$$\psi = \left[\frac{A e^{-KT}}{r} + \frac{B e^{KT}}{r} \right]^{1/2} \quad \text{——— (6)}$$

where A and B are integration constant. The value of B has been found to be zero. So equ. (6) becomes:

$$\psi = \frac{A e^{-KT}}{r} \quad \text{——— (7)}$$

The value of the constant A can be known by the fact that when $K = 0$ the concentration is zero. So:

$$\psi = Z_i \varepsilon / D r$$

r = distance from point
D = Dielectric const.

$$\therefore \frac{Z_i \varepsilon}{D r} = \frac{A}{r}$$

$$\text{or} \quad A = \frac{Z_i \varepsilon}{D}$$

putting the value of A in equ. (7)

$$\psi = \frac{Z_i \varepsilon}{D r} e^{-KT}$$

on expanding above equation and neglecting higher power of K we get:

$$\psi = \frac{Z_i \varepsilon}{D r} - \frac{Z_i \varepsilon K}{D} \quad \text{——— (8)}$$

If the potential at the surface of the ion (radius r) at any stage in the process is ψ then work done in bringing up an element charge $d\varepsilon$ is $\psi \, d\varepsilon$.

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∴ Total work done

$$W = \int_0^{Z_i e} \psi \, d\varepsilon$$

when the ion has the charge ε, the potential ψ at its surface is given by:

$$\psi = \frac{\varepsilon}{D r} - \frac{\varepsilon K}{D}$$

In an infinitly dilute solution, the second term disappears. Since K is then zero. and work done

$$W_1 = \int_0^{Z_i \varepsilon} \frac{\varepsilon}{D r} \cdot d\varepsilon = \frac{Z_i^2 \varepsilon^2}{2 D r}$$

Similarly work done W_2 in charging the ion

$$W_2 = \int_0^{Z_i \varepsilon} \frac{\varepsilon}{D r} \, d\varepsilon - \int_0^{Z_i \varepsilon} \frac{\varepsilon K}{D} \, d\varepsilon$$

$$= \frac{Z_i^2 \varepsilon^2}{2 D r} - \frac{Z_i^2 \varepsilon^2}{2 D} \cdot K$$

∴ work done:

$$\Delta W = W_2 - W_1$$

$$\Delta W = -\frac{Z_i^2 \varepsilon^2}{2 D} K. \quad \text{——— (9)}$$

The corresponding energ E_i for 1 g ion is given by multiplying eqn. (9) by Avagadro no. N. so:

$$E_i = -\frac{Z_i^2 \varepsilon_i^2 K^2}{2 D} \cdot N. \quad \text{(9A)}$$

The chemical potential of a particular ion in an ideal solution is:

$$\mu_i = \mu^0 + RT \log x_i \quad \text{——— (10)}$$

where x_i = mole fraction in the given solution. For non ideal solution.

$$\mu_i = \mu^0 + RT \log a_i \quad \text{——— (11)}$$

$$= \mu^0 + RT \log x_i + RT \log f_i \quad \text{——— (12)}$$

where a_i = activity

f_i = activity coefficient.

The difference between equ. (12) and equ. (10) i.e. $RT \log f_i$ is difference in the free energy change.

on removal of 1 gn ion of the given ionic species from a large volume of real and dilute solution respectively. The difference of free energy may be regarded as equivalent to the electrical energy. Hence equ. (9A)

$$RT \log f_i = -\frac{N z_i^2 \varepsilon_i^2 K}{D}$$

$$-\log f_i = \frac{N z_i^2 \varepsilon_i^2 K}{2DRT}$$

Now putting the value of K from (5A) the number of ions per c.c. may be replaced by. $NC_i/1000$ where C_i is the number of g ions per litre and K may be replaced by R/N

$$-\log f_i = \frac{A'}{(DT)^{3/2}} z_i^2 \sqrt{\mu} \quad \text{——— (13)}$$

where $A' = \left\{ \frac{N^2 \varepsilon^3 \sqrt{2\pi/1000}}{2.3026\, R^{3/2}} \right\}$ and μ = ionic strength

For a given solvent and at a definite temp. D and T are also constant. So equ. (13) takes the form

$$\log f_i = A Z_i^2 \sqrt{\mu} \quad \text{——— (14)}$$

Where $A = A'(DT)^{3/2}$

Suppose 1 mole of an electrolytic dissociates into ν ions consisting of ν_+ cations and ν_- anions, then we have

$$f_\pm = \left(f_+^{\nu_+} \cdot f_-^{\nu_-}\right)^{1/\nu}$$

$$\log f_\pm = \frac{\nu_+ \log f_+ + \nu_- \log f_-}{\nu_+ + \nu_-} \quad \text{——— (15)}$$

If Z_+ and Z_- are valencies of the respective ions we have, by the relationship between the valence and number of ions

$$\frac{\nu_+}{\nu_-} = \frac{Z_-}{Z_+}$$

putting these in equ. (15)

$$\log f_\pm = \frac{Z_- \log f_+ + Z_+ \log f_-}{Z_+ + Z_-}$$

From equ. (14) we get the following for a given solvent at a particular temperature

$$-\log f_\pm = \frac{Z_- A Z_+^2 \sqrt{\mu} + Z_+ A Z_-^2 \sqrt{\mu}}{Z_+ + Z_-}$$

$$= \frac{A Z_+ Z_- \sqrt{\mu}\,(Z_+ + Z_-)}{(Z_+ + Z_-)}$$

$$-\log f_i = A Z_+ Z_- \sqrt{\mu} \quad \text{——— (16)}$$

Equ. (14) and (16) represents the Debye-Huckel law

End.