3. ELECTRO CHEMISTRY

Synopsis:

- It deals with chemical changes involving electricity
- Some chemical reactions require electric current and some chemical reactions produce electric current.

  Conductors : The substances which allow current to pass through them.
- Conductors are of 2 types.
  - i) Electronic conductors : The substances which allow current to pass through them without undergoing any physical or chemical change are called electronic conductors.

    Ex. metals, gas carbon, petroleum coke, CdS and CuS etc.
  - ii) Electrolytic conductors: Substances which conducts electricity in molten state or in aqueous solution because of some chemical change are called electrolytic conductors or electrolytes.

    Ex. – All salts, acids and bases.

Differences between electronic conductors and electrolytic conductors :

Electronic conductors	Electrolytic conductors
1. Flow of electrons.	1. Flow of ions.
2. No chemical change.	2. Chemical change occurs.
3. No transfer of mass.	3. Transfer of mass.
4. Increase in temperature conductance decreases with increase in temperature and resistance increase.	4. Conductance increases with increase of temperature due to decrease in resistance for mobility of ions.

Arrhenius theory of electrolytic dissociation:

- It explains the behaviour of weak electrolytes.
- Any electrolyte must ionise and should be in equilibrium with unionised, substance.

  $AB \rightleftharpoons A^+ + B^- \quad \alpha = \sqrt{\frac{ka}{c}}$

  α = degree of dissociation

  c = concentration

  ka = dissociation constant
- For strong electrolytes $\alpha \approx 1$.

  Ex : All strong acids and strong bases, solutions of all salts.
- For weak electrolytes $\alpha << 1$.

  Ex :All weak acids and weak bases.
- α of weak acids and bases depend on dielectric constant value of solvent.
- Property of solvent to increase the ionisation of solute is called as dielectric constant.

  Degree of ionisation α Dielectric constant.
- Cation $\rightarrow$ cathode (reduced)
- Anion $\rightarrow$Anode (oxidised)

Electrolysis : The decomposition of a chemical compound in the molten state or in the solution state into it's constituent elements under the influence of an applied emf is called electrolysis.

- It is a redox reaction and endo-energic reaction
- It is non – spontaneous.
- At infinite dilution for weak acids and weak bases. $\alpha \approx 1$.
- With increase in dilution interionic attractions decreases and so mobility of ions increases and conductance increases.
- **Electrodes** are of two types.
- Inert electrodes : Which do not take part in electrolysis reaction. Ex: Graphite, pt.
- Active electrodes: Take part in electrolyte reaction.
  Metal present in same electrolyte acts as an active electrode.
  Ex: Cu rods in $CuSO_4$ sol., Ag rods in $AgNO_3$ sol.
- Nature of products of electrolysis : Depends on
  i) Nature of electrolyte.
  ii) Nature of electrodes.
- The ion (cation / anion) with low discharge potential is preferentially discharge first.
- Discharge potential: It is the amount of current required to discharge the ion.
- In case of cations, the cation with high reduction potential is discharged preferentially.
- In case of anions, the anion with higher oxidation potential is discharged preferentially.
- Less reactive cation / anion is readily discharged.

Cations	Anions
1) $Zn^{2+} < Cu^{2+}$	1) $F^- < Cl^- < Bi^- < I^-$
2) $Cu^{2+} < Ag^+$	2) $OH^- < Cl^-$
3) $Zn^{2+} < H^+$	3) $OH^- > SO_4^{2-}$
4) $Cu^{2+} > H^+$	4) $OH^- > NO_3^-$

- The products in the electrolysis will depend on nature of electrolyte, concentration of electrolyte and nature of electrode.

Electrolyte	Product at cathode	Product at anode
1) H_2O	H_2	O_2
2) dil.H_2SO_4	H_2	O_2
3) dil.NaOH	H_2	O_2
4) fused. NaCl	Na	Cl_2
5) aq.NaCl	H_2	Cl_2
6) very dil.NaCl	H_2	O_2
7) aq.NaCl [(Hg) cathode]	Na	Cl_2
8) 50% dil H_2SO_4	H_2	$H_2S_2O_8$
9) Na_2SO_4 sol.	H_2	O_2
10) $CuSO_4$ sol.	Cu	O_2
11) $CuSO_4$ (Cu electrode)	$Cu^{2+} \xrightarrow{2e^-} Cu$	$CU \rightarrow Cu^{2+} + 2e^-$

12) $AgNO_3$ sol.	Ag	O_2
13) $AgNO_3$ sol./ (Ag electrodes)	$Ag^+ \xrightarrow{e^-} Ag$	$Ag \rightarrow Ag^+ + e^-$
14) Stannous chloride (fused)	Sn	$SnCl_4$
15) $Aq.K_2SO_4$	H_2	O_2
16) Aq.KCl	H_2	Cl_2
17) $Aq.CuCl_2$	Cu	Cl_2
18) Fused NaOH	Na	O_2

- **Electrolytic Solution - Resistance - 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.

- **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 or $I = \frac{V}{R}$

- **RESISTANCE(R):** It is the opposition to the flow of current offered by the electrolytic solution. Its units are $\boxed{ohm(\Omega)}$
- The resistance 'R' offered by the electrolytic solution, taken in a conductivity cell, is directly proportional to distance of separation. '' between the two parallel electrodes of the cell and inversely proportional to the area of cross-section (a) of electrode i.e, $R \propto \frac{l}{a}$ or $\boxed{R = S.\frac{l}{a}}$ where S = specific resistance (Resistivity)

- **CONDUCTANCE (C) :**
- It is the reciprocal of the electrical resistance (R) i.e, $\boxed{C = \frac{1}{R}}$
- It measures the ease with which the current flows through a conductor

$$C = \frac{1}{R} \Rightarrow C = \frac{1}{S} \times \frac{1}{l/a}$$

$$= k \times \frac{1}{l/a} \quad \boxed{\therefore k = C \times \frac{l}{a}}$$

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

- **SPECIFIC RESISTIVITY OR RESISTIVITY (S)** :

We know that $R \propto \frac{l}{a} \Rightarrow R = S\frac{l}{a}$

or $\boxed{R = S \times cell\ cons\tan t}$

- Where S = Resistivity
- Length and a = area of cross sction of the conductor
- $\frac{l}{a}$ = cell constant
- 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 (S). Its units are $\boxed{ohm - cm}$

- **SPECIFIC, MOLAR AND EQUIVALENT CONDUTANCE**
- 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 $(\wedge)$

(A) Specific Conductance (k) : It is the reciprocal of specific resistance (S) i.e, $k = \frac{1}{S}$

$$R = S.\frac{l}{a}$$

$$\Rightarrow \frac{1}{C} = \frac{1}{k}.\frac{l}{a} \Rightarrow \boxed{k = C \times \frac{l}{a}}$$

- Where C = conductance
- $\frac{l}{a}$ = cell constant
- Since : $k = C \times \frac{l}{a}$, if l = 1cm ; $a = 1cm^2$ then $\boxed{k = C}$ thus the conductance of of electrolytic solution is called specific conductance (k)

Or

- Similarly, the conductance of the electrolyte in the solution of volume of is known as specific conductance (k)

Or

- The conductance of the solution enclosed between two parallel electrodes of unit area of cross-section separated by a unit distance is called specific conductance (k)
- Its units are : $ohm^{-1} \times cm^{-1}$ (in CGS system)
  or $ohm^{-1}m^{-1} or\ S \times m^{-1}$ (in SI system)
- **Note: -** If l / a (Cell constant) = 1 then k = C

(B) Molar Conductance (μ) : It is the conducting power of all the ions produced by dissolving 1 gram mole of an electrolyte

(or)

- 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 (μ).
- Relation between specific conductance (k) & molar conductance (μ) of an electrolytic solutions, is as follows $\boxed{\mu = \frac{k \times 1000}{Molarity}}$
- Units of μ : $ohm^{-1}.cm^2.mol^{-1}$ (in CGS system)
- (or) $mho.cm^2.mol^{-1}$ (in CGS system)

- (or) S. $cm^2.mol^{-1}$ (in CGS system)
- or) $ohm^{-1}.m^2.mol^{-1}$ (in SI system)

(C) **Equivalent Conductance** $(\wedge)$ **:-** It is the conducting power of all the ions produced by dissolving 1 gram equivalent of an electrolyte (or) 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 $(\wedge)$.

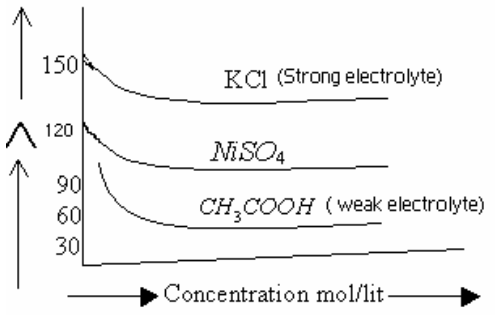
- Relation between 'k' and $\wedge$ is as follows

$$\boxed{\wedge = \frac{k \times 1000}{Normality}}$$

- Units of $\wedge$: - $ohm^{-1}.cm^2.equivalent^{-1}$
- (or) $mho.cm^2.equivalent^{-1}$
- (or) $S.cm^2.equivalent^{-1}$ (in CGS system)
- (or) $ohm^{-1}.m^2.equivalent^{-1}$ (in SI system)

- **Factors Affecting Molar And Equivalent Conductances:**
- Nature of electrolyte i.e, strong or weak
- Nature of the solvent
- Viscosity of solvent
- Temperature
- Concentration of electrolyte
- Size of the ions produced & their salvation

- **Variation Of Conductance With Concentration:**
- Specific conductance of a solution increases with increase in the ionic concentration of the solution.
  Reason : no. of ions per unit volume increases
- But equivalent conductance decrease with increase in concentration
  Reason: decrease in ionic mobility
- The specific conductance (k) or conductance 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 $\wedge$ 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 $(\wedge)$ or molar conductance (μ) of electrolytic solution increases with decrease in concentration.
- For strong uni-univalent electrolytes (Eg. KCl), the decrease in $\wedge$ with increase in concentration is not very large
- If electrolyte is not uni-univalent electrolyte than decrease in $\wedge$ with concentration is more marked as the valency of the ions increases.

$$Eg: NiSO_4, \begin{matrix} K_2SO_4(\text{Uni-bivalent}), \\ BaCl_2(\text{Bi-Univalent}) \end{matrix}$$

behave in an intermediate manner

- Weak electrolytes $(Eg: CH_3COOH, NH_4OH)$ exhibit an apparently different behaviour.
- Effect of Dilution : (1) With dilution "$\wedge$" as well as "μ" of both weak/strong electrolytes increases
- Specific conductivity (k) decreases with dilution because of decrease in no. of ions per cm^3
- At infinite dilution a limiting value of conductivity $(\wedge^0)$ is obtained (conductivity of an electrolyte at infinite dilution or zero concentration is known as limiting molar conductivity).
- $\wedge_0$ 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.

- **Effect Of Temperature:**
- The conductivity of all electrolytes increases with increase in temperature

- **Conductance Ratio** (α) **:** The ratio of the equivalent conductance at any concentration $(\wedge_c)$ to that at infinite dilution $(\wedge_0)$ is called conductance ratio (α). $\boxed{\alpha = \frac{\wedge_c}{\wedge_o}}$ or $\boxed{\alpha = \frac{\wedge_v}{\wedge_\infty}}$.
- For weak electrolytes, α = degree of ionisation.

Note : α is high for 0.01 M , CH_3COOH solution when compared to that of 0.1 M , CH_3COOH because $\wedge_C$ is high incase of 0.01 M

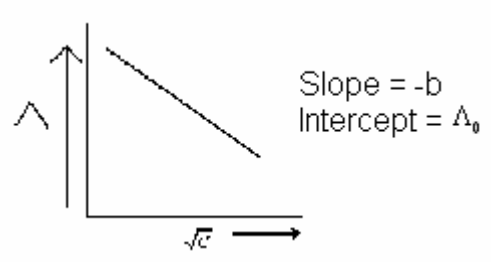
- **Debye - Huckel - Onsagar Equation**:
- In the case of weak electrolytes like, CH_3COOH , α is known as degree of dissociation or degree of ionisation of electrolyte.
- The equivalent conductance at large dilution or at very low concentration is known as equivalent conductance at infinite dilution $(\wedge_\infty)$ or Zero concentration $(\wedge_o)$.
- The equivalent conductance of an electrolytic solution at any concentration (C) is related to $\wedge_o$ for solutions is given by the following Debye-Huckel - onsagar equation.

$$\wedge_C = \wedge_o - \left[\frac{82.4}{(DT)_\eta^{1/2}} + \frac{8.2\times10^5}{(DT)^{3/2}}\wedge_o\right]\sqrt{C}$$

- 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 equiavalent conductance with $\sqrt{concentration}$ is as follows**
- It is a straight line with negative slope.



- This is not applicable for weak electrolytes

- **Kohlrausch's Law**
- Basing on k (specific conductance) value, electrolytes are two types.
- weak electrolytes. These have low 'k' value
- Eg : weak acids, weak bases, carboxylic acids
- Strong electrolytes. These have high 'k' value
- Eg : strong Acids, strong Bases, Salts.
- The conductance of an electrolyte is due to it's ionisation.
- The ionisation extent reaches maximum for weak electrolytes as dilution reaches maximum
  NOTE: Cl. CH_2COOH has higher 'k' value than CH_3COOH since $Cl.CH_2COOH$ is stronger acid than CH_3COOH
- Kohlrausch determined the $\wedge^0$ (equivalent conductance at infinite dilution) for same pairs of strong electrolytes having common anion (or) cation

Ion	**Ionic conductance ($(\Lambda_0)\text{ohm}^{-1}$**	**Ion**	**Ionic conductance $(\Lambda_0)\text{ohm}^{-1}$**
H^+	349.83	Na^+	50.11
K^+	73.52	NH_4^+	73.40
Ag^+	61.92	Cl^-	76.34
Br^-	78.40	I^-	76.80
OH^-	198.50	NO_3^-	71.44
CH_3COO^-	40.89		

- **Statement of Kohlrausch's law :**
- "The equivalent conductance at infinite dilution (λ_∞) of an electrolyte is equal to the algebraic sum of equivalent condutances or mobilities of anion (λ_0^-) and cation (λ_0^+) of the electrolyte at infinite dilution"
- Λ_0 (electrolyte) = $\lambda_0^+ + \lambda_0^-(ions)$
- Eg : $\lambda_\infty(KCl) = \lambda_{k+(\infty)} + {}_{Cl^-(\infty)}$ λ

$\lambda^0\left(MgCl_2\right)=\lambda^0\left(Mg^{+2}\right)+2\ \ ^0\left(Cl^-\right)$ λ

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

- **APPLICATIONS** :
- Determination of $\wedge^0{}_m$ for weak electrolytes
- Eg : NH_4OH is a weak electrolyte $\wedge^0{}_m$ it's is calculated as
  $\wedge^0\left(NH_4OH\right)=\wedge^0\left(NH_4Cl\right)+\wedge^0\left(NaOH\right)-\wedge^0\left(NaCl\right)$
- Degree of dissociation of weak electrolyte is calculated as $\alpha=\frac{\wedge_c}{\wedge_\infty}$ = $\frac{\text{molar conductance at particular concentration 'c'}}{\text{Molar conductance at infinite dilution}}$
- Solubility of spaingly soluble salts can be calculated as
- $\wedge_\infty$ we know $\wedge_\infty=\frac{K\times1000}{Molarity}$
- From kohlrausch's law we can calcuate
- k × v = $\lambda^o m$
- First knowing k (specific conductance), 'v' can be calculated 'v' is volume containing 1 gr.eq. of substance, then solubility is calculated
- Ionic mobilities can be calculated as :
  $\mu_+=\frac{\lambda_+}{F}=\frac{\lambda_+}{96,500}$
  $\mu_-=\frac{\lambda_-}{F}=\frac{\lambda_-}{96,500}$
- Ionic mobility $\mu=\frac{speed}{potential\ gradient}$
- Potentialgradient = $\frac{potential\ difference\ between\ electrodes}{Dis\tan ce\ between\ electrodes}$
- **NOTE:** Λ_∞ of propionic acid cannot be determined experimentally since conductance at low concetrations can not be derermined because it is a weak acid

- **Faradays laws of electrolysis :** (Quantitative laws).
- **First law :** The amount of substance deposited or dissolved or evolved at an electrode in an electrolysis process is directly proportional to the amount of electricity passed through the electrolyte.

  w α Q
  w α ct
  w = ect
  w $\rightarrow$ wt in gms, c $\rightarrow$ current in amp, t $\rightarrow$ time in sec.
  w = e (when c = 1 amp and t = 1 sec)
  e $\rightarrow$ electrochemical equivalent.
- **Electrochemical equivalent :** Weight of the substance deposited or liberated or evolved at an electrode when 1 amp of current is passed in 1 sec through an electrolyte.

  Units: gm / coulomb or gm/ ampere
- **Second law** : When equal amount of electricity is passed through one or more electrolytes connected in series the weights of different substances deposited or liberated or dissolved at the electrodes are directly proportional to the chemical equivalents of the substances.

  : w α E

$$\frac{w_1}{w_2} = \frac{E_1}{E_2}$$

- **Faraday :** The amount of electricity which deposits one gram equivalent of the substance is called Faraday. One faraday = 96500 coulombs.
- **Gram equivalent weight :** Amount of substance deposited when one Faraday (96500C) of electricity is passed through an electrolyte.

$1\ F \rightarrow 1\ GEW$

$96500\ C \rightarrow E$

$1\ Coulomb \rightarrow E/F$

$e \rightarrow E/F\ ;\ w = ect\ ;\ = \frac{E}{F}ct$

$E = \frac{M}{Z}$ ($M \rightarrow$ at. wt , $Z \rightarrow$ valency)

$\therefore w = \frac{MCt}{ZF}$

Applications of Electrolysis :

- To determine the equivalent weights.
- To extract more electropositive metals like Na, K, Mg, Al etc,.
- To extract non – metals like F_2, Cl_2, H_2, O_2.
- To obtain compounds like NaOH, Na_2CO_3.
- In electroplating to prevent corrosion.

Galvanic cells (Voltaic or electrochemical cells) : It is a device which makes use of spontaneous redox reaction for the generation of electrical energy.

- Opposite to electrolytic cells.
- In these cells electricity is generated due to spontaneous redox reaction.

Salt bridge : A 'U' shaped glass jar with Agar agar gelly which contains KCl or KNO_3 or NH_4NO_3 is called salt bridge.

- The purpose of using the above substance in salt bridge is due to free mobility of ions.
- Electrolyte is taken in salt bridge in higher concentration.
- Electrolyte supplies cations and anions.

If salt bridge is not used :

- i) Accumulation of charges will occur, + ve charge at anode and –ve charge at cathode .
- ii) If two solutions come in contact some potential develops at junction of two liquids called "Liquid Junction Potential".
- iii) Electrochemical change stops and every this comes to stand still.

iv) Voltage drops to zero.

If salt bridge is used :

i) It prevents accumulation of charges.

ii) It avoids formation of liquid junction potential.

iii) It prevents mixing of two solutions but permits the flow of ions.

iv) It supplies the ions.

- Generally Galvanic cell contains Zn rod in $ZnSO_4$ solution which acts as anode and Cu rod in $CuSO_4$ solution which acts as cathode.
- To produce more current concentration of $CuSO_4$ should be more.
- As zinc dissolves and Cu deposits thick zinc electrode and thin Cu electrode are to be taken.
- The commercial form of Galvanic cell is Daniel cell.

- **Reversible cells :** When Galvanic cells are connected to external source of EMF.
  i) If cell emf is > ext. emf then $E^0_{cell} \rightarrow +ve$ and cell produces current and spontaneous reaction occurs.
  $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$
  ii) If cell emf is < ext. emf then $E^0_{cell} \rightarrow -ve$ and non spontaneous reaction occurs.
  $Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$
  iii) If cell emf = ext. emf then no current flows in any direction.
- Galvanic cells satisfying the above conditions are called as reversible cells. Daniel cell is a reversible cell.

Electrolytic cell	Electrochemical / Galvanic cell
1) It requires EMF.	1) It produces EMF.
2) Electric energy is converted into chemical energy	2) Chemical energy is converted into electrical energy.
3) Anode is +ve and cathode '-' ve	3) Anode is –ve cathode is '+' ve
4) Oxidation takes place at anode and reduction at cathode	4) Oxidation takes place at anode and reduction at cathode.
5) Electrodes are just metal rods graphite electrode can be used	5) Atoms in contact with ion (graphite electrodes can be used) (Pt, O_2, OH^-)
6) Discharge of ion occur at both electrodes.	6) Discharge of ions occur only at cathode.
7) Non – spontaneous reaction occurs.	7) Spontaneous reaction occurs.
8) These are irreversible.	8) These may be reversible.
9) Flow of electrons is from anode to cathode.	9) Flow of electrons is from anode to cathode.
10) Electrons leave the cell at anode and enter the cell at cathode.	10) Electrons leave the cell at anode and enter the cell at cathode.

- **Electrode potential :** The potential difference that develops between metal atoms and its ions (or) non – metal molecules and the ions is called 'Electrode potential'.
- The tendency of an electrode to undergo oxidation is called oxidation potential (or) the tendency to lose electrons, is called oxidation potential.
- The tendency of an electrode to undergo reduction
  (or) the tendency to gain electron is called reduction potential.
- **Standard electrode potential :** The potential exhibited by a single electrode in the solution of unit concentration of metal ion or non-metal ion at 25°C is called standard single electrode potential.
- The electrode potential measured at 25°C, 1 atm pressure become standard potentials [E°].
- For any electrode the Standard Oxidation Potential(SOP) and Standard Reduction Potential (SRP) values are equal in magnitude and opposite in sign.
  Ex : 1) $E^0_{Zn/Zn^{2}+} \rightarrow +0.76V \ (SOP)$
  $E^0_{Zn^{2+}/Zn} \rightarrow -0.76V \ (SRP)$
  2) $E^0_{Cu^{2+}/Cu} \rightarrow +0.34V \ (SRP)$
  $E^0_{Cu/Cu^{2+}} \rightarrow -0.34V \ (SOP)$
  3) $E^0_{Ag/Ag^{+}} \rightarrow -0.8V \ (SOP)$

$$E^0_{Ag^+/Ag} \rightarrow +0.8V \quad (SRP)$$

- Single Electrode Potentials (SEP) cannot be directly determined because only the potential difference between the two electrodes can be measured by using 'potential metre' or 'volt metre'.
- SEP's can be determined by using 'standard' or 'reference electrodes' (whose potentials are known).
- **Primary reference electrodes :** Standard Hydrogen Electrode (SHE) or Normal Hydrogen Electrode (NHE). It's E° = ± 0.00V.

  Representation of SHE :

  $Pt, H_2 / H^+ \; \frac{1}{2}H_2 \; H^+$ $\rightleftharpoons$

(g) (aq)

- A platinum foil coated with platinum black is half dipped in 1 M HCl(1mH^+) and H_2 gas is bubbled through it at 1atm. This arrangement is called as standard hydrogen electrode. The electrode whose potential has to be determined is connected with SHE.
- Since, it is difficult to maintain 1atm pressure with light gas like H_2, now SHE is replaced by other reference electrodes.

  Ex.Calomel electrode $\rightarrow$ Hg/ $Hg_2Cl_{2(s)}$, $KCl_{(sat)}$

  E° = - 0.2422 V

  Calculating EMF of cell: The potential difference between the two electrodes is called 'cell EMF'.

  $E^0_{cell} = E^0_{right} - E^0_{left}$

  $= E^0_{cathode} - E^0_{anode}$

  = SRP of cathode – SRP of anode

  = SOP of anode – SOP of cathode

  = SOP of anode + SRP of cathode

Electrochemical series (or) EMF series (or) Activity series :

It is the series of electrodes arranged in the increasing water of SRP values.

Electrode system	E°(V) vs (NHE)	Electrode reaction
Li^+| Li	– 3.045	$Li^+ + e^- \; Li$ $\rightleftharpoons$
K^+ | K	– 2.925	$K^+ + e^- \; K$ $\rightleftharpoons$
Ca^{2+} | Ca	– 2.870	$Ca^{2+} + 2e^-$ $\rightleftharpoons$ Ca
Na^+ | Na	– 2.714	$Na^+ + e^-$ Na $\rightleftharpoons$
Zn^{2+} | Zn	– 0.762	$Zn^{2+} + 2e^-$ Zn $\rightleftharpoons$
Fe^{2+} | Fe	– 0.441	$Fe^{2+} + 2e^-$ Fe $\rightleftharpoons$
Cd^{2+} | Cd	– 0.403	$Cd^{2+} + 2e^-$ Cd $\rightleftharpoons$
Co^{2+} | Co	– 0.277	$Co^{2+} + 2e^-$ Co $\rightleftharpoons$
Ni^{2+} | Ni	– 0.250	$Ni^{2+} + 2e^-$ Ni $\rightleftharpoons$
Sn^{2+} | Sn	– 0.140	$Sn^{2+} + 2e^-$ Sn $\rightleftharpoons$
Pb^{2+} | Pb	– 0.126	$Pb^{2+} + 2e^-$ Pb $\rightleftharpoons$
$H^+ + H_2$ | Pt	± 0.00	$H^+ + e^-$ 1/2 H_2 $\rightleftharpoons$
Cu^{2+} | Cu	+ 0.337	$Cu^{2+} + 2e^-$ $\rightleftharpoons$ Cu
Pt, O_2 / OH^-	+ 0.401	$1/2O_2 + H_2O + 2e^-$ $\rightleftharpoons$ $2OH^-$
I_2 | I^- , Pt	+ 0.536	$I_2 + 2e^- \; 2\,I^-$ $\rightleftharpoons$

$Fe^{3+} \mid Fe^{2+}$, Pt	+ 0.771	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$
$Ag^+ \mid Ag$	+ 0.799	$Ag^+ + e^- \rightleftharpoons Ag$
Pt, $Br_2 \mid Br^-$	+ 1.065	$Br_2 + 2e^- \rightleftharpoons 2Br^-$
Pt, $Cl_2 \mid Cl^-$	+ 1.360	$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$
Pt, $F_2 \mid F^-$	+ 2.87	$F_2 + 2e^- \rightleftharpoons 2F^-$

- In the above activity series from top to bottom, SRP value increases.
- SOP values decreases.
- Metallic or electro positive nature decreases.
- Non– metallic or electro negative nature increases.
- Tendency to reduce or reducing nature decreases.
- Tendency to undergo reduction increases.
- Tendency to oxidise (or) oxidising nature, increases.
- Tendency to undergo oxidation decreases.
- The ability to lose electrons decreases.
- The ability to gain electrons increases.
- Above element reduces all the elements below it.
- Below element oxidizes all the elements above it.
- Above metal displaces the below metal from the salt solution.
- Below non – metal displaces the above non – metal from its solution.
- Metals above hydrogen liberate H_2 gas from dil acids and water.
- Metals below hydrogen cannot liberate H_2 gas from dil acids and H_2O.
- Aqueous solution of metals above hydrogen will liberate H_2 but not metal on electrolysis.
- Fused or aq.solution of metal salts below hydrogen will give metal at cathode but not H_2 gas.

Cell Notation :

- The symbolic and short hand form of representation of Galvanic cells is called cell notation.

Anode **cathode**

Solid phase / aq.phase // aq.phase / solid phase

(or)

Solid ; aq.phas / aq. phase; solid

1) Daniel cell :

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

$Zn_{(s)} / Zn^{2+}_{(aq)}$ // $Cu^{2+}_{(aq)} / Cu$

2) $Ni^{2+} + Cd \rightarrow Ni + Cd^{2+}$

$Cd_{(s)} / Cd^{2+}{}_{aq)}$ // $Ni^{2+}{}_{(aq)} / Ni_{(l)}$

3) $Cu + 2Ag^+ \rightarrow Cu^{2+} + Ag$

$Cu_{(s)} + Cu^{2+}{}_{(aq)}$ // $Ag^+{}_{(aq)} + Ag_{(s)}$

4) $Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$

Fe / Fe^{2+} // Cu^{2+} / Cu

5) $2Al + 2Sn^{2+} \rightarrow 2Al^{3+} + 3Sn$

Al / Al^{3+} // Sn^{2+} / Sn

6) $Mg + Cl_2 \rightarrow 2Cl^- + Mg^{2+}$

$Mg_{(s)} / Mg^{2+}{}_{(aq)}$ // $Cl^-{}_{(aq)} / Cl_{2(g)}$, pt

If same electrolyte is used in both the half cells that is kept in between (2) two single vertical lines.

i) pt, H_2 / HCl / Cl_2, pt

cell reaction: $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow H^+ + Cl^- \rightarrow H^+Cl^-$

Nernst equation :

- The electrode potentials or the cell emf depends on
  1) concentration of electrolyte.
  2) Temperature
  3) Number of electrons involved in electrodes reaction.
  4) Pressure (only for gaseous electrodes)
  5) Nature of electrodes.

  Nernst equation will explain how the potential of single electrodes and cell will change with 1) conc. of electrolyte 2) number of electrons.
- The temperature and pressure (25°C, 1atm) are taken as constant for all the calculations.
- **For single electrodes.**

$$E = E^0 - \frac{2.303\ RT}{nF}\log\frac{[products]}{[reactants]}$$

$E \rightarrow$ reduction potential of single electrode; $E^0 \rightarrow$ standard reduction potential

$R \rightarrow 8.314$ J ; $T \rightarrow 25°C$

$n \rightarrow$number of electrons involved ; $F \rightarrow 96500$ C

$2.303RT / F = 0.059$.

$$E = E^0 - 0.059 \log\left[\frac{producst}{reactants}\right]$$

$$E = E^0 - 0.059\log\left[\frac{reduced\ formed}{oxidised\ formed}\right]$$

$$E = E^0 - 0.059\log\left[\frac{M^{n-}}{1}\right]$$

for all metal electrodes and hydrogen electrodes

$$E = E^0 - 0.059\log\left[\frac{1}{M^{n+}}\right]$$

for all non metal electrodes

to calculate cell emf at given concentration of electrolyte.

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{nF}\log\left[\frac{products}{reactants}\right]$$

$E \rightarrow$ Emf of cell ; $E^0 \rightarrow$ Standard emf of the cell

$R \rightarrow 8.314$ J ; $T \rightarrow 25°C$

$n \rightarrow$ number of electrons ; $F \rightarrow 96500$ C

Nernst equation application to various electrodes and various Galvanic cells.

1) Zinc electrode : $E = E^0 - \frac{0.059}{2}\log\left[\frac{1}{Zn^{2+}}\right]$

2) Copper electrode: $E = E^0 - \frac{0.059}{2}\log\left[\frac{1}{Cu^{2+}}\right]$

3) Hydrogen electrode : $E = E^0 - \frac{0.059}{1}\log\left[\frac{1}{H^+}\right]$

$E = E^0 - \frac{0.059}{1} P^H \Rightarrow \quad E^0 - E = \frac{0.059}{1} P^H$

$P^H = \frac{E^0 - E}{0.059} \quad \Rightarrow \quad E^0 \rightarrow$ 'O' V for H_2.

Daniel cell:

1) $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

$E_{cell} = E^0_{cell} - \frac{0.059}{2}\log\left[\frac{Zn^{2+}}{Cu^{2+}}\right]$

2) pt, Mg / Mg^{2+} // Cl^- / Cl_2 , pt

$Mg + Cl_2 \rightarrow 2Cl^- + Mg^{2+}$

$E_{cell} = E^0_{cell} - \frac{0.059}{2}\log\frac{[Mg^{2+}]\,[Cl^-]^2}{1}$

3) pt, $I_2 / I^- \rightarrow$ ½ $I_2 + Cl^-$

$I^- +$ ½ $Cl_2 \rightarrow$ ½ $I_2 + Cl^-$

$E_{cell} = E^0 - \frac{0.059}{1}\log\left[\frac{Cl^-}{I^-}\right]$

(*a*) PRIMARY CELLS:-

i) It is an electrochemical cell which acts as a source of electrical energy without being previously charged up by an electric current from an external source of current.

ii)In which electrode reactions cannot be reversed by external source.

iii) These are not chargeable.

iv) Examples of this type is dry cell or Leclanche cell, voltaic cell.

(b*)* SECONDARY CELLS:-

i) Electrical energy from an external source is first converted into chemical energy (Electrolysis) and when the source is removed then the cell is made to operate in the reverse direction.

ii) Secondary cells are those which can be rechargeable and used again and again.

iii) These are designed to convert the energy from combustion of fuel such as $H_2, CO, CH_4, etc.$, directly into electrical energy.

iv)The common examples are hydrogen- oxygen fuel cell, Alkane-oxygen fuel cell Ni-Cd cell, Pb-accumulator, Li-ion battery.

v) Acid storage cell is Lead accumulator and Alkali storage cell is Edison Battery

S. No.	Name of cell	Type	Anode	Cathode	Electrolite	Anode reaction	Cathode reaction	Overall reaction	Other information
1.	Dry cell or Leclanche cell	Primary	Zinc container	Graphite rod surrounded by MnO_2 Powder	Paste of $NH_4Cl + ZnCl_2$	$Zn \rightarrow Zn^{+2} + 2e^-$	$MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH)^- + NH_3$	$Zn + NH_4^+ + MnO_2 \downarrow Zn^{+2} + MnO(OH)^- + NH_3$	→ To Previent leakage 'Zn' container is coated with Iron or Steel. → Life time is indefinte as NH_4Cl corrodes Zinc → Volltage is 1.2 – 1.5V → Common type of cell.
2.	Mercury cell	Primary	Zn-Hg amalgum	Paste of $(HgO + C)$	Mosist paste of $KOH + ZnO$	$Zn + 2OH^- \rightarrow$ (Amalgum) $ZnO + H_2O + 2e^-$	$HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$	Zn + HgO (Amalgum) ZnO + Hg	→ Voltage is approx 1.35 v → Gives constant Potential through out life.
3.	Lead storage battery. (Acid storage cell) (Lead accumulator)	Secondary	Spongy lead	Grid of 'Pb' Packed with PbO_2	38 % H_2SO_4 by weight	$Pb + SO_4^{-2} \rightarrow PbSO_4 + 2e^-$	$PbO_2 + SO_4^{-2} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$	$Pb + PbO_2 + 4H^+ + 2SO_4^{-2} \rightarrow 2PbSO_4 + 2H_2O$ This is dis-charge reaction while charging reaction is reversed.	→ 38 % H_2SO_4 has density = 1.3 during usage density decreases it it is less than 1.2 it should be charged. → Voltage is 6 – 12 V used in automobiles → Lead storage battery represent as: $Pb / PbSO_4 \; Pb // H_2SO_4 \; (PbO_2) / Pb$
4.	Nickel cadmiuim storage cell (Alkali storage cell)	Secondary	Cadmium	Metal grid containing NiO_2	$KOH_{(aq)}$	$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$	$NiO_2 + 2H_2O + 2e^- \rightarrow Ni(OH)_2 + 2OH^-$	$Cd + NiO_2 + 2H_2O \downarrow Cd(OH)_2 + Ni(OH)_2$	→ cell potential is 1.4V → Lighter portable and costelier has longer life → Used in wincless devices.

FUEL CELLS :

- The cell (or) device that converts combustional energy (obtained by burning H_2, CH_4, CO etc) directly into electrical energy
- first fuel cell was developed by Sir William grove (pt - electrodes, (H_2, O_2 gases used)
- In fuel cells $\Delta G = -nFE$;
- Fuel cells are more advantageous than ordinary batteries in the following respects ;

  i)High efficiency

  In '$H_2 - O_2$' fuel cell 60-70% efficiency has been attained wheres as in convertional methods, only 40% efficiency is attained

  ii)They can be used continuously. There is no need to replace electrodes

  iii) They don't cause pollution problems.

  Eg : '$H_2 - O_2$' in fuel cell, is product

  iv) Silent operation
- Theoretically 100% efficiency
- General reperesentation of fuel cell **:**

• Fuel/electrode/ electrolyte/ electrode / oxidant

• **HYDROGEN-OXYGEN FUEL CELL:**

- H_2 is bubbled through electrolyte at anode. It undergoes oxidation
- O_2 is bubbled through electrolyte at cathode. It undergoes reduction
- Porous graphite rods acts as electrodes. They are coated with Pt, Ag (or) CoO which acts as catalyst
- Reaction at anode : $2\left[\mathrm{H_2(g)^+ 2OH^-_{(aq)} \rightarrow 2H_2O_{(l)+2e^-}} \right]$

• Cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-(aq)$

• Overall reaction : $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

- Electrolyte is concentrated : $NaOH_{(aq)} / KOH_{aq}$
- Fuel cells are even used in space crafts Eg : Apollo gemini air ships utilised '$H_2 - O_2$' fuel cell.
- The heat of combustion is directly converted to electrical energy.

• **HYDROCARBON-OXYGEN FUEL CELL:**

- Hydrocarbons are burned in oxygen at high temperature to get large amount of electrical energy
- Air freed from impurities (or) pure oxygen is oxidant
- $KOH_{(aq)}$ is used as electrolyte
- Pt electrodes are used.
- H_3PO_4 is used as electrolyte if hydrocarbon is burned. It is because the obtained CO_2 in combustion is absorbed by $KOH_{(aq)}$.
- It is costlier
- Fuel cells may be liquid fuel cells (or) gas fuel cells
- In liquid fuel cells $CH_3OH, C_2H_5OH, HCHO, N_2H_4$ are used as fuels. In gas fuel cells - H_2, C_nH_{2n+2} , CO are used as fuels
- Fuel cells a)working below 100°C are low temperature cells

- b)working between 100-250C are medium temperature cells
- c) working above 500°C are high temperature cells.
- O_2, air, H_2O_2, HNO_3 are used as oxidants.
- Pt, Porous PVC, PTFE coated with Ag are used as electrodes.
- In biochemical cells organic compounds disintegrated by micro organisms. These are in use now - a - days.

- **CORROSION**

- The natural tendency of conversion of a metal into its mineral compound form on interaction with the environment (Polluted air, water, associated other Metals etc) is known as corrosion.

- Ex : Iron converts itself into its oxide (Fe_2O_3 , haematite)
- Copper converts itself into its corbonate ($CuCO_3$, Malachite)
- Silver converts itself into its sulPhide (Ag_2S, horn silver)

- Corrosion of iron by conversion into iron oxide is known as rusting
- Corrosion of silver by conversion into its sulphide is known as tarnishing

- **MECHANISM**

- The process of corrosion may be chemical (or) electro chemical in nature
- The anodic dissolution of a metal under the conditions of corrosion is known as electrochemical corrosion $M \rightarrow M^{n+} + ne^-$
- Corrosion occurs if the environmental conditions of the metal favour the formation of an voltaic cell with the metal acting as anode
- Electro - chemical corrosion is basically of two types

- Hydrogen evolution type
- Differential oxygenation type

- **HYDROGEN EVOLUTION TYPE :**

- This type of corrosion is exhibited by metals which can displace H_2 gas from aqueous solution.
- This happens if the electrode potential of the metal under the conditions of corrosion is more negative than that of the hydrogen electode under the given conditions.
- The hydrogen electrode potential depends on the nature of the metal used as the cathode and the P^H of the solution.
- It is almost zero (0V) in 1M acid solution, if the cathode metal is platinised platinum (Black Platinum)
- It is about 0.8 V if the cathode metal is Hg
- For other Metals the value lies in between these two values (0 to 0.8V)
- This type of corrosion depends upon
  1) P^H of the medium
  2) chemical nature of the metal under going corrosion
- Pure zinc does not corrode in salt solutions but in presence of Cu as impurity Zn corrodes.
- Zn corrodes in 2M acid but not in neutral salt solution

- **DIFFERENTIAL OXYGENATION CORROSION**

- This type of corrosion occurs if O_2 concentration is not uniformly distributed on the surface of the metal
- Corrosion of the metal generally occurs at the point where O_2 concentration is less
- The portion of the metal with access to high concentration of O_2 functions as cathode and with access to low concentration of O_2 functions as anode.

- Hence, the metal with differential oxygenation acts as a galvanic cell

Ex : When an iron rod is immersed in NaCl solution the immersed part is corroded due to less oxygenation of the surface of the metal.

- Factors that promote electrochemical corrosion
- The nature of the impurity metal with which the metal under consideration is associated For Ex : Cu favours corrosion of Zn. because Zn is more anodic than copper
- Zn disfavours corrosion of 'Fe' (Galvanization)
- The concentration of O_2 in contact with the surface of the metal
- For Ex : Metal rod half immersed in aqueous salt soln gets corroded at the surface not exposed to O_2, i.e., the immersed part of the Metal gets easily corroded
- Highly conducting solutions favour rapid corrosion

- **PASSIVITY**
- The phenomenon of a metal reaching a stage of non-reactive state in its reaction with concentrated acids may be called passivity.
- Iron group of metals and some other transition metals are rendered passive with concentrated acids.
- Passivity of a metal can be classified into
- chemical passivity
- Mechanical passivity
- Electro - chemical passivity

- **CHEMICAL PASSIVITY**
- Non - reactivity of metals after initial reaction with conc HNO_3 is called chemical passivity
- Eg : If iron is dipped in conc HNO_3 (sp gravity 1.25) it is cattacked for some time and after becomes inactive
- Passive iron don't dissolve in dil HNO_3 and iron don't displace Ag from $AgNO_3$.
- CO,Ni, Cr can also become passive
- Air can also cause passivity to Fe, Cr, Mo, W&V

- **MECHANICAL PASSIVITY**
- In some cases dissolution of metal stops due to visible oxide film formation. This is mechanical passivity
  Eg : $PbO_2 \, on \, Pb$
- Fe, Co, Ni, Mn also exhibits this type of passivity
- **ELECTROCHEMICAL PASSIVITY :**
- Metal with more -ve potential functions as anode in cell.
- Generally Fe, Ni, CO functions as anode
- They dissolve as $M \rightarrow M^{+n} + ne^-$
- At particular stage anode stops dissolving due to formation of invisible metal oxide film. This phenomenon is called electro - chemical passivity.