Handwritten Notes
On
ELECTROCHEMISTRY
(Part-1)

ELECTROCHEMISTRY

→ The branch of chemistry which deals with the production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations is called electrochemistry.

→ The study of electrochemistry is important for creating new technologies which are ecofriendly. The transmission of sensory signals to brain through cells and vice versa and communication between cells have electrochemical origin. Electrochemistry, is therefore very vast and interdisciplinary subject.

Types of substances based on conductivity

(a) Insulator : substances which do not allow electric current to pass through them. example - Pure water, ice, glass, rubber etc.

(b) conductor : Substances which allow electric current to flow through them. Example - Metals, aqueous solution of acids, bases & salts, fused salts & impure water etc.

Types of conductors

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

(ii) Electrolytic conductors : Those substances whose water solution conducts the electric current and which are decomposed by the passage of current. In this case, conduction takes place by movement of ions.

→ Electrolytes also conduct electricity in fused state and undergo decomposition by passage of electric current.

→ Substances whose aqueous solution does not conduct electric current are called non-electrolytes. eg → cane sugar, glycerine, glucose, urea etc.

Classification of electrolytes

Strong electrolyte : Electrolytes which are completely ionized in aqueous solution or in their molten state.
example → all salts, strong acids & bases

weak electrolyte : Electrolytes which are not completely ionized in aqueous solution or in their molten state; ~~ex~~
example ; All carbonic acids, CH_3COOH, HCN, NH_3, amine etc

Differences between Metallic and electrolytic Conduction

Metallic conduction	Electrolytic conduction
1. Metallic conduction is carried by the movement of electrons	Electrolytic conduction is carried by the movement of ions.
2. It involves no change in the chemical properties of the conductor.	It involves the decomposition of the electrolyte as a result of the chemical reaction.
3. It does not involve the transfer of any matter.	It involves the transfer of matter as ions
4. Metallic conduction decreases with increase in temperature.	Electrolytic conduction rises with increase in temperature

ELECTROLYTIC CONDUCTION

(a) RESISTANCE (R) :

→ It measures the obstruction to the flow of current.

→ 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 flowing (I).

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

→ The resistance of any conductor is directly prop to the length (l) & inversly prop. to area of cross section (a).

$R \propto \frac{l}{a}$ $R = \rho \frac{l}{a}$; ρ = specific resistance or resistivity
(rho)
term recomonded by IUPAC

→ unit of resistance = ohm (Ω),

(b) Resistivity

$R = \rho \frac{l}{a}$; $\rho = \frac{Ra}{l}$

→ Defined as the resistance of a conductor of 1 cm length and having area of cross-secton equal to 1 cm^2.

→ unit = ohm cm.

(c) CONDUCTANCE (G)

→ Measure of the ease with which current flows through a conductor.

→ expressed in 'G'

→ $\boxed{G = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}}$; where κ is conductivity (kappa)

→ unit Ω^{-1}, siemens(S) [in SI]

$1\,S = 1\,\Omega^{-1}$

(d) CONDUCTIVITY (κ) / specific conductance.

→ Inverse of resistivity is called conductivity.

→ Defined as conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross section.

$$\boxed{\kappa = \frac{1}{\rho}} = \frac{1}{R}\left(\frac{l}{a}\right)$$

→ unit = $\frac{1}{\Omega\, cm} = \Omega^{-1} cm^{-1}$, Sm^{-1} (SI unit)

The electronic conductance depends on
(i) nature & structure of metal
(ii) no of valence e's per atom
(iii) temp (↓ses with ↑se of temp.)

Electrolytic conductance depends on
(i) nature of electrolyte added
(ii) size of the ions produced & their solvation
(iii) the nature of the solvent & its viscosity
(iv) conc. of the electrolyte
(v) temp (↑ses with ↑se of temp.)

(e) MOLAR CONDUCTIVITY (Λ_m) of electrolytic solution

→ Defined as the conductance of a solution kept between the electrodes at unit distance apart and having area of cross-section large enough to accommodate sufficient volume of the solution that contains one mole of electrolyte.

→ The conductivity of a metallic conductor has a definite value at a given temp. However, in case of electrolytic solution the conductivity not only depends on temperature but also varies with the concentration of the solution. It is due to the fact that conductivity of a solution is attributed to the presence of ions. The number of ions in one centimetre cube of the solution changes with the variation in conc. ∴ in case of electrolytic sol^n, a more appropriate term, molar conductivity is used, which takes into account the concentration of the solution ~~that contains one mo~~ as well as its conductivity.

Relationship between conductivity (K) and Molar conductivity (Λ_m)

$$\boxed{\Lambda_m = \frac{K \times 1000}{C}} \quad \text{or} \quad \boxed{\Lambda_m = \frac{K \times 1000}{M}}$$

$$\text{units of } \Lambda_m = \frac{K(S\,cm^{-1}) \times 1000\,(cm^3/L)}{\text{Molarity}\,(Mol/L)}$$

$$= S\,cm^2\,mol^{-1} \quad \text{or} \quad ohm^{-1}\,cm^2\,mol^{-1}$$

$$\boxed{1\,S\,m^2\,mol^{-1} = 10^4\,S\,cm^2\,mol^{-1}}$$

EQUIVALENT CONDUCTIVITY (Λ_{eq})

→ Defined as the conductance of the solution containing one g-equivalent of the electrolyte such that the entire solution is placed between two parallel electrodes one centimetre apart.

$$\boxed{\Lambda_{eq} = \frac{K \times 1000}{N}} \qquad N = \text{normality}$$

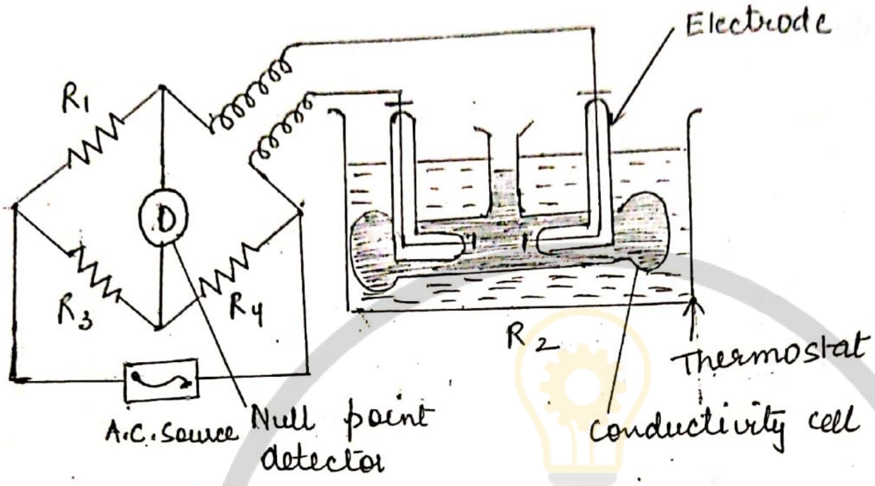
→ units of Λ_{eq} are: $S\,cm^2\,eq^{-1}$ or $ohm^{-1}\,cm^2\,eq^{-1}$ or $\Omega^{-1}\,cm^2\,eq^{-1}$

S. No	Property	Units	S.I. Units
1.	Resistance (R)	ohm (Ω)	Ω
2.	Resistivity (ρ)	ohm-cm	ohm-m
3.	Cell constant (G^*)	cm^{-1}	m^{-1}
4.	Conductance (G)	ohm^{-1} or Ω^{-1}	S
5.	Conductivity (K)	$ohm^{-1}\,cm^{-1}$	$S\,m^{-1}$
6.	Molar conductivity (Λ_m)	$ohm^{-1}\,cm^2\,mol^{-1}$	$S\,m^2\,mol^{-1}$
7.	Equivalent conductivity (Λ_{eq})	$ohm^{-1}\,cm^2\,eq^{-1}$	$S\,m^2\,eq^{-1}$

⇐ Summary of the units of some common Properties

MEASUREMENT OF THE CONDUCTIVITY OF IONIC SOLUTIONS

→ The conductance of the solution is reciprocal of its resistance. Therefore, if resistance of the solution is known, its conductance can be easily calculated. The resistance of the electrolytic solution is measured with the help of <u>wheatstone bridge method</u>.



Arrangement of wheatstone bridge

→ The conductivity cell containing solution of electrolyte is made one arm of wheatstone bridge. The conductivity cell is made of pyrex glass and is fitted with platinum electrodes. These are coated black with finely divided platinum. The fine deposit gives larger surface to the electrodes and improves the sharpness of sound in the null point detector. The cell is placed in thermostat to keep the temp constant. It is because conductance changes with the temperature.

→ After the connections have been made, the A.C. of freq range 1500 - 3000 cps is employed. It may be noted that D.C is not used here, bcz it causes electrolysis and results in the change in conc. of electrolytic solution near the electrodes resulting in polarisation effects.

→ The resistances R_1, R_3 and R_4 are so adjusted that a null point is obtained, which is indicated by detector D. At this point, $\frac{R_1}{R_2} = \frac{R_3}{R_4}$; $R_2 = \frac{R_1 R_4}{R_3}$

where R_2 refers to resistance of electrolytic solution.

→ The reciprocal of R_2 gives the conductance of the solution

Calculation of conductivity (K)

$$K = \frac{1}{R}\left(\frac{l}{a}\right) = G\left(\frac{l}{a}\right)$$

l → distance of separation of two electrodes
a → area of cross-section of the electrodes

$\frac{l}{a}$ = cell constant (G^*)

$$\boxed{K = G \times G^*}$$

$$\boxed{K = \frac{G^*}{R}}$$

$$\boxed{\text{conductivity} = \frac{\text{cell constant}}{R}}$$

Determination of cell constant (G^*)

→ The cell constant is generally not calculated from the values of l and a because these are difficult to be measured for a given cell. It is ∴ more convenient to obtain its value by measuring the conductance of a standard solution whose conductivity is known. For this purpose, a standard solution of KCl is used whose conductivity is known at different concentrations and temp. Suppose the conductance of this solution in the given cell is measured to be X.

Then, cell constant = $\frac{\text{Conductivity}}{\text{conductance}} = \frac{\text{conductivity}}{X}$

$$\boxed{G^* = \frac{l}{A} = RK}$$

→ once the cell constant is known, we can use it for measuring the resistance or conductivity of any solution.

VARIATION OF CONDUCTIVITY AND MOLAR CONDUCTIVITY WITH CONCENTRATION

1. Variation of conductivity (K) with concentration

→ K refers to conductance of one cm^3 of the electrolyte. with the ↑se in dilution the number of ions present in $1 cm^3$ of the solution ↓ses. As a result K also ↓ses with dilution

2. Variation of molar conductivity (Λ_m) with concentration

→ Λ_m for strong electrolytes > Λ_m for weak electrolytes (same conc) due to much lesser extent of dissociation.

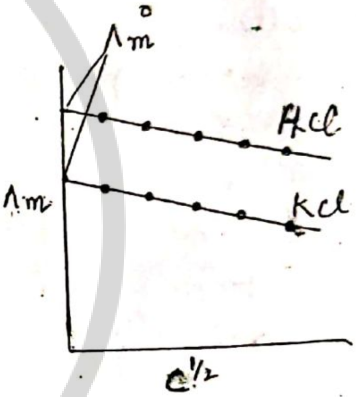
→ Molar conductivity of electrolytes, generally, ↑ses with dilution.

→ Relative ↑se in the value of Λ_m for strong electrolyte is quite small as compared to that for weak electrolytes.

a) For strong electrolytes

→ Λ_m ↑ses slowly with dilution and there is a tendency for Λ_m to approach a certain limiting value when the conc. approches zero or dilution is infinite. i/a molar conductivity at infinite dilution (Λ_m° or Λ_m^∞)

$$\Lambda_m = \Lambda_m^\infty \text{ when } c \longrightarrow 0 \text{ (at infinite dilution)}$$



Explanation : No of ions in solution in case of strong electrolytes does not ↑ses with dilution as they are already almost completely ionised in solution at all conc. but Λ_m ↑ses on dilution as the ions move apart & inter ionic attractions are ↓ses (↑sed ionic mobility). when the conc. of solⁿ becomes very low, the inter ionic attractions becomes negligible and the molar conductance approaches the limiting value called molar conductance at infinite dilution. This value is chracteristic of each electrolyte.

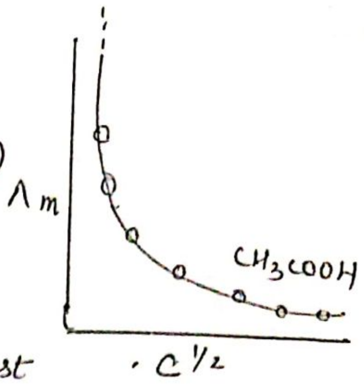
→ Mathamatical relationship b/w Λ_m & Λ_m° for str electrolyte is known as Debye Huckel Onsager equation.

$$\boxed{\Lambda_m = \Lambda_m^\circ - A\sqrt{C}}$$

A = constant which depends upon viscosity & dielectric constant of solution

c = concentration of solution.

(b) For weak electrolyte



→ On dilution for weak electrolytes

i) degree of dissociation ↑ses (no of ions ↑ses)

ii) ionic mobility ↑ses

→ No indication that the limiting value can be attained, because when conc. approaches zero, the graph becomes almost parallel to Y axis. The the value of Λ_m° can not be obtained by extraploting the graph to zero conc. It may however be obtained indirectly from KOHLRAUSCH's law

KOHLRAUSCH'S LAW

"At infinite dilution, when the dissociation of electrolyte is complete, each ion makes a definite contribution towards the molar conductivity of electrolyte, irrespective of the nature of the other ion with which it is associated"

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$

where ν_+ & ν_- → no of +ve & -ve ions furnished by each formula unit of the electrolyte

Examples

1) $\Lambda_m^\circ(NaCl) = \lambda_{Na^+}^\circ + \lambda_{Cl^-}^\circ$

2) $\Lambda_m^\circ(BaCl_2) = \lambda_{Ba^{2+}}^\circ + 2\lambda_{Cl^-}^\circ$

3) $\Lambda_m^\circ(Na_2SO_4) = 2\lambda_{Na^+}^\circ + \lambda_{SO_4^{2-}}^\circ$

APPLICATIONS OF KOHLRAUSCH'S LAW

1. Calculation of Limiting Molar conductivities of weak electrolytes.

→ The value of Λ_m° for CH_3COOH can be calculated from the knowledge of the Λ_m° of str. electrolytes like CH_3COONa, HCl, $NaCl$ as follows:

$$\Lambda_m^\circ(CH_3COOH) = \lambda_{(CH_3COO^-)}^\circ + \lambda_{(H^+)}^\circ$$

Now, add and subtract $\lambda^\circ_{Na^+}$ & $\lambda^\circ_{Cl^-}$ to the expression on RHS & rearrange.

Thus

$$\Lambda_m^\circ(CH_3COOH) = \lambda^\circ_{CH_3COO^\ominus} + \lambda^\circ_{H^+} + \lambda^\circ_{Na^+} - \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-} - \lambda^\circ_{Cl^-}$$

$$= [\lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+}] + [\lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}] - [\lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}]$$

$$= \Lambda_m^\circ(CH_3COONa) + \Lambda_m^\circ(HCl) - \Lambda_m^\circ(NaCl)$$

Similarly

$$\Lambda_m^\circ(NH_4OH) = \Lambda_m^\circ(NH_4Cl) + \Lambda_m^\circ(NaOH) - \Lambda_m^\circ(NaCl)$$

2. Calculation of degree of dissociation of weak electrolyte

If Λ_m^c is the molar conductivity of solution at any conc. and Λ_m° is limiting molar conductivity.

Then, degree of ionisation, α is given as

$$\boxed{\alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ}}$$

3) Calculation of dissociation constant of weak electrolyte

$$A \longrightarrow B + C$$

$t = 0$ 1 0 0

$t = t$ $c(1-\alpha)$ $c\alpha$ $c\alpha$

$$K = \frac{c\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \qquad \left(\because \alpha = \Lambda_m^c/\Lambda_m^\circ\right)$$

$$\boxed{K = \frac{c\,(\Lambda_m^c/\Lambda_m^\circ)^2}{1 - \Lambda_m^c/\Lambda_m^\circ} = \frac{c\,(\Lambda_m^c)^2}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m^c)}}$$

4. Determining the solubility of sparingly soluble salts

$$\Lambda_m^\circ = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{\kappa \times 1000}{\text{Solubility}}$$

$$\boxed{\text{Solubility} = \frac{\kappa \times 1000}{\Lambda_m^\circ}\ (mol\ L^{-1})}$$

5. Calculation of Ionic Product of water (K_w)

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K[H_2O] = [H^+][OH^-] \quad ; \quad K_w = [H^+][OH^-]$$

Limiting ionic conductivities of H^+ & OH^- have been found to be $349.8\ \Omega^{-1}cm^2mol^{-1}$ & $198.5\ \Omega^{-1}cm^2mol^{-1}$. Thus

$$\Lambda^0_{H_2O} = \lambda^0_{H^+} + \lambda^0_{OH^-}$$

$$= 349.8 + 198.5 = 548.7\ \Omega^{-1}cm^2mol^{-1}$$

The conductivity (K) of water at 298 K is $5.54 \times 10^{-8}\ \Omega^{-1}cm^{-1}$

Now, $\Lambda_m^0 = \frac{K \times 1000}{M}$

$$M = \frac{K \times 1000}{\Lambda_m^0} = \frac{5.54 \times 10^{-8} \times 1000}{548.7} = 1 \times 10^{-7}\ mol\ L^{-1}$$

Molarity refers to conc of H^+ or OH^- ion, thus

$$[H^+] = [OH^-] = \text{Molarity} = 1 \times 10^{-7}\ mol\ L^{-1}$$

$$K_w = [H^+][OH^-] = (1 \times 10^{-7})(1 \times 10^{-7}) = \underline{1 \times 10^{-14}}.$$

REDOX REACTIONS

OXIDATION	REDUCTION
1) Addition of oxygen	→ Removal of oxygen
2) Removal of Hydrogen	→ Addition of Hydrogen
3) Removal of electron	→ Addition of electron
4) ↑se in oxidation state	→ ↓se in oxidation state
5) Replacement of electro-ve atom by highly electro-ve atom	→ Replacement of high e.n atom by low e.n atom

REDOX REACTIONS

→ Chemical reactions involving oxidation and reduction processes are called redox reactions. These reactions involve transferrence of electrons from reducing agent to oxidising agent.

→ Oxidation : Process in which a species (atom, molecule or ion) increases oxidation no by losing one or more of electrons. The substance undergoing oxidation is called reducing agent.

→ Reduction : Process in which a species decreases O.N by gaining one ~~one~~ or more electrons. The substance undergoing reduction is called oxidising agent.

→ Example : $\underset{R.A}{Zn} + \underset{O.A}{Cu^{2+}} \longrightarrow Zn^{2+} + Cu$

ELECROCHEMICAL CHANGES

1) Electrochemical cells / Galvanic cells

→ The devices in which chemical energy of a spontaneous redox reaction is converted into electrical energy are called electrochemical cells or galvanic cells.

→ In these devices, the decrease in free energy during the spontaneous redox reaction appears as electrical energy or electrical work which may be used for running a motor or other electrical gadgets like heater, fan, geyser, etc.

2) Electrolytic cells

→ The phenomenon of chemical changes taking place by the passage of electrical energy from an external source is called electrolysis. The devices or cells used to carry out electrolysis are called electrolytic cells.

Example : $2NaCl \xrightarrow[\text{current}]{\text{Electric}} \underset{\text{cathode}}{2Na} + \underset{\text{Anode}}{Cl_2}$

ELECROCHEMICAL CELL OR GALVANIC CELL

In short :→

CELL :→ A device which converts either chemical energy to electrical energy or vice versa.

CELL

Electrolytic
→ Convert E.E to C.E

Electrochemical
→ Convert C.E to E.E.

charges on electrodes —

Electrochemical	Electrolytic
a) Anode −ve	a) Anode +ve
b) cathode +ve	b) cathode −ve

ELECTROCHEMICAL CELL / GALVANIC CELL

→ Also called as <u>voltaic cell</u>.

→ In these cells, oxidation and reduction occurs in separate containers called <u>half cells</u> and the redox reaction is <u>spontaneous</u>.

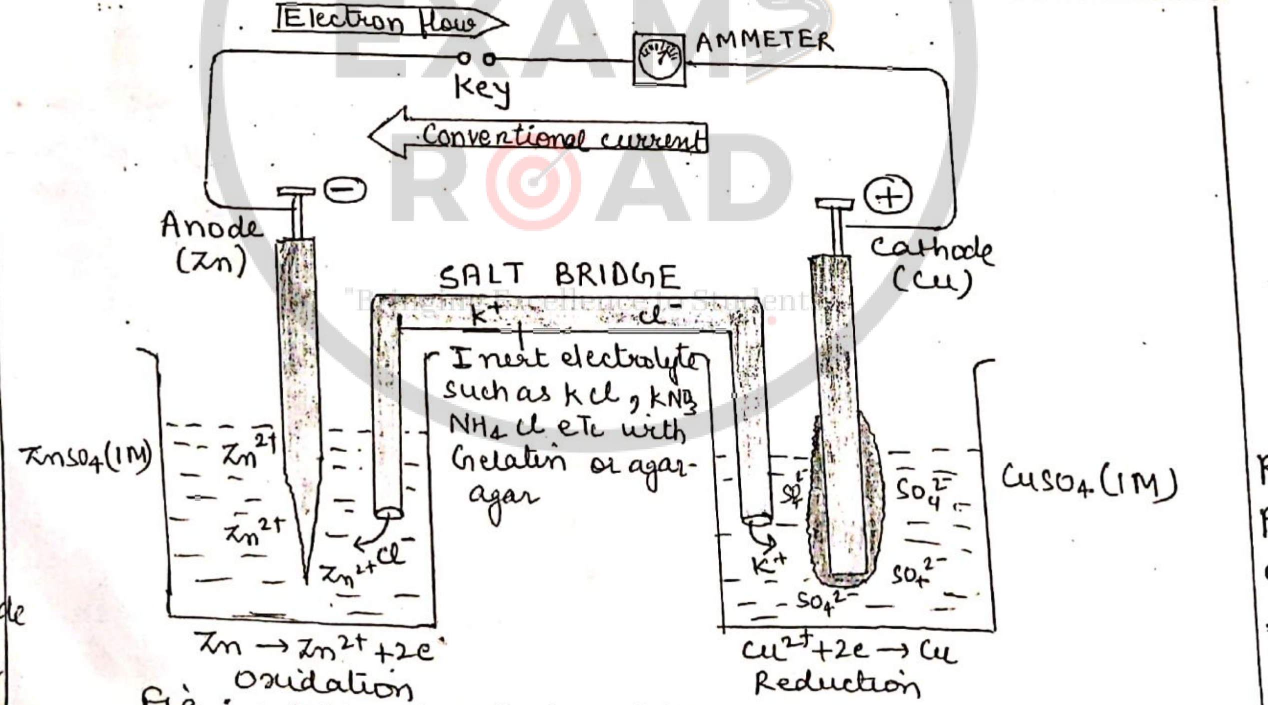
→ In galvanic cell, the decrease in gibbs free energy (ΔG) during the spontaneous chemical process is transformed into electrical energy.

WORKING

→ An indirect redox reaction takes place in a galvanic cell such that the reduction and oxidation processes are carried out in seperate vessels.

→ Redox reaction : $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

→ The arrangement consists of two beakers, one of which contains 1.0 M solution of zinc sulphate and the other 1.0 M copper sulphate. The zinc rod is dipped into $ZnSO_4$ solution while Cu rod is dipped into $CuSO_4$ solⁿ. These metallic rods are known as <u>electrodes</u>.



L→Left
O→oxi
A→Anode
N→-ve

R→Rig
R→Re
C→Ca
P→+

Fig : WORKING OF AN ELECTROCHEMICAL CELL

→ The electrodes are connected to the ammeter by conducting wire through a key. <u>Ammeter</u> is used to know the passage of current which moves in opp. direction to the flow of electrons.

→ The solution in the two beakers are connected by an inverted U-tube containing saturated solution of some electrolyte such as KCl, KNO_3 or NH_4NO_3 which does not undergo a chemical change during the process. The saturated solution is generally taken in agar-agar jelly or gelatin.

→ The U-tube which connects the two glass beakers is called salt-bridge.

→ When the circuit is completed, the electric current flows through external circuit as indicated by ammeter.

→ The following observations are made:

(i) Zinc rod gradually loses its weight.
(ii) The conc of $Zn^{2+}(aq)$ in $ZnSO_4(aq)$ solution increases.
(iii) Copper gets deposited on the electrode
(iv) The conc. of $Cu^{2+}(aq)$ in $CuSO_4(aq)$ decreases.
(v) There is a flow of electrons in the external circuit from Zinc rod to Cu. rod & current from Cu to zic.

These observations are explained as follows:

(i) Zn is oxidised to Zn^{2+} ions which goes into the solution and zinc rod gradually loses its weight.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \quad \text{(oxidation)}.$$

(ii) The electrons librated during oxidation are pushed through the connecting wires to copper strip where they are accepted by Cu^{2+} ions of $CuSO_4$ solution which are reduced to copper thus the metal gets deposited on copper electrode

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

→ The Zn electrode where e^-s are released or oxidation occurs is called anode while Cu electrode where electrons are accepted or reduction occurs is called cathode.

→ As the e^-s move from zinc to Cu rod, the zinc rod is regarded as -ve terminal while copper rod is regarded as positive terminal. The e^- flows from -ve terminal to +ve terminal (anode to cathode).

To sum up,

Oxidation occurs at anode (-ve terminal)
Reduction occurs at cathode (+ve terminal)
Electrons flow from anode to cathode

→ The two containers involving oxidation and reduction half reactions are called half cells or redox couples.

→ Oxidation half cell : Zn rod dipped in $ZnSO_4$ solution

→ Reduction half cell : Cu rod dipped in $CuSO_4$ solution

Characterstics of electrolyte used in salt bridge

1) The electrolyte should be inert.
2) The cations and anions of the electrolyte used should be of the same ionic mobility.

Functions of Salt bridge

1) Salt bridge completes the electrical circuit : The salt bridge connects the two solutions of the half cells whose electrodes are connected by means of a wire. Thus, the salt bridge completes the circuit.

2. Salt bridge maintains electrical neutrality of two half cell solutions.

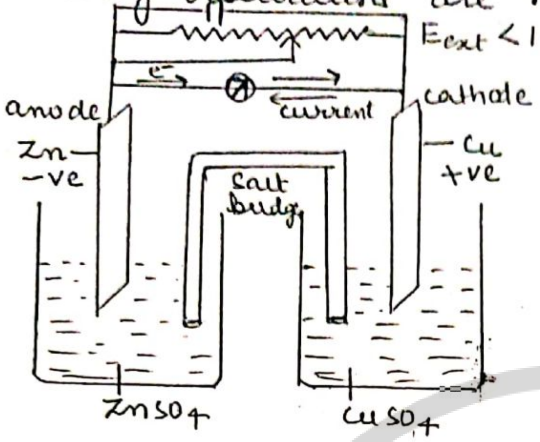
→ In the absence of salt bridge, the transference of electrons from anode to cathode leads to the accumulation of extra positive charge (Zn^{2+}) in the solution around the anode. Similarly, due to reduction of Cu^{2+} ions to Cu, the solution around cathode will aquire extra negative charge due to excess of SO_4^{2-} ions. The accumulation of +ve charge around zinc rod will prevent the further flow of electrons from the zinc rod. Similarly, the accumulation of -ve charge around copper electrode will prevent the flow of e^-s to Cu ions. Thus, the flow of e^-s will occur only momentarily and the cell will stop working.

→ However this can be prevented by using salt bridge, which provides a passage for the flow of charge in the internal circuit. When the conc of Zn^{2+} ions around anode ↑ses, sufficient number of Cl^- ions migrate from salt bridge to the anode half cell. Similarly to neutralise the excess -ve charge due to add. SO_4^{2-} ions in the cathode half cell, sufficient no. of K^+ ions migrate from the salt bridge to this half cell. Thus, the salt bridge provides cations and anions to replace the ions lost or produced in the two half cells.

Functioning of the cell when external opposing potential is applied / EFFECT OF OPPOSING POTENTIAL ON CELL REACTION

→ The electrical potential (called emf) of the cell is 1·10 V when conc of Zn^{2+} & Cu^{2+} ions is 1 M; when an external opposite potential is applied and is increased slowly, the following observations are made.

1)

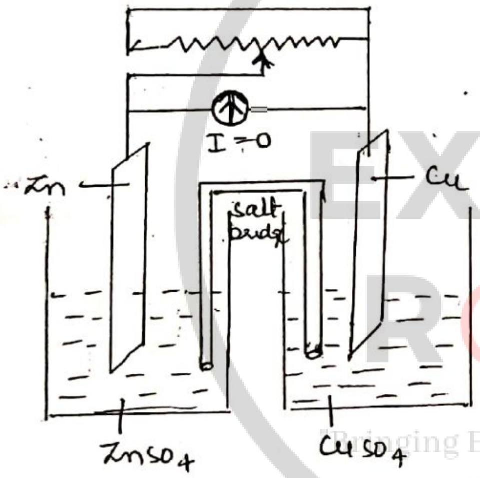


When $E_{ext} < 1 \cdot 1$ V

(i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.

(ii) Zn dissolves at anode and copper deposits at cathode

2)

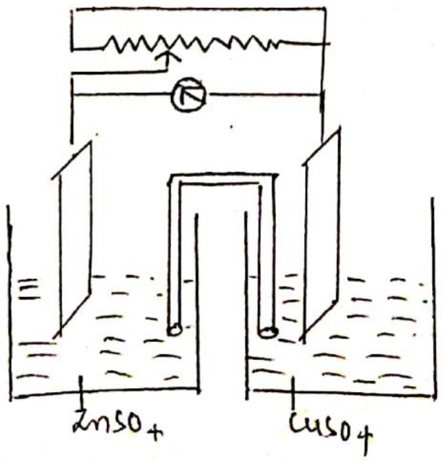


When $E_{xt} = 1 \cdot 1$ V

(i) No flow of electrons or current

(ii) No chemical reaction

3)



When $E_{xt} > 1 \cdot 1$ V

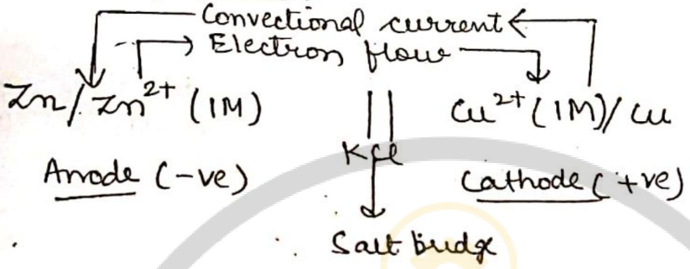
(i) Electrons flow from Cu to Zn and current flows from Zn to Cu.

(ii) Zn is deposited at the zinc electrode and copper dissolves at copper electrode.

(iii) It now functions as electrolytic cell.

NOTATION OF GALVANIC CELL

1) Anode is written on LHS and cathode on RHS
2) Anode is written by writing Metal or solid phase first and then the electrolyte (cation) while cathode is represented by writing electrolyte first (cation) and then Metal & solid phase
3) Metal & the cation are seperated either by a semicolon (;) or by a vertical line.
4) Concentration of the electrolyte is mentioned within bracket after cation.
5) Salt bridge which seperate the two half cells is indicated by two vertical lines.



Examples

(1) **Cu - $AgNO_3$ cell**

$$Cu \longrightarrow Cu^{2+} + 2e \quad \text{(oxidation half)}$$

$$2Ag^+ + 2e \longrightarrow 2Ag \quad \text{(Reduction half)}$$

$$Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag \quad \text{(overall react)}$$

Cell Notation : $Cu(s) \,|\, Cu^{2+}(aq) \,||\, Ag^+(aq) \,|\, Ag(s)$

(2) **Ni - $AgNO_3$ cell**

$$Ni(s) + 2Ag^+(aq) \longrightarrow Ni^{2+} + 2Ag(s)$$

Cell Notation : $Ni(s) \,|\, Ni^{2+}(aq) \,||\, Ag^+(aq) \,|\, Ag(s)$

(3) **Zn - HCl reaction**

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

Cell Notation : $Zn(s) \,|\, Zn^{2+}(aq) \,||\, H^+(aq) \,|\, H_2, Pt$

ELECTRODE POTENTIAL

→ The flow of electric current in an electrochemical cell indicates that a potential difference exists between two electrodes.

→ When a strip of Metal (M) is brought in contact with the solution containing its own ions (M^{n+}), then either of the following three possible process can take place:

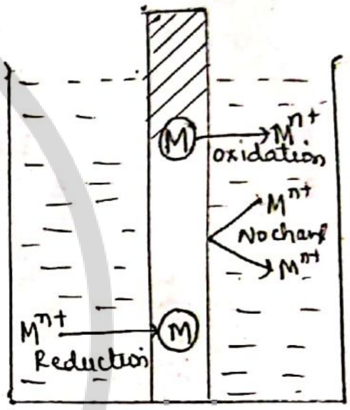
(i) Collision of M^{n+} with metal strip & bouncing back without any change

(ii) Metal ion M^{n+} may collide with the strip & gain n electrons to get converted into metal atom ie it get reduced

$$M^{n+} + ne \longrightarrow M$$

(iii) Metal atom on the strip may lose n electrons and enter the solution as M^{n+} ion, ie it get oxidised.

$$M \longrightarrow M^{n+} + ne^-$$



→ Now if the metal has relatively high tendency to get oxidised, its atoms will lose electrons readily & for M^{n+} ions which go into the solution. The electrons lost on the electrode would be accummulated on the metal electrode and the electrode aquires a slight –ve charge with respect to the soln. Some of the M^{n+} ions from the solution will take up e⁻s & become M atoms. After some time, an eqm will be established as

Electrode equilibrium

$$\underset{\text{Electrode}}{M(s)} \rightleftharpoons \underset{\text{Solution}}{M^{n+}} + \underset{\text{(on electrode)}}{ne}$$

→ When such an eqm is attained, it results in seperation of charges (–ve on the electrode with respect to the solution).

→ Similarly, if the metal ions have relatively greater tendency to get reduced, they will take electrons from the electrode. As a result, a net +ve charge will be developed on the electrode with respect to the solution. This will also result into seperation of charges (+ve on the electrode w.r.t solution).

→ Due to separation of charges b/w the electrode and the Solution, an electric potential is set up between metal electrode and its solution. The electrical potential difference set up b/w the metal & its solution is K/a electrode Potential.

→ Electrode Potential is a measure of the tendency of the electrode in a half cell to gain or loose electrons. It is of two types:

1) OXIDATION POTENTIAL : The tendency of an electrode to loose electrons or to get oxidised is called its oxidation potential. Thus oxidation potential is the tendency of an electrode to loose e's ie

$$M(s) \rightleftharpoons M^{n+}(aq) + ne$$
$$Zn \rightleftharpoons Zn^{2+}(aq) + 2e$$
$$H_2 \rightleftharpoons 2H^{+}(aq) + 2e$$

2. REDUCTION POTENTIAL: The tendency of an electrode to gain electrons or to get reduced is called its reduction potential.

$$M^{n+}(aq) + ne^{-} \rightleftharpoons M(s)$$
$$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$$
$$2H^{+}(aq) + 2e \rightleftharpoons H_2$$

→ The exact potential difference at the eq^{m} depends on the nature of metal, its ions, the conc^{n} of ions and the Temperature.

→ Accor to IUPAC conventions, the half reactions are always written as reduction half reactions and their potentials are represented by reduction potentials. It may be noted that

(i) Reduction potential (tendency to gain electrons) and oxidation potential (tendency to lose electrons) of an electrode are numerically equal but have opposite signs.

(ii) Reduction potential increases with the increase in conc. of ions and ↓ses with the decrease in conc. of ions in solution.

(iii) The red. potential of electrode when the conc. of the ions in solution is 1 mol L^{-1} & temp is 298 K is called standard reduction potential (E°red) or simply standard electrode potential (E°)

In case of gas electrode, the standard cond chosen are 1 bar pressure and 298 K along with 1M conc. of ions in solutions.

(iv) The absolute value of E° cannot be determined because once eq^{m} is reached b/w the electrode and the soln in a half cell, no further displacement of charges can occur unless it is connected to another half cell with diff. electrode potential. This difficulty is overcome by finding the electrode potentials of various electrodes relative to some reference electrode whose electrode potential is arbitarily fixed. The common reference electrode used for this purpose is standard hydrogen electrode (SHE) whose electrode potential is arbitarily taken to be zero.

Electromotive force : It may be defined as the potential difference between the two terminals of the cell when either no current is drawn from it.

or

The difference in the electrode potential of the two electrodes of the cell is termed as electromotive force (EMF) or cell voltage (E_{cell}).

→ Mathematically, it can be expressed as

$$EMF = E_{red}(\text{cathode}) - E_{oxid}(\text{Anode})$$

$$\text{or } E_{cell} = E_{cathode} - E_{anode}$$

$$= E_{Right} - E_{left} = E_R - E_L$$

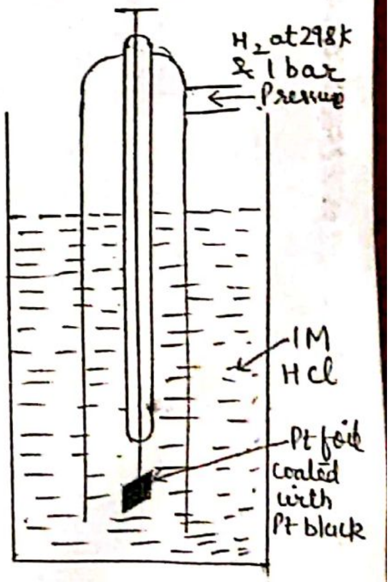
$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

→ The EMF of the cell depends upon

- nature of the reactants
- conc of the solutions of two half cells
- Temperature

STANDARD HYDROGEN ELECTRODE (SHE)

→ It consist of platinum wire sealed into a glass tube and carrying a platinum foil at one end. The platinum foil is coated with finely divided platinum. The electrode is placed in beaker containing an aqueous solution of some acid having 1 molar conc of H^+ ions. H_2 gas a 1 bar pressure is continuously bubbled through the solution at a temp of 298 K. The oxid. or red. in SHE takes place at platinum foil. Hence it can act as anode as well as cathode.



Standard Hydrogen electrode (SHE)

→ It can be represented as

$Pt, \frac{1}{2}H_2(1\,bar)/H^+(1M)$ or (as anode)

$H^+(1M)/\frac{1}{2}H_2(1\,bar), Pt$ (as cathode)

→ If SHE acts as anode then oxidation will take place at it as

$$H_2(g) \rightleftharpoons 2H^+(aq) + 2e$$

→ If SHE acts as cathode then reduction will take place at it as

$$2H^+(aq) + 2e \rightleftharpoons H_2(g)$$

→ By convection SHE is assigned a zero electrode potential ie $E^\circ_{SHE} = 0$

→ The electrode potential of the half cell is equal to the measured EMF of the cell in c / electrode is SHE.

→ The electrode potential of an electrode determined relative to SHE under standard conditions is called standard electrode potential.

SIGN OF THE ELECTRODES :-

→ with reference to SHE if the electrode form the -ve terminal of the cell it is alloted -ve electrode pot. & if it form +ve terminal of the cell, it is alloted +ve electrode potential.

Significance of sign of the electrode potential :-

(1) A +ve value of SEP(E°) tells us that the concerned electrode has more attraction for electron as compare to hydrogen ie reduction on the concerned electrode is more favourable.

(2) The -ve value of E° suggests that hydrogen electrode attract e^- more strongly as compared to the electrode in question ie oxidation on the concerned electrode is more favourable.

How to find standard electrode potential of zinc electrode?

→ In order to find out E°_{Zn}, Zn electrode containing 1M conc. of Zn^{2+} ions is connected to SHE. The

Voltmeter reading shows the potential difference (E°_{cell}) of 0.76 volts. The electron flow is found to be from zinc electrode to SHE. From it it follows that Zn acts as anode while SHE acts as cathode. The net cell reaction is

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

$$\text{Now } E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= E^\circ_{H^+/\frac{1}{2}H_2} - E^\circ_{Zn^{2+}/Zn}, 0.76$$

$$= 0 - E^\circ_{Zn^{2+}/Zn}$$

$$E^\circ_{Zn^{2+}/Zn} = \underline{-0.76 \text{ volts}}$$

To find E°_{Cu}

When standard copper electrode is coupled with SHE, the voltmeter reading shows a potential difference (E°_{cell}) of 0.34 volts. The e^- flow is found to occur from SHE towards Cu electrode. Therefore, SHE in this cell acts as anode & Cu electrode acts as cathode. The cell reaction is :

$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= E^\circ_{Cu^{2+}/Cu} - E^\circ_{H^+/\frac{1}{2}H_2}$$

$$0.34 = E^\circ_{Cu^{2+}/Cu} - 0$$

$$E^\circ_{Cu^{2+}/Cu} = \underline{0.34 \text{ volts}}$$

TABULATION OF STANDARD ELECTRODE POTENTIAL

1) All the dissolved species are at unit molarity.
2) All Gases are at 1 bar pressure
3) All solids are in their most stable form.
4) Temp = 298K
5) $E^\circ_{SHE} = 0$

→ The sign of E° values tells us about the feasibility of the ½ reaction & indicates the types of charge on the electrode in the construction of galvanic cell.

→ The –ve value of E° tells that the concerned electrode is anode (–ve) & SHE is cathode in the galvanic cell constructed for the measurement of SEP.

$$E^\circ_{cell} = E^\circ_R - E^\circ_L = E^\circ_{SHE} - E^\circ_L$$

$$= 0 - E^\circ_L = -E^\circ_L = \text{electrode pot of anode}$$

→ The +ve value of E° tells that the concerned electrode is cathode (+ve) & SHE is anode in the galvanic cell constructed for the measurement of SEP.

$$E^\circ_{cell} = E^\circ_R - E^\circ_L = E^\circ_R - E^\circ_{SHE}$$

$$= E^\circ_R - 0 = E^\circ_R = \text{electrode pot. of cathode.}$$

SELECTION OF ELECTRODES :–

1) For higher cell potential, the electrode c̄ large +ve E° is taken as cathode & anode is chosen c̄ larger –ve E° values.

example : Galvanic cell with Li^+/Li as anode & $F_2/Pt/F^-$ as cathode, the EMF will be

$$E^\circ_{cell} = E^\circ_R - E^\circ_L = 2.870 - (-3.045) = 5.915 \text{ V}$$

2) Two half cells with +ve E° values can be coupled to construct a cell.

example : Cu^{2+}/Cu & Ag^+/Ag can be coupled

$$E^\circ_{cell} = E^\circ_R - E^\circ_L = 0.799 - 0.337 = 0.462 \text{ V}$$

3) Two half cells with –ve E° values can be coupled to construct a cell. The electrode c̄ more –ve E° value is anode & other is cathode