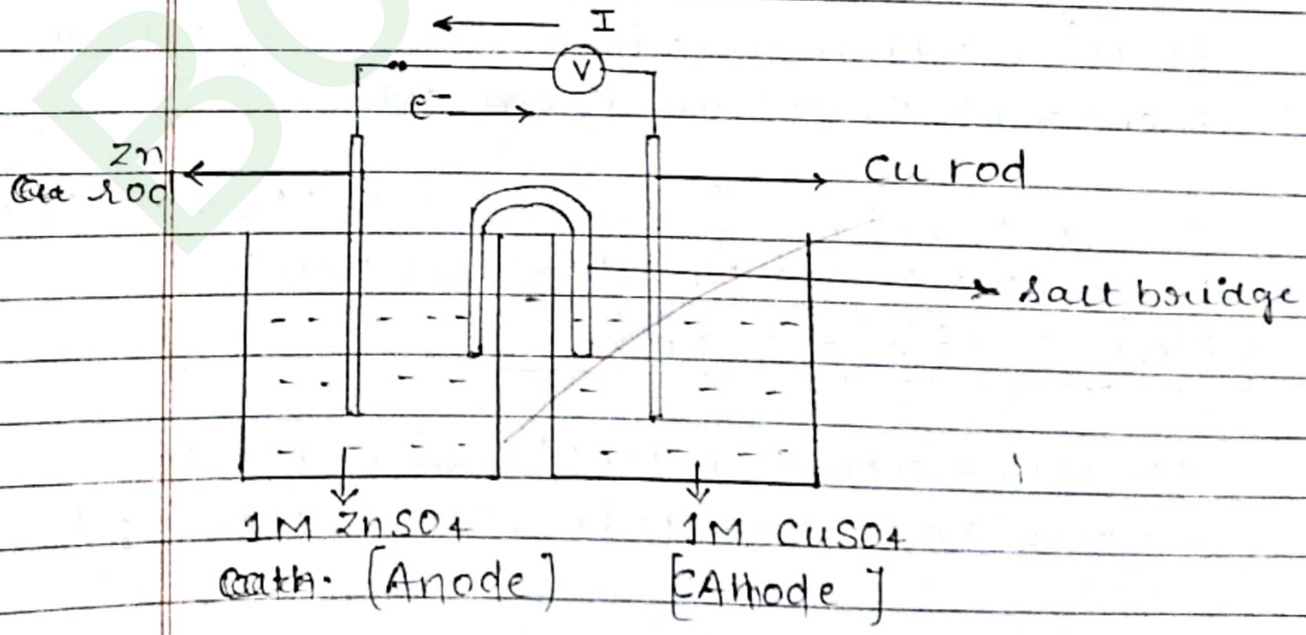
Electrochemistry

Electrochemistry is defined as branch of chemistry which deals with relationship between electrical energy and chemical changes take place in redox reaction, i.e., how chemical energy produced in redox reaction can be converted into electrical energy or how electrical energy can be used to bring about a redox reaction which is otherwise non-spontaneous.

Electrochemical cells : The device which is used to convert chemical energy into electrical energy. into

eg. Daniel cell is a type of galvanic cell in which cell is desingned in such a manner to make used of spontaneous reaction between Zn and cu ion to produce on electric current.

→ Electrochemical cell is also called Galvanic cell or voltaic cell.



Anode — Cathode

oxidation — Reduction

$\downarrow$ — $\downarrow$

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ — $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

$[Zn^{2+}] > [SO_4^{2-}]$ — $[Cu^{2+}] < [SO_4^{2-}]$

Net cell reaction :-

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

Cell Representation :-

$$\underbrace{Zn_{(s)} \mid \underset{1M}{Zn^{2+}_{(aq)}}}_{\text{oxidation Half}} \overset{\text{salt bridge}}{\|} \underbrace{\underset{1M}{Cu^{2+}_{(aq)}} \mid Cu_{(s)}}_{\text{Reduction half}}$$

Cell Potential difference:- is the difference between the electrode potential of the two half cell is known as cell potential or cell voltage.

It is electromotive force (emf) of cell when no current is drawn from cell.

$E^\circ_{cell} = 1.1\,V$ [Standard state : 1atm, 25°C, 1M]

E°_{cell} = Higher Potential − Lower Potential.

$$\boxed{E^\circ_{cell} = (E^\circ_R)_C - (E^\circ_R)_A}$$

→ Standard electrode potential is taken to be standard reduction potential, according to IUPAC.

ionic mobility of cation ≃ ionic mobility of anion.

Salt Bridge :-

Salt bridge is a u-shaped tube containing inert electrolyte and paste of poly saccharide (agar + agar).

Function -

- To maintain electrical nutrality.
- To complete inner circuit without mixing of two solutions.
- To reduce liquid - liquid junction potential.

Inert electrolyte : the electrolyte whose ions do not take part in main cell reaction.

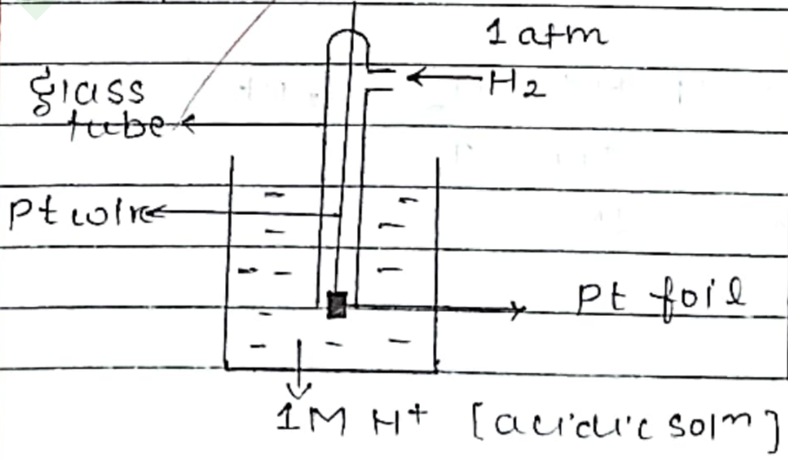
eg. KCL, KNO_3, NH_4NO_3 etc.

Note :- KCL is not used in Ag, TL, Pb, Hg electrode because ppt is formed and affect the reaction.

Standard Hydrogen Electrode :-

→ Standard Hydrogen electrode acts as reference electrode because it's potential is zero.

→ with help of SHE we can measure the standard electrode potential of any metal in electrochemical series.



* electrode potential is the tendency of an electrode to lose or gain electron when it is in contact with solution of its own ions.

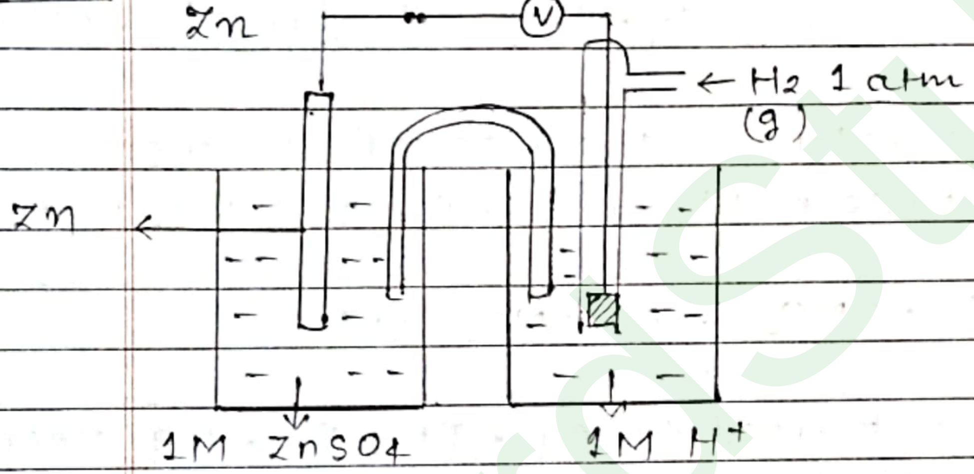
case 1· when SHE acts as anode :

oxidation $H_{2\,(g)} \longrightarrow 2H^{+}_{(aq)} + 2e^{-}$; $E_R^{\circ} = 0$

case 2. when SHE acts as cathode :

reduction $2H^{+}_{(aq)} + 2e^{-} \longrightarrow H_{2\,(g)}$; $E_R^{\circ} = 0$

case ① Calculation of standard electrode potential of Zn



[oxidation] Anode cathode [Reduction]

$Zn \longrightarrow Zn^{2+} + 2e^{-}$ $2H^{+} + 2e^{-} \longrightarrow H_2$

cell reaction -

$Zn_{(s)} + 2H^{+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2\,(g)}$

cell representation -

$Zn_{(s)} \mid \underset{1M}{Zn^{2+}_{(aq)}} \parallel \underset{1M}{H^{+}_{(aq)}} \mid H_{2\,(g)}, Pt$

cell Potential difference :-

$E^\circ_{cell} = (E^\circ_R)_C - (E^\circ_R)_A$

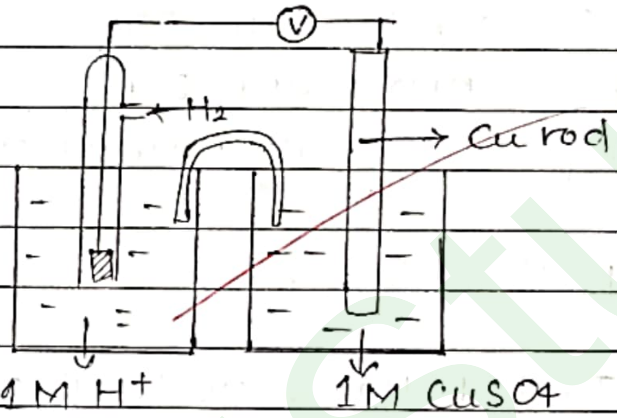
$E^\circ_{cell} = 0 - (E^\circ_{Zn^{2+}|Zn})$

from experiment → $0.76 = -(E^\circ_{Zn^{2+}|Zn})$

$E^\circ_{Zn^{2+}|Zn} = -0.76\ V$

* elements which lie above H in E.C.S. have -ve E°_R.

Case ② Calculation of standard electrode potential of Cu.



Anode [oxidation] cathode [Reduction]

$H_2 \rightarrow 2H^+ + 2e^-$ $Cu^{2+} + 2e^- \rightarrow Cu$

Cell reaction -

$H_{2(g)} + Cu^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Cu_{(s)}$

Cell representation :-

$H_{2(g)} | \underset{1M}{H^+_{(aq)}} || \underset{1M}{Cu^{2+}_{(aq)}} | Cu_{(s)}$

Cell Potential difference :-

$E^\circ_{cell} = (E^\circ_R)_C - (E^\circ_R)_A$

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

$E^\circ_{Cu^{2+}|Cu} = +0.34\ V$

* element which lie below H have +ve E°_R.

Electrochemical series :

Li
K
Ba
Sr
Ca
Na
Mg
Al
Mn
Zn
Cr
Fe
Cd
Co
Ni
Sn
Pb
H
Cu
I
Ag
Hg
Br
Pt
O
Cl
Au
F

increasing oxidising strength ↓

Characterstics :-

(i) Element above H have negative E°_R.
(ii) Element below H have positive E°_R.
(iii) H has zero E°_R.
(iv) Top to bottom, E°_R increases ↑
Li → minimum E°_R
F → maximum E°_R
(v) Top to bottom, reducing power ↓

Application :-

(i). Top to bottom reducing power decreases and oxidising power increases.

(ii). Metal displacement reaction
metal which lie above in electrochemical series can displace the metal from its salt which below E.C.S.

(iii) Non metal displacement reaction
non-metal which lie below in E.C.S can displace the non-metal, which lie above, from its salt.

I
Br
Cl
F
↓

(iv) Top to bottom reactivity decreases.

(v) Top to bottom thermal stability of oxide decreases.

Nernst Equation for Electrode Potential -

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

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

For pure solid or liquid or gases at one atm the molar concentration is taken as UNITY.

$$\text{So, } E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

$$E = E^\circ - \frac{2.303\,RT}{nF} \log \frac{1}{[M^{n+}]}$$

Putting , $R = 8.314\ J\,K^{-1}\,mole^{-1}$

$F = 96500\,C$ and $T = 298\ K$, we get ,

$$\boxed{E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}}$$

Nernst equation for EMF of a cell :-

let us consider example of daniel cell ,

$$E_{Zn^{2+}|Zn} = E^\circ_{Zn^{2+}|Zn} + \frac{RT}{2F} \ln [Zn^{2+}(aq)]$$

$$E_{Cu^{2+}|Cu} = E^\circ_{Cu^{2+}|Cu} + \frac{RT}{2F} \ln [Cu^{2+}(aq)]$$

$$E_{cell} = E_{cathode} - E_{anode}$$

$$E_{cell} = E_{Cu^{2+}|Cu} - E^\circ_{Zn^{2+}|Zn}$$

$$= E_{Cu^{2+}|Cu} + \frac{RT}{2F} \ln[Cu^{2+}\,(aq)] -$$

$$E^\circ_{Zn^{2+}|Zn} + \frac{RT}{2F} \ln[Zn^{2+}(aq)]$$

$$Q = \frac{\text{Product}}{\text{Reactant}} = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$= (E_{Cu^{2+}|Cu} - E_{Zn^{2+}|Zn}) + \frac{RT}{2F} \ln \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$= E^\circ_{cell} - \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

After putting the values -

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\therefore \boxed{E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}}$$

Equilibrium constant from Nernst equation -
when the flow of electron is due to increase in concentration of Zn^{2+} at anode and SO_4^{-} at cathode then cell reaction stops, that condition is called equilibrium constant.

At equilibrium,

$Q = K$ and $E_{cell} = 0$.

also, $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = K$

Putting values in Nernst equation,

$$0 = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E^\circ_{cell} = + \frac{RT}{nF} \ln K$$

$$E^\circ_{cell} = \frac{2.03\, RT}{nF} \log K$$

$$\boxed{E^\circ_{cell} = \frac{0.0591}{n} \log K}$$

→ standard free energy

Relation between ΔG° and E°cell :-

$$\boxed{\Delta G = \Delta G^\circ + RT \ln Q}$$

where,

ΔG → free energy change at T (K)

ΔG° → Standard free energy change.

R → gas constant

T → Temperature (K)

Q → reaction quotient.

At equilibrium, $\Delta G = 0$

$Q = K$

So, $0 = \Delta G^\circ + RT \ln K$

$$\Delta G^\circ = -RT \ln K \quad \text{—①}$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln Q$$

$$0 = E^\circ_{cell} - \frac{RT}{nF} \ln K$$

$$nF E^\circ_{cell} = RT \ln K \quad \text{—②}$$

from equation ① and ② :-

$\Delta G^\circ = -nF E^\circ$cell.

So, $\boxed{\Delta G^\circ = -nF E^\circ_{cell}}$

Calculation of ΔG°, W_{max}, K for Daniel cell —

$\Delta G^\circ = -nF E^\circ$cell

$\Delta G^\circ = -2 \times 96500 \times 1{\cdot}1$

$\Delta G^\circ = -212300$ J/mol

$\Delta G^\circ = -212{\cdot}3$ KJ/mol

$W_{max} = -\Delta G^\circ$

$W_{max} = -(-212{\cdot}3)$

$W_{max} = 212{\cdot}3$ KJ/mol

$\Delta G = -RT \ln K$

$-212300 = \frac{-25}{3} \times 298 \times 2\cdot3 \log_{10} K$

$\frac{212300 \times 3}{25 \times 298 \times 2\cdot3} = \log_{10} K$

$\log_{10} K = 37$

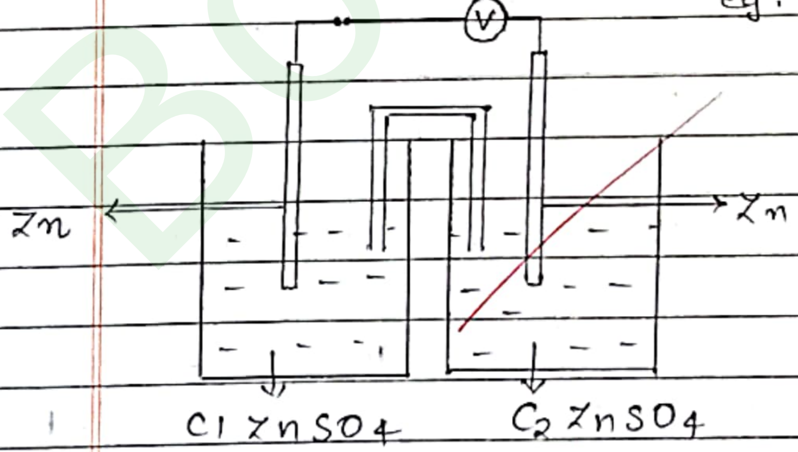
$\boxed{K = 10^{37}}$

Note :- ΔG is an additive quantity but emf of the cell is not.

Concentration Cells :-

are the cells in which either two electrodes are of same material but the concentration of electrolyte in them is different or two electrodes have different concentration but they are immersed in same solution of electrolyte are called electrolytic conc. cell and electrode concentration cell respectively.

eg. when conc. is different



Anode

$\underset{(s)}{Zn} \rightarrow \underset{(aq)}{Zn^{2+}} + 2e^-$
$C_1 M$

cathode

$\underset{(aq)}{Zn^{2+}} + 2e^- \longrightarrow \underset{(s)}{Zn}$
$C_2 M$

Cell reaction :-

$\underset{C_2 M}{\underset{(aq)}{Zn^{2+}}} \longrightarrow \underset{C_1 M}{\underset{(aq)}{Zn^{2+}}}$

Cell representation :-

$Zn \,|\, \underset{(C_1 M)}{\underset{(aq)}{Zn^{2+}}} \,||\, \underset{(C_2 M)}{\underset{(aq)}{Zn^{2+}}} \,|\, Zn$

Cell potential difference :-

Note → $E^\circ cell = 0$

$E cell = 0 - \frac{0.06}{n} \log_{10} Q \quad [n = 2]$

$E cell = -0.03 \log_{10}\left(\frac{C_1}{C_2}\right)$

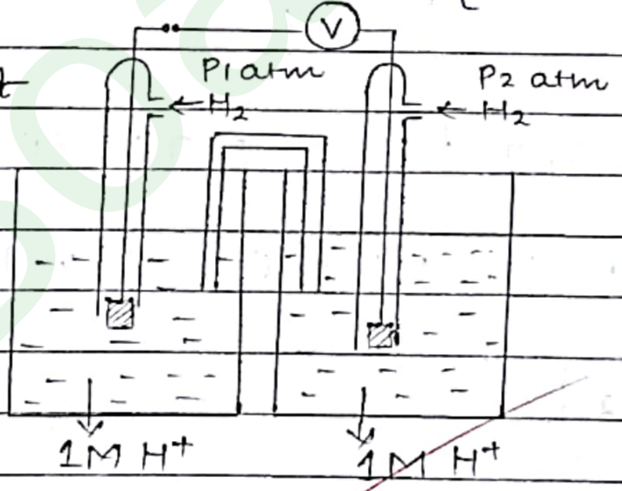
$E cell = +0.03 \log_{10}\left(\frac{C_2}{C_1}\right)$

Condition for spontaneous reaction -

$\Delta G = -nFEcell \quad ; \quad \Delta G < 0$

$E cell > 0 \quad , \quad [C_2 > C_1]$

eg.
on differnt pressure



Anode

$\underset{\text{P1 atm}}{\underset{(g)}{H_2}} \rightarrow \underset{(aq)}{2H^+} + 2e^-$

cathode

$\underset{(aq)}{2H^+} + 2e^- \rightarrow \underset{\text{P2 atm}}{\underset{(g)}{H_2}}$

cell reaction :

$$\underset{P_1\,atm}{\underset{(g)}{H_2}} \longrightarrow \underset{P_2\,atm}{\underset{(g)}{H_2}}$$

Cell representation :

$$Pt, \underset{P_1}{\underset{(g)}{H_2}} | \underset{(aq)}{H^+} || \underset{(aq)}{H^+} | \underset{P_2}{\underset{(g)}{H_2}}, Pt$$

or

$$Pt, \underset{P_1}{\underset{(g)}{H_2}} | HCl | \underset{P_2}{\underset{(g)}{H_2}}, Pt$$

Cell Potential difference :-

$$E_{cell} = 0 - \frac{0.06}{2} \log_{10} \frac{P_2}{P_1}$$

$$E_{cell} = 0.03 \log_{10}\left(\frac{P_1}{P_2}\right)$$

Condition for spontaneous reaction -

$\Delta G = -nFE_{cell}$; $\Delta G < 0$ (-ve)

$E_{cell} > 0$

$\because$ $[P_1 > P_2]$

Electrolysis :-

The process of decomposition of an electrolyte by the passage of electricity through it's aqueous sol^n or molten (fused) state.

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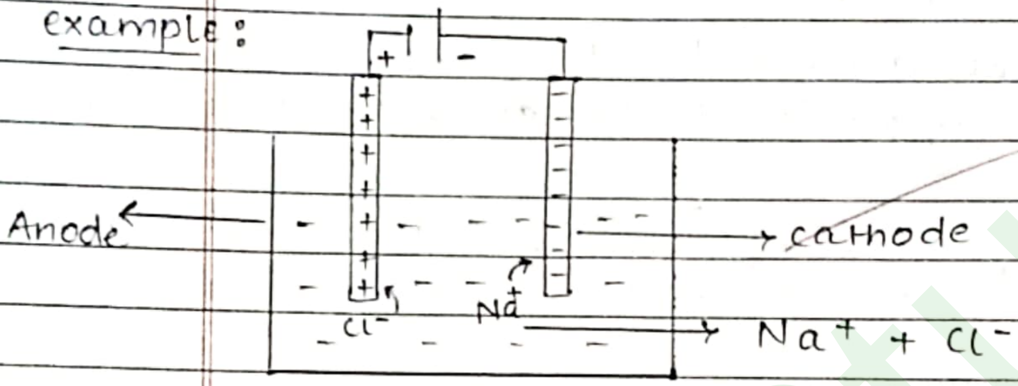
Electrolytic cell :-

The device which is used to convert electrical energy into chemical energy.

or The device in which process of electrolysis occurs.

example :



→ On passing current, positively charged ions move towards cathode, and called cation and negative charged species move at anode and called anion.

→ The conversion of ions into neutral species at their respective electrodes is called primary change.

→ The product formed at their respective electrode as called result of primary change is called as secondary change.

Preferential discharge theory :-

जो नीचे आता है वो जाता है।

case① For cation : when two different ions are present in the solⁿ then that ion will migrate first which have higher reduction potential.

case② For anion : Ease of deposition or tendency to migrate.

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

in case of NaCl (molten),

At cathode $Na^+ + e^- \rightarrow Na$ } primary
At anode $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$ } change.

Product of electrolysis:

- Na metal deposited at cathode.
- Cl_2 gas ~~deposited~~ ~~ext~~ evolved at anode.

eg. Electrolysis of aqueous solution of $CuSO_4$ using inert electrode:

$$CuSO_4 \longrightarrow \underset{(aq)}{Cu^{2+}} + \underset{(aq)}{SO_4^{2-}}$$

$$H_2O \longrightarrow \underset{(aq)}{H^+} + \underset{(aq)}{OH^-}$$

At cathode - discharge potential of Cu^{2+} is lower than H^+ ion, so, Cu^{2+} ions are discharged in preference to H^+ ions.

→ Copper is deposited on electrode.

$$Cu^{2+} + 2e^- \rightarrow Cu$$

At anode - Among SO_4^{2+} and OH^-, so discharge potential of OH^- is lower so,

$$4OH^- \rightarrow 4OH + 4e^-$$
$$4OH \rightarrow 2H_2O\ (l) + O_2\ (g)$$

→ O_2 is liberated at anode.

Faraday's Laws :-

(1) **Faraday' First Law of Electrolysis :-**

The weight of ion discharged is directly proportional to the quantity of electricity passed through the electrolyte.

$$w \propto Q$$

$\boxed{w = zQ}$, where z is a constant of proportionality and it is called electrochemical equivalent of substance deposited.

Electrochemical Equivalent :-

of a substance may be defined as the mass of the substance deposited when a current of one Ampere is passed for one second, i.e. quantity of electricity equal to one coulomb is passed.

(2) Also,

$$w = zQ \qquad \because \left[z = \frac{Ew}{F} \right]$$

$$w = \frac{Ew}{F} \cdot Q$$

$$\boxed{\frac{w}{Ew} = \frac{Q}{F}}$$

no·of gm eq = $\frac{w}{Ew}$

no· of gm eq. = $n \times nf$

$$n \times n \cdot f = \frac{Q}{F}$$

$$\therefore \boxed{n \times nf = \frac{it}{F}}$$

where,

n = number of moles. i = current (Amp.)

nf = number of e⁻ involve in reaction

1 F = charge of one mole e⁻

1 F = $N_A \times 1.6 \times 10^{-19}$

1 F = 96500 C.

(2) Faraday's Second Law of Electrolysis :-

When same quantity of electricity is passed through solution of different electrolyte connected in series, the masses of the substance produced at the electrodes are directly proportional to their equivalent weights.

$w \propto Z$

$w \propto \frac{Ew}{F}$

$w \propto Ew$

$\frac{w_1}{Ew_1} = \frac{w_2}{Ew_2}$

also,

$n \cdot nf = \text{constant}$

$n \propto \frac{1}{nf}$

$$\boxed{n_1 \times nf_1 = n_2 \times nf_2}$$

Current efficiency :- the extent of desired electrochemical reaction divided by the theoretical extent of reaction.

$$\boxed{\text{current efficiency} = \frac{I \text{ actually used}}{I \text{ total supplied}} \times 100}$$

Conductance of Electrolytic Solutions -

Substance which allow electricity to pass through them are known as conductors whereas which do not allow electricity to pass through are insulators.

→ Substance which conduct electricity without undergoing any decomposition, are called electronic conductors.

e.g. Metals, graphite and certain minerals, etc.

→ Those which undergo decomposition when current is passed through them, are known as electrolytic conductors or electrolytes.

e.g. Solution of acid, bases and salts in water, fused salt etc.

Electrolytes are further classified into –

(i) Strong electrolyte :

These dissociate almost completely in aqueous solution or in molten state and hence conduct electricity to large extent.

eg. HCl, HNO_3, H_2SO_4 etc. [Strong acid]
NaOH, KOH etc. [Base strong]
most inorganic salt.

(ii) Weak electrolyte :

These dissociate to a small extent and hence conduct electricity to small extent.

eg. CH_3COOH, HCN, H_2CO_3, H_3PO_4 [weak ~~base~~ acid]
NH_4OH, $Ca(OH)_2$, $Al(OH)_3$ [weak base]

(α) Degree of ionisation :- The fraction of total number of molecule of electrolyte which ionizes in solution.

Strong electrolyte, $\alpha \simeq 1$
weak ,, $\alpha < 1$

Factors affecting electrolytic conduction :

- Nature of electrolyte.
- Size of ions produced and their solvation.
  Greater the size of ions or solvation of ion ; less the conductance.
- Nature of solvent and its viscosity.
- Higher the concentration of solution, less conductance
- On increasing temperature, conduction increases.

Factors affecting electronic conductance :

- Nature and structure of metal.
- Number of valence electrons per atom.
- It decreases with increase of temperature.

(R) Resistance : Hinderance offered by the solution is called resistance.

$$\boxed{R = \frac{\rho l}{A}} \quad ; \quad \text{SI unit} \rightarrow \text{ohm} \ (\Omega)$$

where, R = resistance
ρ = specific resistance.
l = length between electrode
A = Area of cross-section of electrode.

(ρ) Specific Resistance or Resistivity :
It is the resistance when the separation between electrode is 1 cm and area of cross - section is 1 cm^2.

$$\boxed{\rho = \frac{RA}{l}} \quad ; \quad \text{SI unit} \rightarrow (\Omega m)$$

ohm·m

Conductance :-

The reciprocal of electrical resistance is called conductance. It is usually represented by G.

$\boxed{G = \frac{1}{R}}$: unit → ohm^{-1} or mhos or siemens (S)

Conductivity :-

The reciprocal of resistivity.
or
the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section. It is represented by K (Kappa)

$\boxed{K = \frac{1}{\rho} \quad \text{or} \quad K = \frac{l}{RA}}$ $\boxed{K = G\frac{l}{A}}$

unit → $ohm^{-1}cm^{-1}$ or $S\,cm^{-1}$
SI unit → $S\,m^{-1}$

Cell constant : For a particular cell, l/a is constant and this constant is called cell constant.
It is represented by G^* or σ.

$\boxed{G^* = \frac{l}{A} = \text{cell constant}}$

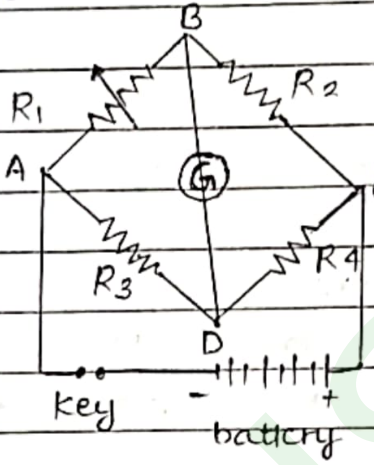
also,
conductivity (K) = conductance (G) × cell constant (G^*)

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

Note: Conductance can be observed by measurement of resistance and also can be found by the Wheatstone Bridge Method.

It consists of four arms containing resistance R_1, R_2, R_3, and R_4.

R_1 is is variable resistance and R_2 is unknown resistance.



$$\boxed{\frac{R_1}{R_2} = \frac{R_3}{R_4}}$$

$$K = \frac{l}{RA} = \frac{G^*}{R}$$

$$\because \quad R_1 = \frac{R_2 R_3}{R_4}$$

Molar conductivity $[\Lambda m]$:-

The conductivity of an electrolyte which is 1 mole when separation between electrode is 1 cm and area is so large that whole solution is contained between them.

$$\boxed{\Lambda m = \frac{K \times 1000}{M}}$$; SI unit → Sm^2mol^{-1}

where Λm = molar conductivity
K = conductivity
M = Molarity (mol/L)

Equivalent conductivity [Λ_{eq}] :-

The conductivity of 1 gmeq of an electrolyte when separation between electrode is 1 cm area is so large that the whole of solution is contained between them.

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

unit : $S\,cm^2 gmeq^{-1}$

where Λ_{eq} = equivalent conductivity
K = conductivity
N = Normality

Relation between Λ_{eq} and Λ_m :-

$$\Lambda_{eq} = \frac{K \times 1000}{M \times nf}$$

$$\Lambda_{eq} = \frac{\Lambda_m}{nf}$$

$$\boxed{\Lambda_{eq} = \frac{\Lambda_m}{nf}}$$

Effect of dilution on conductivity, molar conductivity and equivalent conductivity :-

- On dilution, volume increases and conc. decreases, hence conductivity (K) decreases. because number of ions per unit volume decreases.

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- On dilution, molar conductivity (Λm) and (Λeq) equivalent conductivity increases because degree of dissociation and the total number of ions increases.

Variation of molar conductivity (Λm) with concentration :-

$$\boxed{\Lambda^{c}_{m} = \Lambda^{\circ}_{m} - A\sqrt{C}}$$

The molar conductivity of strong electrolyte is found to vary with given equation.

where,

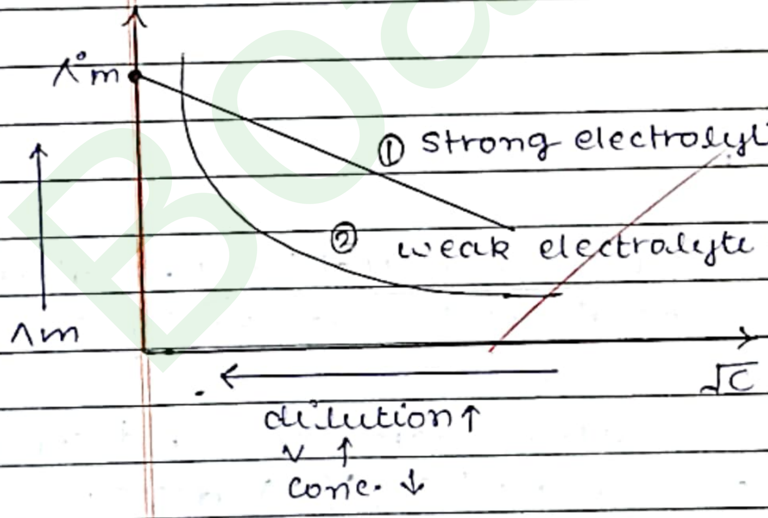
$V \to \infty$
$C \to 0$

$\Lambda^{c}_{m} \to$ molar conductivity at concentration c.

Λ°_{m} or $\Lambda^{\infty}_{m} \to$ limiting molar conductivity

$A \to$ constant and depends on nature of solvent.

$C \to$ concentration.



① For strong electrolyte, we can calculate $\Lambda^{\circ}m$.
② For weak electrolyte, we can't calculate $\Lambda^{\circ}m$.

KOHLRAUSCH Law :-

The limiting molar conductivity of an electrolyte is the sum of ionic molar conductivity of ions (cation and anion) multiply with the number of ions present in one formula unit of electrolyte.

OR

The limiting molar conductivity of an electrolyte is sum of ionic molar conductivity of ions multiply with respective stoichiometric coefficient.

$$A_xB_y \longrightarrow xA^{y+} + yB^{x-}$$

$$\boxed{\Lambda^\circ_m \text{ for } A_xB_y = x \times \lambda^\circ_m A^{y+} + y \times \lambda^\circ_m B^{x-}}$$

eg. Λ°_m for $BaCl_2 = \lambda^\circ_{Ba^{2+}} + 2\lambda^\circ_{Cl^-}$

Λ°_m for $Al_2(SO_4)_3 = 2\lambda^\circ_{Al^{3+}} + 3\lambda^\circ_{SO_4^{2-}}$

In terms of equivalant conductivity,

The limiting equivalent conductivity of an electrolyte is sum of ionic equivalent conductivity.

$$\boxed{\Lambda^\circ_{eq} = \lambda^\circ_{cation} + \lambda^\circ_{anion}}$$

eg. $\Lambda^\circ_{eq}\ Ca_3(PO_4)_2 = \lambda^\circ_{eq}\ Ca^{2+} + \lambda^\circ_{eq}\ (PO_4)^{3-}$

$\Lambda^\circ_{eq}\ BaCl_2 = \lambda^\circ_{eq}\ Ba^{2+} + \lambda^\circ_{eq}\ Cl^{-1}$

Application of KOHLRAUSCH LAW :-

1. To determine degree of dissociation of weak electrolyte.

$$\boxed{\alpha = \frac{\Lambda^c_m}{\Lambda^\circ_m}}$$

2. To find dissociation constant of weak electrolyte.

$$AB \rightleftharpoons A^+ + B^-$$

$$\boxed{K_c = \frac{C\alpha^2}{1-\alpha}}$$

3. To find solubility and solubility product of sparingly (partially) soluble salts.

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

initial $\quad s \quad\quad 0 \quad\quad 0$

$\quad\quad\quad\quad xs \quad\quad ys$

$$Ksp = (xs)^x + (ys)^y$$

$$Ksp = x^x \, y^y \, s^{x+y}$$

$$\boxed{\Lambda^\circ m = \frac{K \times 1000}{S}}$$

4. To find $\Lambda^\circ m$ of an electrolyte when $\Lambda^\circ m$ of other electrolyte is given.

eg. $\Lambda^\circ m$ CH_3COOH = ?

when,

Electrolyte	$\Lambda^\circ m$ Scm^2mol^{-1}
CH_3COONa	91
HCl	426
NaCl	126

$\Lambda^\circ_m\ CH_3COOH = \Lambda^\circ_m\ CH_3COONa + \Lambda^\circ_m\ HCl - \Lambda^\circ\ NaCl$

$\Lambda^\circ_m\ CH_3COOH = 91 + 426 - 126$

$\Lambda^\circ_m\ CH_3COOH = 91 + 300$

$\Lambda^\circ_m\ CH_3COOH = 391\ S\,cm^2\,mol^{-1}$

Similarly, $\Lambda^\circ_m\ Ba(OH)_2$

$\Lambda^\circ_m\ \{Ba(OH)_2 = \Lambda^\circ_m(BaCl_2) + 2\Lambda^\circ_m(NaOH) - 2\Lambda^\circ_m(NaCl)$

$= \lambda^\circ_m\ Ba^{2+} + 2\lambda^\circ_m\ Cl^- + 2\lambda^\circ_m\ Na^+ + 2\lambda^\circ\ OH^- - 2\lambda^\circ_m\ Na - 2\lambda^\circ_m\ Cl^-$

$\Lambda^\circ_m\ Ba(OH)_2 = \lambda^\circ_m\ Ba^{2+} + 2\lambda^\circ\ OH^-$

Batteries :-

If a number of cells are connected in series, the arrangement is called a battery.

The various batteries or cells may be classified mainly into two types —

Ⓐ Primary batteries or cells.
Ⓑ Secondary batteries or cells.

A. Primary Batteries or cells :-

are those in which redox reaction occurs only once and cell become dead after some time and can not be reused. Two common example of this type are dry cell and mercury cells.

B. Secondary cells :-

those which can be recharged by passing electric current through them and hence can be used over again.

Example of secondary cell are -

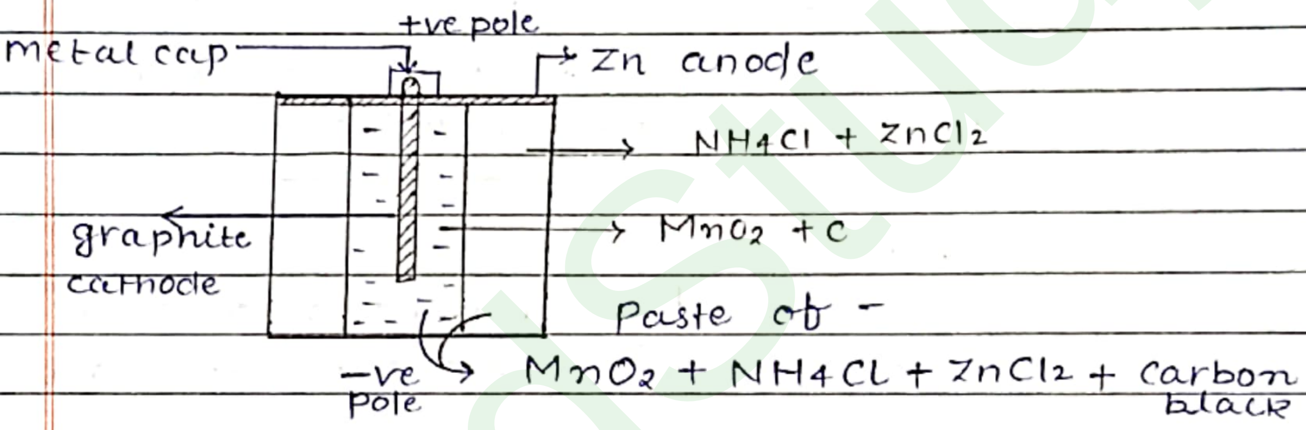
- Lead storage
- Ni - Cd cell
- Fuel cell.

↳ used in transistors and clock

A(i) Dry cell :-

→ compact form of Leclanche cell.

→ voltage range 1.25 V to 1.50 V



At anode :

$\underset{(s)}{Zn} \rightarrow \underset{(aq)}{Zn^{2+}} + 2e^-$

At cathode :

$\underset{(s)}{2MnO_2} + \underset{(aq)}{2NH_4^+} + 2e^- \rightarrow \underset{(s)}{Mn_2O_3} + \underset{(g)}{2NH_3} + H_2O$

Net cell reaction :-

$Zn + MnO_2 + NH_4^+ \rightarrow MnO(OH) + [Zn(NH_3)_4]^{2+}$

Note: NH_3 formed not liberated but combines rapidly with Zn^{2+} and Cl^- to form complex salt $[Zn(NH_3)_2Cl_2]$.

⌐ used in hearing aids and watches

(ii) Mercury cell :-

→ also called Ruben-Mallory cell or Button cell.

→ Voltage 1.35 V.

Anode - Zn (Hg)

Cathode - HgO + C

→ Electrolyte is paste of ~~HgO~~ HgO and KOH.

At cathode :

$Zn(Hg) + 2OH^- \longrightarrow ZnO + 2e^- + H_2O$

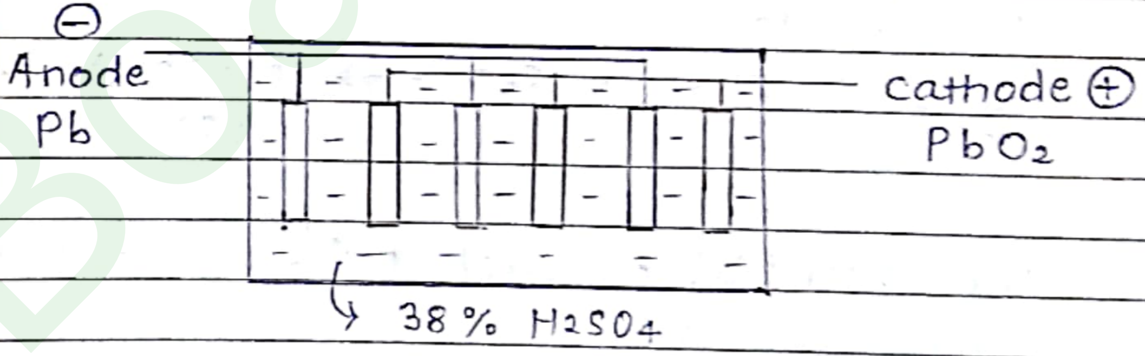
At anode :

$HgO + 2e^- + H_2O \longrightarrow Hg + 2OH^-$

Net cell reaction :

$Zn(Hg) + HgO \longrightarrow ZnO + Hg$

B(i) Lead storage battery :-



→ voltage 1.8 to 2.1 V

At anode [oxidation]

$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

At cathode [reduction]

$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$

Net cell reaction :

$Pb + PbO_2 + 2SO_4^{2-} + 4H^+ \rightarrow 2PbSO_4 + 2H_2O$

[Discharging] $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

[Charging] $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

(ii) Nicad cell or Nickel - Cadmium storage cell :-

It consist of -
Anode - Cd
Cathode - NiO_2 (nickel (IV) oxide)
Electrolyte - KOH

At anode :

$\underset{(s)}{Cd} + \underset{(aq)}{2OH^-} \longrightarrow \underset{(s)}{Cd(OH)_2} + 2e^-$

At cathode :

$\underset{(s)}{NiO_2} + 2H_2O + 2e^- \longrightarrow \underset{(s)}{Ni(OH)_2} + \underset{(aq)}{2OH^-}$

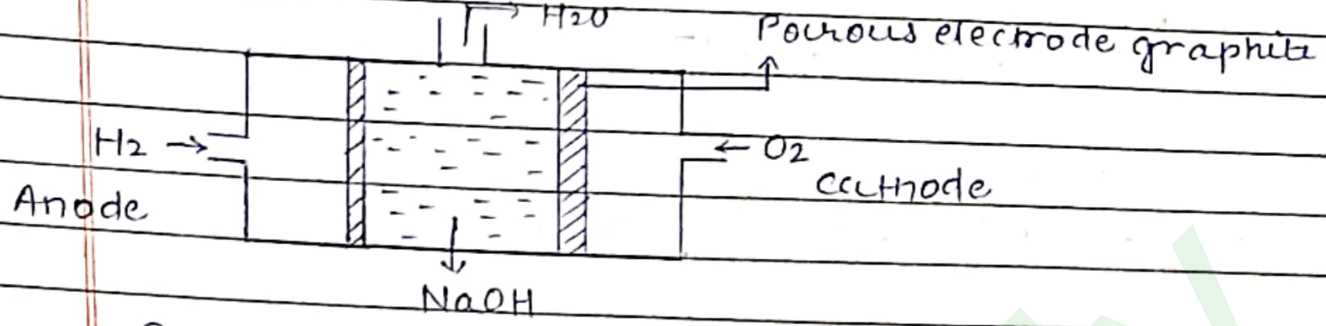
→ The potential of each Ni - Cd cell is 1.4 V approx.

Net cell reaction :

[Discharging] $Cd + 2NiO_2 + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$

[Charging] $Cd(OH)_2 + 2Ni(OH)_2 \longrightarrow Cd + 2NiO_2 + 2H_2O$

(iii) Fuel cells :-



Fuel cell are devices which convert the energy produced during combustion of fuels hydrogen methane, methanol etc. directly into electrical energy.

Such one cell is hydrogen - oxygen fuel cell.

→ Voltage 0.6 to 0.7

At anode :

$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

At cathode :

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Net cell reaction :-

$2H_2 + O_2 \longrightarrow 2H_2O$ + Energy.

→ Fuel cell do not cause any pollution.

→ Efficiency is higher than thermal plants.

CORROSION :-

The process of slowly eating away of metal due to attack of the atmospheric gases on the surface of the metal resulting into the formation of compounds such as oxide, sulphides, carbonates, sulphate etc. is called corrosion.

common example is - Rusting of iron.

Date :
Page

At anode -

$$2Fe \rightarrow Fe^{2+} + 4e^-$$

At cathode -

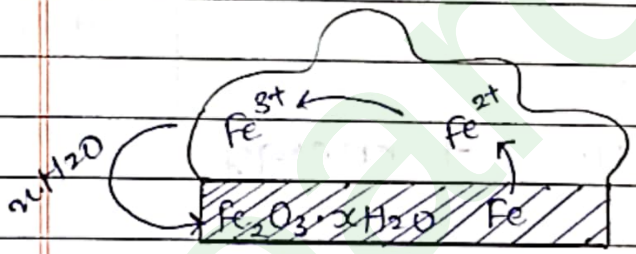
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Net cell reaction -

$$2Fe + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O$$

$$\begin{tikzcd} Fe^{2+} \arrow[r, "\text{oxidation}"] & Fe_2O_3 \arrow[d, "x\cdot H_2O"] \\ & \underbrace{Fe_2O_3\cdot xH_2O}_{\text{rust}} \end{tikzcd}$$

on surface of iron



Factors promoting corrosion

→ More active metals are readily corroded.

→ Presence of impurities enhances chance of corrosion.

→ Air and moisture accelerate corrosion.

→ Electrolyte increases rate of corrosion as, iron rusts faster than pure water.

Prevention from Corrosion

→ Barrier Protection : by applying paint, oil grease, electroplating etc.

→ Sacrificial protection :- means covering the surface with a layer of metal which is more active.

eg. Galvanisation - coating of more active metal which is Zn on iron.

→ Using anti-rust solution.

→ Electrical (cathodic) Protection, by connecting underground iron pipes with a more active metals like Mg with an electrical wire.