Electro Chemistry Part -1

Introduction, Conductors, Conductivity, Electrolysis

Electro Chemistry deals with

i. The use of electrical energy for the dissociation of chemical compounds (electrolysis)

ii. The use of chemical reactions for the production of electrical energy (Electro-chemical cells)

iii. The use of electrical energy in the study and preparation of chemical substances.

iv. The commercial power generating cells, namely secondary cells (batteries & fuel cells)

Electric current is considered as flow of electrons or flow of electrical charges through a conducting system.

1. The Substance which allows the electric current to pass through it is called Electrical Conductor.

The electrical conductors are of two types.

(a)   Electronic Conductors (Metals),

(b)   Electrolytic conductors

Electronic conductors	Electrolytic conductors
1. Conductivity is due to mobility of free electrons from negative to positive end	1.Conductivity is due to mobility of free ions towards oppositely charged electrodes
2. During conduction matter is not	2. During conduction matter is transferred

transferred	in the form of ions
3. Passage of current may bring only as physical changes	3. Passage of current brings in physical well as chemical changes
4. The conductivity power is high	4. The conductivity power is relatively less
5. An increase in temperature decreases conductivity due to increased thermal vibration of particles or resistance increases	5. With an increase in temperature conductivity increases due to the increase in the degree of ionisation and increase in the mobility of ions.

CdS and CuS exhibits electronic conduction due to crystal defect.

Solutions of alkali metals in liquid ammonia are mixed conductors. They contain ammoniated cations (solvated cations) and ammoniated electrons (solvated electrons). They conduct electric current due to the mobility of ions and electrons.

2. Electronic conduction depends on

   (i) The nature and structure of the metal

   (ii) The number of valence electrons per atom

   (iii) Temperature (conductivity decreases with increase of temperature)

* Non-metals like Carbon-black, graphite, organic polymers like polyaniline, polypyrrole, polythiophene, poly acetylene when exposed to vapours of iodine are electronic conductors.

* Metals and their alloys, at very low temperatures (0 to 15 K) were known to behave as superconductors.

3. Electrolytic conduction depends on

   (i) The nature of the electrolyte added

(ii) Size of the ions produced and their solvation

(iii) The nature of the solvent and its viscosity

(iv) Concentration of the electrolyte

(v) Temperature (conductivity increases with the increase of temperature)

.

4. Electrolytic Solution - Resistance and Conductance

Like electronic conductors (Metallic wires) electrolytic solutions obey ohm's law and Aqueous electrolytic solutions offer resistance like metallic wires to the flow of current.

i. Ohm's Law: It states that the current (I) flowing through a conductor at a given temperature is proportional to the potential difference (V) and inversely proportional to resistance (R). Mathematically it can be expressed as V=IR

ii. Resistance (R): It is the opposition to the flow of current offered by the electrolytic solution. Its units are Ohm(Ω)

S.I base units of ohm = $\left(kg\ m^2\right)/\left(S^3 A^2\right)$

The resistance 'R' offered by the electrolytic solution, taken in a conductivity cell, is directly proportional to distance of separation. 'l' between the two parallel electrodes of the cell and inversely proportional to the area of cross-section (a) of electrode i.e,

$R \propto \dfrac{l}{a}$ or $R = \rho . \dfrac{l}{a}$ where ρ = specific resistance (Resistivity). It can be measured with the help of wheat stone bridge.

iii. Conductance (C)

It is the reciprocal of the electrical resistance (R), $C = \dfrac{1}{R}$

It measures the ease with which the current flows through a conductor

$$C = \frac{1}{R} \Rightarrow C = \frac{1}{\rho} \times \frac{1}{l/a} = k \times \frac{1}{l/a} \quad \therefore k = C \times \frac{l}{a}$$

Where C = Conductance, K=Specific conductance (Conductivity), $\frac{1}{a}$ = Constant known as cell constant. Its units are **cm⁻¹ (or) m⁻¹**.

S.I unit of conductance = Siemens (S) or 'mho'

iv. Specific Resistance (or) Resistivity (ρ)

The resistance in ohm of a conductor having length of 1cm and area of cross - section is called resistivity (or) "The resistance offered by 1 solution of an electrolytic solution" is called resistivity ().

Its units are ohm – cm

S.I unit: ohm - metre

$$R = \rho X \frac{l}{a}$$

v. Measurement of Conductivity of Ionic Solutions

Resistance of ionic solution is measured by using conductivity cell.

Conductivity cell consists of two platinum electrodes coated with platinum black, whose area of cross section equal to 'a' and are separated by distance 'l'

Resistance of solution is determined by the equation. $R = \rho \frac{\ell}{a} = \frac{\ell}{ka}$

The quantity $\frac{l}{a}$ is called cell constant denoted by the symbol, G*. It depends on Distance between the electrodes & Area of cross sections

The cell constant is determined by measuring the resistance of the cell containing a solution whose conductivity is already known.

vi. Specific, Molar and Equivalent Conductance

The conductance (or) the current conducting capacity of an electrolytic solution can be expressed as

a) Specific conductance (k),

b) Molar conductance (μ),

c) Equivalent conductance (Λ)

a) Specific Conductance (k): It is the conductance of the solution enclosed between two parallel electrodes of unit area of cross section separated by a unit distance. (or) The conductance of the electrolyte in the solution of volume of $1cm^3$ (CGS units) (or) The conductance of the electrolyte in the solution of volume of $1m^3$ (SI units)

$$k = C \times \frac{\ell}{a}$$

If   Cell constant = 1 then k = C

The conductivity of solutions of different electrolytes in the same solvent and at a given temperature differs due to

(i) Charge and size of the ions in which they dissociate.

(ii) The concentrations of ions (or) ease with which the ions move under a potential gradient.

b) Molar Conductance (μ)

The conductance of a volume of solution containing 1 gram molecular weight of the electrolyte placed between two parallel electrodes separated by a distance of unit length of 1 centimeter (in CGS system) or 1 meter (in SI system) is called molar conductance.

Relation between specific conductance (k) & molar conductance (μ),   of an electrolytic solutions, is as follows

$$\mu = \frac{k \times 1000}{molarity}$$

Units of molar conductance are $ohm^{-1} \, cm^2 \, mol^{-1}$ in CGS system and $S \, m^2 \, mol^{-1}$ in SI system. c)Equivalent conductance (Λ) :- The conductance of a volume of

solution containing 1 gram equivalent of the electrolyte placed between two parallel electrodes separated by unit length of 1 centimeter (in CGS units) (or) 1 meter (in SI units) is called equivalent conductance .

Relation between 'k' and (Λ) is $\wedge = \dfrac{k \times 1000}{normality}$

Units of equivalent conductance are ohm^{-1} cm^{2} eq^{-1} in CGS system and Sm^{2} eq^{-1} in SI system.

If 'k' is given in SI units, then $\mu = \dfrac{k}{1000M}$ and $\Lambda = \dfrac{k}{1000N}$.

For a given solution, $\mu \times Molarity = \Lambda \times Normality$

Note: An electrolytic solution whose molarity is equal to its normality has the same value for molar conductance () & equivalent conductance

Eg: KCl solution, NaCl solution, HCl, NaOH etc

vii. Factors Effecting Molar and Equivalent conductance's

1. Nature of electrolyte i.e, strong (or) weak
2. Nature of the solvent
3. Viscosity of solvent
4. Temperature
5. Concentration of electrolyte
6. Size of the ions produced & their solvation

viii.Variation of Conductance with concentration:

a) Specific conductance of a solution increases with increase in the ionic concentration of the solution (no. of ions per unit volume increases). But equivalent and molar conductance decrease with increase in concentration (

decrease in ionic mobility and increase in interionic attractions)

b) The specific conductance (k) or conductivity at any specified concentration of an electrolyte depends on the nature of the electrolyte.

Strong electrolytes show high conductance while weak electrolytes show low conductance at any given concentration

The variation of equivalent conductance (or) molar conductance () with the concentration of the electrolyte is generally expressed graphically, as follows
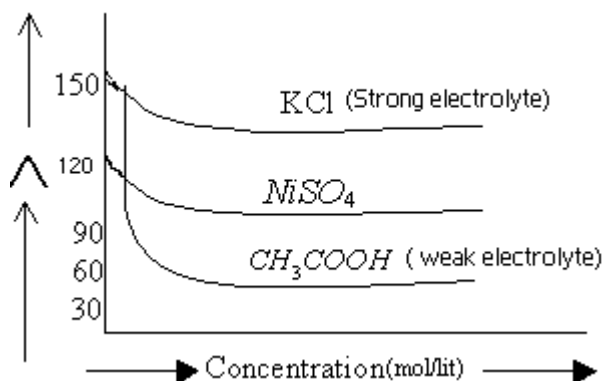
It indicates that the variation of Λ with concentration depends to a great extent on the type of the electrolyte rather than on the actual chemical nature of it.

Thus equivalent conductance (or) molar conductance of electrolytic solution increases with decrease in concentration.

For strong uni-univalent electrolytes (Eg. KCl), the decrease in Λ with increase in concentration is not very large.

If electrolyte is not uni-univalent electrolyte then decrease in Λ with concentration is more marked as the valency of the ions increases. They behave in an intermediate manner.

Eg; $NiSO_4$(Bi-Bivalent),$BaCl_2$(Bi-Univalent)

Weak electrolytes [CH_3COOH,NH_4OH]exhibit an apparently different behaviour as they are not ionised completely.

Effect of Dilution

(1) With dilution "Λ" as well as ""μ of both weak&strong electrolytes increases.

2) Specific conductivity (k) decreases with dilution because of decrease in no. of ions per Ic.c of electrolyte.

3) The molar (or) equivalent conductance of an electrolyte at infinite dilution (or) zero concentration is known as limiting molar conductance (or) limiting equivalent conductance [.Λo]

4) $\Lambda 0$ value for any strong electrolyte is calculated by graphically but for weak electrolyte it is determined by kohlrausch's law.

5. The magnitude of increase in molar conductance for weak electrolyte is much larger than that for a strong electrolyte because strong electrolytes are almost completely ionised in all concentration and increase in μ (or) Λ with dilution is only due to decrease in interionic attractions.

Effect of Temperature

The conductivity of all electrolytes increases with increase in temperature

Conductance Ratio: The ratio of the equivalent conductance at any concentration $\left(\wedge_c\right)$ to that at infinite dilution [$\Lambda 0$]is called conductance ratio[$\propto$] .

$$\alpha = \frac{\wedge_c}{\wedge_o} \quad \text{or} \quad \alpha = \frac{\mu_c}{\mu_0}$$

For weak electrolytes, $\propto$ = degree of ionisation.

\# $\propto$ is high for 0.01 M CH_3COOH solutionwhen compared to that of 0.1 M CH_3COOH , because $\wedge_C$ is high in case of 0.01 M

IX: Debye - Huckel - Onsagar Equation:

In the case of weak electrolytes like CH_3COOH,NH_4OH, $\propto$ is known as degree of dissociation (or) degree of ionisation of electrolyte.

The equivalent conductance at large dilution (or) at very low concentration is known as equivalent conductance at infinite dilution $\left(\wedge_\infty\right)$ or Zero concentration $\left(\wedge_o\right)$

The equivalent conductance of an electrolytic solution at any concentration (C) is related to $\left(\wedge_o\right)$ for a solution is given by the following Debye-Huckel - onsagar equation.

$$\wedge_C = \wedge_o - \left[\frac{82.4}{\left(DT\right)_\eta^{1/2}} + \frac{8.2 \times 10^5}{\left(DT\right)^{3/2}} \wedge_o \right] \sqrt{C} \qquad \text{Where}$$

D = Dielectric constant of water

T = Temperature in Kelvin scale

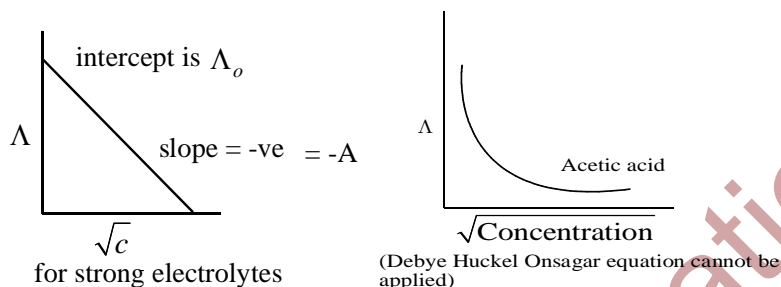$\wedge_c$ = Equivalent conductance at conc. 'c'

$(\wedge_o)$ = equivalent conductance at almost zero concentration or infinite dilution.

η = viscosity co-efficient of solvent.

In short form this equation is represented as $\wedge_c = \wedge_0 - b\sqrt{C}$

Where b is constant and depends on the nature of the solvent and temperature.

variation of equivalent conductance with $\sqrt{c}$ **is** a straight line with negative slope.

At infinite dilution c tends to be zero. $\therefore \wedge_c = \wedge_0$

$(\wedge_o)$ Can be determined by extrapolating the graph to zero concentration. This is

not applicable for weak electrolytes

Basing on k (specific conductance) value, electrolytes are of two types.

1) Weak electrolytes: These have low 'k' value

Eg : weak acids, weak bases.

2) Strong electrolytes:These have high 'k' value

Eg : strong Acids, strong Bases, Salt solutions.

The conductance of an electrolyte is due to its ionisation.

The ionisation extent reaches maximum for weak electrolytes as dilution reaches

maximum

X: Kohlrausch's law

"The equivalent conductance at infinite dilution $(\wedge_\infty)$ of an electrolyte is equal to the algebraic sum of equivalent conductances (or) motilities of anion (Λ_0^-) and cation (Λ_0^+) of the electrolyte at infinite dilution"

$$\Lambda_0 \text{ (electrolyte)} = \Lambda_0^+ + \Lambda_0^- \text{ (ions) and } \Lambda_{eq}^\circ = \frac{1}{n^+}\Lambda_c^\circ + \frac{1}{n^-}\Lambda_a^\circ$$

e.g. (i) $\Lambda_{KCl}^\circ = \Lambda_{K^+}^\circ + \Lambda_{Cl^-}^\circ$

(ii) $\Lambda_{CaCl_2}^\circ = \frac{1}{2}\Lambda_{Ca^{++}}^\circ + \Lambda_{Cl^-}^\circ$

(iii) $\Lambda_{Fe_2(SO_4)_3}^\circ = \frac{1}{3}\Lambda_{Fe^{3+}}^\circ + \frac{1}{2}\Lambda_{SO_4^{2-}}^\circ$

Where n^+ and n^- are charge on each ion furnished by electrolyte. This law is valid at any dilution but is applied only at infinite dilution. Whereas "molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the cations and the anions each multiplied by the number of ions present in one formula unit of electrolyte" e.g. $A_x B_y$

$$\Lambda_M^\circ = x \times \lambda_A^\circ y^+ + y \times \lambda_B^\circ x^-$$

e.g: $\Lambda_{Fe_2(SO_4)_3}^\circ = 2\Lambda_{Fe^{3+}}^\circ + 3\Lambda_{SO_4^{2-}}^\circ$

Note: Ionic conductance is more for hydrated Cs^+ than hydrated Li^+

Applications

i) Determination of Λ_o for weak electrolytes

   Eg: NH_4OH is a weak electrolyte its Λ_o is calculated as

$$\wedge_0 (NH_4OH) = \wedge_0 (NH_4Cl) + \wedge_0 (NaOH) - \wedge_0 (NaCl)$$

ii) Degree of ionisation of weak electrolyte $(\propto) = \dfrac{\mu_c}{\mu_0} = \dfrac{\wedge_c}{\wedge_0}$

   μc = molar conductivity at given concentration

Λ_c = equivalent conductivity at given concentration

μo = limiting molar conductivity

Λ_o = limiting equivalent conductivity Dissociation constant of weak electrolyte

$K = c\alpha^2$

iii) $\mu_m^0 = \wedge_{eq}^0 \times \dfrac{\text{molecular weight}}{\text{equivalent weight}}$

iv) Solubility of sparingly soluble salts, $\mu = \dfrac{k_{salt} \times 1000}{\text{solubility}}$ (or) $S_{\text{in moles/lit}} = \dfrac{k_{salt} \times 1000}{\mu}$

K_{salt} = specific conductance of sparingly soluble salt

Solubility product of salt can be calculated from solubility. $k_{salt} = k_{solution} - k_{solvent}$

$K_{solution}$= Specific conductance of saturated solution

$K_{solvent}$ = Specific conductance of solvent

v) Ionic mobilities can be calculated as :

Ionic mobility $\mu = \dfrac{speed\ of\ the\ ion}{potential\ gradient}$, $\mu_+ = \dfrac{\lambda_+}{F} = \dfrac{\lambda_+}{96,500}$, $\mu_- = \dfrac{\lambda_-}{F} = \dfrac{\lambda_-}{96,500}$

vi) Calculation of dissociation constant of weak electrolytes. $K = \dfrac{C\alpha^2}{1-\alpha}$

XI: Electrolyte: A substance, that is, in the molten state (fused state) or in the dissolved state (in water or any other solvent) containing ions and is functioning as an electrically conducting medium is called an electrolyte.

i. Non Electrolyte:

The substance which does not conduct electricity either in its molten state or in aqueous solution is called a non–electrolyte. Sugar Solution, glucose solution, urea in water, organic solvents, non polar covalent substances, are non electrolytes. Pure water is a poor conductor of electricity.
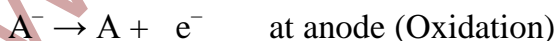
ii. Strong Electrolyte:

Electrolytes, which ionize almost completely at moderate dilutions and have high conductivity, are called Strong Electrolytes. Mineral acids (HCl, H2SO4,HNO3),

alkali and alkaline earth metallic hydroxides and most of the salts are strong electrolytes in aqueous solution.

iii. Weak Electrolytes: Electrolytes, which ionize partially and have low conductivity, are called Weak Electrolytes. Most of the organic acids, bases and salts like CH_3COONH_4, $HgCl_2$, $BaSO_4$, NH_4OH, H_3BO_3 are weak electrolytes.

XII: Mechanism of electrolysis–its application

a) The decomposition of an electrolyte at the electrodes as a result of the passage of electric current is called electrolysis. (or)The process of decomposition of an electrolyte by passing electric current is called electrolysis.

b) The cell in which electrolysis is carried out is called electrolytic cell.

c) In an electrolytic cell, electrical energy is converted into chemical energy.

d) In the electrolytic cell, an external source of emf (battery) is used.

e) The medium through which the electrons enters and leaves the electrolyte is called electrode.

i. Cathode (–): It is the electrode which is connected to the –ve terminal of the battery, and through which the electrons enter the electrolyte.

ii. Anode (+): It is the electrode, which is connected to the +ve terminal of the battery, and through which the electrons leave the electrolyte.

f) In an electrolytic cell oxidation of anions takes place at anode and reduction of cations takes place at cathode. Electrons flow from anode to cathode, but current flow from cathode to anode.

$MA \rightleftharpoons M^+ + A^-$ (Ionisation)

$M^+ + e– \rightarrow M$ at cathode (Reduction)

$A^- \rightarrow A + e^-$ at anode (Oxidation)

When a solution contains two (or) more anions and cations, the ion with the lower discharge potential will deposit first.

g) Decreasing order of discharge potentials for various anions

$SO4^{-2} > NO^{3-} > OH^- > Cl^- > Br^- > I^-$

Decreasing order of discharge potentials for various cations

$$K^+ > Na^+ > Ca^{2+} > Mg^{2+} > Al^{3+} > Mn^{2+} > Zn^{2+} > Cr^{3+} > Fe^{2+} > H+ > Cu^{2+} > Hg+$$

$$> Ag+ > Au3^+$$

h) ORDER OF DEPOSITION OF ANIONS

$$CO_3^{-2} > I^- > Br^- > Cl^- > OH^- > NO_3^- > SO_4^{-2}$$

ORDER OF DEPOSITION OF CATIONS

$$Au^+ > pt^{+2} > Ag^+ > Hg^+ > Cu^{+2} > H^+ > Fe^{+3} > Cr^{+3} > Zn^{+2} > Mn^{+2} > Al^{+3} > Mg^{+2} >$$

$$Ca^{+2} > Na^+ > K^+ > Li^+$$

I) Electrodes which do not involve in chemical reaction during electrolysis are called inert electrodes.

eg. Graphite, Platinum, etc

In some cases, the electrodes also may take part in the electrolysis reaction. Such electrodes are called active electrodes.

eg: In the electrolysis of NiCl2(fused) using nickel electrodes, the anode nickel dissolves electrolytically as nickel ion.

eg. Cu Anode in aqueous CuSO$_4$

Electrolysis of some substances and the respective products

Electrolyte used	Anode used	Anode reaction	Cathode used	Cathode reaction
Fused NaCl	Pt	$2Cl^- \rightarrow Cl_2 + 2e^-$	Pt	$Na^+ + e^- \rightarrow Na$
Aq. NaCl	Pt	$2Cl^- \rightarrow Cl_2 + 2e^-$	Hg	$Na^+ + e^- \rightarrow Na$
Aq. NaCl	Pt	$2Cl^- \rightarrow Cl_2 + 2e^-$	Pt	$2H^+ + 2e^- \rightarrow H_2$
Fused NaOH	Pt	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	Pt	$Na^+ + e^- \rightarrow Na$
Aq. NaOH	Pt	$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$	Pt	$2H^+ + 2e^- \rightarrow H_2$
Aq. HCl	Pt	$2Cl^- \rightarrow Cl + 2e^-$	Pt	$2H^+ + 2e^- \rightarrow H_2$
Aq. H_2SO_4	Pt	$2H_2O \rightarrow O_2 + 4e^- + 4H^+$	Pt	$2H^+ + 2e^- \rightarrow H_2$
50% H_2SO_4	Pt	$2HSO_4 \rightarrow H_2S_2O_8 + 2e^-$	Pb	$2H^+ + 2e^- \rightarrow H_2$
Aq. Na_2SO_4	Pt	$2H_2O \rightarrow O_2 + 4e^- + 4H^+$	Pt	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
Fused $CuCl_2$	Pt	$2Cl^- \rightarrow Cl_2 + 2e^-$	Pt	$Cu^{2+} + 2e^- \rightarrow Cu$
Aq. $CuCl_2$	Pt	$2Cl^- \rightarrow Cl_2 + 2e^-$	Pt	$Cu^{2+} + 2e^- \rightarrow Cu$
Aq. $CuCl_2$	Cu	$Cu \rightarrow Cu^{2+} + 2e^-$	Cu	$Cu^{2+} + 2e^- \rightarrow Cu$
Aq. $CuSO_4$	Pt	$2H_2O \rightarrow O_2 + 4e^- + 4H^+$	Pt	$Cu^{2+} + 2e^- \rightarrow Cu$
Fused $MgCl_2$	C	$2Cl^- \rightarrow Cl_2 + 2e^-$	Steel	$Cu^{2+} + 2e^- \rightarrow Cu$
Fused MgO	C	$2O^{2-} \rightarrow O_2 + 4e^-$	Fe	$Mg^{2+} + 2e^- \rightarrow Mg$
Fused NaH	Pt	$2H^- \rightarrow H_2 + 2e^-$	Pt	$Na^+ + e^- \rightarrow Na$
Aq. $AgNO_3$	Pt	$2H_2O \rightarrow O_2 + 4e^- + 4H^+$	Pt	$Ag^+ + e^- \rightarrow Ag$
Aq. $AgNO_3$	Ag	$Ag \rightarrow Ag^+ + e^-$	Ag	$Ag^+ + e^- \rightarrow Ag$
Aq. $ZnSO_4$	Zn	$Zn \rightarrow Zn^{2+} + 2e^-$	Zn	$Zn^{2+} + 2e^- \rightarrow Zn$