

Conductance

❖ Resistance:

The tendency of materials to stop the flow of current is known as resistance. It is measured in ohm (Ω).

According to Ohm's law, the resistance offered by a substance is directly proportional to its length (l), but inversely proportional to its cross-sectional area (A), i.e.

$$R \propto \frac{l}{A}$$

In case of electrolytic solutions, l represents the distance between two electrodes & A is the cross-sectional area of the electrodes.

Unit: *ohm*

❖ Specific Resistance:

We know,

$$R \propto \frac{l}{A}, \quad \text{Or,} \quad R = \rho \left(\frac{l}{A} \right)$$

where ρ = Proportionality constant & is known as specific resistance.

$$\text{If } A = 1\text{cm}^2 \text{ \& } l = 1\text{cm, then } R = \rho$$

Therefore, specific resistance can be defined as follows:

It is the resistance offered by a material or solution occupying one c.c. volume.

Unit: *Ohm.cm (in C. G. S.) or Ohm.m (in S. I.)*

❖ Conductance:

It is the tendency of a material or solution to allow the flow of current through it. It is the reciprocal of resistance, i.e.

$$\begin{aligned} \text{Conductance } (G) &= \frac{1}{\text{Resistance}(R)} \\ &= \left(\frac{1}{\rho} \right) \times \left(\frac{A}{l} \right) \\ &= \kappa \times \left(\frac{A}{l} \right) \end{aligned}$$

$$\text{where } \kappa = \frac{1}{\rho} = \text{specific conductance}$$

Unit: $\text{ohm}^{-1} = \text{mho} = \text{Siemens } (S)$

❖ Specific Conductance:

We know,

$$G = \kappa \times \left(\frac{A}{l}\right)$$

If $A = 1\text{cm}^2$ & $l = 1\text{cm}$, then $\kappa = G$

So, specific conductance is defined as the conductance of a solution at a constant temperature in a given solvent when two parallel electrodes of 1cm^2 cross – sectional area are placed in a solution 1cm apart.

Unit: $\text{ohm}^{-1}\text{cm}^{-1}$ (C. G. S.) or Siemens m^{-1} (S. I.)

❖ Cell Constant:

The ratio of the distance (l) between the electrodes to the cross – sectional area (A), of the electrodes is known as cell constant, i.e.

$$\text{Cell constant} = \left(\frac{l}{A}\right)$$

$$\text{Again, } G = \kappa \times \left(\frac{A}{l}\right)$$

$$\text{Or, } \left(\frac{l}{A}\right) = \left(\frac{\kappa}{G}\right)$$

$$\text{So, cell constant} = \frac{\kappa}{G} = \frac{\text{specific conductance}}{\text{observe conductance}}$$

Unit: cm^{-1} (C. G. S.) or m^{-1} (S. I.)

- If the conductance of a solution is measured using different conductivity cells, then specific conductance values are different. Justify or criticize.

We know,

$$\text{specific conductance} = \text{cell constant} \times \text{observed conductance.}$$

Since for different cells cell constant will be different, so specific conductance values are different in different cell.

❖ Equivalent Conductance:

The equivalent conductance of an electrolyte at a given temperature in a given solvent is the conductance of the solution containing 1gm . Equivalent of the electrolyte placed between two parallel electrodes at 1cm . apart & large enough cross – sectional area to accommodate the whole solution between the two electrodes. Mathematically, it is expressed as –

$$\Lambda_{eq.} = \frac{1000 \kappa}{C \text{ (in normality)}}$$

Unit: $\text{cm}^2 \cdot \text{ohm}^{-1} \cdot \text{equivalent}^{-1}$ (in C. G. S.) or $\text{m}^2 \cdot \text{siemens} \cdot \text{equivalent}^{-1}$

❖ Molar Conductivity:

The conductance of that volume of solution containing one mole of an electrolyte is known as molar conductivity. Mathematically, it is expressed as –

$$\Lambda_m = \frac{1000 \kappa}{C \text{ (in molarity)}}$$

Unit: $cm^2 \cdot ohm^{-1} \cdot mol^{-1}$ (in C.G.S.) or $m^2 \cdot siemens \cdot mol^{-1}$

➤ Which will have greater molar conductance & why?

(i) 1mol. KCl dissolved in 200 cc of the solution.

(ii) 1mol. KCl dissolved in 500 cc of the solution.

We know $\Lambda_m = K \times V$. So, higher the volume of solution higher will be the value of molar conductance. So, solution B has higher value of molar conductance.

❖ Relation between Equivalent & Molar Conductance:

$$1(M) = (n_+ \cdot z_+) 1(N)$$

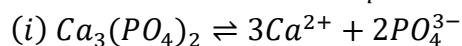
n_+ = number of cations

z_+ = charge of cations

$$\text{So, } \Lambda_m = (n_+ \cdot z_+) \Lambda_{eq.}$$

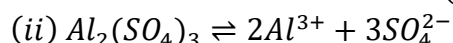
➤ Let the molar conductance of a $Ca_3(PO_4)_2$ solution be M_1 & that of a $Al_2(SO_4)_3$ solution be M_2 respectively. Express the respective equivalent conductance of the solutions, in terms of M_1 & M_2 .

We know $\Lambda_m = (n_+ z_+) \Lambda_{eq}$



So, $n_+ = 3$ & $z_+ = 2$

$$\text{So, } \Lambda_m = (3 \times 2) \Lambda_{eq}, \text{ Or, } \Lambda_{eq} = \left(\frac{M_1}{6}\right)$$



So, $n_+ = 2$ & $z_+ = 3$

$$\text{So, } \Lambda_m = (2 \times 3) \Lambda_{eq}, \text{ Or, } \Lambda_{eq} = \left(\frac{M_2}{6}\right)$$

❖ Variation of Equivalent Conductance with Dilution:

1. For strong electrolyte: Equivalent conductance of a strong electrolyte increases with dilution & attains a limiting value which does not change further with dilution. This value is called the equivalent conductance at infinite dilution (Λ_0). The explanation is as follows:

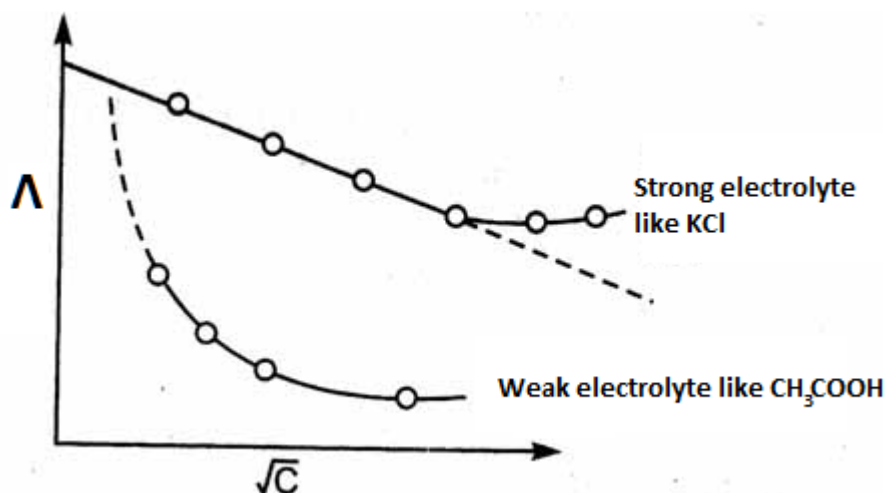
Strong electrolytes are fully ionized at all dilutions & so the number of ions is the same at all dilutions. The decrease of Λ with increase of concentration is attributed to decrease of speed due to strong interionic attraction which decreases with dilution. Hence, the equivalent conductance increases with dilution & attains a limiting value in sufficiently dilute solution, when the effect of interionic attraction becomes negligible.

Conductance (VJRC)

2. For weak electrolyte: As a weak electrolyte dissociate to a much lesser extent as compared to a strong electrolyte, therefore the conductance of weak electrolyte is much lower than that of a strong electrolyte at the same concentration.

Further the curve obtained for a weak electrolyte shows that there is a very large increase in conductance with dilution especially near infinite dilution. This is because as the concentration of weak electrolyte is reduced, more of it ionizes. Thus increase in conductance with decrease in concentration is due to the increase in the number of ions in the solution.

Graphical Representation:



❖ Variation of Specific Conductance with Dilution:

1. For Strong electrolyte: In case of strong electrolyte number of ions remain practically unchanged due to dilution. So number of ions per unit volume of solution decrease due to dilution. So specific conductance decreases with dilution for strong electrolyte.
 2. For weak Electrolyte: In case of weak electrolyte, the number of ions in the solution increases due to increased dissociation with dilution. But increase in the number of ions on dilution of weak electrolyte is much less than the increase in the volume of the solution. So, the number of ions per unit volume decreases. So, in case of weak electrolyte specific conductance decreases on dilution. So, the rate of decrease of specific conductance due to dilution is higher for strong electrolyte because with dilution number of ions increase for weak electrolyte but number of ions remain same for strong electrolyte.
- Solution of two electrolytes A & B are diluted. The Λ_m of B increases 1.5 times while that of A increases 25 times. Which is strong electrolyte?
B is strong electrolyte because on dilution of a strong electrolyte, number of ions remain almost same only asymmetric effect decrease, so increase of Λ_m will be very small with respect to weak electrolyte.

- Why the equivalent conductance at infinite dilution values cannot be obtained by plotting equivalent conductance *vs.* \sqrt{C} for weak electrolytes.

For weak electrolyte extrapolation to zero concentration is not possible as it is clear from the diagram. Experimentally also it is not possible to determine the Λ_c^0 value for weak electrolyte because though the dissociation is complete, the concentration of ions per unit volume is so low that the conductivity can't be measured accurately.

❖ Kohlrausch's Law of Independent Migration of Ions:

According to Kohlrausch's law of independent migration of ions at infinite dilution when the dissociation of electrolyte is completed & no inter-ionic effect is present, each ion in the solution migrates independently of its co-ions & contribute a definite share to the total equivalent conductance of the electrolyte that depends only on the nature of ion itself but not with its co-ion.

Mathematically, the law can be explained as –

$$\Lambda_{eq}^0 = \lambda_+^0 + \lambda_-^0$$

Where λ_+^0 & λ_-^0 are ionic equivalent conductance of cation & anion respectively.

Determining Λ_0 of a weak acid, HA : Here, $HA \rightleftharpoons H^+ + A^-$. According to Kohlrausch's law

$$\Lambda_{(HA)}^0 = \lambda_{H^+}^0 + \lambda_{A^-}^0$$

The equivalent conductance can be arrived by knowing the molar conductance at infinite dilution for the strong electrolyte KCl , HCl & KA . Now according to this law

$$\Lambda_{KCl}^0 = \lambda_{K^+}^0 + \lambda_{Cl^-}^0$$

$$\Lambda_{HCl}^0 = \lambda_{H^+}^0 + \lambda_{Cl^-}^0$$

$$\Lambda_{KA}^0 = \lambda_{K^+}^0 + \lambda_{A^-}^0$$

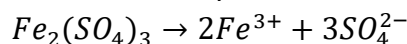
Hence we have –

$$\lambda_{H^+}^0 + \lambda_{A^-}^0 = (\lambda_{H^+}^0 + \lambda_{Cl^-}^0) + (\lambda_{K^+}^0 + \lambda_{A^-}^0) - (\lambda_{K^+}^0 + \lambda_{Cl^-}^0)$$

$$\text{So, } \Lambda_{(HA)}^0 = \Lambda_{HCl}^0 + \Lambda_{KA}^0 - \Lambda_{KA}^0$$

- Find the expression for Λ_0 (molar) of $Fe_2(SO_4)_3$ when λ_0 (molar) of cation & anion are x & y respectively.

Kohlrausch law of limiting molar conductivity is defined as the sum of the limiting ionic conductivities of the cation & the anion each multiplied with the number of ions present in one formula unit of electrolyte.



$$\text{So, } \Lambda_0 = 2x + 3y$$