

The free energy associated with the additional potential arising from the ionic atmosphere is equal to the reversible electrical work,  $w_{el}$ , required to form the ionic atmosphere.

This is obtained by integrating the second term the equation

$$w_{el} = \int_0^{ze} \left( \frac{-ze\kappa}{\epsilon_r} \right) d(ze) \quad \text{--- (1)}$$

$$= \frac{-\kappa}{2\epsilon_r} (ze)^2 \quad \text{--- (2)}$$

For dilute solution,  $w_{el}$  can be written as,

$$w_{el} = kT \ln \gamma_i = \frac{-z_i^2 e^2 \kappa}{2\epsilon_r} \quad \text{--- (3)}$$

where  $\gamma_i$  is the activity coefficient,  $w_{el}$  can be written as

$$w_{el} = z_i kT \ln \gamma_i = \frac{-\sum_i z_i^2 e^2 \kappa}{2\epsilon_r kT} \quad \text{--- (4)}$$

Accordingly, mean ionic activity coefficient,  $\gamma_{\pm}$  is

$$\gamma_{\pm}^{\nu} = \gamma_{+}^{\nu_{+}} \gamma_{-}^{\nu_{-}} \quad \text{--- (5)}$$

where  $\nu_{+}$  is the number of positive ions,  $\nu_{-}$  is the number of negative ions and

$$\nu = \nu_{+} + \nu_{-} \quad \text{--- (6)}$$

Hence

$$\ln \gamma_{\pm} = \frac{\nu_{+}}{\nu} \ln \gamma_{+} + \frac{\nu_{-}}{\nu} \ln \gamma_{-} \quad \text{--- (7)}$$

And,  $\nu_{+} z_{+} = \nu_{-} z_{-} \quad \text{--- (8)}$

Hence using above equations

$$\ln \gamma_{\pm} = -|z_+ z_-| \frac{e^2 K}{2 \epsilon_r k T} \quad \text{--- (9)}$$

using the definition of ionic strength,  $I$ , as

$$I = \frac{1}{2} \sum c_i z_i^2 \quad \text{--- (10)}$$

Since  $n_i = c_i N_A / 1000$

$N_A \rightarrow$  Avogadro's number

$c_i = m_i \rho_0$  ( $\rho_0 \rightarrow$  density of the solvent)

$$K^2 = \frac{8 \pi N_A^2 e^2 \rho_0 I}{1000 \epsilon_r R T} \quad \text{--- (11)}$$

or  $K = \left( \frac{8 \pi N_A^2 e^2 \rho_0 I}{1000 \epsilon_r R T} \right)^{1/2} \quad \text{--- (12)}$

Substituting for  $K$  in eq. (9),  $\rho_0 = 1 \text{ g ml}^{-1}$  for water and changing from  $\ln$  to  $\log$ , we have

$$\log \gamma_{\pm} = -A |z_+ z_-| I^{1/2} \quad \text{--- (13)}$$

where the constant  $A$  is given by expression

$$A = \frac{N_A^2 e^3}{2.303 \epsilon_r R T} \left( \frac{2 \pi}{1000 \epsilon_r R T} \right)^{1/2}$$

$$= \left( \frac{\pi N_A}{500} \right)^{1/2} \frac{e^3}{2.303 k^{3/2} (\epsilon_r T)^{3/2}} \quad \text{--- (14)}$$

Substituting the value of  $N_A$ ,  $k$  and charge  $e$ , we get

$$A = 1.8246 \times 10^6 / (\epsilon_r T)^{3/2} \quad \text{--- (15)}$$

At  $25^\circ\text{C}$ , the dielectric constant  $\epsilon_r$  for water 78.54 so that Debye-Huckel constant  $A$  become equal to 0.509.

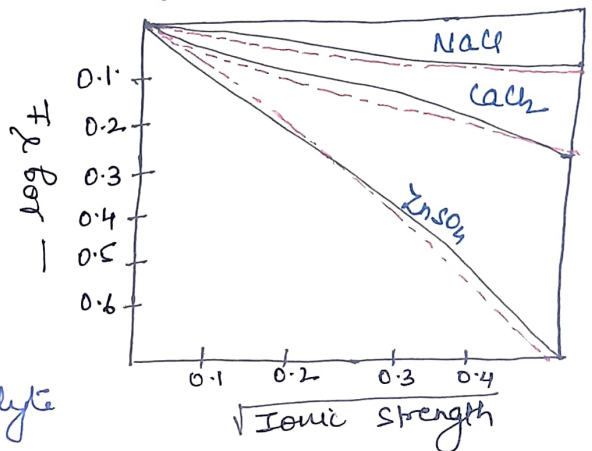
$$\log \gamma_{\pm} = -0.509 |z_+ z_-| I^{1/2} \quad \text{--- (16)}$$

$$\log \gamma_{\pm} = -0.509 |z_+ z_-| I^{1/2}$$

This is called Debye-Huckel limiting law (DHLL).

- This is the law for mean ionic activity coefficient to ionic strength of the solution.
- The negative value for log in this equation implies that mean activity coefficient is less than unity. This is mainly applicable for the dilute solutions of the ~~co~~ electrolyte, as at higher concentrations the value even exceeds unity.

- According to DHLL if  $z_+$  and  $z_-$  are the same, the activity coefficients should vary only with ionic strength of the solution and not the nature of the electrolyte



- The graphical analysis represents that by varying the valency of various electrolytes for solutions with  $\log \gamma_{\pm}$  plotted against  $\sqrt{I}$ .
- According to DHLL, the plot of all the electrolytes should straight line passing through the origin is expected and slope ~~is~~ depends on  $z_+ z_-$ . For univalent electrolytes, the slope should be 0.509, for uni-~~bi~~valent electrolyte and bi-univalent electrolyte the value should be equal to  $2 \times 0.509$  and for tri-univalent or

electrolytes it should be  $3 \times 0.509$  and so on.

- This is quite evident and valid for the plots in dilute aqueous solutions. The dotted lines are the deviations from ideal behaviour and expected from limiting law.
- As the ionic strength decreases the ideality of the solution increases.

Although some empirical corrections have been suggested for making this equation applicable.

$$\log \gamma_{\pm} = -A z_{+} z_{-} \sqrt{I} + CI \quad \text{--- (A)}$$

where  $C \rightarrow$  empirical constant depending on the nature (valency) of the electrolyte.

The results have been found to be valid for electrolytes upto 1 molar concentration in case of uni-univalent electrolytes.

- Eq. (A) also explains why activity coefficients start to rise again after touching a minimum value as both the terms in equation contain ionic strength.
- for  $\gamma > 1$  ( $\because \gamma = a/c$ ) at high conc. the ion-solvent dipole interaction is large and some solvent molecules are isolated from bulk. The effective conc. hence increases.