ELECTROCHEMISTRY

CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

ELECTRO-CHEMICAL AND GIBB'S ENERGY: -

Electrochemistry: It is a branch of chemistry that deals with the relationship between chemical energy and electrical energy and their interconversions.

Redox Reactions: Oxidation is the process that involves the loss of electrons & reduction is a process in which it involves the gain of electrons. The reactions which involve both that reaction simultaneously is called a redox reaction.

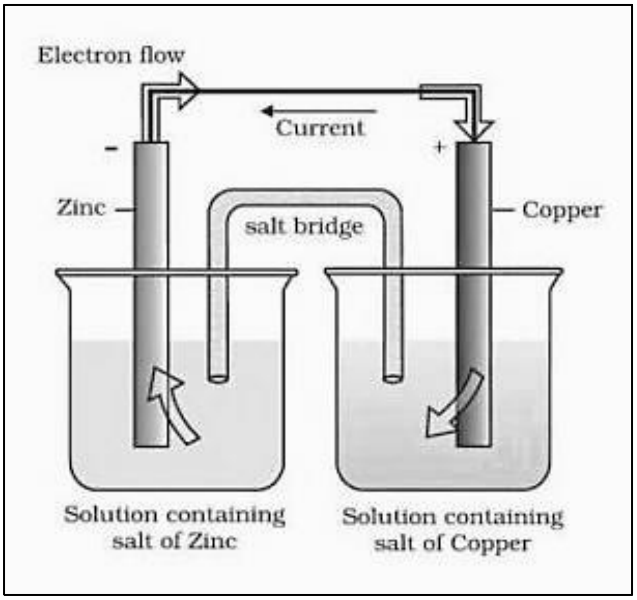
Electrochemical Cells: These are devices that convert the chemical energy of some redox reactions to electrical energy. They are also called Galvanic cells or Voltaic cells. An example for a Galvanic cell is Daniel cell.

It is constructed by dipping a Zn rod in $ZnSO_4$ solution and a Cu rod in $CuSO_4$ solution. The two solutions are connected externally by a metallic wire through a voltmeter and a switch and internally by a salt bridge.
A salt bridge is a U-tube containing an inert electrolyte like $NaNO_3$ or KNO_3 in a Gilly like substance.

The functions of a salt bridge are:

1. To complete the electrical circuit
2. To maintain the electrical neutrality in the two half cells.

- $Cu^{2+} + 2e^- \rightarrow Cu(s)$ (reduction half reaction)
- $Zn(s) \rightarrow Zn^{2+} + 2e^-$ (oxidation half reaction)



These reactions occur in two different portions of the Daniel cell. The reduction half-reaction occurs on the copper electrode while the oxidation half-reaction occurs on the zinc electrode. These two portions of the cell are also called half-cells or redox couples. The copper electrode may be called the reduction half-cell and the zinc electrode, the oxidation half-cell.

Electrochemical Cells Nernst Equation and Gibbs Energy

Electrode Potential: This tendency of a metal to lose or gain an electron when it is in contact with its own solution is called electrode potential.

Standard electrode potential (E0): The electrode potential measured at standard conditions.ie at 298K,1 atm pressure, and at 1 molar concentration.

Standard hydrogen electrode (SHE): The reference electrode used to measure single electrode potential. Its potential is assumed to be zero. It consists of a platinum wire dipped in HCl of 1 molar concentration. Hydrogen gas at 1 atm. is passed through the solution. The electrode can be represented as Pt, H_2 /H^+(1M).

Nernst Equation for A Cell Reaction: -

Let us consider a general equation

$aA + bB \rightarrow cC + dD$

$$E = E^0_{cell} - \frac{2.303\ RT}{nF} \times \log \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

Where E^0 is the standard electrode potential,

R is the gas constant (8.314 $JK^{-1}\ mol^{-1}$)

F is Faraday constant (96500 C mol^{-1})

T is the temperature in Kelvin.

Nernst equation can be written as:

Putting the above values Nernst equations can be written as

$$\mathrm{Ecell} = E^0\ \mathrm{cell} + \frac{0.0591}{n} \log \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

Equilibrium Constant from Nernst Equation:

For a Daniel cell, the emf of the cell at 298 K is given by

$$E_{eell} = E^0_{cell} + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

When the cell reaction attains equilibrium, $E_{cell} = 0$

$$\text{So, } 0 = E^0_{cell} + \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$Or,\ E^0_{cell} = \frac{-0.0591}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$= \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2}]}$$

But at equilibrium, $\frac{[Zn^{2+}]}{[Cu^{2+}]} = Kc$

So the above equation becomes,

$$E^0_{cell} = \frac{0.0591}{2} \log Kc$$

In General, $E^0_{cell} = \frac{2.303RT}{nF} \log Kc$

or, $E^0_{cell} = \frac{0.0591}{n} \log Kc$ at 298 K

Electrochemical Cells Nernst Equation and Gibbs Energy

Electrochemical Cell and Gibbs Energy of the Reaction:

Electrical work done in one second is equal to electrical potential multiplied by total charge passed. The reversible work done by a galvanic cell is equal to a decrease in its Gibbs energy and therefore if the emf of the cell is E and nF is the amount of charge passed and ΔG is the Gibbs energy of the reaction, then

$\Delta G = - nFE_{cell}$

If the concentration of all the reacting species is unity, then $E_{cell} = E^0_{cell}$ and we have

$\Delta G^0 = - nFE^0_{cell}$

Thus, from the measurement of E^0_{cell}, we can calculate the standard Gibbs energy of the reaction.

CONDUCTANCE OF ELECTROLYTIC SOLUTIONS: -

ELECTROLYTIC CONDUCTANCE

(a) **Resistance (R):** Metallic and electrolytic conductors obey ohm's law according to which the resistance of a conductor is the ratio of the applied potential difference **(V)** to the current following**(I)**.

$R = \frac{V}{I}$ • R is expressed in ohms.

(b) **Conductance (C):** The conductance of a conductor is equal to reciprocal of resistance

$C = \frac{1}{R}$ • C is expressed in mho.

(c) **Specific resistance (ρ):** The resistance (R) of a conductor of uniform cross section is directly proportional to its length(λ) and inversely proportional to its area of cross section (A)

$R \propto \frac{\ell}{A}$ $R = \rho \frac{\ell}{A}$

where ρ is a constant and called resistivity or specific resistance.

When $\lambda = 1$, $A = 1$, then $\rho = R$ thus the specific resistance may be defined as the resistance of a conductor of unit length and unit area of cross section.

- Unit of ρ → ohm .cm

(d) Specific conductance (κ): It is defined as the reciprocal of specific resistance $K=\frac{1}{\rho}$

The above definitions apply to metallic conductors and electrolytes.

- In the case of solution of electrolytes, the resistance offered by the solution to the flow of current is –
- Directly proportional to the distance between the electrodes

$$R \propto \lambda$$

- Inversely proportional to the area of cross section of the electrodes

$$R \propto \frac{1}{A} \quad R = \rho \frac{\ell}{A}$$

The conductance $C = \frac{A}{\rho\ell}$

$\because \frac{1}{\rho} = \kappa$

so $\kappa = \frac{C\ell}{A}$

If $\ell = 1$ cm and $A = 1$ cm^2 then

$\kappa = C$

Hence specific conductivity of a solution is defined as the conductance of one centimeter cube of the solution of the electrolyte.

- $\kappa = \frac{C\ell}{A}$

Where $\frac{\ell}{A}$ = cell constant

- Cell constant (x) is a fixed quantity for a particular cell and is defined as the distance between two parallel electrodes of a cell divided by the area of cross section of the electrodes.

$\kappa = C \times$ cell constant

cell constant $= \frac{K}{C} = \kappa R$ = Specific conductivity × resistance

- Unit of κ → ohm^{-1} cm^{-1}

(e) Equivalent Conductance (λeq) : It is defined as the product of specific conductance (κ) and the volume (V in mL) of the solution which contain one gram equivalent of the electrolyte.

$$\therefore \lambda eq = \kappa \times V$$

If concentration of solution is C - gram equivalent per liter then $\lambda eq = \frac{\kappa}{C} \times 1000$

- Unit $ohm^{-1}\ cm^{2}$ per gram equivalent

CLASSIFICATION OF CONDUCTIVITY: -

Depending on the magnitude of their (material) conductivity, they

1. conductors

2. Insulators

3. Semi-conductors

Conductors

- Metals and their alloys have large conductivity and are known as conductors.
- Their conductivity ranges from 104 to 107 $ohm^{1}\ m^{1}$

Ex:

All metals, alloys of metals, certain non-metals like carbon-black, graphite and some organic polymers like polyaniline, polypyrene and polythiophene etc.

Insulators

- Substances like glass, ceramics etc having very low conductivity are known as insulators.
- Their conductivity ranges from 10^{-20} to 10^{-10} $ohm^{-1}\ m^{-1}$

Semi-conductors

- Substance like silicon, doped silicon and gallium arsenide having resistivity in the range 1-106 conductors. ohm.cm are called semi
- These are very important materials used in electronic industry.

Superconductors

- The substance having zero resistivity or infinite conductivity are superconductors.
  Ex: A number of ceramic materials and mixed metal oxide conductors act as Superconductors at 150k.

TYPES OF CONDUCTANCE: -

Conductor: Substances which allow electric current to flow through them are called conductors.
Examples - Metals, Aqueous solution of acids, bases and salts, fused salts and impure water etc.

CONDUCTORS ARE OF TWO TYPES

(i) Metallic conductors

(ii) Electrolytic conductors or electrolytes.

(i) Metallic conductors: The conductors which conduct electric current by movement of electrons without undergoing any chemical change are known as metallic conductors. Metals (Cu, Ag, Fe, Al etc), non-metals (graphite) and various alloys and minerals are examples.

(ii) Electrolytic conductors: Those substances whose water solution conducts the electric current and which are decomposed by the passage of current are called electrolytes. In this case, conduction takes place by movement of ions.
electrolytes also conduct electricity in fused state and undergo decomposition by passage the electric current. Substances whose aqueous solution does not conduct electric current are called non-electrolytes.

They do not conduct electricity in the fused state also. Solutions of cane sugar, glycerin, glucose, urea etc. are the examples of non-electrolytes.

Strong electrolyte: Electrolytes which are completely ionized in aqueous solution or in their molten state, are called strong electrolytes.
Example – all salts, strong acid and strong base

Weak electrolyte: Electrolytes which are not completely ionized in aqueous solution or in their molten state, are called weak electrolytes.
Examples: - All carbonic acids (except sulphonic acid), CH_3COOH, HCN, NH_3 , amine, etc.

Difference between metallic and electrolytic conduction

S.No.	Metallic conduction	Eectrolytic conduction
(i)	Flow of electricity takes place without the decomposition of the substance	Flow of electricity takes place by chemical changes at electrodes.
(ii)	No transfer of matter takes place.	Transfer of matter takes place in the form of ions
(iii)	The resistance to the flow of current increases with the increase in temperature and hence the increase in temperature decreases the conduction.	The resistance to the flow of current decreases with the increase in temperature and hence increase in temperature increases the conduction.

CONDUCTIVITY OF IONIC SOLUTIONS & MOLAR CONDUCTIVITY: -

In this article, you will get to know about molar conductivity. What is the ionic solution? Moreover, the ways to determine the conductivity of ionic solutions. At first, we will understand the two types of compounds, namely, ionic and covalent.

The properties of ionic and covalent compounds vary according to different factors, which we will be discussing in this article. Let us first understand what ionic solutions are and any difference between ions and electrolytes. So, let us dive in together.

IONIC SOLUTIONS

The ionic solution is defined as the type of solution that contains ions for the conduction of electricity through them. Whenever an electrolyte breaks into a solution, it disintegrates into ions. The electrolytes which break into ions can only conduct electricity in molten or aqueous forms. These types of ions do not conduct electricity in the solid form. There are various ionic solutions like KNO_3, NaCl, KCl, etc.

Factors affecting the conductivity of Ionic Solutions

The conductivity of ionic solutions helps in the formation of batteries and other important devices. The conductivity of an ionic solution depends on various factors.

CONCENTRATION OF IONS

The main reason behind the conduction of electricity is the ions. As you increase the number of ions in a solution, the conductivity of these solutions will also increase. Due to the increased number of ions, there will be more carriers of charge, which will help the solution conduct better.

NATURE OF ELECTROLYTE

The nature of electrolytes varies with the conductance of ionic solution. As there will be more dissociation of ions in the solution, there will be an increase in the number of ions in the solution, which indicates the name conductivity of ionic solutions. Let us take an example of the compound CH_3COOH. The acetic acid has a very small degree of separation, which is why there are fewer ions of acetic acid in the solution.

All compounds of these types with a small degree of separation fall into the category of weak electrolytes. However, the electrolytes like KNO_3 have a high degree of dissociation, due to which they can easily break into ions. The solution would contain more ions as compared to other solutions. These types of solutions that contain compounds of a high degree of dissociation are termed good ionic solutions.

TEMPERATURE

Temperature plays a crucial role in the formation of an ionic solution. According to the observations, if you increase the temperature of a solution, then better will be the solubility of ions in the solution. The more solubility of ions will result in increased ionic conduction.

MOLAR CONDUCTIVITY: -

When you dissolve one mole of an electrolyte in a solution, the power of conducting a solution is termed molar conductivity. The molar conductivity of ionic solution depends upon various factors. To calculate the conducting electricity of an ionic solution, molar conductivity comes into play. The formula of molar conductivity is.

$$\lambda_m = \frac{\mathrm{K}}{c}$$

Where,

λ_m is the molar conductivity

MEASUREMENT OF THE CONDUCTIVITY OF IONIC SOLUTIONS

For the measurement of the molar conductivity of ionic solution, we take the help of a Wheatstone bridge. In order to calculate the unknown resistance, a Wheatstone bridge is the only option.

The conductivity cell comprises two platinum electrodes with a coating of platinum black. The area of cross-section of the electrodes is “A”, and the distance between them is “l”. Hence, the resistance of the column of the solution will be.

$R=P(l/A)$

CONCLUSION

Conductivity is the reverse of resistivity and its unit is ohm-1 cm-1. In SI units, l is addressed in m, and the space of the cross-area in m2, bringing about conductivity upsides of Sm-1. The substance controls the greatness of conductivity. The ionic solution is a solution containing ions for the conduction of electricity through them. Molar conductivity, also known as molar conductance, is a kind of electrical conductivity. It is the leading force of the relative multitude of particles made by dissolving one mole of an electrolyte in an arrangement.

EFFECT OF CONCENTRATION ON CONDUCTIVITY & MOLAR CONDUCTIVITY: -

On dilution, molar conductivity increases but conductivity decreases because on dilution rate of increase in volume is more than rate of inc. of ions.

VARIATION OF MOLAR CONDUCTIVITY WITH CONCENTRATION

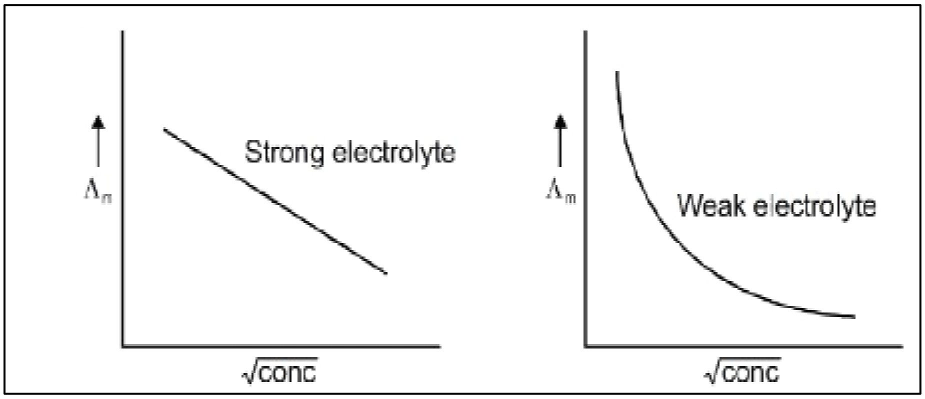
The values of both conductivity and molar conductivity of an electrolyte in solution change with the concentration of the electrolyte. Conductivity of all electrolytes always decreases with decrease in concentration because it is the conductance of all the ions present in unit volume and the number of ions per unit volume decreases with the decrease in concentration.

Molar conductivity of an electrolyte not only depends on the nature of electrolyte but also on its concentration. Depending upon the values of molar conductivity, the electrolytes can be divided into two groups, namely

(i) strong electrolytes

(ii) weak electrolytes.

For the same concentration, the molar conductivity of a strong electrolyte is higher than that of weak electrolyte because a strong electrolyte is completely ionised at all concentrations and a weak electrolyte is partially ionised in the high concentration region. As concentration of an electrolyte decreases the molar conductivity of a strong electrolyte marginally increases whereas it increases appreciably in case of a weak electrolyte. The former is due to increase in interionic distance on dilution which reduces the influence of cation on anion and vice versa whereas the latter is due to increase in the extent of ionisation of weak electrolytes on dilution. The plot of a graph between molar conductivity (A_m) vs $\sqrt{conc}$. for a strong electrolyte and a weak electrolyte is shown in the figure.

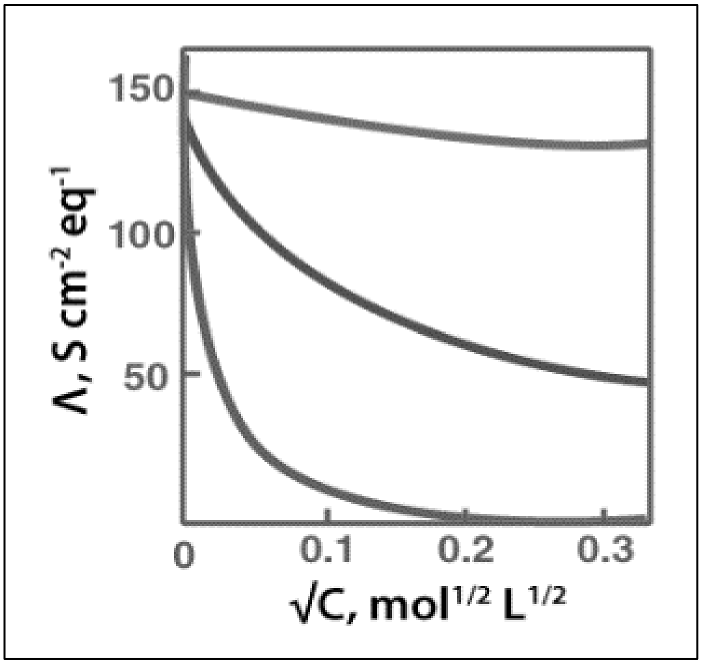


Molar conductivity of a strong electrolyte varies linearly with $\sqrt{concentration}$. It can be extrapolated when concentration approaches zero. The molar conductivity at infinite dilution is known as limiting molar conductivity and is represented by A_m^o or A_m^∞.It can be experimentally determined for strong electrolytes only because A_m slowly increases linearly with dilution and can be represented as

$A_m = 40\text{-}A\sqrt{C}$

The intercept of the plot along Y-axis is $A_m^o$and slope equal to (-A). The magnitude of slope for a given solvent and temperature depends on the charges on cations and anions produced on dissociation of the electrolyte in the solution. Thus, all electrolytes having same type of charges have same value for A.

Molar conductivity: increases with decrease in concentration as the total volume, V, of a solution containing one mole of electrolyte also increases. Upon dilution, the concentration decreases. When the concentration approaches zero, the molar conductivity of the solution is known as limiting molar conductivity, Ë°m. Variation of molar conductivity with concentration is different for strong and weak electrolytes



Variation of Molar Conductivity With concentration for strong electrolytes:

For strong electrolytes, the molar conductivity increases slowly with the dilution. The plot between the molar conductivity and $c^{1/2}$ is a straight-line having y-intercept equal to Ë°m. The value of limiting molar conductivity, Ë°m can be determined from the graph or with the help of Kohlrausch law. The general equation for the plot is given as:

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Λ_m = Ë°$_m$ -A$c^{1/2}$

Where -A is a constant equal to the slope of the line. For a given solvent, the value of “A” depends on the type of electrolyte at a particular temperature.

KOHLRAUSCH LAW OF INDEPLENDENT MIGRATION OF IONS: -

Kohlrausch's Law?

Kohlrausch's law states that the equivalent conductivity of an electrolyte at infinite dilution is equal to the sum of the conductance's of the anions and cations.

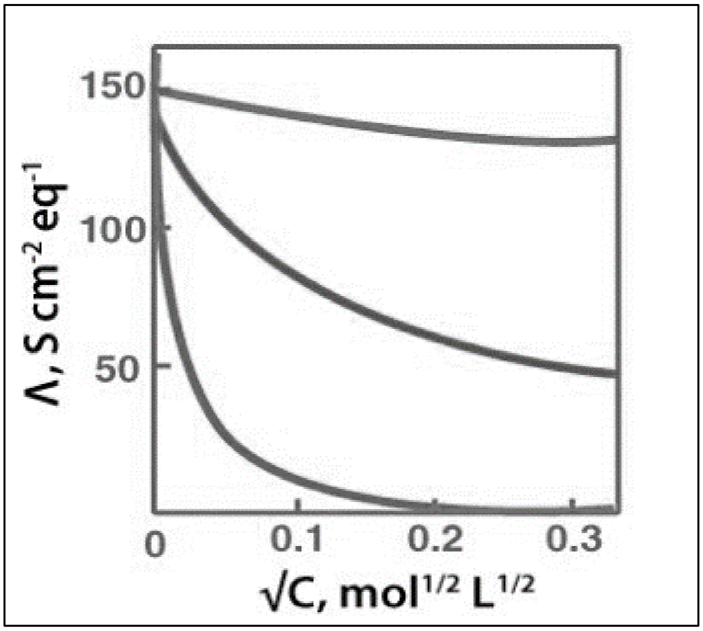
The molar conductivity of a solution at a given concentration is the conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with the unit area of cross-section and distance of unit length. The molar conductivity of a solution increases with the decrease in concentration. This increase in molar conductivity is because of the increase in the total volume containing one mole of the electrolyte. When the concentration of the electrolyte approaches zero, the molar conductivity is known as limiting molar conductivity, Ë$_{m}$°.

Kohlrausch observed certain regularities while comparing the values of limiting molar conductivities of some strong electrolytes. On the basis of his observations, Kohlrausch proposed "limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anions and cations of the electrolyte". This law is popularly known as Kohlrausch law of independent migration of ions. For example, limiting molar conductivity, Λ of sodium chloride can be determined with the knowledge of limiting molar conductivities of sodium ion and chloride ion.

$$\Lambda^{\circ}_{\mathrm{NaCl}} = \Lambda^{\circ}_{\mathrm{Na+}} + \Lambda^{\circ}_{\mathrm{Cl-}}$$

Some important applications of Kohlrausch law of independent migration of ions are:

Kohlrausch law helps us in the determination of limiting molar conductivities for any electrolyte. Weak electrolytes have lower molar conductivities and lower degree of dissociation at higher concentrations. The graph plotted between molar conductivity and $c^{1/2}$ (where c is the concentration) is not a straight line for weak electrolytes. The molar conductivity of weak electrolyte increases steeply at lower concentrations. Therefore, limiting molar conductivity, Λ cannot be obtained by extrapolation of molar conductivity to zero concentration. Hence, we use the Kohlrausch law of independent migration of ions for the determination of limiting molar conductivity, Λ for weak electrolytes.



Kohlrausch law also helps us in determining the value of dissociation constant from the value of molar conductivity and limiting molar conductivity for a weak electrolyte at a given concentration.

$\alpha \frac{\Lambda}{\ddot{E}m^{\circ}}$Where,

α = dissociation constant

Λ = molar conductivity

$\ddot{E}_m^{\circ}$ = limiting molar conductivity

Uses of Kohlrausch's law

- Calculation of Degree of dissociation
- Calculation of solubility of sparingly soluble salt
- Calculation of Dissociation Constant for weak electrolytes
- Calculation of Molar Conductivity for weak electrolytes at infinite dilution