ELECTROCHEMISTRY

1. INTRODUCTION :

Electrochemistry deals with the study of electrical properties of solutions of electrolytes and the inter-relation of chemical phenomenon and electrical energies.

* Electric 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 free electrons without undergoing any chemical change are known as metallic conductors.

eg. Metals : Cu,Ag,Fe,Al etc., non metals : graphite and various alloys.

(ii) Electrolytic conductors :

Those substances whose aqueous solution conducts the electric current and which are decomposed by the passage of DC 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.

Strong electrolyte :

Electrolytes which are completely ionized in aqueous solution or in their molten state, are called *strong electrolytes*. Their aqueous solutions are strongly conducting.

Ex : All salts, strong acids and strong bases.

* Weak electrolyte :

Electrolytes which are not completely ionized in aqueous solution are called *Weak electrolytes*. Their aqueous solutions are weakly conducting.

Ex: Organic acids CH₃COOH, HCN (Except : Alkyl sulphonic acids, RSO₃H)

Organic base : Amines, Aniline etc.

Note : Ostwald's dilution law is only applicable for weak electrolytes according to which degree of dissociation(α) increases on dilution.

- For weak electrolyte : $\alpha \ll 1 \Rightarrow$ lesser ions \Rightarrow weakly conducting
- For strong electrolyte : $\alpha = 1$ (always) \Rightarrow more ions \Rightarrow strongly conducting

* Difference between metallic and electrolytic conduction :

	Metallic conduction	Electrolytic conduction
(i)	Flow of electricity takes place due to	Flow of electricity takes place by ions.
	free electrons without the decomposition	
	of the substance.	
(ii)	No transfer of matter takes place.	Transfer of matter takes place.
(iii)	The resistance to the flow of current	The resistance to the flow of current decreases
	increases with the increase in	with the increase in temperature and hence
	temperature and hence the increase in	increase in temperature increases the conduction.
	temperature decreases the conduction.	

2. ELECTROCHEMICAL CELL :

It is device for inter-converting chemical energy in to electrical energy or vice versa.

Electrochemical cells are of two types



Galvanic cell or Voltaic cell

- A spontaneous chemical reaction generates an electric current | EMF
- Chemical energy converted into electrical energy.

Electrolytic cell.

- An electric current drives a non-spontaneous reaction.
- Electrical energy converted into chemical energy.

3. GALVANIC CELL | VOLTAIC CELL

- A cell in which the chemical energy is transformed into electrical energy.
- The chemical reaction occurring in a galvanic cell is a spontaneous redox reaction.
- During the chemical process, the reduction in Gibbs free energy is converted in the form of electrical energy.

$$(\mathbf{DG})_{\mathrm{T,P}} = \mathbf{W}_{\mathrm{Useful}|\mathrm{max.}} = -\mathbf{nF} \mathbf{E}_{\mathrm{cell.}}$$

Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It may be represented by Daniel cell which is a type of Galvanic cell. Zinc rod immersed in $ZnSO_4$ behaves as anode and copper rod immersed in $CuSO_4$ behaves as cathode.



Solution Solution Constant and Solution Constan

$$Zn(s) \longrightarrow Zn^{2+} + 2e^{-}$$

(Loss of electron : Oxidation)

***** Reduction takes place at cathode :

 $Cu^{2+} + 2e^{-} \longrightarrow Cu(s)$

(Gain of electron ; Reduction)

3.1 Construction of Cell :

- It has two half-cells, each having a beaker containing a metal strip that dips in its aqueous solution.
- The metal strips are called *electrodes* and are connected by a conducting wire.
- Two solutions are connected by a *salt bridge*.
- 3.2 Construction | Working principle of Daniel cell :
- I. Anode of Daniel cell : Zn rod is placed in $ZnSO_4$ solution are found to have tendency to go into the solution phase when these are placed in contact with their ions or their salt solutions.



The Zn atom or metal atoms will move in the solution to form Zn^{+2} . After some time following equilibrium will be established.

 $Zn(s) \rightleftharpoons Zn^{2+} + 2e^{-}$

There will be accumulation of sufficient negative charge on the rod which will not allow extra zinc ions to move in the solution. i.e. solution will be saturated with Zn^{+2} ions.

The positive charge will be more concentrated near the rod.

The extra positive charge of the solution will be more concentrated around the negatively charged rod. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution which is known as electrode potential

This particular electrode is known as anode :

- At anode oxidation will take place. (Release of electron).
- To act as source of electrons.
- It is of negative polarity.
- The electrode oxidation potential is represented by $E_{Zn(s)/Zn_{2m}^{2+}}$ & reduction potential by $E_{Zn^{2+}/Zn}$.

II. Cathode of Daniel cell :



Cu, when placed in contact with their aqueous ions, the ions (Cu^{2+}) from the solution will get deposited on the metal rod.

The following equilibrium will be established :

 $Cu^{2+}(aq) + 2e^{-} \implies Cu(s)$

So rod will have deficiency of electron (positive charge). Extra negative charge will surround this positively charged rod and form double layer. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution which is known as electrode potential. This will be known as cathode.

- At cathode reduction will take place. (Gain of e⁻ will take place)
- Cathode acts as sink of electron.
- Positive polarity will be developed.
- Their electrode reduction potential can be represented by : $E_{Cu^{2+}(aq)|Cu(s)}$.

• Anode : {Is where oxidation occurs Has a negative sign
• Cathode : {Is where reduction occurs Has a positive sign
•

Overall process :

 $Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$

In Galvanic cell like Daniel cell ; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit ; zinc dissolves as Zn^{2+} ; Cu^{2+} ion in the cathode cell picks up two electron and is deposited at cathode.

Note: The electrode potential will keep on decreasing with time as Zn²⁺ ions increase & Cu²⁺ ions decrease in solution therefore tendency of cell reaction decreases and cell attains equilibrium.

3.3 Functions of Salt Bridge :

- A salt bridge is a U-shaped inverted tube that contains a gel permeated with an inert electrolyte.
- It connects the solution of two half cell to complete the circuit.
- It minimise the liquid junction potential, the potential difference between the junction of two liquids)
- It maintains the electrical neutrality of the solution in order to give continuous flow or generation of current " The simultaneous electrical neutrality of the anodic oxidation chamber and cathodic reduction chamber is due to almost same mobility or velocity of K⁺ and NO₃⁻ ions taken into salt bridge.
- If the salt bridge is removed then voltage drops to zero & cell stops working.
- The ions of the inert electrolyte should not react with other ions in the solution and the ions are not oxidised or reduced at the electrodes.
- Generally tube is filled with a paste of agar-agar powder with neutral electrolyte generally not common to anodic compartment with porous plugs at each mouth of tube.
- It prevents mechanical mixing of two electrolytic solutions.

Liquid Junction Potential :

The potential difference which arises between two solutions when in contact with each other. Salt bridge removes effects of junction potential by providing appropriate migration of ions.

* Characteristics of electrolyte used in salt bridge :

- 1. The electrolyte should be inert.
- 2. The cations and anions of the electrolyte used should be of ionic mobility.
- 3. Ions of electrolyte should not react with ions involved in cell reaction.

3.4 Representation of galvanic cell (IUPAC)

The anode is written on the LHS & cathode on the RHS.

we denote salt bridge by two vertical parallel lines (||), if used, in between anode & cathode.

- **Ex.** $Pt(s) | H_2(g) | H^+(aq.) || H^+(aq.) | H_2(g) | Pt(s)$
- **Ex.** Daniel cell : $Zn(s) | Zn^{2+}(aq) || Cu^{2+}(aq.) | Cu(s)$
- **Ex.** For cell reaction : $H_2(g) + Cu^{+2}(aq) \longrightarrow 2H^+(aq) + Cu(s)$

Pt $| H_2(g) | H^+(aq) || Cu^{2+}(aq.) | Cu(s).$

3.5 Electrode potential :

When a strip of metal is brought in contact with the solution containing its own ions then the strip of metal gets positively charged or negatively charged and results into a potential being developed between the metallic strip and its solution which is known as electrode potential.

- At anode: $M \rightarrow M^{+n} + ne^{-}$ (Oxidation Potential)
- At cathode: $M^{+n} + ne^- \rightarrow M$ (Reduction Potential)
- The value of electrode potential depends upon :
 - (i) the nature of electrode
 - (ii) the concentration of solution
 - (iii) the temperature

3.6 Standard electrode potential (E°) :

If the concentration of ions is unity, temperature is 25°C (or any constant temperature) and pressure is 1 bar (standard conditions), the potential of the electrode is called *standard electrode potential*.

• The given value of electrode potential is regarded as reduction potential unless it is specifically mentioned that it is an oxidation potential.

3.7 Electromotive force of cell or cell voltage :

The difference in the electrode potentials of the two electrodes of the cell is termed as electro motive force [EMF] or cell voltage which causes current to flow.

$$E_{cell} = E_{red} (cathode) - E_{red} (anode) = E_{oxi.} (anode) - E_{oxi.} (cathode) = E_{oxi.} (anode) + E_{red} (cathode) = E_{oxi.} (anode) + E_{red} (cathode) = E_{oxi.} (anode) + E_{red} (cathode) = E_{oxi.} (c$$

Electrode Reduction Reaction	Standard electrode Reduction
	potential \mathbf{E}° , Volts
$Li^+ + e \rightarrow Li$	- 3.05
$K^+ + e^- \rightarrow K$	- 2.93
$Ba^{+2} + 2e^{-} \rightarrow Ba$	- 2.90
$Ca^{+2} + 2e^{-} \rightarrow Ca$	- 2.87
$Na^+ + e^- \rightarrow Na$	- 2.71
$Mg^{+2} + 2e^- \rightarrow Mg$	-2.37
$Al^{+3} + 3e^- \rightarrow Al$	- 1.66
$Mn^{+2} + 2e^- \rightarrow Mn$	- 1.18
$H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH$	- 0.83
$Zn^{+2} + 2e^{-} \rightarrow Zn$	- 0.76
$Cr^{+3} + 3e^- \rightarrow Cr$	- 0.74
$Fe^{+2} + 2e^{-} \rightarrow Fe$	- 0.44
$Cd^{+2} + 2e^{-} \rightarrow Cd$	-0.40
$Ni^{+2} + 2e^{-} \rightarrow Ni$	- 0.25
$\mathrm{Sn}^{+2} + 2\mathrm{e}^{-} \rightarrow \mathrm{Sn}$	- 0.14
$Pb^{+2} + 2e^{-} \rightarrow Pb$	- 0.13
$2D^+ + e^- \rightarrow D_2$	– 0.01 V
$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \rightarrow \mathrm{H}_{2}$	0
$AgBr(s) + e^- \rightarrow Ag(s) + Br^-$	+0.09 V
$AgCl + e^- \rightarrow Ag + Cl^-$	0.22 V
$Cu^{+2} + 2e^{-} \rightarrow Cu$	+ 0.34
${}^{1}/_{4} O_{2} + {}^{1}/_{2} H_{2}O + e^{-} \rightarrow OH^{-}$	+0.401 V
$I_2 + 2e^- \rightarrow 2I^-$	+0.54
$Q + 2H^+ + 1e^- \rightarrow H_2Q$	+ 0.70
$\mathrm{Hg_2}^{+2} + 2\mathrm{e} \to 2\mathrm{Hg}$	+ 0.79
$Ag^+ + e^- \rightarrow Ag$	+ 0.80
$\mathrm{Hg}^{+2} + 2e^{-} \rightarrow \mathrm{Hg}$	+0.85
$Br_2 + 2e^- \rightarrow 2Br^-$	+ 1.08
${}^{1}/_{4} O_{2} + H^{+} + e^{-} \rightarrow {}^{1}/_{2} H_{2}O$	+1.23 V
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.36
$Pt^{+2} + 2e^- \rightarrow Pt$	+ 1.20
$Au^{+3} + 3e \rightarrow Au$	+ 1.50
$Au^+ + e \rightarrow Au$	+ 1.69
$S_2O_8^{} + 2e^- \rightarrow 2SO_4^{}$	+2.0 V
$F_2 + 2e^- \rightarrow 2F^-$	+ 2.87

Application of electrochemical series :

(i) Activity of metal : From electrochemical series, the activity of any metal can easily be determined. All the metals which are placed above hydrogen are stronger reducing agents & can easily evolve H_2 gas whereas metals lying below hydrogen are weaker reducing agents cannot lose electrons to H^+ ions & hence can't evolve H_2 gas. For e.g. Na, K, Zn etc. can easily evolve H_2 whereas Cu, Hg, Ag etc. do not have tendency to evolve H_2 gas.

$$Na + H_2SO_4 \rightarrow Na_2SO_4 + H_2\uparrow$$

$$Na + H_2O \rightarrow NaOH + \frac{1}{2} H_2\uparrow$$

$$Cu + H_2SO_4 \longrightarrow CuSO_4 + H_2\uparrow$$

(ii) **Displacement reaction :** The active metal can easily displace less active metal from their aq. salt solution for e.g. Zn can replace Cu^{2+} from an aq. solution of $CuSO_4$. But Cu cannot displace Zn^{2+} from solution similarly,

$$2AgNO_{3} + Cu \rightarrow Cu(NO_{3})_{2} + 2Ag,$$
$$CuSO_{4} + Ag \xrightarrow{} Ag_{2}SO_{4} + Cu$$

(iii) Feasibility of redox reaction : The feasibility of particular redox reaction can be easily find out from electrochemical series. The metal placed higher or have more reducing property can easily lose electrons to the metal ion present below in series, hence redox reaction become feasible i.e. cell will serve as source of electrical energy. For e.g. NiSO₄ solution cannot be placed in Fe vessel because, the redox reaction between them is feasible.

Note: If emf of the cell for redox reaction comes out to be positive, it suggest the redox reaction is spontaneous or feasible. Negative value indicate that redox reaction is not feasible.

$$\begin{array}{c} -0.25V \\ Ni^{+2} + Fe \longrightarrow Ni(s) + Fe^{+2} \\ +0.44V \end{array} \qquad \qquad \begin{array}{c} -1.36V \\ Cl^{-} + Cr_{2}O_{7}^{--} \longrightarrow Cl_{2} + Cr^{+3} \\ 1.33V \end{array}$$

- (iv) Oxidising & reducing powers : The metals placed above hydrogen in the electrochemical series are strong reducing agents whereas non-metals placed after hydrogen, are strong oxidising agents.
- (v) Displacement of one non-metal from its salt solution by another non-metal : A non metal lower in the series will have more reduction potential and will displace another non-metal with lower reduction potential. e.g. F₂ can displace all halide ion from solution.

$$F_2 + 2KCI \longrightarrow 2KF + Cl_2$$
$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

EXERCISE #1

1. A standard reduction electrode potentials of four metal cations are -				
	$A^+ = -0.250 V$,	$B^+ = -0.140 V$	$C^+ = -0.126 V$,	$D^+ = -0.402 V$
	The metal that displace	es A ⁺ from its aqueous	solution is :-	
	(A) B	(B) C	(C) D	(D) None of the above
2.	The standard reductio	n potentials for two ha	alf-cell reactions are gi	ven below,
	$Cd^{2+}(aq) + 2e^{-} \rightarrow Cd^{2+}(aq)$	$d(s), E^{\circ} = -0.40^{\circ}$	V	
	$Ag^{+}(aq) + e^{-} \rightarrow Ag($	s), $E^{\circ} = 0.80V$		
	The standard free ene	ergy change for the rea	iction	
	$2Ag^{+}(aq) + Cd(s) \rightarrow$	$2Ag(s) + Cd^{2+}$ (aq) is	given by :	
	(A) 115.8 KJ	(B) –115.8 KJ	(C) –231.6 KJ	(D) 231.6KJ
3.	The reduction potenti	al values are given be	low:	
	$Al^{3+} Al = -1.67$ vo	$lt,Mg^{2+} Mg = -2.34$	volt	
	$Cu^{2+} Cu = +0.34$ vo	olt, $I_2 \mid 2I^- = + 0$	0.53 volt	
	Which one is the best	t reducing agent ?		
	(A) Al	(B) Mg	(C) Cu	(D) I ₂
4.	E° for $F_2 + 2e^- = 2F$	E^{-} is 2.8 V, E° for E°	$V_2F_2 + e^- = F^-$ is ?	
	(A) 2.8 V	(B) 1.4 V	(C) –2.8 V	(D) –1.4 V
5.	If ΔG° of the cell rea	ction,		
	$\operatorname{AgCl}(s) + \frac{1}{2}\operatorname{H}_2(g) \to A$	$Ag(s) + H^+ + CI^-$ is -21.5	52 KJ	
	then ΔG° of $2 \text{AgCl}(s)$	$+H_2(g) \rightarrow 2Ag(s) +2$	$H^+ + 2Cl^-$ is :	
	(A) –21.52 KJ	(B) –10.76 KJ	(C) –43.04 KJ	(D) 43.04 KJ
6.	Given electrode poten	tials :		
	$\operatorname{Fe}_{(aq)}^{3+} + e^{-} \longrightarrow \operatorname{Fe}_{(a}^{2+}$	$_{q}$; E° = 0.771 volts	$I_{2(g)} + 2e^{-} \longrightarrow 2I_{(a)}^{-}$	$_{q)}$; $E^{\circ} = 0.536$ volts
	E°_{cell} for the cell react	ion,		
	$2Fe_{(aq)}^{3+} + 2I_{(aq)}^{-}$	$\rightarrow 2Fe^{2+}_{(aq)} + I_{2(g)}$ is -		
	(A) $(2 \times 0.771 - 0.53)$	6) = 1.006 volts	(B) $(0.771 - 0.5 \times 0.5)$	(536) = 0.503 volts
	(C) $0.771 - 0.536 = 0$.235 volts	(D) 0.536 – 0.771 =	–0.235 volts
3.9	NERNST EQUATION	ON:		
	For a reaction aA + bI	B = cC + dD		
	$DG = DG^{o} + RTlnQ$			
	$-nFE = -nFE^{\circ} + RTh$	nQ		
	With the help of Nernst equation, we can calculate the non-standard electrode potential of electrode			
	or EMF of cell. Nernst equation predicts effects of concentration. pressure or temperature changes			

or EMF of cell. *Nernst equation predicts effects of concentration, pressure or temperature changes on cell EMF.* Nernst equation can be applied on half-cell as well as complete Galvanic cells reaction.

$$E_{cell} = E^{0} - \frac{RT}{nF} lnQ = E^{o} - \frac{2.303RT}{nF} logQ$$

9

Where -

 E^0 = Standard electrode potential R = Gas constantT = Temperature (in K) $F = Faraday (96500 \text{ coulomb mol}^{-1})$ $n = No. of e^{-}$ gained or lost in balanced equation. Q = Reaction quotent

 $\frac{2.303 \times 8.314 \times 298}{96500} = 0.059 \text{ volt (At 298 K)}$

Note: (i) For writing Nernst equation, first write balanced cell reaction.

(ii) Nernst equation can be applied on half-cell as well as complete Galvanic cells.

3.10 **THERMODYNAMIC TREATMENT OF CELL:**

(i) Determination of equilibrium constant : We know, that

$$E = E^{\circ} - \frac{0.0591}{n} \log Q$$
 ...(i)

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. $E = 0 \& Q = K_{eq}$. \therefore From E (i), we have

$$0 = E^{0} - \frac{0.0591}{n} \log K_{eq} \text{ or } K_{eq} = \text{anti} \log \left[\frac{nE^{0}}{0.0591} \right] = 10^{\frac{nE^{0}}{0.591}}$$

(ii) Heat of Reaction inside the cell: Let n Faraday charge flows out of a cell of e.m.f. E, then

(i)

$$-\Delta G = nFE$$

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_{p}$$
(ii)

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T \left[\frac{\partial (-nFE)}{\partial T} \right]_{p} = \Delta H - nFT \left[\frac{\partial E}{\partial T} \right]_{p}$$

$$\therefore \qquad \Delta H = -nFE + nFT \left[\frac{\partial E}{\partial T} \right]_{p}$$

Entropy change inside the cell : We know that G = H - TS or $\Delta G = \Delta H - T\Delta S$...(i) (iii) where ΔG = Free energy change ; ΔH = Enthalpy change and ΔS = entropy change. According to Gibbs Helmoholtz equation,

$$\Delta G = \Delta H + T \left[\frac{\partial \Delta G}{\partial T} \right]_{p} \qquad \dots (ii)$$

From Eqs. (i) and (ii), we have

$$-T\Delta S = T \left[\frac{\partial \Delta G}{\partial T} \right]_{p} \qquad \text{or} \qquad \Delta S = - \left[\frac{\partial \Delta G}{\partial T} \right]_{p}$$
$$\Delta S = nF \left[\frac{\partial E}{\partial T} \right]_{p}$$

or

where
$$\left[\frac{\partial E}{\partial T}\right]_{p}$$
 is called temperature coefficient of cell.

3.11 DIFFERENT TYPES OF ELECTRODES

I. Metal - Metal ion electrode : Ex. - $M^{+n} | M$ $M^{n^+} + ne^- \longrightarrow M(s)$

$$E_{M^{n+}/M} = E_{M^{n+}/M}^0 - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

II. Gas - ion Electrode :

Andoe : Pt , $H_2(P \text{ atm}) | H^+(cM)$ Cathode : $H^+(cM) | H_2(P \text{ atm}) | Pt$

Cathodic raction : $H^+(aq) + e^- \longrightarrow \frac{1}{2} H_2(P \text{ atm})$

$$\mathbf{E} = \mathbf{E}^{\circ} - 0.0591 \log \frac{\mathbf{P}_{\mathrm{H}_{2}}^{\frac{1}{2}}}{[\mathrm{H}^{+}]} = -0.0591 \mathrm{pH} \left[\because \mathbf{E}_{\mathrm{H}^{+}/\mathrm{H}_{2}}^{0} = 0 \& \mathrm{pH}_{2} = 1 \mathrm{bar} \right]$$

III. Oxidation - reduction Electrode (or redox electrode) :

It has same metal (or element) in two different oxidation states in same solution. Pt | Fe^{2+} , Fe^{3+}

As a reduction electrode

$$Fe^{3^+} + e^- \longrightarrow Fe^{2^+}$$
$$E = E^\circ - 0.0591 \log \frac{[Fe^{2^+}]}{[Fe^{3^+}]}$$

Also, $Pt | Cr_2O_7^{-2}(aq.), Cr^{+3}(aq.), H^+$ $Pt | Mn^{+2}(aq.), MnO_4^{-}(aq.), H^+$

IV. Metal - metal insoluble salt-anion electrode :

In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell:

This half cell is represented as Cl⁻|AgCl|Ag. The equilibrium reaction that occurs at the electrode is

$$AgCl(s) + e^{-} \rightleftharpoons Ag(s) + Cl^{-}(aq)$$
$$E^{0}_{Cl^{-}/AgCl/Ag} = E^{0}_{Ag^{+}/Ag} + \frac{0.0591}{1} \log K_{sp}$$
$$E_{Cl^{-}/AgCl/Ag} = E^{0}_{Cl^{-}/AgCl/Ag} - \frac{0.0591}{1} \log \left[Cl^{-} \right]$$

potential of such cells depends upon the concentration of anions. Such cells can be used as **Reference Electrode**.

3.12 Reference Electrode :

Absolute values of electrode potentials can not be measured. Reference electrodes is an electrode used to measure the electrode potential of other electrodes.

(a) Standard Hydrogen Electrode (SHE) :

It consist of a platinum electrode over which H_2 gas (1 bar pressure) is bubbled and the electrode is immersed in a solution that is 1 M in H^+ at any specified temperature.

 $2H^+(1 M) + 2e^- \longrightarrow H_2(g)(1 atm)$

The potential of this electrode at all temperature is taken as Zero volt.

$$[\text{IUPAC convention}: E_{H^{+}/H_{2}}^{*} = E_{H_{2}/H^{+}}^{*} = 0]$$
Calculation of electrode potential :

At Anode

 $H_{2}(g) \Longrightarrow 2H^{+} + 2e^{-}$

Oxidation potential O.P. = $E_{H_{2}(g)/H^{+}(sq)}$

 $E^{0}_{H_{2}(g)/H^{+}(sq)} = \text{SOP} = 0$

 $E_{H_{2}/H^{+}} \neq 0$

 $H_{2}(g) = \text{SOP} = 0$

 $H_{2}(g) = \text{Constant of the set o$

- To calculate standard potential of any other electrode a cell is coupled with standard hydrogen electrode (SHE) and it's potential is measured that gives the value of electrode potential of that electrode.
- Ex. Anode : Zinc electrode

Cell : Zinc electrode || SHE

$$E_{cell} = E_{H^{+}/H_{2}(g)} - E^{\circ}_{Zn2^{+}|Zn}$$

= 0.76 V (at 298 K experimentally)

So, $E^{\circ}_{Zn2^+|Zn} = -0.76 \text{ V} (SRP)$ $E^{\circ}_{Zn|Zn2^+(aq)} = 0.76 \text{ V} (SOP)$

(b) Calomel Electrode :

Cathode : $Cl^{-}(c M) |Hg_{2}Cl_{2}(s)| Hg(l)| Pt(s)$

It is prepared by a Pt wire in contact with a paste of Hg and Hg₂Cl₂ present in a KCl solution. reaction Hg₂Cl₂(s) + 2e⁻ \longrightarrow 2Hg(l) + 2Cl⁻; E⁰ = + 0.27 V

$$\Rightarrow \qquad E_{Cl^{-}/H_{g_{2}}Cl_{2}/H_{g}} = E_{Cl^{-}/H_{g_{2}}Cl_{2}/H_{g}}^{0} - \frac{0.059}{2} \log[Cl^{-}]^{2}$$

4. CONCENTRATION CELL

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cells.

4.1 Electrode concentration cell :

Pt, $H_2(P_1) | H^+(C) | H_2(P_2)$, Pt

Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

Cell process : $1/2H_2(p_1) \rightarrow H^+(c) + e^-$ (Anode process)

or

For spontanity of such cell reaction, $p_1 > p_2$

4.2 Electrolyte concentration cells:

 $Zn(s) | ZnSO_4(C_1) || ZnSO_4(C_2) | Zn(s)$

In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,

 $Zn(s) \rightarrow Zn^{2+}(C_1)+2e$ (Anodic process)

$$\frac{Zn^{2+}(C_2) + 2e \longrightarrow Zn(s)}{Zn^{2+}(C_2) \rightleftharpoons Zn^{2+}(C_1)}$$
 (Cathodic process, Over all process)

\therefore From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F} log \left[\frac{C_1}{C_2} \right] \quad or \qquad E = \frac{2.303RT}{2F} log \left[\frac{C_2}{C_1} \right]$$

For spontanity of such cell reaction, $C_2 > C_1$

EXERCISE # 2 **Representation of Cell diagrams, complete and half cell reactions :** The reduction potential of hydrogen electrode ($P_{H_{\gamma}} = 1 \text{ atms}$; [H⁺] = 0.1 M) at 25°C will be -1. (A) 0.00 V (B) -0.059 V (C) 0.118 V (D) 0.059 V 2. Which of the following represents the reduction potential of silver wire dipped into 0.1 MAgNO₃ solution at 25° C? (A) E°_{red} (B) $(E_{red}^{\circ} + 0.059)$ (C) $(E_{oxi}^{\circ} - 0.059)$ (D) $(E_{red}^{\circ} - 0.059)$ For a reaction - A(s) + $2B_{(aq)}^+ \rightarrow A_{(aq)}^{2+} + 2B_{(s)}$ K_c has been found to be 10¹². The E°cell is: 3. (C) 0.0098 V (A) 0.354 V (B) 0.708 V (D) 1.36 V 4. For the cell reaction $Mg_{(s)} + Zn^{2+}_{(a0)}(1M) \longrightarrow Zn(s) + Mg^{2+}_{(a0)}(1M)$ The emf has been found to be 1.60 V, E° of the cell is : (B) 1.60 V (A) -1.60 V (C) 0.0 V (D) 0.16 V 5. The emf of the cell in which the following reaction, $Zn(s) + Ni^{2+}_{(a0)} (a = 0.1) \rightarrow Zn^{2+}_{(a0)} (a = 1.0) + Ni(s)$ occurs, is found to be 0.5105 V at 298 K. The standard e.m.f. of the cell is :-(A) -0.5105 V (B) 0.5400 V (C) 0.4810 V (D) 0.5696 V Given electrode potentials : 6. $\operatorname{Fe}_{(aq)}^{3+} + e^{-} \longrightarrow \operatorname{Fe}_{(aq)}^{2+}$; $\operatorname{E}^{\circ} = 0.771 \text{ volts}$ $I_{2(g)} + 2e^{-} \longrightarrow 2I_{(aq)}^{-}$; $\operatorname{E}^{\circ} = 0.536 \text{ volts}$ E°_{cell} for the cell reaction, $2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I^{-}_{2(q)}$ is -(A) $(2 \times 0.771 - 0.536) = 1.006$ volts (B) $(0.771 - 0.5 \times 0.536) = 0.503$ volts (C) 0.771 - 0.536 = 0.235 volts (D) 0.536 - 0.771 = -0.235 volts SOME COMMERCIAL BATTERIES 5. Any battery or cell that we use as a source of electrical energy is basically an electrochemical cell where

oxidising and reducing agents are made to react by using a suitable device. In principle, any redox reaction can be used as the basis of an electrochemical cell, but there are limitations to the use of most reactions as the basis of practical batteries. A battery should be reasonably right and compact and its voltage should not vary appreciably during the use.

There are mainly two types of cells :

(i) primary cells and (ii) secondary cells. In primary cells, the reaction occurs only once and the battery then becomes dead over a period of time and cannot be used again. (For example, dry cell, mercury cell.) Contrary to this, secondary cells can be recharged by passing a current through them so that they can be used again and again.(For example, lead storage battery, nickel- cadmium storage cell.)

5.1 Primary Batteries

5.1.1 Dry cell or Laclanche cell :

The most familiar type of battery is the dry cell which is a compact of Leclanche cell known after its discoverer Leclanche (fig.) : In this cell, the anode consists of a zinc container and the cathode is a graphite rod surrounded by powdered MnO_2 and carbon. The space between the electrodes is filled with a moist paste of NH_4Cl and $ZnCl_2$. The electrode reactions are complex, but they can be written approximately as follows.



• Anode
$$Zn(s) \longrightarrow Zn^{+2} + 2e^{-1}$$

Cathode $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

In the cathode reaction, manganese is reduced from the +4 oxidation state to the +3 state. Ammonia is not liberated as a gas but combines with Zn^{2+} to form $Zn(NH_3)_4^{2+}$ ion. The cell has a potential of nearly 1.5 V.

5.1.2 Mercury cell :

Mercury cell, suitable for low current devices like hearing aids, watches, etc.consists of zinc & mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions for the cell are given below:

Anode : $Zn(Hg) + 2OH \rightarrow ZnO(s) + H_2O + 2e$

Cathode : HgO + 2H₂O + 2e⁻ \rightarrow Hg(I) + 2OH⁻

The overall reaction is represented by

 $Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(I)$

The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.



5.2 Secondary Batteries

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles.

5.2.1 Lead storage cell :

The most important secondary cell is the lead storage battery commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

The cell reactions when the battery is in use are given below:

Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^{-}$

Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(\ell)$

i.e., overall cell reaction consisting of cathode and anode reactions is:

 $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(I)$

On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO₂, respectively.



5.2.2 Nickel-cadmium cell :

Another important secondary cell is the nickel-cadmium cell which has longer life than the lead storage cell but more expensive to manufacture. We shall not go into details of working of the cell and the electrode reactions during charging and discharging. The overall reaction during discharge is:

 $Cd (s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$



A rechargeable nickel-cadinium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide

5.3 FUEL CELLS

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity. We know that a galvanic cell directly converts chemical energy into electricity and is highly efficient. It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment. Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells. One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water . The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:

Cathode: $O_2(g) + 2H_2O(I) + 4e^- \rightarrow 4OH^-(aq)$

Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(I) + 4e^-$

Overall reaction being :

 $2H_2(g) + O_2(g) \rightarrow 2H_2O(I)$

The cell runs continuously as long as the reactions are supplied Fuel cells produce electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. These have been used in automobiles on an experimental basis. Fuel cells are pollution free and in view of their future importance, a variety of fuel cells have been fabricated and tried. H_2O



Fuel cell using H₂ and O₂ produces electricity

6. CORROSION :

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion. It It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. We lose crores of rupees every year on account of corrosion. In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction



Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$ Reduction: $O_2(g) + 4H^+(aq) + 4e^{-} \rightarrow 2H_2O(I)$ Atmospheric

Corrosion of iron in atmosphere

Anode: $2Fe(s) \longrightarrow 2Fe^{2+} + 4e^{-1}$

$$E_{(Fe^{2+}/Fe)}^{\Theta} = -0.44 \text{ V}$$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(I)$ $E_{H^+|O_2|H_2O} = 1.23 \text{ V}$ The overall reaction being:

 $2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(I) \qquad \qquad E_{(Cell)}^{\Theta} = 1.67 \text{ V}$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide (Fe₂O₃·xH₂O) and with further production of hydrogen ions.

Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion. One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmoshphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol). Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.). Which corrodes itself but saves the object.

SOLVED EXAMPLES

Ex.1	E° of some oxidants are given as :			
	$I_2 + 2e^- \longrightarrow 2I^-,$	$E^\circ = + 0.54 V$		
	$\mathrm{MnO}_{4}^{-}+8\mathrm{H}^{+}+5e^{-}\longrightarrow Mn^{2+}+4H_{2}O,$	$E^{\circ} = + 1.52 V$		
	$Fe^{3+} + e^- \longrightarrow Fe^{2+},$	$E^{\circ} = + 0.77 V$		
	$Sn^{4+} + 2e^{-} \longrightarrow Sn^{2+},$	$E^\circ = + 0.1 V$		
	(a) Select the strongest reductant and oxidant in these.			
	(b) Select the weakest reductant and oxidant in these.			
	(c) Select the spontaneous reaction from the changes given below.			
	$(i) Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$			
	$(\ddot{u})2Fe^{2+} + I_2 \longrightarrow 2Fe^{3+} + 2I^-$			
	$(iii) Sn^{4+} + 2I^{-} \longrightarrow Sn^{2+} + I_{2}$			
	$(iv) Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^{-}$			
Sol.	(a) More the $E^{\circ}_{\Omega P}$, more is the tendency for oxidation. Therefore, since maximum $E^{\circ}_{\Omega P}$ stands for :			
	$\operatorname{Sn}^{2+} \longrightarrow \operatorname{Sn}^{4+} + 2e^{-} \qquad \operatorname{E}^{\circ}_{OP} = -$	0.1V		
	\therefore Strongest reductant : Sn^{2+}			
	and weakest oxidant : Sn^{4+}			
	(b) More +ve is E°_{RP} , more is the tendency for reduction. Therefore, since maximum E°_{RP} stands for			
	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O E_{RP}^\circ = +1.52 V$			
	$\therefore Strongest oxidant \qquad : \qquad MnO_4^{-}$			
	and weakest reductant : Mn^{2+}			
	Note :- Stronger is oxidant, weaker is its conjugate reducant and vice-versa.			

(c) For (i) $E_{Cell}^{\circ} = E_{OP_{Fe^{2^+}/Fe^{3^+}}}^{\circ} + E_{RP_{Sn^{4^+}/Sn^{2^+}}}^{\circ} = -0.77 + 0.1$

Fe²⁺ oxidizes and Sn⁴⁺ reduces in change.

$$\therefore \qquad E_{\text{Cell}}^{\circ} = E_{\text{OP}_{\text{Fe}^{2_{+}}/\text{Fe}^{3_{+}}}}^{\circ} + E_{\text{RP}_{\text{Sn}^{4_{+}}/\text{Sn}^{2_{+}}}}^{\circ} = -0.77 + 0.1 = -0.67 \text{ V}$$

 E_{Cell}° is negative.

 \therefore (i) Is non-spontaneous change.

For (ii)
$$E_{Cell}^{\circ} = E_{OP_{re^{2+}/re^{3+}}}^{\circ} + E_{RP_{lg/l^{-}}}^{\circ} = -0.77 + 0.54 = -0.23 \text{ V}$$

 \therefore (ii) reaction is non-spontaneous change.

For (iii)
$$E_{Cell}^{\circ} = E_{OP_{\Gamma/l_2}}^{\circ} + E_{RP_{Sn^{4+}/Sn^{2^+}}}^{\circ} = -0.54 + 0.1 = -0.44 \text{ V}$$

- \therefore (iii) Reaction is non-spontaneous change.
- For (iv) $E_{Cell}^{\circ} = E_{OP_{Su^{2+}/Su^{4+}}}^{\circ} + E_{RP_{12/1}}^{\circ} = -0.1 + 0.54 = +0.44 \text{ V}$
 - (iv) Reaction is spontaneous change.
- Ex.2 Given the standard electrode potentials; $K^{+}|K = -2.93 V, Ag^{+}|Ag = 0.80 V, Hg^{2+}|Hg = 0.79 V, Mg^{2+}|Mg = -2.37 V, Cr^{3+}|Cr = -0.74V.$ Arrange these metals in their increasing order of reducing power.
- Sol. More is E°_{RP} , more is the tendency to get reduced or more is the oxidising power or lesser is reducing power. Ag < Hg < Cr < Mg < K
- *Ex.3* A cell is prepared by dipping a copper rod in 1 M $CuSO_4$ solution and a nickel rod in 1M $NiSO_4$ The standard reduction potentials of copper and nickel electrodes are + 0.34 V and -0.25 V respectively.
 - (i) Which electrode will work as anode and which as cathode ?
 - (ii) What will be the cell reaction ?
 - (iii) How is the cell represented ?
 - (iv) Calculate the EMF of the cell.
- Sol. (i) The nickel electrode with smaller E° value (-0.25 V) will work as anode while copper electrode with more E° value (+0.34V) will work as cathode.
 - (ii) The cell reaction may be written as :

At anode:Ni (s) \longrightarrow Ni²⁺ (aq.) + 2e⁻At cathode:Cu²⁺ (aq) + 2e⁻ \longrightarrow Cu (s)Cell reaction:Ni (s) + Cu²⁺ (aq) \longrightarrow Ni²⁺ (aq) + Cu (s)

- (iii) The cell may be represented as : $Ni(s)|Ni^{2+}(aq)||Cu^{2+}(aq)|Cu(s)|$
- (iv) EMF of cell = $E_{cathode}^{\circ} E_{anode}^{\circ} = (+0.34) (-0.25) = 0.59 \text{ V}$

Ex.4Predict whether the following reaction can occur under standard conditions or not. $Sn^{2+}(aq) + Br_{2}(\ell) \longrightarrow Sn^{4+}(aq) + 2Br^{-}(aq)$ *Given*: $E^{\circ}_{Sn^{4+}|Sn^{2+}} = +0.15; E^{\circ}_{Br^{2}|Br^{-}} = 1.06V.$ $E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = 1.06 - 0.15 = 0.91 V.$ Sol. Since, E_{coll}° comes out be positive, this means that the reaction can occur. Given that, $Co^{3+} + e^- \longrightarrow Co^{2+} E^\circ = +1.82V$ Ex.5 $2H_{2}O \longrightarrow O_{2} + 4H^{+} + 4e^{-}$; $E^{\circ} = -1.23V$. Explain why Co^{3+} is not stable in aqueous solutions. The E_{cell}° can be calculated as follows : Sol. $4 \times [\text{Co}^{3+} + e^{-} \longrightarrow \text{Co}^{2+}]$: $E^{\circ} = +1.82\text{V}$ $1 \times [2H_2O \longrightarrow O_2 + 4H^+ + 4e^-]; E^\circ = -1.23 V.$ Add: $4\text{Co}^{3+} + 2\text{H}_2^{2}\text{O} \longrightarrow 4\text{Co}^{2+} + 4\text{H}^{+} + \text{O}_2$; $\text{E}^\circ = 1.82 - 1.23 = +0.59\text{V}$. Since, E_{cell}° is positive, the cell reaction is spontaneous. This means that Co^{3+} ions will take part in the reaction. Therefore, Co^{3+} is not stable. The 0.1 M copper sulphate solution in which copper electrode is dipped at 25°C. Calculate the Ex.6 electrode reduction potential of copper electrode. [Given: $E_{Cv^{2+|Cv|}}^0 = 0.34$ V] $Cu^{+2} + 2e^{-} \rightarrow Cu$ Sol: $E_{red} = E_{red}^{0} - \frac{0.059}{n} \log Q = E_{Cu^{2+}|Cu}^{0} - \frac{0.0591}{2} \log \frac{1}{|Cu^{2+}|}$ So E = $0.34 - \frac{0.0591}{2} \log 10$ = 0.34 - 0.03 = 0.31 volts Calculate the EMF of the cell : $Cr[Cr^{+3}(0.1M) || Fe^{+2}(0.01M)]Fe$ **Ex.7** (Given : $E^{\circ}_{Cr^{+3}|Cr} = -0.75 V$, $E^{\circ}_{Fe^{+2}|Fe} = -0.45 V$) Sol. Half cell reactions are : $[Cr \rightarrow Cr^{+3} + 3e^{-}] \times 2$ • At anode : $[Fe^{+2} + 2e^{-} \rightarrow Fe] \times 3$ At cathode : Over all reaction : $2Cr(s) + 3Fe^{+2}(aq_{.}) \rightarrow 2Cr^{+3}(aq_{.}) + 3Fe(s_{.})$ $E^{\circ}_{cell} = E^{\circ}_{Cr|Cr^{+3}} + E^{\circ}_{Fe^{+3}|Fe} = 0.75 + (-0.45) = 0.30 V$ $E_{cell} = E^{0} - \frac{0.0591}{n} \log Q = 0.30 - \frac{0.0591}{6} \log \frac{\left[Cr^{+3}\right]^{2}}{\left[Fe^{+2}\right]^{3}} = 0.30 - \frac{0.0591}{6} \log \frac{\left[0.1\right]^{2}}{\left[0.01\right]^{3}} = 0.26 V$

- Ex.8 The measured e.m.f. at 25°C for the cell reaction, $Zn(s) + Cu^{2+}_{(aq)}(1.0M) \longrightarrow Cu(s) + Zn^{2+}_{(aq)}(0.1 M)$ is 1.3 volt, Calculate E° for the cell reaction.
- **Sol.** Using Nernst equation (at 298 K), $E_{cell} = E_{cell}^{\circ} \frac{0.059}{2} \log \frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$

Here, $E_{cell} = 1.3 \text{ V}$, $[Cu^{2+} (aq)] = 1.0 \text{ M}$, $[Zn^{2+} (aq)] = 0.1 \text{ M}$, $E_{cell}^{\circ} = ?$

Substituting the values , $E_{cell}^0 = 1.27 \text{ V}$

Ex.9 The emf of a cell corresponding to the reaction $Zn + 2H^{+}(aq) \longrightarrow Zn^{2+}(0.1M) + H_{2}(g) \ 1 \ atm$ is 0.28 volt at 25°C. Calculate the pH of the solution at the hydrogen electrode. $E_{7a^{2+}|Zn}^{\circ} = -0.76 \ volt \ and \ E_{H^{+}|H_{2}}^{\circ} = 0$

Sol. $E_{cell}^{\circ} = 0.76 \text{ volt}$

Applying Nernst equation, $E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]P_{H_2}}{[H^+]^2}$

$$0.28 = 0.76 - \frac{0.0591}{2} \log \frac{(0.1) \times 1}{[H^+]^2}$$
, pH = 8.62

Ex.10 The half cell oxidation potential of a half-cell A^{x+} , $A^{(x+n)+}$ | Pt were found to be as follows :

% of reduced form	24.4	48.8
Cell potential V	0.101	0.115

Determine the value of n. [Take $\frac{2.303 \text{ RT}}{\text{F}} = 0.06$, $\log_{10} 24.4 = 1.387$, $\log_{10} 75.6 = 1.878$, $\log_{10} 48.8$

 $= 1.688, \log_{10} 51.2 = 1.709$]

The half-cell reaction is -

 $A^{x+} \rightarrow A^{(x+n)+} + ne^{-1}$

Sol.

Its Nernst equation is -

$$E = E^{\circ} - 2.303 \frac{RT}{nF} \log \frac{[A^{(x+n)+}]}{[A^{x+}]} = E^{\circ} - \left(\frac{0.06V}{n}\right) \log \left(\frac{\text{oxidized form}}{\text{reduced form}}\right)$$

Substituting the given values, we get

$$0.101 \text{ V} = \text{E}^{\circ} - \left(\frac{0.06\text{V}}{n}\right) \log \frac{75.6}{24.4} = \text{E}^{\circ} - \left(\frac{0.06\text{ V}}{n}\right) (0.491) \dots (i)$$

$$0.115 \text{ V} = \text{E}^{\circ} - \left(\frac{0.06\text{ V}}{n}\right) \log \frac{51.2}{48.8} = \text{E}^{\circ} - \left(\frac{0.06\text{ V}}{n}\right) (0.021) \dots (ii)$$
eq. (ii) - (i), n = 2

What is the standard electrode potential for the electrode $MnO_4^{-1}|MnO_2$ in solution $E_{MnO_4|Mn^{2+}}^{\circ} =$ Ex.11 **1.51 volt**, E[°]_{MnOolMn²⁺} =1.23 volt $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$; $E^\circ = 1.51$ volt Sol. $MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$; $E^\circ = 1.23$ volt $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O; E^\circ = ?$ $E^{\circ} = \frac{5 \times 1.51 - 2 \times 1.23}{3} = \frac{7.55 - 2.45}{3} = \frac{5.09}{3} = 1.70$ volt Calculate ΔG° for the reaction : $Cu^{2+}(aq) + Fe(s) \rightleftharpoons Fe^{2+}(aq) + Cu(s)$. Ex.12 Given that $E^{\circ}_{Cu^{2+}|Cu} = +0.34 V$, $E^{\circ}_{Fe^{+2}/Fe} = -0.44 V$ Sol. The cell reactions are : Fe (s) \longrightarrow Fe²⁺ (aq) + 2e⁻at (anode) $Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$at (cathode) We know that : $\Delta G^{\circ} = -nF E_{cell}^{0}$; n = 2 $E_{cell}^{\circ} = \left[E_{(C_1)^{2+}/(C_1)}^{\circ} - E_{(Fe^{2+}/(Fe))}^{\circ} \right] = (+0.34 \text{ V}) - (-0.44 \text{ V}) = +0.78 \text{ V} \text{ and } F = 96500 \text{ C}$:. $\Delta G^{\circ} = -nF E_{cell}^{\circ} = -(B) \times (96500 C) \times (+0.78 V) = -150540 CV = -150540 J$ At 298 K the standard free energy of formation of H₂O(l) is-256.5 kJ|mol & OH⁻ is 80 kJ|mol. What *Ex.13* will be emf at 298 K of the cell $H_2(g, 1 bar) | H^+(1M) | OH^-(1M) | O_2(g, 1 bar)$ $H_2 + H_2O + \frac{1}{2}O_2 \longrightarrow 2H^+ + 2OH^ \Delta G^{\circ} = -256.5 + 2 \times 80 = -96.5 \text{ kJ}$ $-\Delta G^{\circ} = nFE^{\circ}$ $+96.5 \times 1000 = 2 \times 96500 \times E^{\circ}$ $E^\circ = 0.5$ Volt Calculate the equilibrium constant for the reaction at 298 K. *Ex.14* $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ Given, $E_{7n^{2+}/7n}^{\circ} = -0.76 \text{ V}$ and $E_{Cu^{2+}/Cu}^{\circ} = +0.34 \text{ V}$ We know that, $\log K_c = \frac{nE_{cell}^0}{0.0591}$ Sol. $E_{cell}^{\circ} = [E_{Cathode}^{\circ} - E_{Anode}^{\circ}] = [(+0.34 \text{ V}) - (-0.76 \text{ V})] = 1.10 \text{ V}, n = 2,$ $\therefore \qquad \log K_c = \frac{2 \times (1.10 \text{ V})}{(0.0591 \text{ V})} = 37.29 \text{, } K_c = \text{Antilog } 37.29 = 1.95 \times 10^{37}$

Calculate the cell e.m.f. and ΔG for the cell reaction at 298 K for the cell. Ex.15 $Zn(s) | Zn^{2+} (0.0004M) | | Cd^{2+} (0.2M) | Cd(s)$

Given, $E_{7n^{2+1/7n}}^{\circ} = -0.763 V$; $E_{Cd^{2+1/6}}^{\circ} = -0.403 V$ at 298 K. $F = 96500 C mol^{-1}$.

Sol. Step I. Calculation of cell e.m.f.: According to Nernst equation,

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[Zn^{2+}(aq)]}{[Cd^{2+}(aq)]}$$

 $E_{cell}^{\circ} = E_{(Cd^{2+}/Cd)}^{\circ} - E_{(Zn^{2+}/Zn)}^{\circ} = (-0.403) - (-0.763) = 0.36 \text{ V}$ $[Zn^{+}(aq)] = 0.0004 \text{ M}, [Cd^{2+}(aq)] = 0.2 \text{ M}, n = 2$

$$E = (0.36) - \frac{(0.059V)}{2} \log \frac{0.0004}{0.2} = 0.36 - \frac{(0.059V)}{2} \times (-2.69990) = 0.36V + 0.08 = 0.44V$$

Step II. Calculation of $\triangle G$:

$$\Delta G = - nFE_{cell}$$

$$E_{cell} = 0.44 \text{ V}, n = 2 \text{ mol}, F = 96500 \text{ c mol}^{-1}$$

$$\Delta G = - (2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.44 \text{ V})$$

$$= -84920 \text{ CV} = -84920 \text{ J}$$

The cell $Pt \mid H_2(g) (1 \text{ atm}) \mid H^+$; $pH = x \mid |Normal calomal electrode has EMF of 0.64 volt at$ *Ex.16* 25°C. The standard reduction potential of normal calomal electrode is 0.28 V. What is the pH 2.303RT of solution in anodic compartment. Take 0.06 at 298 K.

 $E_{H^+/H_2} = -0.06 \log \frac{1}{[H^+]} = -0.06 \text{pH}$ Sol. $\Rightarrow 0.64 = E_{cathode} - E_{Anode} = 0.28 - (-0.06 \text{ pH})$ $\Rightarrow pH = \frac{0.64 - 0.28}{0.06} = \frac{0.36}{0.06} = 6$

Consider a Galvenic cell, *Ex.*17

$$Zn(s) | Zn^{2+}(0.1 M) | | Cu^{2+}(0.1 M) | Cu(s)$$

by what factor, the electrolyte in anodic half cell should be diluted to increase the emf by 9 milli volt at 298 K.

Ans.
$$E = E_{cell}^{\circ} - \frac{0.06}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

 $E_1 = E_{cell}^{\circ} - 0.03 \log \frac{(0.1)}{(0.1)}$
 $E_2 = E_{cell}^{\circ} - 0.03 \log \frac{(0.1/x)}{(0.1)}$ {x is the factor by which electrolyte is diluted.}

 $E_2 - E_1 = 9 \times 10^{-3} = 0 - 0.03 \log\left(\frac{1}{x}\right)$ 0.009 = 0.03 log X $\frac{9 \times 10^{-3}}{3 \times 10^{-2}} = 0.3 = \log X$ X = 2

Ex.18 A disposable galvanic cell $Zn |Zn^{2+}||Sn^{2+}|Sn$ is produced using 1.0 mL of 0.5 M $Zn(NO_3)_2$ and 1.0 mL of 0.50 M $Sn(NO_3)_2$. It is needed to power a pace-maker that draws a constant current of 10^{-6} Amp to run it and requires atleast 0.50 V to function. Calculate the value of $[Zn^{2+}]$ when cell reaches 0.5 V at 298 K.

$$(Given : E^{\circ}(Zn^{2+}|Zn) = -0.76V; E^{\circ}(Sn^{2+}|Sn) = -0.14V)$$

Ans.

1

$$E = 0.5 V = 0.62 - \frac{0.059}{2} \log \frac{0.5 + x}{0.5 - x}$$

$$\therefore Zn + Sn^{2+} \rightleftharpoons Sn + Zn^{2+} One Sn + Zn^{2+} One$$

Ex.19 An alloy of Pb-Ag weighing 54 mg was dissolved in desired amount of HNO_3 & volume was made upto 500ml. An Ag electrode was dipped in solution and then connected to standard hydrogen electrode anode. Then calculate % of Ag in alloy.

Given:
$$E_{cell} = 0.5 V$$
; $E_{Ag^+|Ag} = 0.8V$ $\frac{2.303RT}{F} = 0.06$

Ans. $Ag^{+} + 1e^{-} \longrightarrow Ag$ $E_{cell} = 0.5 = 0.8 + \frac{0.06}{1} \log [Ag^{+}]$ $\log [Ag^{+}] = \frac{-0.30}{0.06} = -5$ $[Ag^{+}] = 10^{-5} \text{ mol}|L$ moles of Ag^{+} in 500 ml $= \frac{10^{-5}}{2}$ Mass of $Ag = \frac{10^{-5}}{2} \times 108$ $\% Ag = \frac{\frac{10^{-5}}{2} \times 108}{54 \times 10^{-3}} \times 100 = 1$ *Ex.20.* A solution contains A^+ and B^+ in such a concentration that both deposit simultaneously. If current of 9.65 amp was passed through 100 ml solution for 55 seconds then find the final concentration of A^+ ions if initial concentration of B^+ is 0.1M.

 $Given: A^{+} + e^{-} \longrightarrow A \qquad E^{\circ} = -0.5 \text{ volt}$ $B^{+} + e^{-} \longrightarrow B \qquad E^{\circ} = -0.56 \text{ volt}$ $\frac{2.303\text{RT}}{\text{F}} = 0.06$ Sol. $-0.5 - \frac{0.06}{1} \log \frac{1}{[A^{+}]} = -0.56 - \frac{0.06}{1} \log \frac{1}{[B^{+}]}$ $0.06 = \frac{0.06}{1} \log \frac{[B^{+}]}{[A^{+}]}$ $\frac{[B^{+}]}{[A^{+}]} = 10$ $[A^{+}]_{\text{initial}} = 0.01\text{M}$

Ex.21 While the discharging of a lead storage battery following reaction take place. $PbO_2 + Pb + 4H^+ + 2SO_4^{-2} \rightarrow 2PbSO_4 + 2H_2O$; $E^\circ = 2.01$ Calculate the energy (in kJ) obtained from a lead storage battery in which 0.014 mol of lead is consumed. Assume a constant concentration of 10.M H₂SO₄ (log2 = 0.3)

Ans.
$$E = E^{\circ} - \frac{0.059}{n} \log \frac{1}{[H^+]^4 [SO_4^{-2}]^2} = 2.01 - \frac{0.059}{2} \log \frac{1}{[20]^4 [10]^2} = 2.22 \text{ V}$$

Energy = qE = $2 \times 0.014 \times 96500 \times 2.22$ = 6000 J = 6 kJ

Ex.22 Consider the following standard reduction potentials :-

$Fe^{2+} + 2e^{-} \rightleftharpoons Fe$;	$E^{\circ} = -0.41 V$
$Ag^+ + e^- \rightleftharpoons Ag$;	$E^\circ = 0.80 V$
$O_2 + 2H_2O + 4e^- \rightleftharpoons$	<i>40H</i> ⁻;	$E^\circ = 0.40 V$

What would happen if a block of silver metal is connected to a buried iron pipe via a wire:-

- (A) The silver metal would corrode, a current would be produced in the wire, and O_2 would be reduced on the surface of the iron pipe.
- (B) The silver metal would corrode, a current would be produced in the wire, and Fe²⁺ would be reduced on the surface of the iron pipe.
- (C) The iron pipe would corrode, a current would be produced in the wire, and Ag^+ would be reduced on the surface of the silver metal.
- (D) The iron pipe would corrode, no current would be produced in the wire, and O₂ would be reduced on the surface of the iron pipe.

Sol. (D)

7. ELECTROLYSIS :

The process of decomposition of an electrolyte by the passage of electricity is called *electrolysis* or electrolytic dissociation. It is carried out in electrolytic cell where electrical energy is converted into chemical energy. For electrolysis to take place two suitable electrodes are immersed in the liquid or solution of an electrolyte containing ions. When an electric potential is applied between the electrodes, the positively charged ions move towards the negative cathode and negatively ions move towards the positive anode, when a cation reaches the cathode, its takes up electron(s) and thus gets its charge neutralised. Thus the gain of electrons (decrease in oxidation number) means reduction takes place at the cathode.

Similarly when an anion it reaches the anode, gives up electron(s) and thus gets discharged. Loss of electrons (Increase in oxidation number) means oxidation takes place at anode.

- The tendency of an electrode to lose electrons is known as the *oxidation potential*.
- The tendency of an electrode to gain electrons is known as the *reduction potential*.
- Greater oxidation potential means stronger is tendency to get oxidised and act as a reducing agent or reductant.
- Greater reduction potential means stronger is tendency to get reduced and act as an oxidising agent (oxidant).

(a) Electrolysis of fused sodium chloride :

When fused sodium chloride is electrolysed, Na^+ ions moves towards the cathode and Cl^- ions moves towards the anode. At cathode Na^+ ions accept electrons to form sodium metal. At anode each Cl^- ion loses an electron to form Cl_2 gas.

- At anode : $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$; $E_{OP}^0 = -1.36V$
- At cathode: $Na^+ + e^- \longrightarrow Na(s)$; $E^0_{RP} = -2.71V$

(b) Electrolysis of aqueous solution of KBr

The solution of KBr contain K^+ , Br^- & small amounts of H^+ , OH^- (due to small dissociation of water)

- At anode : $2Br(aq.) \longrightarrow Br_2(g) + 2e^-$
- At cathode : $2H_2O(\ell) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
- If more than one types of ions are present at a given electrode, then the one ion is the liberated which requires least energy. The energy required to liberate an ion is provided by the applied potential between electrodes. This potential is called *discharge or deposition potential*.

Note :

- 1. In aqueous solution most electropositive metal cations for eg. (s-block & Al^{3+}) will not discharg at cathode instead H_2O is reduced. $2H_2O(\ell) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
- 2. In aqueous solution cations of moderately electropositive metals (Mn, Co, Fe, Zn etc.) and least electropositive metals (Cu, Hg, Au, Ag, Pt) get discharged at cathode first.

3. Active vs Inactive electrodes :

- Sometimes the metal electrodes in the cell are active and the metals themselves are components of the half reactions or influence the reaction of electrode.
- For many redox reactions, however, there are no reactants or products capable of serving as electrodes. Inactive electrodes are used, most commonly rods of graphite or platinum, materials that conduct electrons into or out of the cell but cannot take part in the half-reactions.
- Platinum is used : highly conducting, unreactive.

highly malleable and ductile.

Examples of Electrolysis :

• **Electrolysis of aq. PbBr**₂(Using inert (Pt|graphite) electrodes).

Cathode :	$Pb^{2+} + 2e^- \rightarrow Pb(s)$	$E^0 = 0.126V$
Anode :	$2Br^{-} \rightarrow Br_2 + 2e^{-}$	$E^0 = -1.08 V$
	$E_{cell} = -0.126 - (0.108) \times 10 = -1.206 V$	7
	$E_{ext} > 1.206 V$	

• Electrolysis of aq. CuSO₄(Using inert (Pt|graphite) electrodes).

 $Cu^{2+} + 2e^- \rightarrow Cu(s)$

Cathode :

Anode

	$2e + 2H_2O(\ell) \rightarrow H_2(g) + 2OH^-(aq)$	$E^0 = -0.83V$
:	$2 \mathrm{SO}_4^{2-} \rightarrow \mathrm{S}_2 \mathrm{O}_8^{2-} + 2 \mathrm{e}^-$	$E^0 = -2.05 V$
	$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$	$E^0 = -1.23 V$

 $E^0 = 0.34 V$

- \therefore Cu discharged at cathode and O₂ at anode.
- Electrolysis of aq. NaCl (Using inert (Pt|graphite) electrodes).

Cathode :	$Na^+ + e^- \rightarrow Na$	$E^0 = -2.71 V$
	$2e^- + 2H_2O(\ell) \rightarrow H_2(g) + 2OH^-$	$E^0 = -0.83 V$
Anode :	$2Cl^{-} \rightarrow Cl_2 + 2e^{-}$	$E_{OX}^0 = -1.30 V$
	$2\mathrm{H}_{2}\mathrm{O}(\ell) \rightarrow \mathrm{O}_{2} + 4\mathrm{H}^{+} + 4\mathrm{e}^{-}$	$E_{ox}^{0} = -1.23 V$

Rate of production of Cl_2 is more than rate of production of O_2 gas because of greater activation energy barrier for O_2 production, therefore Cl_2 is released at anode and H_2 at cathode.

Note:(i) As observed from electrode potential values discharge potential for O_2 is less than for Cl_2 . According to thermodynamics, oxidation of H_2O to produce O_2 should take place on anode but experimentally (experiment from chemical kinetics) the rate of oxidation of water is found to be very slow. To increase it's rate, the greater potential difference has to be is applied called over voltage or over potential.

Because of this oxidation of Cl^- ions also become feasible and this takes place at anode. Electrode potential values do not take into account such effects as : Activation energy of process or non-uniform ionic concentration in solution.

(ii) Electrode potentials are thermodynamic intensive properties obtained experimentally under ideal & standard conditions. Sometimes in working conditions additional potentials are required for discharging. This difference is termed as overvoltage or overpotential.

pure Ag

aq. AgNO₃

***** Electrolysis using attackable (reactive) electrodes :

Electrolysis of aq. CuSO₄ using Cu electrode.

Anode (oxidation) :	$SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$	$E_{ox}^{0} = -2.05 V$	
	$2\mathrm{H}_{2}\mathrm{O}(\ell) \rightarrow \mathrm{O}_{2} + 2\mathrm{H}^{+} + 4\mathrm{e}^{-}$	$E^0 = -1.23 V$	
	$Cu(s) \rightarrow Cu^{2+} + 2e^{-}$	$E^0 = -0.34 V$	
Cathode (reduction) : $Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = +0.34 V$			
	$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-$	$E^0 = -0.83 V$	

:. Both oxidation and reduction of copper occurs and density of solution remains constant.

Impure

Ag

Electrolytic Refining

Electrolysis of AgNO₃(aq) using Ag cathode & Ag anode.

Impure metal \rightarrow Anode;

Pure Metal \rightarrow Cathode ;

Metal salt solution \rightarrow Electrolyte

Anode : $NO_3^- \rightarrow X$ (No reaction)

 $2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$ Ag(s) $\rightarrow Ag^+(aq) + e^-$ (impure)

Cathode:
$$Ag^+ + e^- \rightarrow Ag(s)$$
 (pure) $E^0 = 0.8V$
 $2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^ E^0 = -0.83V$

... Both oxidation and reduction of Ag occurs and mass transfer of Ag occurs from anode (impure Ag) to cathode (pure Ag). Electrical energy provided by battery is used for mass transfer of Ag from anode to cathode.

 $E^{0} = -1.23V$ $E^{0} = -0.80V$

S.No. Electrolyte		Electrode	Product obtained	Product obtained
			at anode	at cathode
(i)	Fused NaCl(molten)	Pt or Graphite	Cl ₂	Na
(ii)	Aqueous NaCl(conc.)	Pt or Graphite	Cl ₂	H ₂
(iii)	dil.NaCl	Pt or Graphite	0 ₂	H ₂
(iv)	Aqueous NaOH	Pt or Graphite	0 ₂	H ₂
(v)	Fused NaOH	Pt or Graphite	0 ₂	Na
(vi)	Aqueous CuSO ₄	Pt or Graphite	O ₂	Cu
(vii)	Dilute HCl	Pt or Graphite	Cl ₂	H ₂
(viii)	Dilute H_2SO_4	Pt or Graphite	O ₂	H ₂
(ix)	Aqueous AgNO ₃	Pt of Graphite	O ₂	Ag
(x)	Aqueous CH ₃ COONa	Pt of Graphite	CH ₃ -CH ₃ +CO ₂	H ₂

PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

8. FARADAY'S LAWS OF ELECTROLYSIS :

Michael Faraday on basis of experiments deduced two important laws :

(a) Faraday's first law of electrolysis : This law states that "The amount of a substance deposited or discharged at an electrode is directly proportional to the charge passing through the electrolytic solution".

If a current of **I** amperes is passed for **t** seconds, (the quantity of charge Q in coulombs). If W gram of substances is deposited by Q coulombs of electricity, then

$$W \propto Q \propto i \times t$$
$$W = Z \times i \times t = \frac{E}{96500} \times i \times t = \eta \times \frac{E}{F} \times i \times t$$

moles of $e^- = n_e = \frac{\eta \times i \times t}{F}$ = *no. of equivalents of species discharged* During electrolysis :

Where 1 Faraday (1F) is defined as charge of 1 mole electrons = $eN_A = 1 F \cong 96500 C$

Hence faraday (F) is the quantity of charge in coulombs required to deposit one g equivalent of any substance.

E = Equivalent mass of species discharged

 η = current efficiency in fraction if current efficiency is not mentioned, by default it is assumed to be 1 (100%).

Z is constant of proportionality and is known as *electrochemical equivalent*. Its value is different for different species, when Q = 1 coulomb, W = Z, thus electro chemical equivalent may be defined as the weight in grams of an element liberated by the passage of 1 coulomb of electricity.

Electrochemical equivalent of species (Z) = $\frac{E}{96500}$ gm | coulomb.

(b) **Faraday's second law :** This law states that the amounts of different substances deposited in different solutions connected in series at electrodes by passage of the same quantity of electricity are proportional to their equivalent masses(E).

$W \propto E$ (E = equivalent mass)

If W_1 and W_2 be the amounts of two different substances deposited at electrodes and E_1 and E_2 be the equivalent weights respectively then -

$$\frac{W_{1}}{W_{2}} \!=\! \frac{E_{1}}{E_{2}}$$

9. APPLICATION OF ELECTROLYSIS

(i) Electroplating : Metal used for plating → ANODE
 Object to be plated → CATHODE
 (ii) Electrorefining : Impure metal → ANODE (see fig.)
 Pure metal → CATHODE

Metal salt solution \rightarrow electrolyte

Ag-Anode (-) AgNO_{3(aq.)} (+)

(iii)	Electro-metallurgy	Electro-metallurgy : (Electrolytic reduction) Ex. Electrolysis of NaCl (from seawater) Using Hg-cathode.							
	Ex. Electrolysis of N								
	Anode: $2Cl^- \longrightarrow C$	Anode : $2Cl^- \longrightarrow Cl_{2(g)} + 2e$							
	Cathode : $Na^+ + e^-$	\xrightarrow{Hg} Na–Hg							
		EXEI	RCISE # 3						
1.	Which of the substan	ices Na, Hg, S, Pt and gra	aphite can be used as ele	ctrodes in electrolytic cells having					
	aqueous solution?								
	(A) Hg and Pt								
	(B) Hg, Pt and grap	hite							
	(C) Na, S								
	(D) Na, Hg, S								
2.	When an electric cur	When an electric current is passed through acid diluted water, 112 ml. of hydrogen gas at STP collects							
	at the cathode in 96	5 second. The current p	bassed, in ampere is :						
	(A) 1.0	(B) 0.5	(C) 0.1	(D) 2.0					
3.	A factory produces $40 \mathrm{kg}$. of calcium in two hours by electrolysis. How much aluminium can be produced								
	by the same current	t in two hours- (At wt.	of $Ca = 40$, $Al = 27$)						
	(A) 22 kg.	(B) 18 kg.	(C) 9 kg.	(D) 27 kg.					
4.	Calculate the volume water for 30 minutes	of hydrogen at STP obtained.	ined by passing a curren	t of 0.536 ampere through acidified					
	(A) 0.1135 litre	(B) 0.227 litre	(C) 0.057 litre	(D) 0.454 litre					
5.	An electric current is p the silver voltameter w is:	assed through silver voltar reighed 0.108g more at the	neter connected to a wate end of the electrolysis. T	r voltameter in series. The cathode of he volume of oxygen evolved at STP					
	(A) 56.75 cm ³	(B) 567.5 cm^3	(C) 5.675 cm^3	(D) 113.5 cm^3					
6.	When, during electro	lysis of a solution of AgN	O ₂ 9650 coulombs of ch	arge pass through the electroplating					
	bath, the mass of silv	ver deposited on the cath	node will be :	[AIEEE 2003]					
	(A) 21.6g	(B) 108g	(C) 1.08g	(D) 10.8g					
7.	Aluminium oxide m	hay be electrolysed at 10	000°C to furnish alum	inium metal (1 Faraday = 96500					
	Coulombs).The cath	ode reaction is		[AIEEE 2005]					
	$Al^{3+} + 3e^{-} \longrightarrow Al$								
	To prepare 5.12 kg o	f aluminium metal by th	is method would requir	e,					
	(A) 5.49×10^4 C of	electric charge							
	(B) 5.49×10^{1} C of	electric charge							
	(C) 5.49×10^7 C of	electric charge							
	(D) 1.83×10^7 C of	electric charge							

SOLVED EXAMPLES

How much charge is present on 1 mole of Cu^{+2} ion in faraday. (1 Faraday = 96500 coulomb) *Ex.23*

 $1 \text{ mole } e^- = 1 \text{ mol proton} = 1 \text{ F}$ Ans.

2 Faraday

+3

For an element 'X' the process of oxidation is : $X_2 O_4^{-2} \longrightarrow$ product *Ex.24* If 965 A current when passed for 100 seconds for 0.1 mol of $X_2O_4^{-2}$, find oxidation state of X in new compound?

Ans.

- $\begin{array}{c} \textbf{+3} \\ X_2 O_4^{-2} \longrightarrow 2X^{+n} \\ \therefore \\ \text{oxidation process } 3 < n \text{, N-factor} = 2 (n-3) \end{array}$ $0.1 \times 2(n-3) = \frac{i \times t}{96500} = \frac{965 \times 100}{96500}$ so 2(n-3) = 10, n-3 = 5, n = 8
- How many litres of chlorine at 1atm & 273K will be deposited by 100 amp. current flowing for *Ex.*25 5 hours through molten NaCl?
- $O = It = 100 \times 5 \times 60 \times 60 = 18 \times 10^5 C$ Sol:

W = ZQ =
$$\frac{E}{96500} \times 18 \times 10^5 = \frac{18E}{96500} \times 10^5 = 662.2 \text{ g}, \left(E_{Cl_2} \frac{71}{2} = 35.5\right)$$

Volume of 71 g Cl_2 at 1atm & 273K = 22.4 L ÷

- Volume of 662.2 g Cl₂ at NTP = $\frac{22.4}{71} \times 662.2 = 208.9$ L *.*..
- How much time is required for complete decomposition of two moles of water at anode using 4 *Ex.26* amperes current ?

Sol.
$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$$

For H₂: 2 × 2 =
$$\frac{4 \times t}{96500}$$
 \Rightarrow t = 96500 sec,

How much charge (in F) must flow through solution during electrolysis of aq. Na₂SO₄ at 0°C *Ex.27* and 1 atm to produce 33.6 L of product gases at 50% current efficiency?

Ans.
$$H_2O \xrightarrow{2F} H_2 + \frac{1}{2}O_2$$

 $V \quad V|2 \quad P \quad \frac{3}{2}V = 33.6L \quad P \quad V = 22.4 \quad L$
 $Q \times \frac{50}{100} = 2F \quad P \quad Q = 4F$

- *Ex.28* Calculate the time required to coat a metal surface of 80 cm² with 0.005 mm thick layer of silver (density = 10.5 g cm^{-3}) with the passage of 3A current through silver nitrate solution.
- **Sol.** : Volume of layer of silver = $0.005 \times 10^{-1} \times 80 = 0.04$ cm³
 - \therefore Mass = Density \times volume = 10.5 \times 0.04 = 0.42 g

So
$$w = \frac{E}{96500} \times It \Rightarrow 0.42 = \frac{108}{96500} \times 3 \times t$$

$$t = \frac{0.42 \times 96500}{108 \times 3} = 125.09 \text{ seconds.}$$

- Ex.29 A Solution of copper (II) sulphate is electrolysed between copper electrodes by a current of 10.0 amperes passing for one hour. What changes occur at the electrodes and in the solution?
- **Sol.** According to Faraday's first law of electrolysis : The reaction at eathede : $Cu^{2+} + 2e^{-}$

The reaction at cathode :
$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

63.5 $2 \times 96500 \text{ C}$

The quantity of charge passed = $I \times t = (10 \text{ amp}) \times (60 \times 60 \text{s}) = 36000 \text{ C}.$

 2×96500 C of charge deposit copper - 63.5 g

36500 C of charge deposit copper = $\frac{(63.5 \text{ g})}{(2 \times 96500 \text{ C})} \times (36000 \text{ C}) = 11.84 \text{ g}$

Thus, 11.84 g of copper will dissolve from the anode and the same amount from the solution will get deposited on the cathode. The concentration of the solution will remain unchanged.

- *Ex.30* An aqueous solution of Na_2SO_4 was electrolysed for 10 min. 82 ml of a gas was produced at anode and collected over water at 27°C at a total pressure of 580 torr. Determine the current that was used in amp., Given : Vapour pressure of H_2O at 27°C = 10 torr, R = 0.082 atm L|mol-K
- Ans (1.6A)

At anode reaction will be

 $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

 Vo_2 collected = 82 ml

By PV = nRT
$$\frac{(580-10)}{760} \times \frac{82}{1000} = (n_{o_2}) \times 0.0821 \times 300$$
, $n_{o_2} = \frac{1}{400}$

By Faraday law $\frac{W}{E} = \frac{i \times t}{96500}$

$$\left(\frac{W}{M}\right) \times n = \frac{i \times t}{96500}$$
, $\left(\frac{1}{400} \times 4\right) = \frac{i \times 10 \times 60}{96500}$, $i = 1.6$ A

- Ex.31 The same current if passed through solution of silver nitrate and cupric salt connected in series. If the weight of silver deposited is 1.08 g. calculate the weight of copper deposited.
- Sol. According to faradays second law

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \Rightarrow \frac{1.08}{W_2} = \frac{108}{31.75} \Rightarrow W_2 = 0.3175 \text{ g}$$

10 ELECTROLYTIC CONDUCTANCE

10.1 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

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

(b) Inversely proportional to the area of cross section of the electrodes

$$R \propto \frac{1}{A}$$

10.2 Conductance or resistivity (G) :

The conductance of a conductor is equal to reciprocal of resistance.

$$G = \frac{1}{R}$$
 • G is expressed in mho or Ω^{-1} or Siemen(S). [1S = 1W^{-1} S.I. unit]

10.3 Specific resistance or conductivity (ρ) :

The resistance (R) of a conductor of uniform cross section is directly proportional to its length(ℓ) 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 $\ell = 1$, 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 $\rho \rightarrow \text{ohm.cm}$

10.4 Specific conductance (κ) :

It is defined as the reciprocal of specific resistance

$$\kappa \stackrel{-}{=} \frac{1}{\rho}$$
,

$$G = \kappa / G^*$$
, $G^* = \frac{l}{a} = cell constant$

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

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

• Cell constant 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.

$\kappa = G \times cell constant$

- Unit of $\kappa \rightarrow ohm^{-1} cm^{-1}$
- SI unit of $\kappa \to S m^{-1}$ 1 S m⁻¹ = 100 ohm⁻¹ cm⁻¹

10.5 Molar conductance $(\lambda_m \text{ or } \wedge_m)$: It is defined as the product of specific conductance (κ) and the volume (V in mL) in which contains one mole of the electrolyte.

$$\Lambda_{\rm m} = \kappa \times v \quad \text{and} \quad \Lambda_{\rm m} = \frac{\kappa \times 1000}{M} \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \qquad [SI \text{ unit} : S \text{ m}^2 \text{ mol}^{-1}]$$

- It can also be defined as conductance of 1 mole electrolyte completely dissolved between two plates separated by unit distance.
- **10.6 Equivalent conductance** $(\lambda_{eq} \text{ or } \wedge_{eq})$: It is defined as the product of specific conductance (κ) and the volume (V in mL) in which contains one equivalent of the electrolyte.

 $\Lambda_{\rm m} = \kappa \times v \quad \text{and} \quad \Lambda_{\rm m} = \frac{\kappa \times 1000}{M} \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1} \qquad [SI unit : S \text{ m}^2 \text{ eq}^{-1}]$

- It can also be defined as conductance of 1 equivalent electrolyte completely dissolved between two plates separated by unit distance.
- Relation between $\Lambda_{eq.}$ and Λ_m :

 $\Lambda_{\rm m} = \frac{\kappa \times 1000}{M} \quad and \quad \Lambda_{\rm eq.} = \frac{\kappa \times 1000}{N}$

We know that, *Normality* = *Valency Factor* × *Molarity*

or
$$N = n \times M \Rightarrow \lambda_{eq} = \frac{\lambda_M}{n}$$

n = total cationic (or anionic) charge of salt.

Ex.
$$\Lambda_{eq}[Al_2(SO_4)_3] = \frac{\Lambda_m[Al_2(SO_4)_3]}{6}, L_{eq \ NaCl} = \frac{\Lambda_m NaCl}{1}, L_{eq.CaCl_2} = \frac{\Lambda_m CaCl_2}{2}$$

11 EFFECT OF DILUTION ON THE CONDUCTIVITY OF ELECTROLYTES

- (i) The degree of ionisation of weak electrolytes increases with the increase of dilution of the solution the conductivity is increases due to increasing the number of ions.
- (ii) Effect of dilution on specific conductance :
 Specific conductance decreases with the increase of dilution of the solution due to the presence of no. of ions in 1 cm³ solution decreases conductance also decrease on dilution.
- (iii) Effect of dilution on equivalent|molar conductivity : The equivalent|molar conductivity increases with dilution. For strong electrolyte λ_m or λ_{eq} increases very slowly but for weak electrolytes $\lambda_m \& \lambda_{eq}$ increase sharply on dilution.
- When the whole of the electrolyte has ionised, further addition of the water brings a small change in the value of equivalent|molar conductance. This stage is called *infinite dilution*.
- The ratio of equivalent conductivity at any dilution to equivalent conductivity at infinite dilution is called *conductivity ratio* or degree of dissociation of solute -

$$\alpha = \frac{\lambda_{eq.}}{\lambda_{m}^{\infty}} = \frac{\lambda_{m}}{\lambda_{m}^{\infty}}$$
[λ_{m}^{∞} = molar conductance at ∞ dilution.]

* Variation of conductivity and molar conductivity with concentration :

- Conductance and conductivity always decreases with the decrease in concentration both for weak and strong electrolytes.
- It is because the number of ions per unit volume that carry the current in a solution decreases on dilution decreasing I, C and K.

Strong Electrolytes :

• For strong electrolytes. A increases slowly with dilution and can be represented by the equation $A = A C^{1/2} A = constant$

 $\mathbf{\Lambda} = \mathbf{\Lambda}^{\circ} - \mathbf{A} \mathbf{C}^{1|2}. \mathbf{A} = \text{constant}$

On dilution interionic separation increases causing free movement & less hindrance. This increases $\Lambda_m \& \Lambda_{eq.}$

For strong electrolytes Λ° or Λ^{∞} can be calculated graphically from y-intercept.

It can be seen that if we plot . L_m against $c^{1|2}$, we obtain a straight line with intercept equal to A°_m and slope equal to -A. The value of the constant A for a given solvent and temperature depends on the type of the electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus, NaCl, CaCl₂, MgSO₄ are known as 1 - 1, 2 - 1 and 2 - 2 electrolytes respectively. All electrolytes of a particular type have the same value for A.

***** Weak electrolytes :

• Weak electrolytes like acetic acid have lower degree of dissociation at higher concentration and hence for such electrolytes, the change in ∧ with dilution is due to increase in the number of ions solution containing a given amount of electrolyte.





Note : (A) Weaker the electrolyte more sharp will be increase of Λ_{m} or Λ_{eq} on dilution.

(B) same plot is also observed for Λ_m vs. molarity of respective electrolytes.

12. KOHLARAUSCH'S LAW

"At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions."

i.e., for
$$A_{n+} B_{n-}$$

$$\begin{array}{c} \Lambda_{eq.}^{\infty} = \Lambda_{eq.}^{\infty}(+) + \Lambda_{eq.}^{\infty}(-) \\ \Lambda_{m}^{\infty} = \nu_{+} \Lambda_{m}^{\infty}(+) + \nu_{-} \Lambda_{m}^{\infty}(-) \end{array}$$

 $v_{\perp} =$ no. of cation in one formula unit of electrolyte.

 v_{-} = no. of anions in one formula unit of electrolyte.

Note :
$$\lambda^{\infty} = \lambda^{\circ}$$

$$\lambda_{eq+}^{0} = \frac{\lambda_{m}^{0}}{\text{charge on the cation}} \qquad \lambda_{eq}^{0} \cdot Al^{3+} = \frac{\lambda_{m}^{0} Al^{3+}}{3}$$
$$\lambda_{eq}^{0} = \frac{\lambda_{m}^{0}}{\text{chargeon the anion}} \qquad \lambda_{eq}^{0} \cdot \text{electrolyte} = \frac{\lambda_{m}^{0} \cdot \text{electrolyte}}{\text{total +ve charge on cations in electrolyte}}$$

total -ve charge on anions in electrolyte

The Independent Migration of Ions. A survey of equivalent conductances at infinite dilution of a number of electrolytes having an ion in common will bring to light certain regularities;

COMPARISON OF EQUIVALENT CONDUCTANCES AT INFINITE DILUTION

Electrolyte	Λ_0	Electrolyte	Λ_0	Difference
KCl	130.0	NaCl	108.9	21.1
KNO ₃	126.3	NaNO ₃	105.2	21.1
K_2SO_4	133.0	Na_2SO_4	111.9	21.1

Observations of this kind were first made by *Kohlrausch (1879, 1885)* by comparing equivalent conductances at high dilutions; described them to the fact that under these conditions every ion makes a definite contribution towards the equivalent conductance of the electrolyte, irrespective of the nature of the other ion with which it is associated in the solution. The value of the equivalent conductance at infinite dilution may thus be regarded as made up of the sum of two independent factors, one characteristic of each ion; this result is known as Kohlrausch's law of independent migration of ions.

The ion conductance is a definite constant for each ion, in a given solvent, its value depending only on the temperature.

It will be seen later that the ion conductances at infinite dilution are related to the speeds with which the ions move under the influence of an applied potential gradient.

* Applications of Kohlarausch's law :

Calculate Λ° for any electrolyte from the Λ° of individual ions.

An important use of ion conductances is to determine the equivalent conductance at infinite dilution of certain electrolytes which cannot be, or have not been, evaluated from experimental data. For example, with a weak electrolyte the extrapolation to infinite dilution is very uncertain, and with sparingly soluble salts the number of measurements which can be made at appreciably different concentrations is very limited. The value of Λ° can, however, so obtained by adding the ion conductances. For example, the equivalent conductance of acetic acid at infinite dilution is the sum of the conductances of the hydrogen and acetate ions; the former is derived from a study of strong acids and the latter from measurements on acetates. It follows, therefore, that at 25°.

 $\Lambda^{\circ}_{(CH_3CO_2H)} = \lambda^0_{H^+} + \lambda^0_{CH_2CO_2} = 349.8 + 40.9 = 390.7 \text{ ohms}^{-1} \text{ cm}^2$

The same result can be derived in another manner which is often convenient since it avoids the necessity of separating the conductance of an electrolyte into the contributions of its constituent ions. The equivalent conductance of any weak electrolyte MA at infinite dilution it follows, therefore, that $\Lambda^{\circ}(MA) = \Lambda^{\circ}(MCl) + \Lambda^{\circ}(NaA) - \Lambda^{\circ}(NaCl)$, [MCl, NaA, NaCl are strong electrolytes] where Λ° (MCl), $\Lambda^{\circ}(NaA)$ and $\Lambda^{\circ}(NaCl)$ are the equivalent conductances at infinite dilution of the chloride of the metal M, i.e., MCI, of the sodium salt of the anion A, i.e., NaA, and of sodium chloride, respectively. Any convenient anion may be used instead of the chloride ion, and similarly the sodium ion may be replaced by another metallic cation or by the hydrogen ion. For example, if M⁺ is the hydrogen ion and A⁻ is the acetate ion, it follows that

 $\Lambda^{\circ}(CH_{3}COOH) = \Lambda^{\circ}(HCl) + \Lambda^{\circ}(CH_{3}COONa) - \Lambda^{\circ}(NaCl)$ = 426.16 + 91.0 - 126.45 = 390.71 ohms⁻¹ cm² at 25.

Similarly:

 $\Lambda_{m}^{\circ}[BaSO_{4}] = \Lambda_{m}^{\circ}[BaCl_{2}] + \Lambda_{m}^{\circ}[Na_{2}SO_{4}] - 2\Lambda_{m}^{\circ}[NaCl]$

• Degree of dissociation :

... Degree of dissociation

equivalent conductance at a given concentration equivalent conductance at infinite dilution

$$\alpha = \frac{\Lambda_{\rm m}^{\rm c}}{\Lambda_{\rm m}^{\rm c}} = \frac{\Lambda_{\rm eq}^{\rm c}}{\Lambda_{\rm eq}^{\rm c}}$$

• **Dissociation constant** of weak electrolyte :

$$K_{c} = \frac{C\alpha^{2}}{1-\alpha} \frac{C\left(\frac{\Lambda_{m}^{c}}{\Lambda_{m}^{c}}\right)^{2}}{1-\frac{\Lambda_{m}^{c}}{\Lambda_{m}^{0}}}$$

Solubility(s) and K_{CD} of any sparingly soluble salt. Sparingly soluble salt = Very small solubility Solubility = molarity \cong S \rightarrow 0 So, solution can be considered to be of zero conc or infinite dilution. $\Lambda_{\rm m}^{\rm s}\simeq\Lambda_{\rm m}^{\rm s}=\kappa=\frac{1000}{\rm s}$ $s = \frac{\kappa \times 1000}{\Lambda_m^0}$ EXERCISE #4 1. Electrolytic conduction differs from metallic conduction from the fact that in the former (A) The resistance increases with increasing temperature (B) The resistance decreases with increasing temperature (C) The resistance remains constant with increasing temperature (D) The resistance is independent of the length of the conductor 2. Which of the following solution of KCl has the lowest value of specific conductance : (A) 1 M (B) 0.1 M (C) 0.01 M (D) 0.001 M 3. Which of the following solutions of KCl has the lowest value of equivalent conductance ? (A) 1 M (B) 0.1 M (C) .01 M (D) .001 M 4. The molar conductance at infinite dilution of AgNO₃, AgCl and NaCl are 115, 120 and 110 respectively. The molar conductance of NaNO₃ is :-(A) 110 (B) 105 (C) 130 (D) 150 5. The equivalent conductivity of 0.1 N CH, COOH at 25 °C is 80 and at infinite dilution 400. The degree of dissociation of CH₂COOH is : (C) 0.1 (D) 0.5 (A) 1 (B) 0.2 The specific conductance of a 0.01 M solution of KCl is 0.0014 ohm⁻¹ cm⁻¹at 25° C. Its equivalent 6. conductance (cm² ohm⁻¹ equiv⁻¹) is :-(A) 140 (B) 14 (C) 1.4 (D) 0.14 The resistance of 0.1 N solution of a acetic acid is 250 ohm. When measured in a cell of cell constant 7. 1.15 cm⁻¹. The equivalent conductance (in ohm⁻¹ cm² equiv.⁻¹) of 0.1 N acetic acid is (A) 46 (B) 9.2 (C) 18.4 (D) 0.023 If 0.01 M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant 8. of 0.4 cm⁻¹ then its molar conductance in ohm⁻¹ cm² mol⁻¹ is : (B) 10^2 (C) 10³ (D) 10⁴ (A) 10 Abnormal ion conductances of H⁺ and OH⁻: \div It is supposed, as already indicated, that the hydrogen ion in water is $H_{2}O^{+}$ with three hydrogen atoms attached to the central oxygen atom. When a potential gradient is applied to an aqueous solution containing hydrogen ions, the latter travel to some extent by the same mechanism as do other ions, but there is in addition another mechanism which permits of a more rapid ionic movement. This second process is believed to involve the transfer of a proton (H^+) from a H_3O^+ ion to an adjacent water molecule; thus

$$\begin{array}{c} H \\ H - \underset{(\textcircled{+})}{O} - H + \underset{(\overbrace{+})}{H} - H \end{array} \longrightarrow \begin{array}{c} H \\ H - \underset{(\overbrace{+})}{H} + H \\ H - \underset{(\fbox{+})}{H} - \underset{(\fbox{+})}{H} - H \end{array}$$

The resulting H_3O^+ ion can now transfer a proton to another water molecule, and in this way the positive charge will be transferred a considerable distance in a short time. The electrical conductance will thus be much greater than that due solely to the normal mechanism.

13. CONDUCTOMETRIC TITRATION :

The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invari ably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added. In order to reduce the influence of errors in the c onductometric titration to a minimum, the angle between the two branches of the titration curve should be as small as possible (see Fig. 6.2). If the angle is very obtus e, a small error in the conductance data can cause a large deviation. The following app roximate rules will be found

- The smaller the conductivity of the ion which replaces the reacting ion, the more accurate will be the result. Thus it is preferable C to titrate a silver salt with lithium chloride rather than with HCl. Generally, cations should be titrated with lithium salts and anions with acetates as these ion s have low conductivity
- The larger the conductivity of the anion of the reagent which reacts with the cation to be determined, or vice versa, the more acute is the angle of titration curve.
- The titration of a slightly ionized salt does not g ive good results, since the conductivity increases continuously from the commen cement. Hence, the salt present in the cell should be virtually completely dissociated; for a similar reason; the added reagent should also be as strong electrolyte. The main advantages to the conductometric titration are its applicability to very dilute, and coloured solutions and to system that involver elative incomplete reactions. For example, which neither a potentiometric, nor indica tor method can be used for the neutralization titration of phenol ($K_a \times 10^{-10}$) a conductometric endpoint can be successfully applied.

Cation	H_3O^+	NH_4^+	\mathbf{K}^{+}	Na ⁺	Ag^{+}	Ca ²⁺	Mg^{2+}
$\lambda_{m}^{\infty}/(\Omega^{-1} \mathrm{cm}^{2} \mathrm{mol}^{-1})$	350.0	73.5	73.5	50.1	62.1	118.0	106.1
Anion	OH⁻	Br	Cl⁻	NO_3^-	CH ₃ COO ⁻	${\rm SO_4}^{2-}$	
$\lambda_{m}^{\infty}/(\Omega^{-1} cm^{2} mol^{-1})$	199.2	78.1	76.5	71.4	40.0	159.6	

Some Typical Conductometric Titration Curves are :

13.1 Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H⁺ ions react with OH - ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the so lution contains only NaCl. After the equivalence point, the conductance increases due to the large.



13.2 Weak Acid with a Strong Base, e.g. acetic acid with NaOH: Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H⁺ by Na⁺ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH₃ COOH to CH₃OONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH₃ COONa. Beyond the equivalence point, conductance in creases more rapidly with the addition of NaOH due to the highly conducting OH ions.



13.3 Strong Acid with a Weak Base, e.g. sulphuric acid with dilute ammonia : Initially the conductance is high and then it decre ases due to the replacement of H⁺. But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate.



13.4. Weak Acid with a Weak Base : The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting



13.5 Precipitation Titration and Complex Formation Titration : A reaction may be made the basis of a conductometric precipitation titration provided the reaction product is sparingly soluble or is a stable complex . The solubility of the precipitate (or the dissociation of the complex) should be less than 5%. The addition of ethanol is sometimes recommended to reduce the solubility in the precipitations. An experimental curve is given in F ig. 6.8 (ammonium sulphate in aqueous-ethanol solution with barium acetate).

If the solubility of the precipitate were negligibly small, the conductance at the equivalence point should be given by AB and not the observed AC. The addition of excess of the reagent depresses the solubility of the precipitate and, if the solubility is not too large, the position of the point B can be determine d by continuing the straight portion of the two arms of the curve until they intersect



14. IONIC MOBILITY :

It is the speed of ion under unit potential gradient applied through solution.

 $u = \frac{speed of ion(s)}{Potential gradient} = \frac{cm^2}{volt - sec.} = \frac{\Lambda}{ZF}$

 $u/10^{-8} \text{ m}^2\text{-s}^{-1}\text{-v}^{-1}$ in H₂O at 298 K

Li ⁺	4.01 4.65	Ca^{+2}	6.17	Rb^{+}	7.92	$\rm CH_3 COO^-$	7.92	CO ₃	7.91	$\mathrm{SO}_4^{}$	8.29	OH⁻	20.64
Na ⁺	5.19	Ag^{+}	6.24	$\mathrm{H}^{\scriptscriptstyle +}$	7.92	F^{-}	7.92	Cl ⁻	7.96	$[Fe(CN)_6]^{3-}$	7.96		
Cu⁺	² 5.47 5.56	NH_4^+	7.43	$\mathrm{H}^{\scriptscriptstyle +}$	36.23	NO_3^{-}	7.40	I_	7.91	$[Fe(CN)_6]^{4-}$	11.4		

SOLVED EXAMPLES

- Ex.32 The resistance of a 1 N solution of salt is 50 Ω. Calculate the equivalent conductance of the solution, if the two platinum electrodes in solution are 2.1 cm apart and each having an area of 4.2 cm².
- Sol: $\kappa = \frac{1}{\rho} = \frac{1}{R} \left(\frac{\ell}{A} \right) = \frac{1}{50} \times \frac{2.1}{4.2} = \frac{1}{100}$ and $\lambda_{eq.} = \frac{\kappa \times 1000}{N} = \frac{1}{100} \times \frac{1000}{1} = 10 = \Omega^{-1} \text{cm}^2 \text{eq}^{-1}$
- Ex.33 Which of the following have maximum molar conductivity. (i) 0.08 M solution and its specific conductivity is $2 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$. (ii) 0.1 M solution and its resistivity is 50 Ω cm.
- **Sol.** (i) $\wedge_{\rm m} = \frac{\kappa \times 1000}{M} = 2 \times 10^{-2} \times \frac{1000}{0.08} = 250 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1}$

(ii)
$$\wedge_{\rm m} = \frac{\kappa \times 1000}{\rm M}$$
 \therefore $\kappa = \frac{1}{\rho}$ \therefore $\Lambda_{\rm m} = \frac{1}{50} \times \frac{1000}{0.1} = 200 \ \Omega^{-1} \ {\rm cm}^2 \ {\rm mol}^{-1}$

So, the molar conductivity of 0.08 M solution will be greater than 0.1 M solution.

- Ex.34 The equivalent conductivity of H_2SO_4 at infinite dilution is 384 Ω^{-1} cm² eq⁻¹. If 49 g H_2SO_4 per litre is present in solution and specific resistance is 18.4 Ω -cm then calculate the degree of dissociation.
- **Sol:** Equivalent of $H_2SO_4 = \frac{49}{49} = 1 N$

Specific conductance = $\frac{1}{\text{specific resistance}} = \frac{1}{18.4}$

$$\Rightarrow \lambda_{eq.} = \frac{1000 \times \kappa}{N} = \frac{1000 \times 1}{18.4} = 55$$

Degree of dissociation (α) = $\frac{\lambda_{eq.}^{C}}{\lambda_{eq.}^{\infty}} = \frac{55}{384} = 0.14 \Rightarrow \alpha \% = 14\%$

Ex.35 Explain following ionic conductance data of 25°C for various fatty acid anions.

Anion	Formula	λ_{-}^{0} AT 25°C (in ohm ⁻¹ cm ² eq ⁻¹)
Formate	HCO ₂ ⁻	-52
Acetate	CH ₃ CO ₂ ⁻	40.9
Propionate	$CH_3CH_2CO_2^-$	35.8
Butyrate	$CH_3(CH_2)_2CO_2^-$	32.6
Valerianate	$CH_3(CH_2)_2CO_2^-$	~29
Caproate	$CH_3(CH_2)_4CO_2^-$	~28

- **Sol.** With increasing chain length bulk increases decreasing ionic mobility and thus equivalent conductance decreases.
 - \therefore Charge is identical λ_m also decreases.
- Ex.36 The resistance of a 0.01 N solution of an electolyte was found to 210 ohm at 298 K using a conductivity cell with a cell constant of 0.88 cm⁻¹. Calculate specific conductance and equivalent conductance of solution.

Sol. Given, for 0.01 N solution.

$$R = 210 \text{ ohm}$$
, $\frac{\ell}{a} = 0.88 \text{ cm}^{-1}$

Specific conductance,

$$\therefore \qquad \kappa = \frac{1}{R} \times \frac{\ell}{a} \implies \kappa = \frac{1}{210} \times 0.88 = 4.19 \times 10^{-3} \text{ mho cm}^{-1}$$
$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} = \frac{4.19 \times 10^{-3} \times 1000}{0.01} = 419 \text{ mho cm}^2 \text{ eq}^{-1}$$

- *Ex.37* The conductivity of pure water in a conductivity cell with electrodes of cross-sectional area 4 cm^2 placed at a distance 2 cm apart is $8 \times 10^{-7} \text{ S cm}^{-1}$. Calculate;
 - (a) The resistance of water.
 - (b) The current that would flow through the cell under the applied potential difference of 1 volt.
- **Sol.** Cell constant = $\frac{\ell}{a} = \frac{2}{4} = \frac{1}{2} \text{ cm}^{-1}$
 - (a) Also, $\kappa = \frac{1}{R} \times \frac{\ell}{a}$

$$R = \frac{1}{\kappa} \times \frac{\ell}{a} = \frac{1}{8 \times 10^{-7}} \times \frac{1}{2} = 6.25 \times 10^5 \text{ ohm}$$

(b) From Ohm's law,
$$\frac{V}{i} = R$$

i =
$$\frac{1}{6.25 \times 10^5}$$
 = 1.6 × 10⁻⁶ ampere

Ex.38 Molar conductance of 1 M solution of weak acid HA is 20 ohm⁻¹ cm² mol⁻¹. Find % dissocaition of HA:

$$\begin{pmatrix} \Lambda_{\rm m}^{\circ}(H^{\scriptscriptstyle +}) = 350 \mbox{ S cm}^2 \mbox{ mol}^{-1} \\ \Lambda_{\rm m}^{\circ}(A^{\scriptscriptstyle -}) = 50 \mbox{ S cm}^2 \mbox{ mol}^{-1} \end{cases}$$

Ans. $\Lambda_{\rm m}^{\circ}({\rm HA}) = 350 + 50 = 400$

$$\alpha = \frac{\Lambda_{\rm m}^{\rm C}}{\Lambda_{\rm m}^{\rm o}} \times 100 = \frac{20}{400} \times 100 = 5 \%$$

- *Ex.39* Conductivity of an aqueous solution of 0.1 M HX (a weak mono-protic acid) is $5 \times 10^{-4} \text{ Sm}^{-1}$. Find $pK_a[HX. \text{ Given} : \Lambda_m^{\infty}[H^+] = 0.04 \text{ Sm}^2 \text{mol}^{-1}$; $\Lambda_m^{\infty}[X^-] = 0.01 \text{ Sm}^2 \text{mol}^{-1}$
- Ans. HX \rightleftharpoons H⁺ + X⁻ $0.1(1-\alpha)$ 0.1α 0.1α $^{\rm M} = k \times \frac{1000}{C} \Rightarrow 5 \times 10^6 \times \frac{1000}{0.1} = 0.05\Omega^{-1} \text{cm}^2 \text{-mol}^{-1}$ $a = \frac{\Lambda_{\rm m}}{\Lambda_{\rm m}} = \frac{0.05}{50}\Omega^{-1} - \text{cm}^2 \text{mol}^{-1} = 10^{-4}$ $K_a = C\alpha^2 = 0.1 \times (10^{-4})^2 = 10^{-9}$ $pK_a = 9$

Ex.40 Specific conductance of 10^{-4} M n-Butyric acid aqueous solution is 1.9×10^{-9} S m⁻¹. If molar conductance of n-Butyric acid at infinite dilution is 380×10^{-4} S m² mol⁻¹, then K_a for n-Butyric acid is :

Sol.
$$\Lambda_{\rm m} = 1000 \times \frac{1.9 \times 10^{-9}}{10^{-4}} = 1.9 \times 10^{-2}$$

$$\alpha = \frac{1.9 \times 10^{-2}}{380 \times 10^{-4}} = 0.5$$

$$K_{a} = \frac{10^{-4} (0.5)^{2}}{1 - 0.5} = 5 \times 10^{-5} \text{ M}$$

- Ex.41 The specific conductance of a saturated AgCl solution is found to be 2.12×10^{-6} S cm⁻¹ and that for water is 6×10^{-8} S cm⁻¹. The solubility of AgCl is : $(l_{eq.}^{Y} = 103 \text{ S equiv}^{-1} \text{ cm}^{2})$
- **Sol.** So.= $241.67 \text{ S cm}^2 \text{ mol}^{-1}$

$$S = \frac{(F_{\rm Ag \, sol.} - F_{\rm H_2O}) \times 1000}{(\Lambda^{\rm o}_{\rm eq.})_{\rm Ag Cl}} = 2 \times 10^{-5} \, M$$

- *Ex.*42 The value of μ^{∞} for NH_4Cl , NaOH and NaCl are 129.8, 248.1 and 126.4 ohm⁻¹ cm² mol⁻¹ respectively. Calculate μ^{∞} for NH_4OH solution.
- Sol. $\mu_{\text{NH}_4\text{OH}}^{\infty} = \mu_{\text{NH}_4\text{CI}}^{\infty} + \mu_{\text{NaOH}}^{\infty} \mu_{\text{NaCI}}^{\infty}$ = 129.8 + 248.1 - 126.4

 $\mu_{\rm NH,OH}^{\infty} = 251.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$

- *Ex.43* Calculate molar conductance for NH_4OH , given that molar conductances for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 523.28, 280.0 and 129.8 ohm⁻¹ cm² mol⁻¹ respectively.
- Sol. $\mu_{Ba(OH)_{2}}^{\infty} = \lambda_{Ba^{2+}}^{\infty} + 2\lambda_{OH^{-}}^{\infty} = 523.28 \qquad \dots \dots (i)$ $\mu_{BaCl_{2}}^{\infty} = \lambda_{Ba^{2+}}^{\infty} + 2\lambda_{CI^{-}}^{\infty} = 280.00 \qquad \dots \dots (ii)$ $\mu_{NH_{4}CI}^{\infty} = \lambda_{NH_{4}^{+}}^{\infty} + \lambda_{CI^{-}}^{\infty} = 129.80 \qquad \dots \dots (iii)$ $\mu_{NH_{4}OH}^{\infty} = \lambda_{NH_{4}^{+}}^{\infty} + \lambda_{OH^{-}}^{\infty} = ?$ $Eq.(iii) + \frac{Eq.(i)}{2} \frac{Eq.(ii)}{2} \text{ will gives}$ $\lambda_{NH_{4}^{+}}^{\infty} + \lambda_{OH^{-}}^{\infty} = \lambda_{NH_{4}OH}^{\infty} = \frac{502.88}{2} = 251.44 \text{ ohm}^{-1} \text{ cm}^{2} \text{ mol}^{-1}$

Ex.44 The equivalent conductivities of acetic acid at 298 K at the concentrations of 0.1 M and 0.001 M are 5.20 and 49.2 S cm² eq.⁻¹ respectively. Calculate the degree of dissociation of acetic acid at these concentrations. Given that, $\lambda^{\infty}(H^+)$ and $\lambda^{\infty}(CH_3COO^-)$ are 349.8 and 40.9 ohm⁻¹ cm² mol⁻¹ respectively.

Sol. Degree of dissociation is given by $\alpha = \frac{\lambda^c}{\lambda^{\infty}}$

(i) Evaluation of $\lambda_{CH_3COOH}^{\infty}$:

$$\lambda_{CH_{3}COOH}^{\infty} = \lambda_{CH_{3}COO^{-}}^{\infty} + \lambda_{H^{+}}^{\infty}$$
$$= 40.9 + 349.8 = 390.7 \text{ ohm}^{-1} \text{ cm}^{2} \text{ eq.}^{-1}$$

(ii) Evaluation of degree of dissociation :

At C = 0.1 M
$$\alpha = \frac{\lambda^{c}}{\lambda^{\infty}} = \frac{5.20}{390.7} = 0.013$$

i.e. 1.3%
At C = 0.001 M $\alpha = \frac{\lambda^{c}}{\lambda^{\infty}} = \frac{49.2}{390.7} = 0.125$
i.e. 12.5%

*Ex.*45 At infinite dilution the molar conductance of AI^{+3} and SO_4^{-2} ion are 189 and 160 Ω^{-1} cm² mole⁻¹ respectively. Calculate the equivalent and molar conductivity at infinite dilute of $AI_2(SO_4)_3$.

Sol.
$$\lambda_{eq.[Al_2(SO_4)_3]}^{\infty} = \frac{1}{3}\lambda_{Al^{+3}}^{\infty} + \frac{1}{2}\lambda_{SO_4^{-2}}^{\infty}$$

 $= \frac{1}{3} \times 189 + \frac{1}{2} \times 160$
 $= 143 \ \Omega^{-1} \ cm^2 \ eq^{-1}$
Molar conductivity $= \lambda_{eq} \times V. \ F. = 143 \times 6$
 $= 858 \ \Omega^{-1} \ cm^2 \ mol^{-1}$

Ex.46 Find $\Lambda_{\rm m}^{\infty}$ (in Ω^{-1} cm² mol⁻¹) for strong electrolyte AB₂ in water at 25° from the following data.

	Conc.C(mole/L)	0.25	1
	$\[mm] m(W^{-1}cm^2/mol)\]$	160	150
Sol.	$160 = \Lambda_{\rm m}^{\infty} - b \times \sqrt{.25}$	((A)
	$150=~\Lambda^{\infty}_{m}~-b\times~\sqrt{1}$	((B)
	$b = 20$ and $\Lambda_m^{\infty} = 170$		
	y = 170 - 20x		
	Intercept = 170		
	$\Lambda_{\rm m}^{\infty}=170\Omega^{-1}{\rm cm}^2{\rm mol}^{-1}$		

Ex.47 For any sparingly soluble salt $[M(NH_3)_4Br_2]H_2PO_2$

Given: $\lambda_{M(NH_3)_4Br_2^+}^0 = 400 \text{ S-m}^2 - mol^{-1}$,

 $\lambda_{\rm H_2PO_2^-}^0 = 100 \ S - m^2 - mol^{-1}$

Specific resistance of saturated $[M(NH_3)_4Br_2]H_2PO_2$ solution is 200 Ω -cm. If solubility product constant of the above salt is 10^{-x} . What will be the value of x.

Ans. $\wedge_{\rm m}^{\infty} = \kappa \times \frac{1000}{\rm m} \times 10^{-6}$ $500 = \frac{1}{200} \times \frac{1000}{5} \times 10^{-6}$ $\rm S = 10^{-8} \ mol|L$, $\rm K_{sp} = \rm S^2 = 10^{-16}$

Ex.48 20 mL of KOH solution was titrated with $0.2 M H_2 SO_4$ solution in a conductivity cell. The data obtained were plotted to given the graph shown below :



the concentration of KOH solution was -

(A) 0.3 M (B) 0.15 M (C) 0.12 M (D) 0.075 M Sol. (A)

 $20 \times M = 0.2 \times 2 \times 15 \Rightarrow M = 0.15$

48	JEE-C	hemistry
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	ANSWER KEY								
	EXERCISE # 1								
1.	Ans.(C)	2.	Ans. (C)	3.	Ans.(B)				
4.	Ans.(A)	5.	Ans.(C)	6.	Ans.(C)				
		Ε	XERCISE #	2					
1.	Ans.(B)	2.	Ans.(D)	3.	Ans.(A)				
4.	Ans.(B)	5.	Ans.(B)	6.	Ans.(C)				
		E	EXERCISE # 3	3					
1.	Ans.(B)	2.	Ans.(A)	3.	Ans.(B)				
4.	Ans.(A)	5.	Ans.(C)	6.	Ans.(D)				
7.	Ans.(C)								
		F	EXERCISE # 4	4					
1.	Ans.(B)	2.	Ans.(D)	3.	Ans.(A)				
4.	Ans.(B)	5.	Ans.(B)	6.	Ans.(A)				
7.	Ans.(A)	8.	Ans.(C)						