Debye-Huckel-Onsager worked out on the magnitudes of assymmetry and electrophoretic effects in terms of factors as valency of the ion, ionic concentration and dielectric constant and viscosity of the medium.

For uni-univalent ionic electrolytes such as KCl, furnishing two univalent ions the equation was

$$\Lambda_m = \Lambda_m^\circ - \left\{ \frac{82 \cdot 4}{(\epsilon_r T)^{1/2} \eta} + \frac{8 \cdot 20 \times 10^5 \, \Lambda_m^\circ}{(\epsilon_r T)^{1/2}} \right\} \sqrt{c} \quad - ①$$

  where $\epsilon$ is the dielectric constant of the medium

  and $\eta$ is the viscosity of the medium
at    temperature $T$ and concentration $c$.

The above equation is known as <u>Debye Huckel Onsager equation</u>.

This equation is very well explains the difference between $\Lambda_m$ and $\Lambda_m^\circ$.

since $\Lambda_m < \Lambda_m^\circ$ due to assymmetry and electrophoretic effect.

  $\dfrac{82 \cdot 4}{(\epsilon_r T)^{1/2} \eta}$  is the measure of electrophoretic

effect and   $\dfrac{8 \cdot 20 \times 10^5}{(\epsilon_r T)^{1/2} \eta} \Lambda_m^\circ$ is assymmetry effect

These two terms gives the value of $\Lambda_m$ when multiplied with $\sqrt{c}$ and tells the decrease of $\Lambda_m$ from $\Lambda_m^\circ$.

For a particular solvent at a certain given temperature $\epsilon_r$ and $\eta$ are fixed.

Hence the terms

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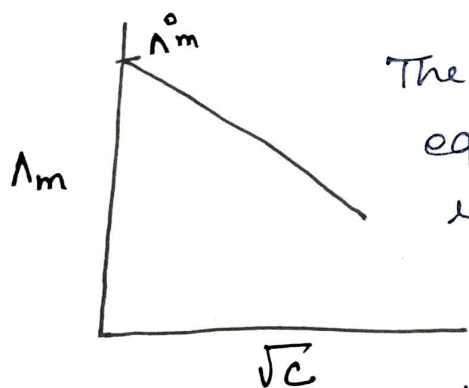
$$\frac{8.20 \times 10^5}{(\epsilon_r T)^{1/2}} = B \quad\quad -③$$

The equation becomes

$$\Lambda_m = \Lambda^\circ_m - (A + B\Lambda^\circ_m)\sqrt{c} \quad -④$$

For water at 25°c the value of $A = 60.2$ and $B = 0.229$, Hence

$$\Lambda_m = \Lambda^\circ_m (60.2 + 0.229\,\Lambda^\circ_m)\sqrt{c} \quad -⑤$$



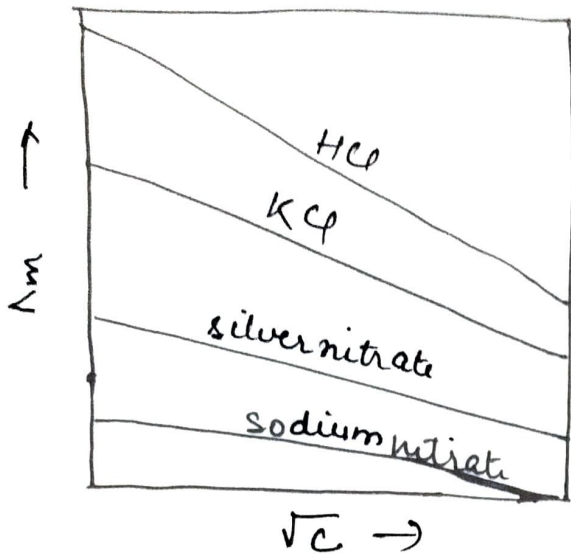The equation ④ follows a linear equation and when plotted gives intercept $= \Lambda^\circ_m$ and slope $= (A + B\Lambda^\circ_m)$ This has been proved in case of various uni-univalent ions upto a concentration range of 0.02 M in water as solvent.

Various deviations has been reported at higher concentrations which further increased with increase in the concentration.

At very low concentration the value of second term is equation ④ is almost negigible and reduced to a greater extent and $\Lambda_m$ is nearly same as $\Lambda^\circ_m$.

Verification of Debye-
~~Huttell~~ Huckel equation

There are many deviations that have been observed in the cases where concentration are either very high or the electrolytes are not univalents. This graph also shows the various effect of cations on the molar conductance when plotted versus $\sqrt{c}$.

## Debye-Falkenhagen effect:-

Debye and Falkenhagen examined the conductance behaviour of a solution of strong electrolyte by applying alternating current of difference frequencies. They predicted that if the frequency of alternating current is very high as compared to ~~frequency of~~ time of oscillation and as the relaxation time is small, the assymetry effect is virtually absent. In other words, the ionic atmosphere around the central ion is higher.

The ~~ced~~ conductance of solution varies with the variation in frequency of alternating current. The higher the frequency, the higher will be conductance. This effect is known as dispersion of conductance and has been verified experimentally.

The conductance remains free of frequency upto to cycle per second.

As the increasing frequency happens the conductanc starts increasing to a certain limiting value rate · indicating complex absence of asymmetry effect.

## Wein effect:

It is study of conductance under high potential gradient.

Speed of ion in electric field varies with applied potential gradient.

Under the potential gradient of 20000 V/cm, an ion may have a speed of 100 cm/sec. The ion passes several time through the thick ionic atmosphere during time of relaxation. The ion will be free from effect of ~~moving ion~~ oppositely charged ionic atmosphere.

Thus ~~o~~ asymmetric and electrophoretic effects are small or ~~nego~~ negligible. The conductance increases to a certain limiting value with the increase in potential gradient applied. The experiments have performed by wein and known as wein effect.