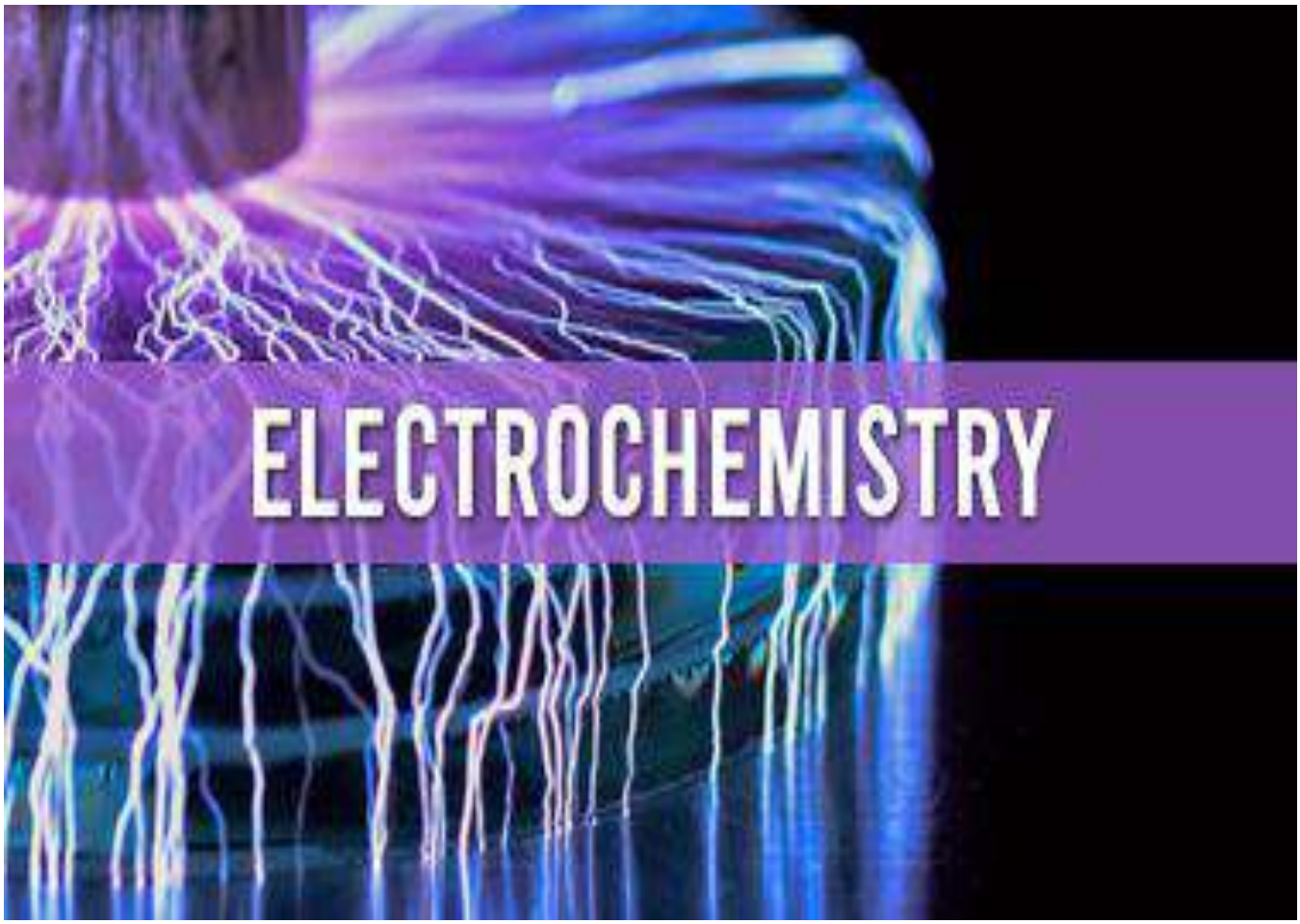
R.C.Patel College Of Engineering & Polytechnic, Shirpur

Department of Applied Science & Humanities

Course Title- Basic Science (Chemistry) **Course Code -** 311305

Department Name – Applied Science **Semester-** First -1K

Unit	Title	COs	Learning hours	R Level	U Level	A Level	Total Marks
2	Electrochemistry & Metal Corrosion ,Its Prevention	CO5	12	03	04	05	12



∘ Electrochemistry & Metal Corrosion, It's Prevention ∘

∘ **Electrolytes** -

An Electrolyte is a substance that produces ions when dissolved in water or in molten state and allows electricity to pass through it. (aq)

For e.g. Acids, bases & Electrovalent salts.

∘ Electrolytes are two types -

(1) Strong Electrolyte

(2) Weak Electrolyte

∘ **Strong Electrolyte** -

- The electrolytes which are completely ionized in it's aq. solution and have high degree of Ionization are known as Strong Electrolytes.

∘ For e.g. - Strong acids - H_2SO_4, HCl, HNO_3

Strong bases - $NaOH$, KOH

Salts - $NaCl$, KCl

∘ **Weak Electrolytes** -

- It is defined as the electrolyte which are incompletely ionized in it's aq. solution and have Low degree of Ionization are known as weak electrolyte.

∘ For e.g. - Weak acid - CH_3COOH, oxalic acid.

Weak base - NH_4OH, NH_3

Salts - $BaSO_4$, $Al(OH)_3$

∘ **Non-Electrolytes** -

- These are substance which in solution or fused State are non-conductor of Electricity.

∘ For e.g. Alcohol, petrol, oils, starch, sugar ~~are~~ etc.

Strong Electrolyte	Weak Electrolyte
∘ Electrolytes which are completely ionized in aq. are known as Strong Electrolytes	∘ Electrolytes which are partially ionized in aq. solution are known as Strong Electrolytes
∘ Large ~~Numeb~~ Number of ions produced (High degree of Ionization)	∘ Small Number of ions produced i.e. Low degree of Ionization.

• Their solution shows high conductivity • for e.g. - • H_2SO_4 HCl, HNO_3 (Strong Acids) • Strong bases - NaOH, KOH • Salts - NaCl, KCl	• Their solution shows Low conductivity. for e.g. - CH_3COOH, oxalic acid. (weak Acid), NH_4OH, NH_3 (Weak base) Salts - $BaSO_4$, $Al(OH)_3$

Ionization & Dissociation -

• Ionization - Process in which neutral molecules ~~fo~~ form ions when dissolved in water.
• occurs mainly in covalent ~~bo~~ compounds
• It is chemical change.
For e.g. $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

• Dissociation :- Process in which an ionic compound seperates into it's existing ions in water.
- occurs mainly in ionic compound.
- It is mainly physical change.
For e.g. $NaCl \longrightarrow Na^+ + Cl^-$

Ionization → Ions are formed
Dissociation → Ions are seperated

Electrolytic Cell or Voltmeter -

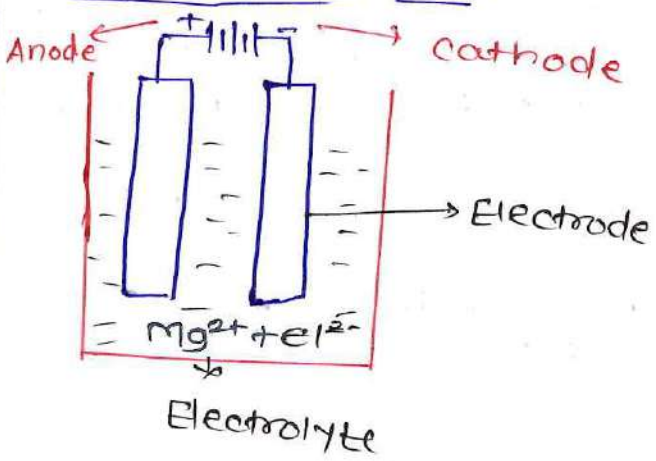
• An Electrolytic cell is device that uses electrical energy used to carry out chemical change.

(a) Battery - supplies Electrical energy

(b) Electrode - ~~Et~~ these are metalic or Non-Metallic rods, plates or foils immersed in an electrolyte. (electric current / ions carrier)
• Electrode acts as electron carries & also take part in chemical reaction called Active electrode
For e.g. Copper, silver etc.
• the electrode which simply acts as electrons carries are called inert electrode.
For e.g. - Platinum & graphite.

• Anode → Positive pole of battery
• Cathode → Negative pole OF battery

° Electrolytic cell :-



- oxidation at Anode +ve pole of Battery
- Reduction at cathode -ve pole of Battery

- **Reaction**

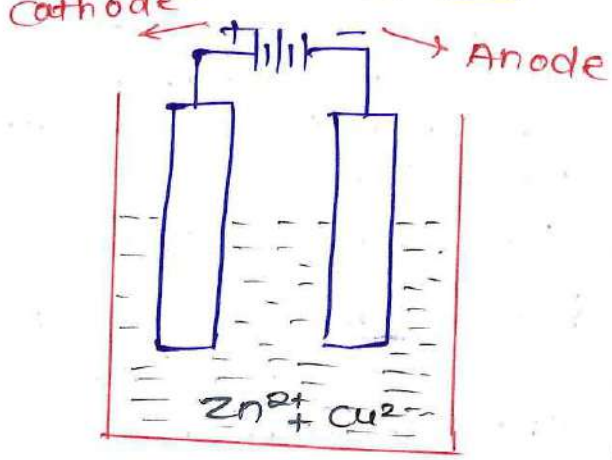
- At Anode -

$2Cl^- \longrightarrow Cl_2 + 2e^-s$ --- (oxidation)

- At cathode -

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

° Electrochemical cell -



- oxidation occurs at Anode - -ve pole of Battery
- Reduction occurs at cathode +ve pole of Battery

- **Reaction**

- At Anode -

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

- At cathode -

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

- **oxidation** - Loss of electrons
- **Reduction** - Gain of electrons

- **Electrochemical cell** -

The device that converts chemical energy into electrical energy through redox reaction.

- **Electrode Potential** :-

Tendency of metalic electrode to lose or gain electrons, when it immersed into it's own salt solution.

- **oxidation potential** -

the tendency of electrode to loses electrons & It's direct measure of it tendency to get oxidised is called oxidation potential.

For e.g. zinc (Zn) rod dipped into $ZnSO_4$ solution.

◦ Reduction potential -

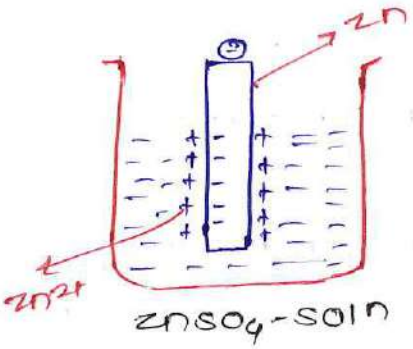
The tendency of electrode to gain electrons or accept electrons is direct measure of It's tendency to get reduced & is called Reduction potential

for e.g. - copper (Cu) rod in $CuSO_4$ solution,

* when metal Rod immersed in It's own salt solution then 2-Possibilities -

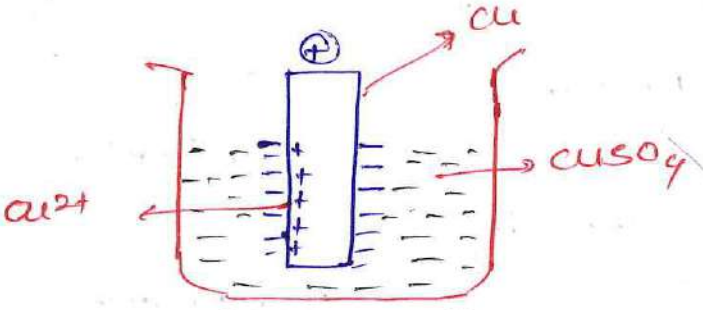
(I) Posibility - (I)

- the metal atoms present on the surface of the metal rod have tendency to pass into solution then loss equivalent number of electrons on the surface of metal rod the metal aquired -ve charges is called oxidation or de-electronation.



$ZnSO_4$-soln

De-electronation
(oxidation)



$CuSO_4$-soln

Electronation
(reduction)

(II) Posibility - (II)

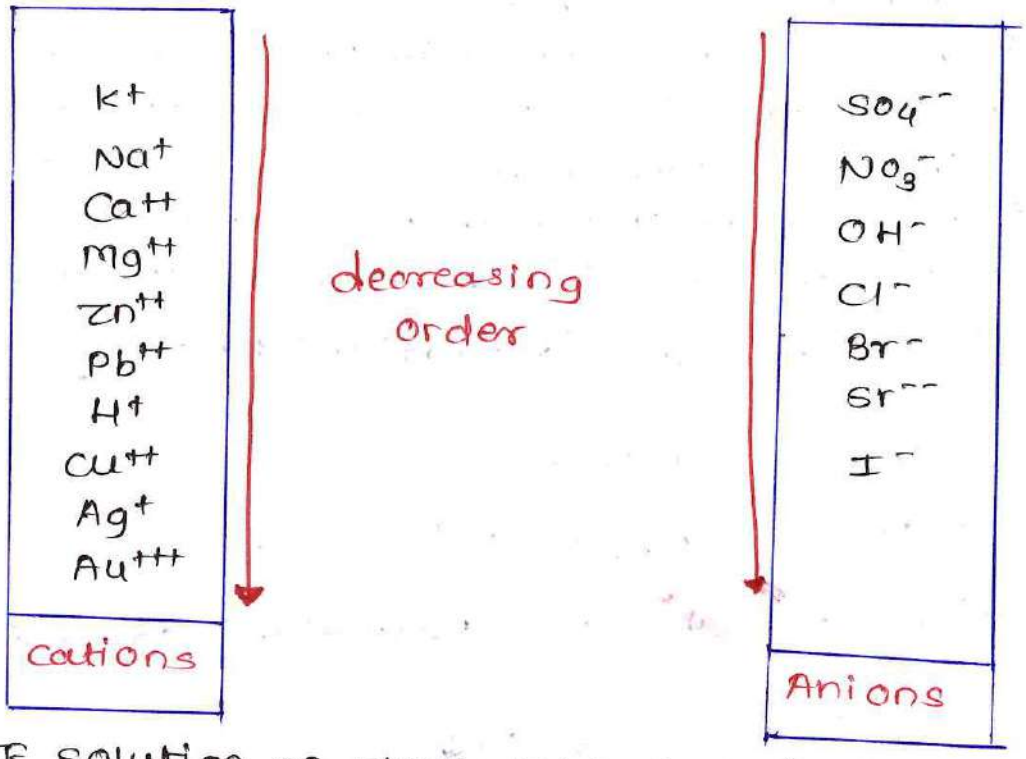
The positive metal ions present in the soln have tendency to accept electrons from metal rod the & get deposite on metal atoms then aquire +ve charge, therefore this reaction is called reduction reaction or electronation

* Electrochemical series of cations & Anions -

- cations & Anions are arranged in the order of their decreasing activity,
- more active metal readily form It's ion (cation) By loss of electron & such ion has tendency to accept electron.

∴ cation is difficulty discharged at the cathode.

• Electrochemical series of cations & Anion -

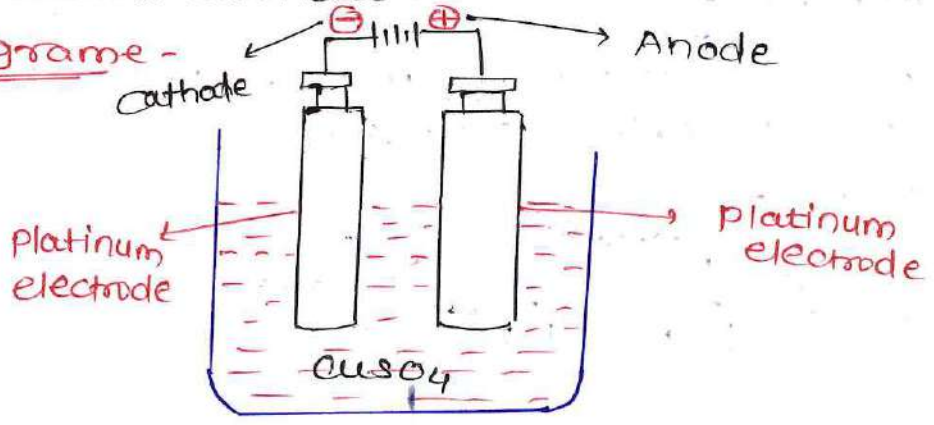


• IF solution of electrolyte contain two or more cations & Anion, then the ion which placed at the bottom of electrochemical series is preferably discharged at respective electrode during electrolysis.

(1) * Electrolysis of aq. copper sulphate solution ($CuSO_4$) using platinum electrode -

- Electrolysis - A process of chemical decomposition of the substance due to the passage of electric current.

- Diagrame -



• Ionisation - $CuSO_4$ solution ionized to $Cu^{2++} + SO_4^{--}$ ions

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

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

- $CuSO_4$ solution contain Cu^{++}, SO_4^{--}, H^+, OH^-

ions.

- According to electrochemical series Cu^{2+} ion are discharged at cathod in preference to H^+ ions & copper is deposited on cathode
- According to electrochemical series, OH^- ions are discharged at anode in preference to SO_4^{--} ions & oxygen gas is Librated at anode.

° Reaction at Anode - (oxidation) Anodic

$$2OH^- \longrightarrow 2OH + 2e^- \quad \text{(Primary reaction)}$$

$$4(OH) \longrightarrow 2H_2O + O_2\uparrow \quad \text{(secondary reaction)}$$

° Reaction at Cathode - (Reduction) Cathodic

$$Cu^{++} + 2e^- \longrightarrow Cu\downarrow$$

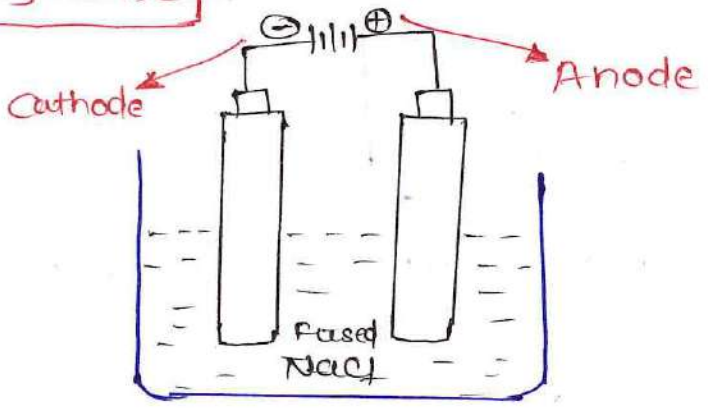
- Net Result -

① At cathode, Cu-metal is deposited
② At Anode, O_2-gas is evolved
③ In electrolytic cell, colourless, sulphuric acid is formed - $(2H^+ + SO_4 \longrightarrow H_2SO_4)$
∴ Blue colour of $CuSO_4$, becomes faint & finally turns to colourless after electrolysis.

② Example-2

- Electrolysis of fused (molten) NaCl - using carbon (graphite) electrodes

- Diagram



- Fused NaCl contains Na^+, Cl^- ions.
- At Cathode Na^+ ions discharged at & Na^+ is deposited
- At anode, Cl^- ions are discharged & Cl^-

gas librated.

- Ionisation - NaCl is Ionized to $Na^+ + Cl^-$

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

- Reaction at cathode -

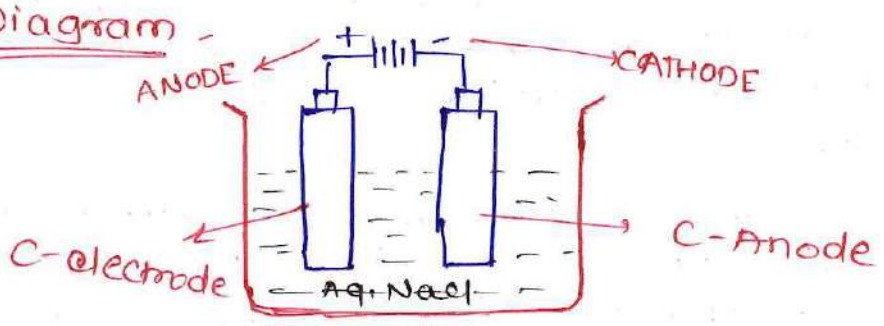
$$Na^+ + 1e^- \longrightarrow Na \downarrow$$

- Reaction at Anode -

$$2Cl^- \longrightarrow Cl_2 \uparrow + 2e^-$$

Electrolysis of aq. NaCl using Carbon electrode-

- Diagram -



- Contain Na^+, Cl^-, H^+, OH^- ions.
- According to electrochemical series, H^+ ions Are discharged at the electrochemical series, H^+ ions are discharged at the cathode in preference to Na^+ ions & H-gas librated at cathode.
- According to electrochemical series Cl^- ions are discharged at Anode to OH^- ions & Cl-gas librated at anode.

- Ionisation -

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

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

- Reaction at Cathode -

$$2H^+ + 2e^- \longrightarrow H_2$$

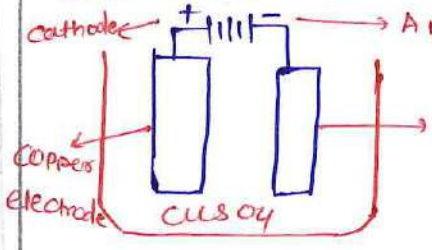
- Reaction at Anode -

$$2Cl^- \longrightarrow Cl_2 \uparrow + 2e^-$$

- Net Result -

- At Cathode - H-gas is librated
- At Anode - Cl-gas is librated
- In electrolytic cell, conc. of Na^+ & OH^- ions increases & NaOH is Formed

• Electrolysis of copper sulphate using copper Electrode -



- Ionisation -

$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$

- Reaction at cathode -

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

- Reaction at Anode -

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

- In these mechanism instead of sulphate or OH^- ion being oxidised, the copper metal of the anode oxidised itself & dissolved into the solution as Cu^{2+} ions

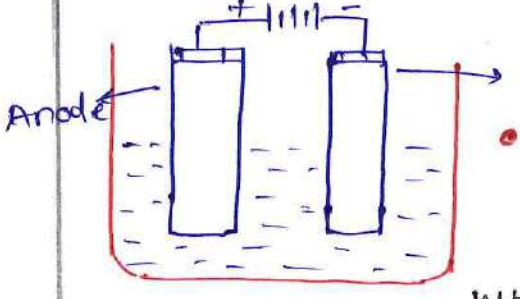
• **Observation** -

- the copper anode loses, mass & diminishesh in size while copper metal is deposited on the cathode & the $CuSO_4$ solution blue colour remain unchanged therefore this process used to purification of Cu.

Faraday's first Law & second Law -

① Faraday's first Law -

• Statement - the weight of the substance deposited or librated at respective electrode during electrolytesis is directly proportional to quantity of electricity passed through an electrolyte



• Mathematically -

$\therefore$ $\boxed{W \propto Q}$

Where, - W - weight of substance Librated or diposited

Q - quantity of electricity passed through Electrolyte.

But, $\boxed{Q = C \cdot t}$

C - current in Amperes

t - time in seconds.

∴ substitude value of Q in equation

$$\therefore \boxed{W = Z \times C \times t}$$

'Z' is constant, it is called as electrochemical equivalent (E.C.E) of substance in equation.

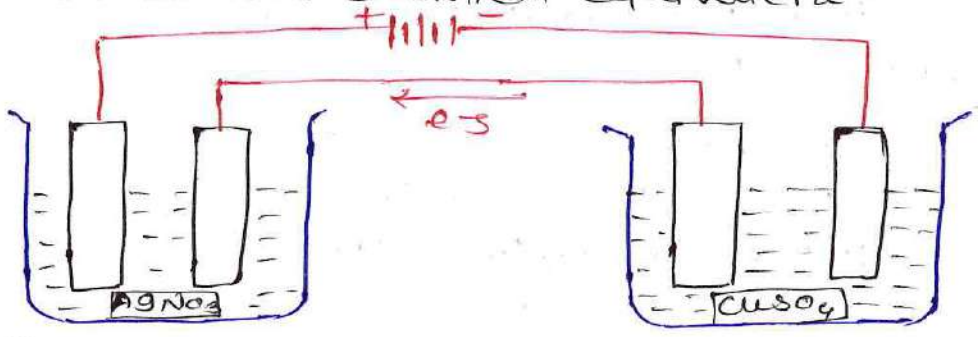
If C = 1A & t = 1 sec. then, $W = Z \times 1 \times 1$

$$\therefore \boxed{W = Z}$$

∴ Electrochemical equivalent (Z) is defined as, the weight of substance librated or deposited when current 1 A is passed 1 sec. through electrolyte.

Faraday's second law -

- **Statement** - When same quantity of electricity passed through different electrolytes arrange in series, then the amount of substance librated or diposited at resp. electrode is directly proportional to it's chemical equivalent.



- If same quantity of current passed through 2 electrolytes $CuSO_4$ & $AgNO_3$ arranged in series then (W_1) weight of the (Cu) copper & W_2-weight of silver (Ag) deposited, will be equal to their chemical equivalents of Cu & Ag resp.

$$\therefore \boxed{\frac{\text{weight of Cu deposited}}{\text{weight of Ag deposited}} = \frac{\text{C.E. of Cu}}{\text{C.E of Ag}}}$$

- C.E - Chemical equivalent / equivalent wt.

$$\therefore \boxed{\frac{W_{Cu}}{W_{Ag}} = \frac{E_{Cu}}{E_{Ag}}} \qquad \therefore \boxed{\frac{W_1}{W_2} = \frac{E_1}{E_2}}$$

⊛ Relation between C.E & E.C.E.

- **Faraday** - one faraday is the quantity of electricity required to deposite or librated one gm equivalent weight of Substance.

- Coulomb - the quantity of electricity that passed through circuit when current of 1A is passed through the circuit for second is called Coulomb.

∴ C.E = (equivalent weight) = 96,500 × E.C.E.

- Ampere - S.I Unit of electric current.

If represent the rate of flow of electric charge. 6.24×10^{18} e-s (1 Colowomb) passed through conducter in one second.

Problems -

(1) A current of 3A passing through silver Nitrate ($AgNO_3$) solution for 20 min, deposited 4.09 gms of silver, Nitrate solution fo what is the E.CE & C.E of silver.

⇒ According Faraday's First Law.

$W = z.C.t$

Given : current (C) = 3A

time (t) = 20 min = 20 × 60 = 1200 sec

Weight (W) = 4.09 gms.

Find - E.C.E = ?, CE = ?

solution - $W = z.C.t$

$4.09 = z \times 3 \times 20 \times 60$

$z = \frac{4.09}{3 \times 20 \times 60} = 0.001136$ gm/columbs

∴ C.E = 96500 × E.C.E = 96500 × 0.001136

CE = 109.24 gms

∴ Electrochemical equivalent (z) = 0.001136 gm/C and chemical equivalent (CE) = 109.24 gms.

(2) Calculate the time in second in which 0.3 gm of copper is librated from copper sulphate when a current of 0.5 Ampere is passed (Equivalent weight of Cu = 31.6 gm)

⇒ Given - W = 0.3 gms, t = ?

C = 0.5A, z = ?

C.E OF Cu = 31.6 gms.

ECE (Z) OF copper = $\frac{\text{Equivalent weight OF copper}}{96500}$

$\therefore Z = \frac{31.6}{96500} = 0.000327$ gm/C.

According to faraday's first Law,

$W = Z \cdot C \cdot t$

$= 0.000327 \times 0.5 \times t$

$0.3 = 0.000327 \times 0.5 \times t$

$\therefore t = \frac{0.3}{0.000327 \times 0.5}$

$t = 1834.862$ sec

(3) A given quantity OF electricity is passed through 2-cells containing $CuSO_4$ & $AgNO_3$ solution resp, IF 0.99 gm Ag & 0.29 gm OF Cu are deposited, Find equivalent weight OF Ag. (equivalent weight OF Cu = 31.6)

⇒ Weight OF Ag-deposit = 0.99 gm

weight OF Cu-deposit = 0.29 gm

Equivalent weight OF Cu = 31.6 gm

Equivalent weight OF Ag = ?

∴ By using Faraday's IInd Law:

$\frac{W_{Ag}}{W_{Cu}} = \frac{E_{Ag}}{E_{Cu}}$

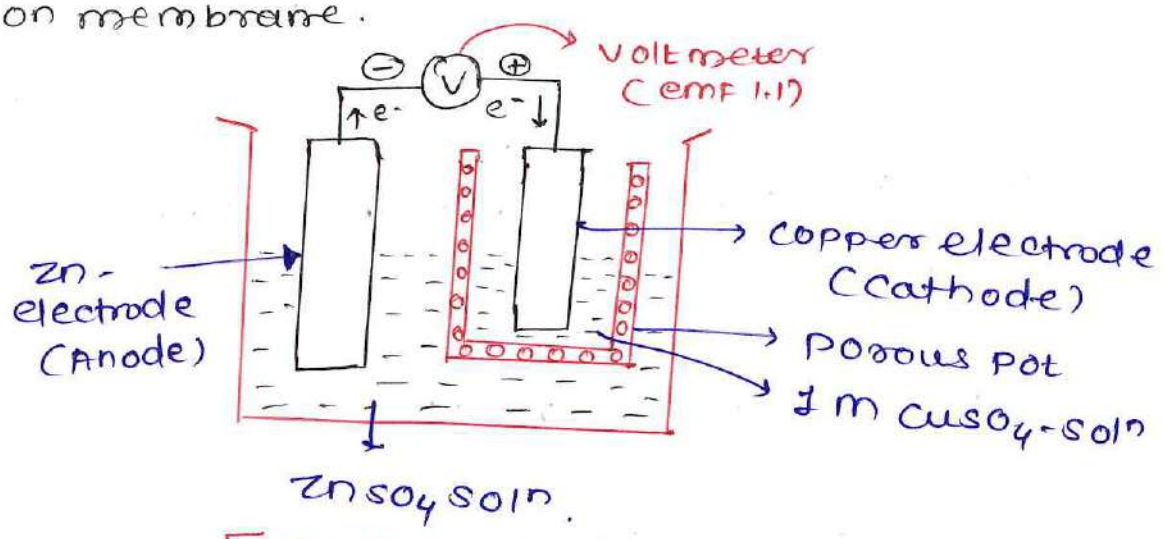
∴ Equivalent weight OF Ag-deposited $= \frac{0.99}{0.29} \times 31.6$

$= 107.87$ gm

Construction & working OF Daniel cell -

• The most common e.g. OF electrochemical or galvanic cell is Daniel cell.

It consis of zn electrode immersed in $ZnSO_4$ - solution & copper electrode dipped in copper sulphate ($CuSO_4$) solution Both electrolytes $ZnSO_4$ & $CuSO_4$ are seperated by porous partition membrane.



[Daniel cell]

- Because of High oxidation potential zn acts as anode & copper acts as Cathode.
- the emf developed is due to the reactions occuring at Cathode & Anode.
  - Anodic oxidation - $Zn \longrightarrow Zn^{2+} + 2e^-$
  - Cathodic reduction - $Cu^{2+} + 2e^- \longrightarrow Cu\downarrow$
- Copper ions in ~~these~~ $CuSO_4$ solution accepts the librated es, undergoes reduction & get deposited on Cathode.
- the surface atom of zinc rod pass into solution & undergoes corrosion.

Daniel cell with salt bridge -

The cell consist of two Half cells. the zn plate dipped in $ZnSO_4$ solution while the copper plate dipped in $CuSO_4$ solution.

- These plates are known as electrodes the soln in the two beakers are connected by an inverted U-tube called a salt bridge.
- A salt Bridge connected solutions in the two Half cells & complete the cell circuit. salt brige keeps the solution in the two Half cells electrically neutral.
- oxidation Half cells - Zn-atom $\longrightarrow Zn^{2+}$

reduction Half cells - Cu^{+2} atom $\longrightarrow$ Cu

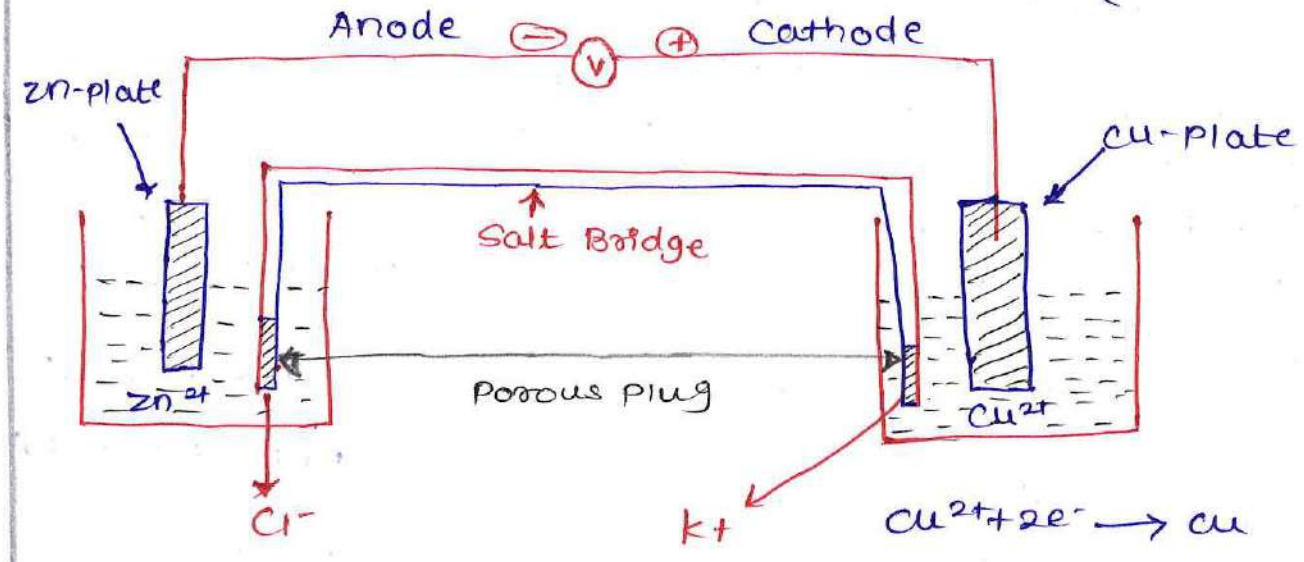
∴ Zn^{2+} ions around Anode prevents flow of e's from Cu e⁻s & cells stop working.

∴ accumulation of 2-Half cells prevented by using salt bridge. because of sufficient No. of Cl^- ions migrate from the salt bridge to one Half cell & K^+ ions migrate ~~bridge to one Half cell from~~ another Half cells to maintain neutral.

∴ $Zn(s) \longrightarrow Zn^{+2} + 2e^-s$ ... (Oxidⁿ Half cell rean)

$Cu^{+2} + 2e^- \longrightarrow Cu(s)$ ... (Redⁿ Half cell rean)

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



aq. $Zn \longrightarrow Zn^{2+} + 2e^-s$

Application of Electrolysis -

(1) Electrorefining of copper

It is process of obtaining extrapure metal from impure metal by using electric current.

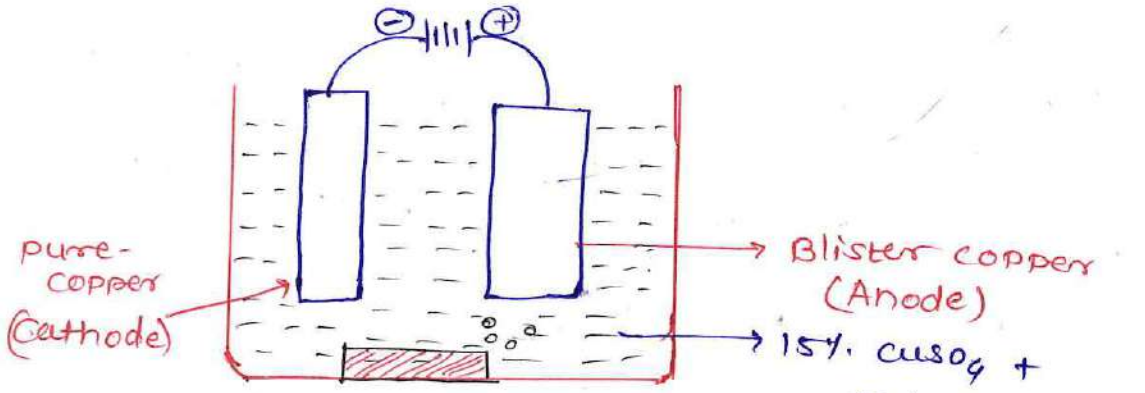
For e.g. **Electrorefining of blister copper** -

- Blister copper contain 3-5% impurities of active metal like zinc, iron, nickel & passive metal like Pt, gold, antimony, silver.

- **Process :-**

(1) The process is carried out in large tank, the thick block of blister copper is connected to anode

and thin wire of pure copper is connected to the cathode. mixture of 15% $CuSO_4$ & 5-10% H_2SO_4 is used in electrolyte.



(Process of electrorefining)

(2) A direct current of low voltage passed through electrolyte, at this voltage, impurities of more active metals pass into solution in the ~~form~~ form of ions & less active metals like Ag, Au, Pt gets settle down at the bottom forming 'anode mud' from which they are extracted.

(3) At proper voltage only Cu^{+2} ions are discharged at cathode, undergoes reduction & get deposit on on cathode.

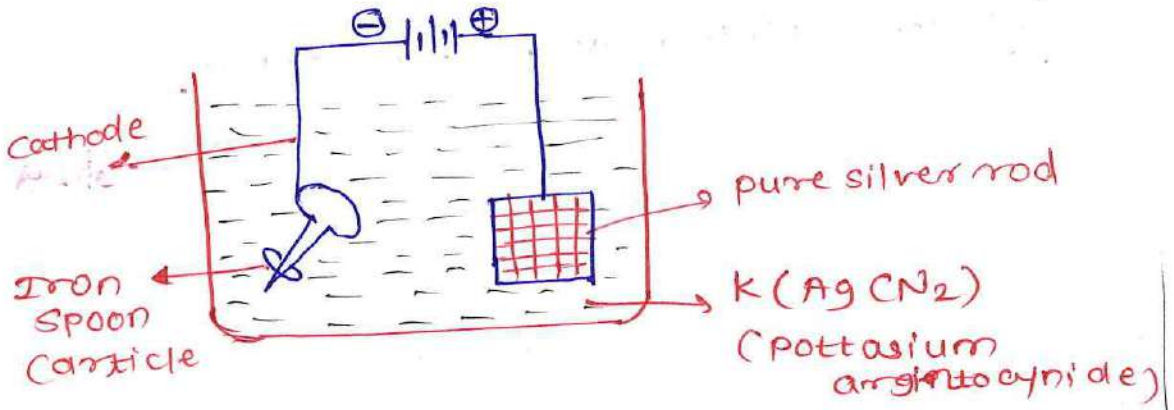
$$Cu^{+2} + 2e^- \longrightarrow Cu\downarrow \quad \text{---(Cathodic redn}$$

$$Cu \longrightarrow Cu^{2+} + 2e^- \quad \text{--(Anodic oxidn}$$

∴ 99.99% pure copper is obtained by this process.

Electroplating :- "It is process of coating of superior metal on inferior metal by electric current is called "electroplating"

For e.g. **Silver plating**



• process -

(1) Article is electroplated is clean by using alkali, acid & finally with water to remove impurities present on the surface of article.

(2) Cleaned Article or spoon is connected to negative terminal of the battery (cathode) pure silver rod is connected to the positive terminal of battery (Anode)

(3) Both cathode & Anode are immersed in pottasium argentocynide solution which acts as an electrolyte.

(4) Dissociation reaction of $K[Ag(CN)_2]$ is follows -

$$K[Ag(CN)_2] \longrightarrow K^+ + [Ag(CN)_2]^-$$

$$\downarrow$$

$$Ag^+ + 2CN^-$$

After passing electric current Ag^+ ions from electrolyte gets deposite on iron spoon & undergoes reduction.

• Cathodic reduction :-

$$Ag^+ + e^- \longrightarrow Ag \downarrow$$

at the same time surface silver atoms at anode undergoes oxidation & pass into solution.

• Anodic oxidation :-

$$Ag \longrightarrow Ag^+ + 1e^-s$$

Here, Coating of silver metal is obtained on iron spoon, & more active K^+ & H^+ ions remain in the solution as they required very High voltage for discharge.

Corrosion

Corrosion is defined as "Destruction of metal through chemical or electrochemical action (Enviornment & surrounding) starting from It's surface"

• There are mainly two Types -

(1) Atmospheric Corrosion / Direct chemical Corrosion or Dry Corrosion

(2) Immersed corrosion / Electrochemical Corrosion or wet corrosion.

① Dry / Direct chemical corrosion / Atmospheric corrosion -

- This type of corrosion occurs when metal surface come in contact directly with atmospheric gases like oxygen, halogen, Hydrogen sulphide, carbon-dioxide, sulphur dioxide & Nitrogen.
- metal surfaces are attache attacked by gases present in surrounding medium & get coated with corresponding compounds like oxides, sulphides, & basic carbonates.
- Such type of corrosion brought about by atmospheric condition due to oxygen gas is called 'atmospheric corrosion'.
- There are 2-types of Atmospheric corrosion -
  1. Corrosion due to oxygen - oxidation Corrosion
  2. Corrosion due to other gases - S, Cl etc.
  3. Liquid metal corrosion - attack by Liquid metals at high temperatures.

① Corrosion due to oxygen -

Corrosion due to oxygen is called oxidation corrosion. Based on the nature of the oxide film formed on the metal surface, it is classified into 3-types -

① Stable oxide film corrosion -

- The oxide layer formed is compact, adherent (tightly) & Non-porous.
- It protects the underlying metal from further oxidation
- Corrosion rate becomes very slow.

For e.g. Aluminium oxide on Al & Cro on Cr.

② Unstable oxide film corrosion -

- The oxide formed is unstable & decomposes back into metal & oxygen
- No protective film is produced
- Continues corrosion occurs.

For e.g. silver oxide on silver (at elevated temp.)

③ Volatile oxide film corrosion -

- The oxide formed is volatile & Evaporates from the surface
- Fresh metal continously exposed to oxygen
- corrosion proceeds rapidly.

For e.g. Molybdenum Trioxide formed on molybdenum at High temperatures.

- Stable oxide film
  - → Porous oxide film
  - → Non-Porous oxide film

(I) Porous oxide film - (Non Protective oxide film)

- Alkali & Alkaline earth metals on oxidation reaction produce metal oxide having smaller volm than the metal. & Formation of porous oxide film - Due to porous nature oxygen gets penetrate through pores & destroys bulk metal & this process of corrosion is rapid & continuous.

for e.g. Li, Na, Mg, K.

(II) Non-Porous oxide film (Protective oxide film):

- the metal like Aluminium (Al) forms oxide film having greater volume than the corresponding metal. this type of oxide film is smooth, continuous & Non-porous. This Non-porous oxide film acts as a protective layer & restricts further corrosion of bulk metal.

For e.g. Al (Aluminium), Cr (Chromium), Cu (Copper)

Mechanism of Atmospheric Corrosion -

- Atmospheric oxygen gas is responsible for oxidation corrosion.

- Mechanism of oxide film formation involve following steps -

1) When metal surface is exposed to atmospheric oxygen gas, it loses it's valence electrons & undergoes oxidation reaction

a) $M \longrightarrow M^{2+} + 2e^-$ ---- oxidation Reaction.

ii) Atmospheric oxygen gas accepts these electro-ns undergo reduction reaction.

b) $\frac{1}{2} O_2 + 2e^- \longrightarrow O^{2-}$ --- reduction Reaction.

Combining (a) + (b), we will get net cell reaction

∴ Net cell Reaction -

$$M + \frac{1}{2} O_2 \longrightarrow \underbrace{M^{2+} + O^{2-}}_{MO}$$

MO (Metal oxide film).

Wet corrosion :-

Defination - "The corrosion which brought about through ionic reactions when two disimilar metals are in contact with each other in presence of conducting medium is called as electrochemical or immersed or wet corrosion"

- Immersed corrosion takes place by formation of following types of cell-
  - (a) Galvanic cells.
  - (b) Concentration cells.

(a) Galvanic cells - when two dissimilar metals are in contact with each other in presence of Liquid conducting medium or moist air

(b) concentration cells - when single metals is in contact with different atmospheric condition.

Mechanism of wet corrosion -

(a) Hydrogen Evalution Mechanism [Galvanic cell action]

i) For example, a steel tank containing acidic industrial waste with small piece of copper scrap is in contact with it.

a) $Fe \longrightarrow Fe^{+2} + 2e^-$ ---oxidation Rean.

- water droplet accepts liberated electrons & undergoes reduction.

b) $2H_2O + O_2 + 4e^- \longrightarrow 4(OH^-)$ ---- Red^n rean

Fe^{2+} ions & OH^- ions combine to form ferrous Hydroxide.

c) $Fe^{2+} + 2(OH^-) \longrightarrow Fe(OH)_2$ -- ferrous Hydroxide.

d) In presence of oxygen ferrous ~~oxide~~ Hydroxide undergoes further oxidation to form ferric Hydroxide, followed by decomposition to get ferric oxide, which is called yellow rust. $4Fe(OH)_2 + 2H_2O + O_2 \longrightarrow 4Fe(OH)_3$

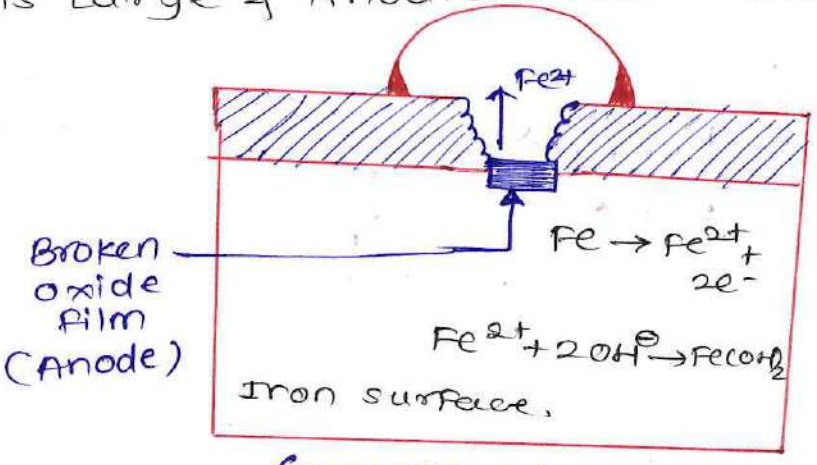
Ferric oxide.

↓ decomposition

$Fe_2O_3 \cdot H_2O$

yellow rust

- In this type cathodic area is Large & Anodic area is small



(oxygen absorption mechanism)

Factors Affecting the rate of corrosion -

(I) Factors Related to the metal

(1) Position in the electrochemical series.

- Metals Higher in the series (more reactive) Corrode more easily than less reactive metal.

(2) Purity of the metal -

- Impurities create tiny galvanic cells on the metal surface, increasing corrosion.

ii) In presence of acidic conducting medium piece of copper acts as cathode & steel tank as anode.

∴ Anode undergoes oxidation reaction with Libration of e⁻s a) $Fe \longrightarrow Fe^{2+} + 2e^{\ominus}$ ..(oxidation)

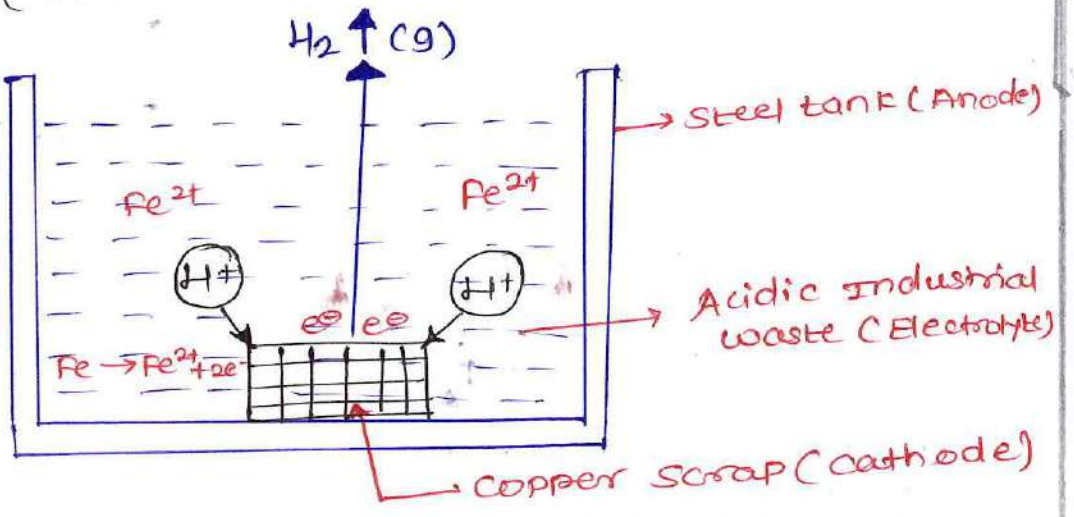
iii) Librated electrons flow from anode to cathode through metal Hydrogen ions (H^+) from electro-lyte accepts these liberated electrons & undergoes reduction reaction with Liberation H-gas.

b) $2H^+ + 2e^{\ominus} \longrightarrow H_2\uparrow$ (Reduction)

∴ Net reaction is -

c) $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2\uparrow$

iv) In this type of corrosion cathodic area is small & Anodic area is large.



Hydrogen liberation mechanism

(b) Oxygen Absorption mechanism (concentration cell action) -

- For e.g. rusting of iron in Neutral aq. solution in presence of atmospheric oxygen, when a drop of water is resting on an iron or steel surface.
- Usually iron surface is coated with a thin film of iron oxide. If the film develops a crack, ~~presence~~ acts as anode & remaining iron oxide film acts as cathode.
- The surface metal atom of anode (Fe) undergoes oxidation with liberation of e⁻s

(3) Nature of the oxide film
- Stable, Non-porous oxide layer (e.g. aluminium) protects the metal
- Porous oxide layer (e.g. iron rust) allow continued corrosion.

(4) Surface area of Anode & cathode.
- A small anodic area with cathodic area result in rapid corrosion.

(5) Physical State of metal
- Cold-worked or stressed metals corrode faster than unstressed metals.

(2) Factors Related To environment -

(1) Moisture (Humidity) -

Higher Humidity ↑ Increase corrosion

(2) Temperature - Temperature ↑ corrosion ↑

(3) pH of Medium - Acidic soln ↑ corrosion

(4) Presence of Electrolytes, Dissolved oxygen & corrosive Gases - Corrosion increases due to More oxygen, corrosive Gases Like SO_2, H_2S (Hydrogen sulphide) & CO_2.

Corrosion control :-

(1) Modification of Environment -

The corrosion of the metal can be reduced by modifying the environment by using following ways
(1) Removal of Harmful corrosion stimulants
(2) Use of corrosion inhibitors

(1) Removal of Harmful Corrosion Stimulants

- Alkaline Neutralization - Prevention of corrosion because of acidic environment is done by using neutralizers like NH_3, Lime etc. in vapour or liquid form.
- Dehumidification - Moisture or Humidity in atmosphere is one of the important factor which is responsible

for corrosion dehumidication is done by using silica gel to prevent corrosion due to moisture.

(II) Use of corrosion inhibitors:

- Inhibitors are the organic or inorganic substances, which added in small quantity to the corrosive environment effectively minimises the corrosion of metal.

- corrosion inhibitors are following Types -

(1) Anodic inhibitors - e.g. Phosphates, Chromates

(2) Cathodic inhibitors - e.g. Amines, Urea

(3) Vapour phase inhibitors - e.g. Dichlorohexylammonium nitrate.

(B) Use of Protective coatings

(I) Use of Less active metal for Coating (Tinning)

(II) Use of more active metal for Coating (Galvanizing)

(I) Use of Less active metal for coating (Tinning)

- In this process tin is used as coating metal. "Tinning is the process of coating steel sheets with thin & uniform coat of thin to prevent it from corrosion."

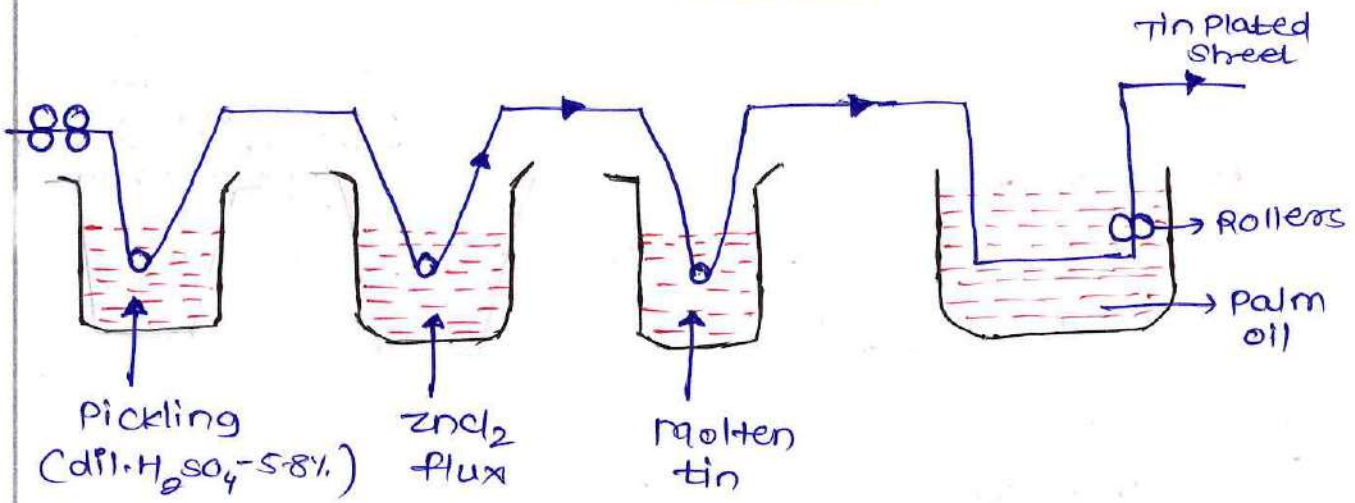
- Tin is low M.P. metal (M.P - 232°C), less electro-positive than iron. & therefore it is more resistant to chemical attack.

- process -

- To remove oxide film & impurities present on the surface of steel sheet, it is cleaned by dil. H_2SO_4.
- cleaned sheet is passed through bath containing molten flux of Zinc oxide | Zinc Chloride which helps the molten metal to get adhered to the sheet.
- then steel sheet passed through tank of molten tin & prevent by palm oil from oxidation of Hot tin coated surface.
- To remove excess of tin & to get uniform coating the sheet is passed through a series of Hot

rollers.

- Tinning process Diagram -



- Advantages of Tinning -

(1) Corrosion resistance - protect the base metal from rust & environmental damage.

(2) Non toxic surface - used for coating steel container which are used to store foodstuff as tin resistant action organic acid & water, thus avoids food poisoning.

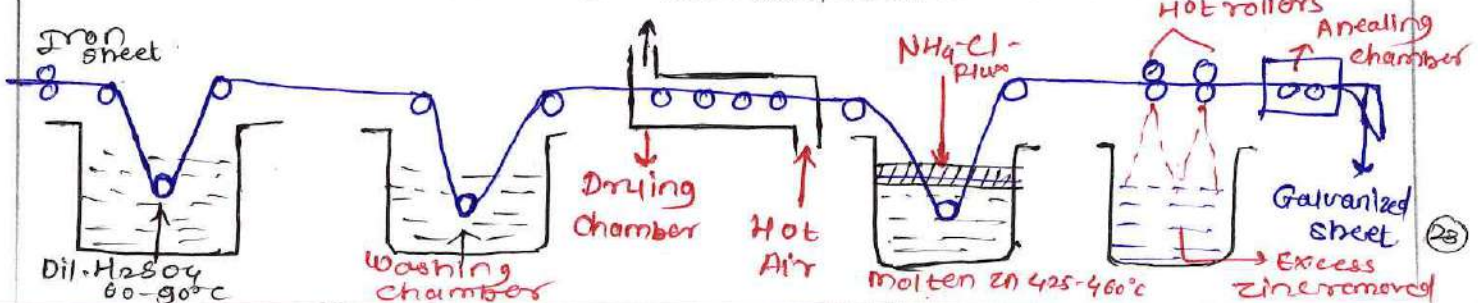
(3) Reduced wear & friction - tin coating can provide smoother surface & reduce friction betn parts.

Use of more active metal Coating (Galvanizing) -

"The process of coating iron or steel sheet with thin coat of zinc by hot dipping process to prevent corrosion is called as Galvanizing."

- Process -

- The iron sheet to be galvanized is first cleaned with H_2SO_4 then washe in washing bath & then dried in drying chamber.
- clean iron sheet is then dipped in the bath of molten zinc at 425-460°C which is covered with NH_4Cl flux to prevent atmospheric oxidation.



- To remove excess of zinc, coated sheet is passed through pair of rollers where, uniform coating of zinc is obtained.
- Coated sheet is finally annealed at 650°c temp. & slowly cooled.

Annealing - Alters material physical & chemical properties increase ductility & reduce Hardness.

- **Advantages**

- Even protective zinc coating is broken, iron is protected because Zn is more electropositive than iron & therefore does not allow iron to pass into the solution.

- **Disadvantages**

- Galvanised containers are not used to store food stuffs because zinc gets dissolved in dil. H_2SO_4 acids forming Hazardous zinc compounds which are Harmful to health.

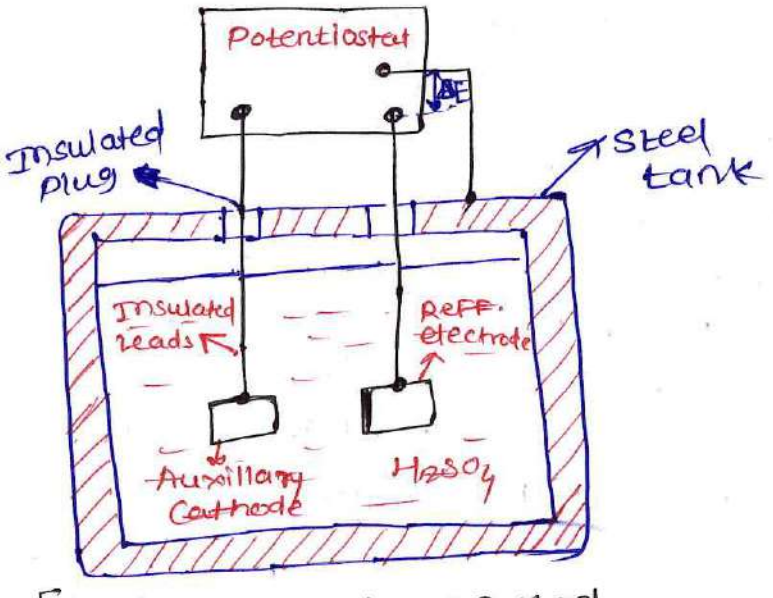
Galvanizing	Tinning
① It is process of coating iron or steel with a layer of Zn.	① It is process of coating iron or steel with layer of Tin.
② Metal used zinc (Zn)	② Metal used Tin (Sn)
③ Galvanized containers are not used to store food stuffs. Zinc	③ Tinned containers are used to store food stuffs.
④ Zinc is more reactive than iron, so it corrodes first & protects the iron even if the coating is scratched	④ Tin is less reactive than iron; If the coating is damaged, iron may rust faster.
⑤ Uses - Roofing sheets, water pipes, fences, transmission towers.	⑤ Uses - Food cans, kitchen utensils, containers for storing food.
⑥ Galvanizing cost is cheaper.	⑥ Tinning cost is more expensive.

Anodic Protection (AP)

- Anodic protection is technique to control the corrosion of metal surface by making it the Anode of an electrochemical cell & controlling the electrode potential zone where the metal is passive
- To anodically protect the structure, potentiostat is required.

• Process

- anodic protection is based on formation of protective film on metals by externally applied anodic currents.
- It appears that the rate application of anodic current to structure should tend to increase the dissolution rate of metal & decrease the rate of Hydrogen evalution,
- If carefully controlled the anodic currents are applied to these materials they are passivated & the rate of metal dissolution is decreased,



[Anodic protection of steel storage tank containing H_2SO_4]

(1) The potentiostat has 3-terminals, one is connected to the tank or structure to be protected
(2) second terminal is connected to Auxilliary cathode & third terminal is connected to the reff. electrode.

- Actualy potentiostat maintains constant potential between structure to be protected & reff. electrode, resulting to decreases in corrosion rate.

Cathodic protection -

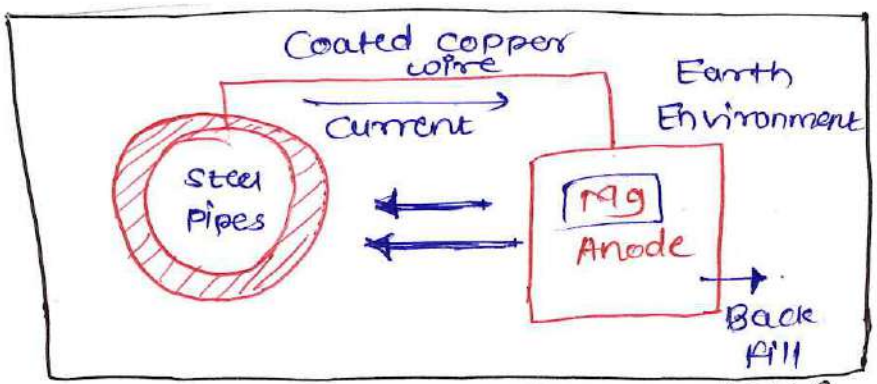
- "The reduction or prevention of corrosion by making metalic structure as cathode in electrolytic cell is called cathodic protection"

- Methods of applying cathodic protection to metalic structure -

(I) sacrificial anodic protection (Galvanic Protection)
(II) Impressed current Cathodic protection.

(I) sacrifical anodic protection method -

- In these method, metalic structure connected to more anodic metal.
- Hence, corrosion concentrated as active metal only and active metal gets corroded slowly.
- The article protected is connected to more active metal by using insulating wire, it is called 'sacrifical Anode'. To increase electrical contact sacrifical anode is kept in back fill (Coal + NaCl).
- Metals commonly used as sacrifical anodes are Mg, Zn, Al. & their alloys.
- Sacrifical Anode is consumed completely, it is replaced by fresh piece.
- these method is used in industry to protect underground pipelines, underground cables, ship hulls & hot water tank.



protection of underground pipe with Mg-anode.

Choice of material : using pure metal & using metal alloys :

- selection of the right type material is the main factor for corrosion control

- **Using pure metal** –

-Noble or inert metals are most immune to corrosion but they cannot be used for general purpose they are costly. next option is use purest possible metal, which is done by using refining process. pure metal resist the process of corrosi-on, refining process is used to get extra pure metal & to minimise corrosion.

- **Using metal Alloys :**

-the metals can be made corrosion resistant by alloying them with suitable alloying elements. for e.g. Steel becomes resistant to corrosion on addition of Cr, Ni, elements.

Difference between primary & secondary cell :

Primary cell	Secondary cell
① Primary cells are Non-rechargeable cells.	① secondary cells are rechargeable cells.
② The cell reaction is irreversible	② The cell reaction is reversible.
③ once the active components are used up, they cannot be reused	③ Electrical energy is stored in the form of chemical energy hence they are also called as storage cells.
④ They have short life.	④ They have Long life.
⑤ It's cost it low.	⑤ It's cost is High
⑥ e.g. Dry cell	⑥ e.g. Ni-Cd cell.

Electrochemical cell	Electrolytic cell.
① It is device which converts chemical energy into electrical energy.	① It is a device which converts electrical energy into chemical energy.
② spontaneous chemical reaction is used to generate electricity	② Non-spontaneous chemical reaction is carried out by using electric current
③ In this, cathode is the positive terminal & anode is the negative terminal of the battery	③ In this, cathode is the negative terminal & anode is the positive terminal of the battery
④ e.g. : Galvanic cell, Daniel cell.	④ e.g.: Electroplating, Electrolysis of $CuSO_4$,

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Ms. S.N. Patil
Mrs. M.R. Patil

[Question Bank]

Unit -2] Electro Chemistry & Metal Corrosion, It's Prevention

Q.1] Define - Electrolyte & Write It's types.

Q.2] Distinguish strong Electrolyte and weak Electrolyte.

Q.3] Define 1] Electrode potential 2] Oxidation potential
3] Reduction potential

Q.4] Write the mechanism of aq. NaCl using carbon Electrode.

Q.5] State Faraday's 1st Law & 2nd Law.

Q.6] Show the relation between C.E and E.C.E.

Q.7] Write the construction and working of Daniel cell

Q.8] Define Electroplating and Explain it?

Q.9] What is Corrosion & Write their types?

Q.10] Explain the mechanism of wet corrosion?

Q.11] Difference between Primary cell and secondary cell?

Q.12] State factors affecting on the ~~wet~~ corrosion?

Q.13] Explain the corrosion control by using more active metal for coating i.e. Galvanising?

Q.14] Distinguish Galvanisig and Tinning?

Q.15] ~~State~~ Define Sacrificial Anode & Explain the term sacrificial Anode(Aniodic protection).

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