* Onsager Equation —

Onsager calculated the relaxation force as —

$$\text{Relaxation force} = \frac{e^3 Z_i K}{6 D k T} \omega V$$

and

$$\text{Electrophoretic effect} = \frac{K V K_i}{6 \pi \eta} \cdot e Z_i$$

where,

η = viscocity coefficient of the medium.

K_i = coefficient of fractional resistance of the solvent opposing the motion of ith kind and 'ω' is defined by —

$$\omega = Z_+ Z_- \frac{2q}{1 + q^{1/2}}$$

and the value of q is given by-

$$q = \frac{z_+ z_- (\lambda_+ + \lambda_-)}{(z_+ + z_-)(z_+ \lambda_- + z_- \lambda_+)}$$

If an ions of ith kind moving through a solution with a steady velocity 'U_i' thus, driving force appears due to the applied electric field is $= \varepsilon z_i V$ and this is opposed by-

Frictional force + Relaxation force + Electrophoretic force

$$\varepsilon z_i V = k_i U_i + \frac{\varepsilon z_i \kappa}{6\pi\eta} k_i V + \frac{\varepsilon^3 z_i \kappa}{6DkT} \omega V.$$

dividing through out by $k_i V$ and rearranging we get-

$$U_i/V = \frac{\varepsilon z_i}{k_i} - \frac{\varepsilon z_i \kappa}{6\pi\eta} - \frac{\varepsilon^3 z_i \kappa}{6DkT} \omega/k_i$$

If the potential gradient (V) is taken as 1 volt/cm, then-

$$V = 1/300 \text{ (in esu)}$$

$$U_i = \frac{\varepsilon z_i}{300 k_i} - \frac{\varepsilon \kappa}{300}\left(\frac{z_i}{6\pi\eta} + \frac{\varepsilon^2 z_i}{6DkT} \cdot \omega/k_i\right) \quad \text{—(1)}$$

At infinite dilution κ is zero and hence eqn becomes-

$$U_i^0 = \frac{\varepsilon z_i}{300 k_i}$$

But $\lambda_i^\circ = F U_i^\circ$ or $U_i^\circ = \frac{\lambda_i^\circ}{F}$

$$\therefore \frac{\varepsilon Z_i}{300 K_i} = \lambda_i^\circ / F$$

again,

$$U_i = \frac{\lambda_i}{\alpha F}$$

then eqn – (I) becomes –

$$\therefore \frac{\lambda_i}{\alpha F} = \frac{\lambda_i^\circ}{F} - \frac{\varepsilon K}{300}\left(\frac{Z_i}{6\pi\eta} + \frac{\varepsilon}{6DkT} \cdot \frac{\varepsilon Z_i}{K_i}\omega\right)$$

when the electrolyte is completely ionised, i.e. $\alpha = 1$

therefore above eqn – becomes –

$$\lambda_i = \lambda_i^\circ - \frac{\varepsilon K}{300}\left(\frac{Z_i}{6\pi\eta} F + \frac{300\varepsilon}{6DkT} \cdot \lambda_i^\circ \omega\right)$$

since, $\frac{\varepsilon Z_i}{K_i} = \frac{300\lambda_i^\circ}{F}$ therefore the above

equation reduced to –

$$\lambda_i = \lambda_i^\circ - \left(\frac{29.15 Z_i}{(DT)^{1/2}\eta} + \frac{9.90\times10^5}{(DT)^{3/2}} \cdot \lambda_i^\circ \omega\right)\sqrt{c(z_+ + z_-)}$$

In terms of equivalent conductance we can write –

$$\text{or} \quad \Lambda = \Lambda_0 - \left(\frac{29.15 (z_+ + z_-)}{(DT)^{1/2}\eta} + \frac{9.90\times10^5}{(DT)^{3/2}} \Lambda_0 \omega\right)\sqrt{c(z_+ + z_-)}$$

In uni-univalent electrolyte –

$$Z_+ = Z_- = 1$$

$$\& \quad \omega = 2 - \sqrt{2}$$

$$\therefore \boxed{\Lambda = \Lambda_0 - \left(\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.20\times10^5}{(DT)^{3/2}} \Lambda_0\right)\sqrt{c}} \quad \text{(II)}$$

This expression (II) is known as – ONSAGER EQUATION

$$\text{or} \quad \Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{c} \quad \text{(III)}$$

where,

$$A = \frac{82.4}{(DT)^{1/2}\eta}$$

$$B = \frac{8.20\times10^5}{(DT)^{3/2}}$$

* Testing of Onsager Equation –

* Validity of Onsager equation –

A/C to Onsager eqⁿ –

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{C} \quad \text{—— (I)}$$

where, A & B are Debye – Huckel constant.

$$A = \frac{82.4}{(DT)^{1/2}\eta} \quad \& \quad B = \frac{8.20 \times 10^5}{(DT)^{3/2}}$$

The value of A & B for water at 25°C is 60.2 and 0.229 respectively.

if C = 0 (i.e. infinite dilution)

then eqⁿ – (I) becomes –

$$\Lambda = \Lambda_0$$

$$\therefore \quad \Lambda = \Lambda_0 - (60.2 + 0.229\Lambda_0)\sqrt{C}$$

Graph –

* When equivalent conductance is plotted against the square root of the concentration, a straight line should be obtained with slope $A = B\Lambda_0$. These value closely agreed with experimental values.