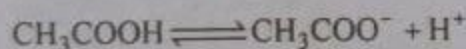
or $\quad HAc \rightleftharpoons H^+ + Ac^-$

The thermodynamic equilibrium constant, denoted by K_{th} is given

$$K_{th} = \frac{(a_{H^+})(a_{AC^-})}{(a_{HAc})}$$

$$K_{th} = \frac{\gamma_+ \gamma_- [H^+][Ac^-]}{\gamma_{HAc}[HAc]} \tag{9.93}$$

This expression is simplified when it is realized that the electrostatic interactions are primarily responsible for the non-ideality which produces activity coefficient different from unity. The uncharged HAc molecule should therefore behave relatively ideally, and we can set $\gamma_{HAc} = 1$

$$K_{th} = \frac{\gamma_\pm^2 [H^+][Ac^-]}{[HAc]} \tag{9.94}$$

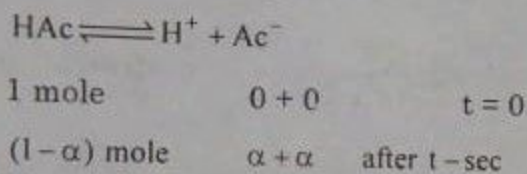Taking log of the above expression and on rearranging we get

$$\log K_{th} = \log \left[\frac{\gamma_\pm^2 \, [H^+][Ac^-]}{[HAc]} \right]$$

$$\log K_{th} = \log \gamma_\pm^2 + \log \frac{[H^+][Ac^-]}{[HAc]}$$

$$\log K_{th} = 2 \log \gamma_\pm + \log \frac{[H^+][Ac^-]}{[HAc]}$$

$$\log \frac{[H^+][Ac^-]}{[HAc]} = \log K_{th} - 2 \log \gamma_\pm \tag{9.95}$$

Since HAc is partially dissociated, so the concentration of dissociated and un-dissociated acetic acid may be substituted in the above expression by considering the degree of dissociation (α). Let

$$HAc \rightleftharpoons H^+ + Ac^-$$

1 mole $0 + 0$ $t = 0$

$(1-\alpha)$ mole $\alpha + \alpha$ after $t - sec$

Where α =no of moles converted to ions and it is also known as degree of dissociation. Let the concentration of CH_3COOH is taken as "C" moles liter. Then at equilibrium stage.

$$C(1-\alpha) \rightleftharpoons C\alpha + C\alpha$$

Substitute then values of concentration in Eq. (9.95) we get

$$\log \frac{C\alpha . C\alpha}{C(1-\alpha)} = \log K_{th} - 2 \log \gamma_\pm$$

$$\log \frac{C\alpha^2}{(1-\alpha)} = \log K_{th} - 2 \log \gamma_\pm \tag{9.96}$$

For solutions that are very dilute in ions one can still use the Arrhenius expression to obtain the degree of dissociation from the conductivity measurement.

$$\alpha = \frac{\Lambda}{\Lambda_o} = \frac{\text{equivalent conductance at given cancentration}}{\text{equivalent conductance at inf inite dilution}}$$

In this way, the left side of Eq. (9.96) is determined for various acetic acid concentrations. The right side consists of a constant term $\log K_{th}$ and a term which the D.H. theory suggests will, at low concentrations, be proportional to the square root of the ionic strength.

$$-\log \gamma_\pm \propto \sqrt{\mu}$$

If the solution contains only the H^+ and Ac^- ions from the dissociation of

$$\mu = \frac{1}{2}\left[(C\alpha)(1)^2 + (C\alpha)(-1)^2\right]$$

$$\mu = C\alpha$$

and $$\sqrt{\mu} = \sqrt{C\alpha}$$

so $$\log \frac{C\alpha^2}{1-\alpha} = \log K_{th} + 2(0.5091\, Z_+ Z_- \sqrt{\mu})$$

$$\log \frac{C\alpha^2}{1-\alpha} = \log K_{th} + 1.018\, Z_+ Z_- \sqrt{C\alpha} \tag{9.97}$$

Equation (9.97) is an equation of straight-line,

$$\log \frac{C\alpha^2}{1-\alpha} = \log K_{th} + 1.018\sqrt{C\alpha} \quad \therefore \text{ electrolyte is 1:1 type } Z_+ = Z_- = 1$$

If a graph is plotted between $\log \dfrac{C\alpha^2}{1-\alpha}$ v/s $\sqrt{C\alpha}$ a straight-line is obtained

with slope 1.018 and intercept log K_{th}.

Extrapolation to zero ionic strength, when $\gamma_\pm = 1$ and $\log \gamma_\pm = 0$, gives

$$\log K_{th} = -4.7565$$

and $$K_{th} = \text{antilog}\,(-4.7565)$$

$$K_{th} = 1.752 \times 10^{-5}$$

$$K_{th} = 1.752 \times 10^{-5} \text{ (theoretical)}$$

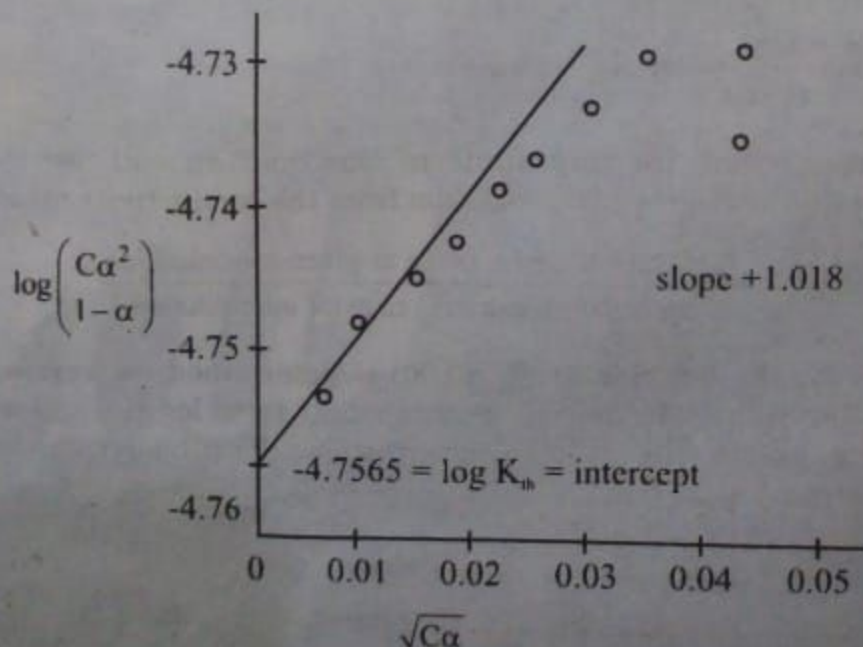$$K_{th} = 1.8 \times 10^{-5} \text{ (experimental)}$$

Fig. 9.9. Representation of experimental data for weak electrolyte

The value of K_{th} is very close to experimental value, so D.H.L can be used to calculate the thermodynamic equilibrium constant of weak electrolyte.

Equation (9.96) can also be now rearranged to give.

$$\log \gamma_\pm = \frac{1}{2} \log K_{th} - \frac{1}{2} \log \frac{C\alpha^2}{1-\alpha}$$

$$\log \gamma_\pm = -2.3782 - \frac{1}{2} \log \frac{C\alpha^2}{1-\alpha} \tag{9.98}$$

From equation (9.98), we can determine $\gamma_\pm$ for the dissociation products of CH_3COOH at any concentrations for which values of α can be obtained.