Factors affecting the electrolytic conductance.

In general, conductance of an electrolyte depends upon the following factors,

(1) Nature of electrolyte

(2) Concentration of the solution

(3) Temperature

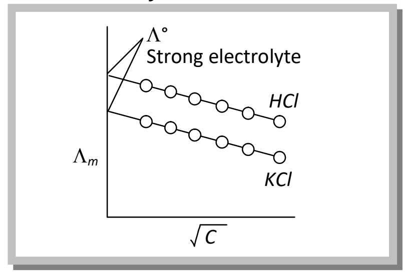
(1) **Nature of electrolyte:**The conductance of an electrolyte depends upon the number of ions present in the solution. Therefore, the greater the number of ions in the solution the greater is the conductance. The number of ions produced by an electrolyte depends upon its nature. The strong electrolytes dissociate almost completely into ions in solutions and, therefore, their solutions have high conductance. On the other hand, weak electrolytes, dissociate to only small extents and give lesser number of ions. Therefore, the solutions of weak electrolytes have low conductance.

(2) **Concentration of the solution:**The molar conductance of electrolytic solution varies with the concentration of the electrolyte. In general, the molar conductance of an electrolyte increases with decrease in concentration or increase in dilution. The molar conductance of a few electrolytes in water at different concentrations are given in table

C	**HCl**	**KCl**	**KNO_3**	**CH_3COOH**	**NH_4OH**
0.1	391.3	129.0	120.4	5.2	3.6
0.05	399.1	133.4	126.3	–	–
0.01	412.0	141.3	132.8	16.3	11.3
0.005	415.8	143.5	131.5	–	–
0.001	421.4	146.9	141.8	49.2	34.0
0.0005	422.7	147.8	142.8	67.7	46.9
0(Infinite dilution)	426.2	149.9	146.0	390.7	271.0

Inspection of table reveals that the molar conductance of strong electrolyte (HCl, KCl, KNO_3) as well as weak electrolytes (CH_3COOH, NH_4OH)increase with decrease in concentration or increase in dilution. The variation is however different for strong and weak electrolytes.

(i) **Variation of conductivity with concentration for strong electrolytes:** In case of strong electrolytes, there is a tendency for molar conductivity to approach a certain limiting value when the concentration approaches zero i.e., when the dilution is infinite. The molar conductivity when the concentration approaches zero (Infinite dilution) is called molar conductivity at infinite dilution. It is denoted by Λ^0.



Thus, $\Lambda = \Lambda^0$ when C $\rightarrow 0$ (At infinite dilution)

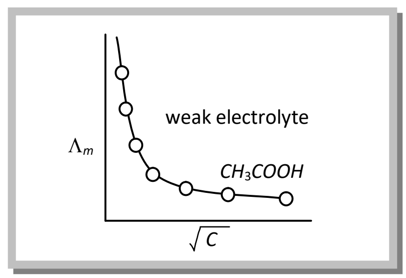
It has been observed that the variation of molar conductivity with concentration may be given by the expression

$$\Lambda = \Lambda^0 - Ac^{1/2}$$

Where, A is a constant and Λ^0 is called molar conductivity at infinite dilution.

The variation of molar conductivity with concentration can be studied by plotting the values of Λ_m against square root of concentration $(\sqrt{C})$. The plots of variation of molar conductivity with $\sqrt{C}$ for KCl and HCl are given in fig. It has been noticed that the variation of Λ_m with concentration, $\sqrt{C}$ is small (Between 4 to 10% only) so that the plots can be extrapolated to zero concentration. This gives the limiting value of molar conductance when the concentration approaches zero, called molar conductivity at infinite dilution.

(ii) **Variation of molar conductivity with concentration for weak electrolytes**:



The weak electrolytes dissociate to a much lesser extent as compared to strong electrolytes. Therefore, the molar conductivity is low as compared to that of strong electrolytes.

However, the variation of Λ_m with $\sqrt{C}$ is very large and so much so that we cannot obtain molar conductance at infinite dilution (Λ^0) by extrapolation of the Λ_m versus $\sqrt{C}$ plots. The behavior of weak electrolytes such as CH_3COOH is shown in figure.

Note: The Λ^0 value for weak electrolytes can be obtained by an indirect method based upon Kohlrausch law.

Explanation for the variation: The variation of molar conductance with concentration can be explained on the basis of conducting ability of ions for weak and strong electrolytes.

For weak electrolytes the variation of Λ with dilution can be explained on the bases of number of ions in solution. The number of ions furnished by an electrolyte in solution depends upon the degree of dissociation with dilution. With the increase in dilution, the degree of dissociation increases and as a result molar conductance increases. The limiting value of molar conductance

(Λ^0) corresponds to degree of dissociation equal to 1 i.e., the whole of the electrolyte dissociates.

Thus, the degree of dissociation can be calculated at any concentration as,

$$\alpha = \frac{\Lambda^c}{\Lambda^0}$$

Where α the degree of dissociation is, Λ^c is the molar conductance at concentration C and Λ^0 is the molar conductance at infinite dilution.

For strong electrolytes, there is no increase in the number of ions with dilution because strong electrolytes are completely ionized in solution at all concentrations (By definition). However, in concentrated solutions of strong electrolytes there are strong forces of attraction between the ions of opposite charges called inter-ionic forces. Due to these inter-ionic forces the conducting ability of the ions is less in concentrated solutions. With dilution, the ions become far apart from one another and inter-ionic forces decrease. As a result, molar conductivity increases with dilution. When the concentration of the solution becomes very-very low, the inter-ionic attractions become negligible and the molar conductance approaches the limiting value called molar conductance at infinite dilution. This value is characteristic of each electrolyte.

(3) **Temperature:** The conductivity of an electrolyte depends upon the temperature. With increase in temperature, the conductivity of an electrolyte increases.