

$$\nabla^2 \psi = \frac{4\pi n_0 e^2}{\epsilon_1} \left(-\frac{ze\psi}{kT} \right)$$

$$\nabla^2 \psi = \left[\frac{8\pi n_0 e^2}{\epsilon_1 kT} \right] \psi \quad \text{--- (8)}$$

Defining a quantity k by

$$k^2 = \frac{8\pi n_0 e^2}{\epsilon_1 kT} \sum_i \sigma_i z_i^2 \quad \text{--- (9)}$$

where z_i is the charge on the ion. For uni-univalent electrolyte

$$k^2 = \frac{8\pi n_0 e^2}{\epsilon_1 kT} \quad \text{--- (10)}$$

Thus equation (8) becomes

$$\nabla^2 \psi = k^2 \psi, \text{ which has the solution}$$

$$\psi = \frac{ze}{\epsilon_1 r} e^{-kr} \quad \text{--- (11)}$$

The exponential equation (11) can be expanded, retaining only the first two terms to give

$$\psi(r) = \frac{ze}{\epsilon_1 r} - \frac{zek}{\epsilon_1} \quad \text{--- (12)}$$

In equation (12), the first term on the right-hand side is the potential due to the charge on the ion itself, while the second term can be thought of as the potential due to charge $-ze$ at a distance $\frac{1}{k}$. The quantity $\frac{1}{k}$, which has the dimension of length and it is known as effective radius of the ionic atmosphere or Debye length.

The free energy associated with the additional potential arising from the ionic atmosphere is equal to the reversible electrical work W_{el} , it is required to form the ionic atmosphere. This is obtained by integrating the second term in equation (12) from 0 to full charge ze .

$$W_{el} = \int_0^{ze} \left(-\frac{zek}{\epsilon_1} \right) d(ze) = -\frac{k}{2\epsilon_1} (ze)^2 \quad \text{--- (13)}$$

For dilute solution, W_{el} can also be written as

$$W_{el} = kT \ln \gamma_i = -\frac{z_i^2 e^2 k}{2\epsilon_1} \quad \text{--- (14)}$$

where γ_i is the activity coefficient of the i th ion component.

$$\text{Thus, } \ln \gamma_i = \frac{z_i^2 e^2 k}{2\epsilon_1 kT} \quad \text{--- (15)}$$

Since the mean ionic activity coefficient is defined as

$$\gamma_{\pm}^{\nu} = \gamma_+^{\nu_+} \gamma_-^{\nu_-} \quad \text{--- (16)}$$

where ν_+ and ν_- are the numbers of positive and negative ions respectively and $\nu = \nu_+ + \nu_-$.