Pb:- II
Physical
Electrochemistry

Ionic strength

It is measure of Electrical intensity due to the presence of ions in the solution.

It is given by

$$I = \frac{1}{2}(m_1 z_1^2 + m_2 z_2^2 + \cdots)$$

$$= \frac{1}{2}\left(\sum_{i=1}^{i=n} c_i z_i^2\right)$$

Where $m_1, m_2, m_3 \cdots$ are molalities

c_i = concentration of ions

$z_1, z_2, z_3^2 \cdots$ are valencies of various ions present in solution.

Ex- Calculation of Ionic strength of (i) 0.15 m KCl solution
(ii) 0.25 molal K_2SO_4 solution
(iii) mixture of 0.1m NaCl and 0.2 Na_2SO_4 solution.

$KCl \rightarrow K^+ + Cl^-$

$$I = \frac{1}{2}(0.15 \times 1^2 + 0.15 \times 1^2) = 0.15$$

$K_2SO_4 = 2K^+ + SO_4^{-2}$

$$I = \frac{1}{2}(0.5 \times 1^2 + 0.25 \times 2^2) = 0.75$$

Activity & Activity coefficient of Electrolytes

The effective concentration of an ion or the electrolyte in a solution is called activity, it is usually denoted by a and given by

$$a = \gamma \times m$$

where m = molality

γ = activity coefficient

$$\gamma = \frac{a}{m} = \frac{\text{activity}}{\text{molality of solution}}$$

$\therefore a < m$ for real solutions

$\gamma < 1$

$a = m$, $\gamma = 1$ for ideal solutions

For electrolyte $a = a_+ a_-$ = product of activity of ions.

The activity of individual ion cannot be determined hence mean ionic activity ($a_\pm$) is considered

$$a_\pm = \sqrt{a} = \sqrt{a_+ a_-}$$

mean activity coefficient $= \gamma_\pm = \sqrt{\gamma_+ \cdot \gamma_-}$

$$a_\pm = \sqrt{\gamma_+ m_+ \times \gamma_- m_-}$$

for univalent ions $m_\pm = m_- = m_+$, $\gamma_+ = \gamma_- = \gamma_\pm$

$$\sqrt{a} = \sqrt{m^2 \gamma_\pm^2}$$

$$a = m^2 \gamma_\pm^2$$