

Debye Huckel Theory : This theory is based on the assumption that strong electrolytes are completely dissociated into ions. The increase in eq. conductance of a weak electrolyte is due to the increase in the no. of ions with dilution. But the increase in equivalent conductance for strong electrolyte is due to the electrical interactions between the ions. At ordinary concentration, the ions are close proximity to each other and hence there are interionic forces which render them unable to move with a high speed. With dilution, the interionic forces diminish and hence the conductance increases. In 1923, Debye and Huckel treated the interionic effects for a solution carrying an electrical current quantitatively. This is known as Debye-Huckel theory.

Let us consider an ion in a solution with charge $+e$. Let E be the intensity of the external electric field which directs the ion to move in x direction. There are really four different forces which play on the given ion.

(1) Firstly, there is the electric force Ee acting on the ion in the direction of x -axis.

(2) Secondly, as the ion moves forward, there is a frictional force which retards its motion i.e. viscous force. If the velocity of the ion be u in the x direction and medium is assumed to be at rest, the frictional force would be

$$f = -kV$$

$$= -6\pi\eta r u$$

where η is the viscosity of the medium and r is radius of the ion, assumed to be spherical. This frictional force would be counterbalanced by the electrical force and expressing E in volts

$$6\pi\eta r u \times 300 = Ee$$

$$\text{Hence mobility of the ion} = \frac{u}{E} = \frac{e}{6\pi\eta r \times 300}$$

$$= \frac{\kappa_1}{r\eta}$$

$$\left(\text{where } \kappa_1 = \frac{e}{6\pi \times 300}\right)$$

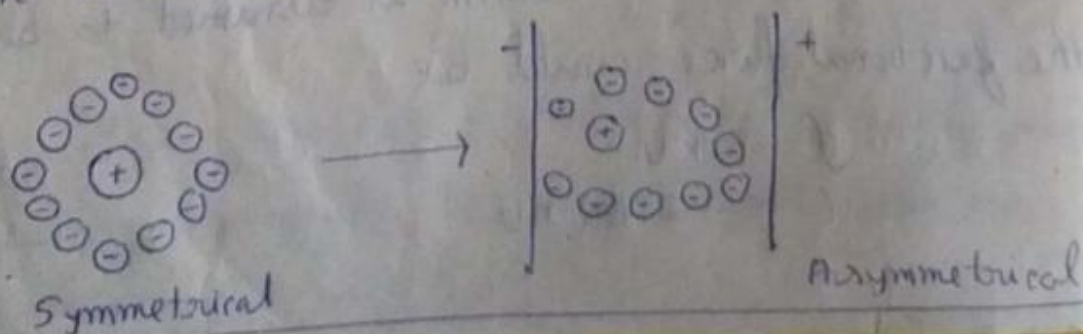
The equivalent conductance of the solution is

$$\pi = F(u+v) = \frac{\kappa_1 F}{\eta} \left(\frac{1}{r_+} + \frac{1}{r_-}\right) \text{ where}$$

$$F = 96500 \text{ e.}$$

This is Walden's rule

③ Asymmetric or relaxation effect: According to Debye and Huckel, each ion in the solution of an electrolyte is surrounded by an atmosphere of oppositely charged ions. On the application of the electrical field, the ions present in solution move towards their respective electrodes. The central +ve ion will tend to move towards the cathode while its -vely charged ionic atmosphere will move towards anode. As a result, the symmetry of the ion atmosphere is destroyed.



As long as the ion atmosphere about the central ion is symmetrical, it will exert uniform force of attraction on the central ion from all possible directions and net effect will be nil. But in case of the unsymmetrical ion atmosphere, the force of attraction is not uniform. Therefore, the central +ve ion experiences a backward pull as a retarding force. Its mobility is ~~stayed~~ ^{stowed} down and hence the effective conductance of the solution decreases. This backward pull of the central ion is known as relaxation or asymmetric effect. Once the ion atmosphere is destroyed, a finite time is required for rebuilding another symmetric ion atmosphere. This time is called relaxation time. This time of relaxation is considered to explain the retardation in the motion of the central moving ion by the ion atmosphere when the dielectric constant of the solvent is large, the force between the ions is ~~is~~ reduced and hence the effect of ionic atmosphere is less. Onsager calculated in terms of ionic charges, concentration of the solution, dielectric constant of the ~~is~~ solvent and temperature, the force which opposes the motion of the central ion. This may be expressed as $-K_1 E \sqrt{c}$, the magnitude of K_1 depends upon n , T and ϵ .

④ Electrophoretic effect : In addition to asymmetric effect, there is another factor which retards the mobility of ions. The ion atmosphere of the central ion always remains associated with solvent molecules.

In case of water, the ion atmosphere remains associated with water of hydration. Since the ion atmosphere is oppositely charged with respect to central ion, there is a tendency of the ion atmosphere moves with its associated solvent molecules. Thus a cation migrates towards cathode through the medium while the -vely charged ion atmosphere with associated molecules of water moves towards the anode. These counter-movements have a retarding influence on the mobility of the central ion. This effect is known as electrophoretic effect. This causes an additional viscous force ~~which~~ which further lowers down the conductance. This viscous force $f = -kU$. Debye-Huckel and also Onsager expressed this opposing force due to electrophoretic effect as $-k_2 E \sqrt{c}$

Under equilibrium conditions, the four forces may be equated as

$$Ee = kU + k_1 E \sqrt{c} \text{ and } + k_2 E \sqrt{c}$$

$$\text{or } U = \frac{Ee}{k} - \frac{k_1 + k_2}{k} E \sqrt{c}$$

Debye-Huckel equation : Debye and Huckel mathematically worked out the magnitude of relaxation and electrophoretic effects in terms of such factors as ionic concentration, the valency, valency of the ion and viscosity of the medium. The expression of equivalent conductance of a dilute solution of conc. c is given by

$$\Pi = \Pi_0 - \left[\frac{0.9834 \times 10^6}{(DT)^{3/2}} \omega \Pi_0 + \frac{28.94 (z_1 + z_2)}{\eta (DT)^{1/2}} \right] \sqrt{z_1 + z_2}$$

where $\omega = \frac{2q}{1 + \sqrt{q}} z_1 z_2$ and $q = \frac{z_1 z_2 (\lambda_+^\circ + \lambda_-^\circ)}{(z_1 + z_2)(z_1 \lambda_+^\circ + z_2 \lambda_-^\circ)}$

z_1 and z_2 are valencies of two ions of the electrolyte. D is dielectric constant, η is viscosity coefficient, T is absolute temperature and c is concentration of the solution in moles/litre.

The Debye-Huckel theory is based upon the following assumptions -

- ① All strong electrolytes are completely dissociated.
- ② The ratio Π_c/Π_0 is not equal to degree of dissociation for the strong electrolyte but it is a conductivity ratio.
- ③ The increase in conductivity Π_c on dilution is due to increase in the ionic mobilities of ions.
- ④ Each ion is surrounded by oppositely charged ions and solvent molecules.

Debye - Falkenhagen effect : (conductance under high A.C frequencies)

Debye - Falkenhagen studied the conductance behaviour of a solution of strong electrolytes. They applied A.C of different frequencies on the solution. According to them, "if the frequency of A.C is high so that the time of relaxation is high, then asymmetry effect will be absent." Under such

conditions, the retarding effect due to asymmetry will be absent and conductance will be high. Hence, the conductance of a solution changes with the frequency of A.C. used. Higher the frequency of A.C., higher is the conductance.

Wein effect :- The speed of the ions depends upon the applied potential gradient. An ion may have a speed of 100 cm sec^{-1} under potential gradient of 20,000 volt per cm. Under such conditions, the ion will be moving so fast that there will be no time for the ionic atmosphere to be built up. Hence, the ~~the~~ asymmetry and electrophoretic effects will be absent. The conductance of strong electrolyte in aqueous solution will increase with the increase in applied potential gradient. This is known as Wein effect.