

DR. A.P.J. ABDUL KALAM TECHNICAL UNIVERSITY, LUCKNOW



**ENGINEERING- CHEMISTRY (BAS- 102/ 202)
B. TECH. I YEAR**



COURSE OUTCOMES

CO- 1	Students will be able to explain the formation and stability of homo and hetero di atomic molecules. They will understand the concept of liquid crystals and nanomaterials.
CO-2	Students will be able to apply basic concept of spectroscopy to identify various molecular structures.
CO- 3	Students will be able to apply the concept of Nernst equation, Gibbs Helmholtz equation, EMF and thermodynamic functions to solve various problems based on electrochemistry. They will be able to identify the causes of corrosion and best methods to reduce it as well as to understand the phase rule and apply it to the water system.
CO 4	Students will be able to analyze water sample for its type and amount of hardness. They will be able to analyze coal sample qualitatively and quantitatively.
CO- 5	Students will be able understand the importance of polymers in our day to day life. They will be able to understand how various organic compounds can be synthesized using Grignard's Reagent.





ELECTROCHEMISTRY, CORROSION AND PHASE RULE



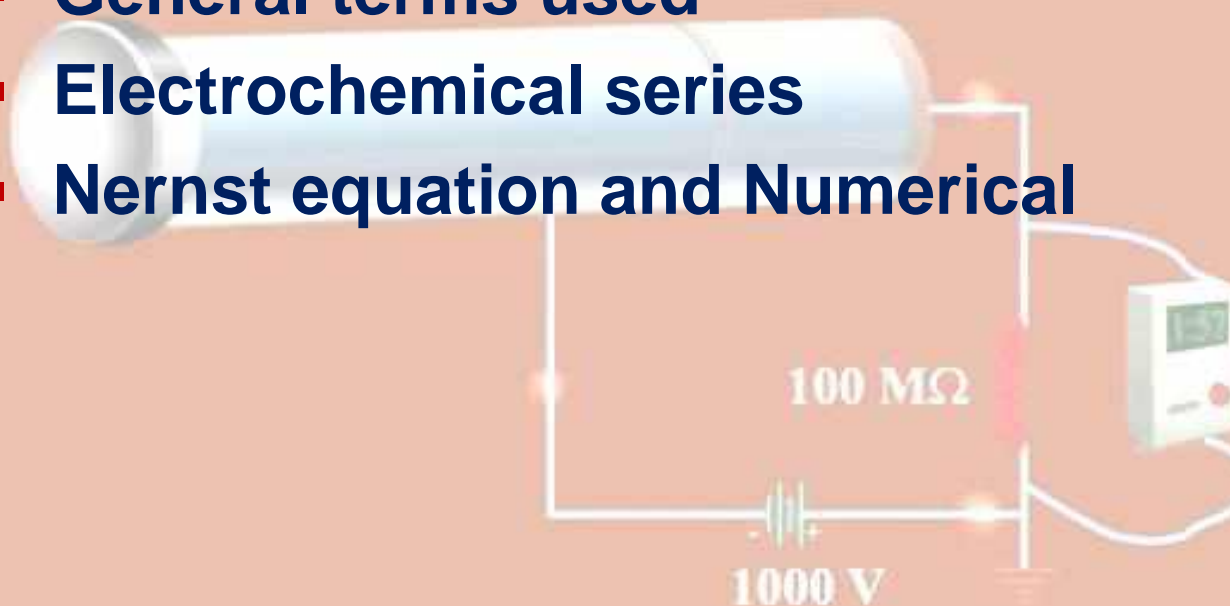
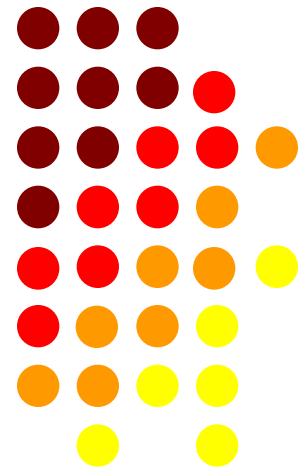
Contents

- Basic concepts of electrochemistry, general terms used, electrochemical series, Nernst equation and numericals.
- Gibb's Helmholtz equation, relation between ΔH and ΔS and with E_{cell} and numericals.
- Batteries and their types, Lead acid storage battery
- Definition and cause of corrosion, factors affecting it, electrochemical theory of corrosion.
- Prevention of corrosion and types of corrosion.
- Corrosion issues in specific industries (Power generation, Chemical processing industry, Oil & gas industry and Pulp & paper industries).
- Cement; Constituents, manufacturing, hardening and setting, deterioration of cement, Plaster of Paris (POP).



LECTURE - 20

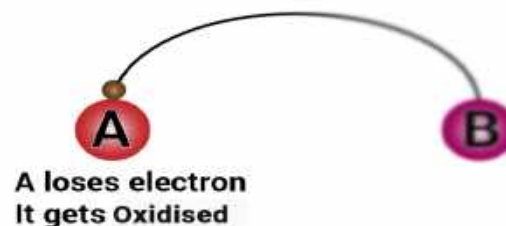
- Basic concepts of electrochemistry
- General terms used
- Electrochemical series
- Nernst equation and Numerical



Basic Concepts Of Electrochemistry

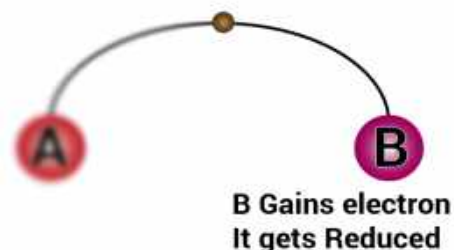
Oxidation:

- Addition Of O_2
- Loss of e^-
- Increase in Oxidation No.

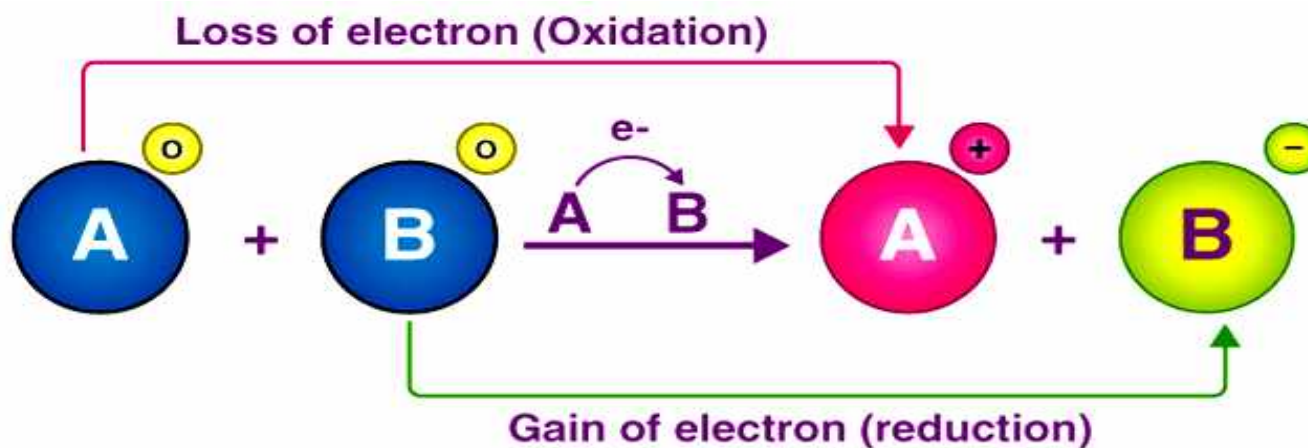


Reduction:

- Removal Of O_2
- Addition of e^-
- Decrease in Oxidation No.



OXIDATION	REDUCTION
Addition of oxygen	Addition of hydrogen
Loss of electron (s) by any species	Gain of electron (s) by any species
Increase in oxidation number of the element in given substance	Decrease in oxidation number of the element in given substance



IF	Meaning
$E^{\circ}_{\text{Cu} \text{Cu}^{2+}} = - 0.34\text{V}$ <p style="text-align: center;">or</p> $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^{-}$ $E^{\circ} = - 0.34\text{V}$	Oxidation Potential (OP) is given.
$E^{\circ}_{\text{Cu}^{2+} \text{Cu}} = +0.34\text{V}$ <p style="text-align: center;">or</p> $\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}$ $E^{\circ} = +0.34\text{V}$	Reduction Potential (RP) is given.

OP and RP of a species are equal in Magnitude but Opposite in sign.

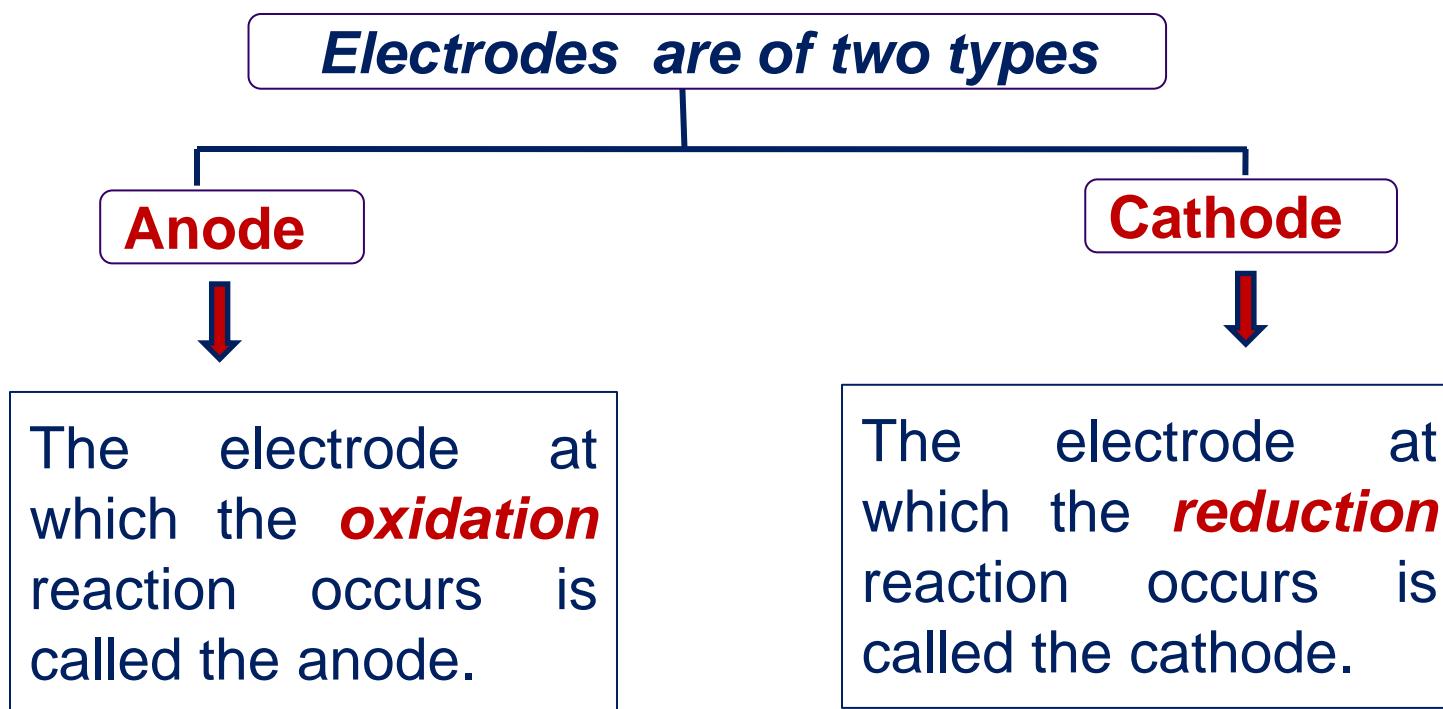
$$\therefore E^{\circ}_{\text{Cu} | \text{Cu}^{2+}} = - (E^{\circ}_{\text{Cu}^{2+} / \text{Cu}})$$

$$\therefore E^{\circ}_{\text{OP}} = - (E^{\circ}_{\text{RP}})$$

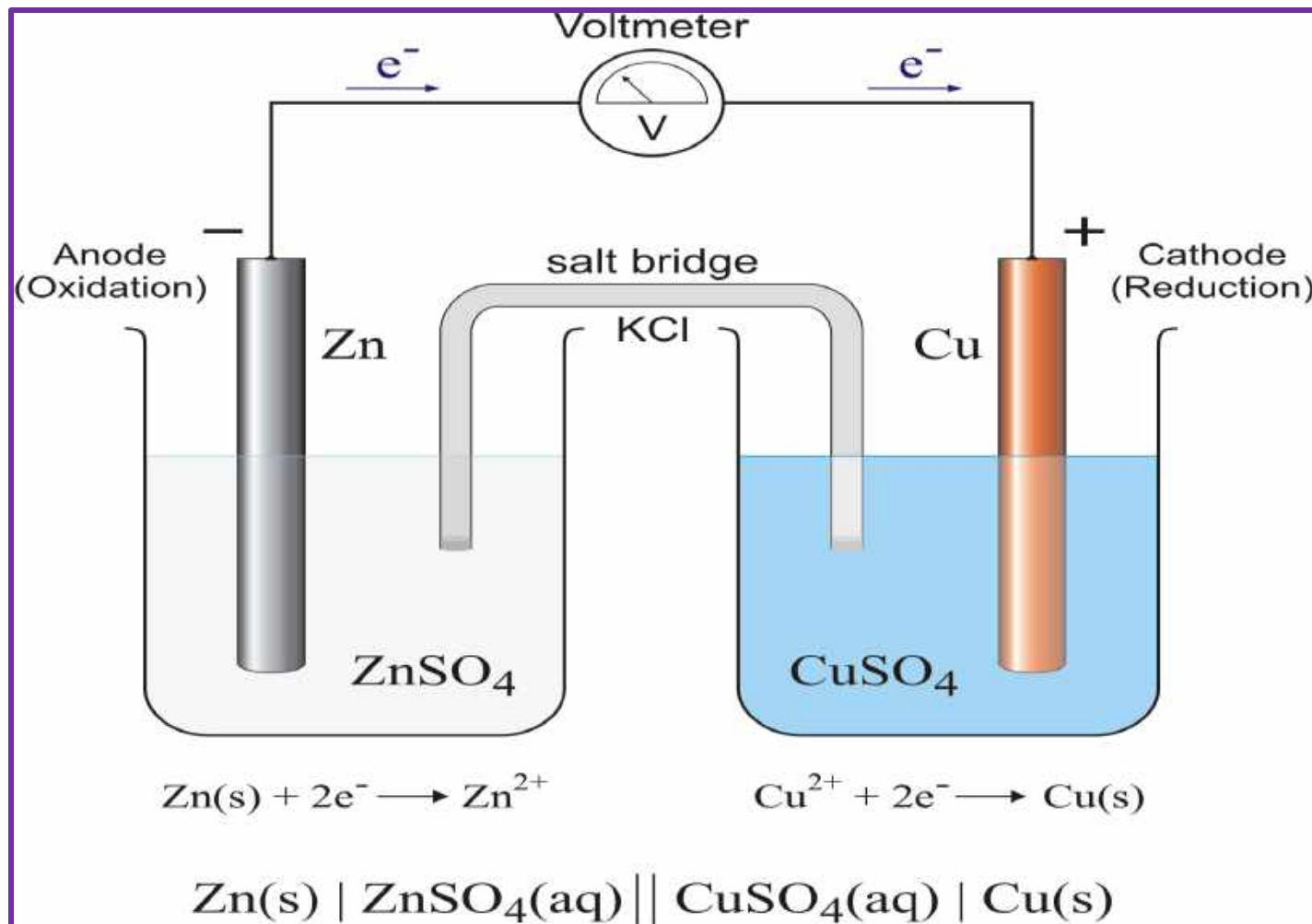


General Terms:

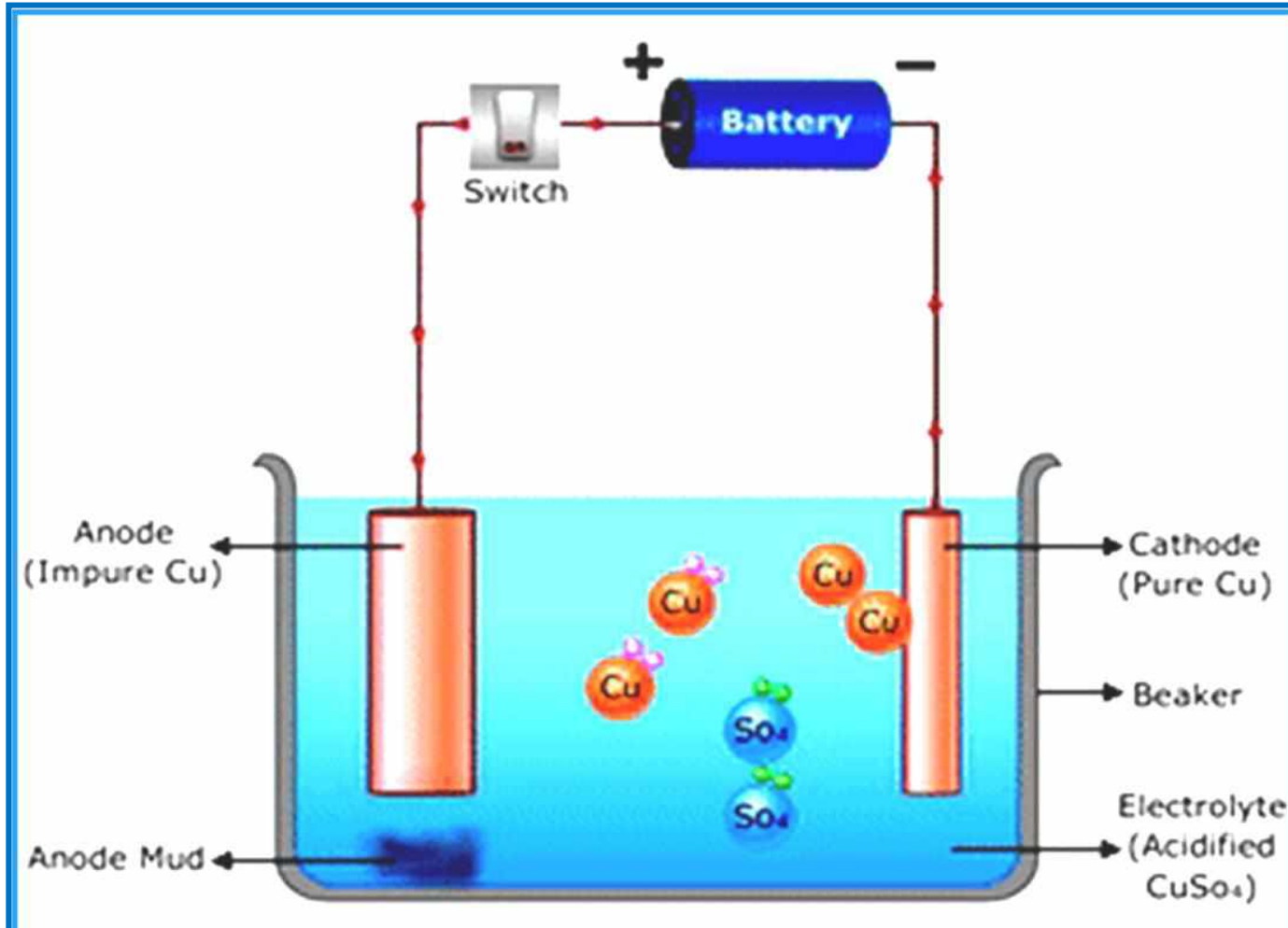
Electrode: It is any solid on the surface of which oxidation-reduction reactions occur.



Galvanic cell



Electrolytic cell



Difference between a Galvanic cell and an electrolytic cell

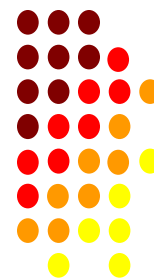
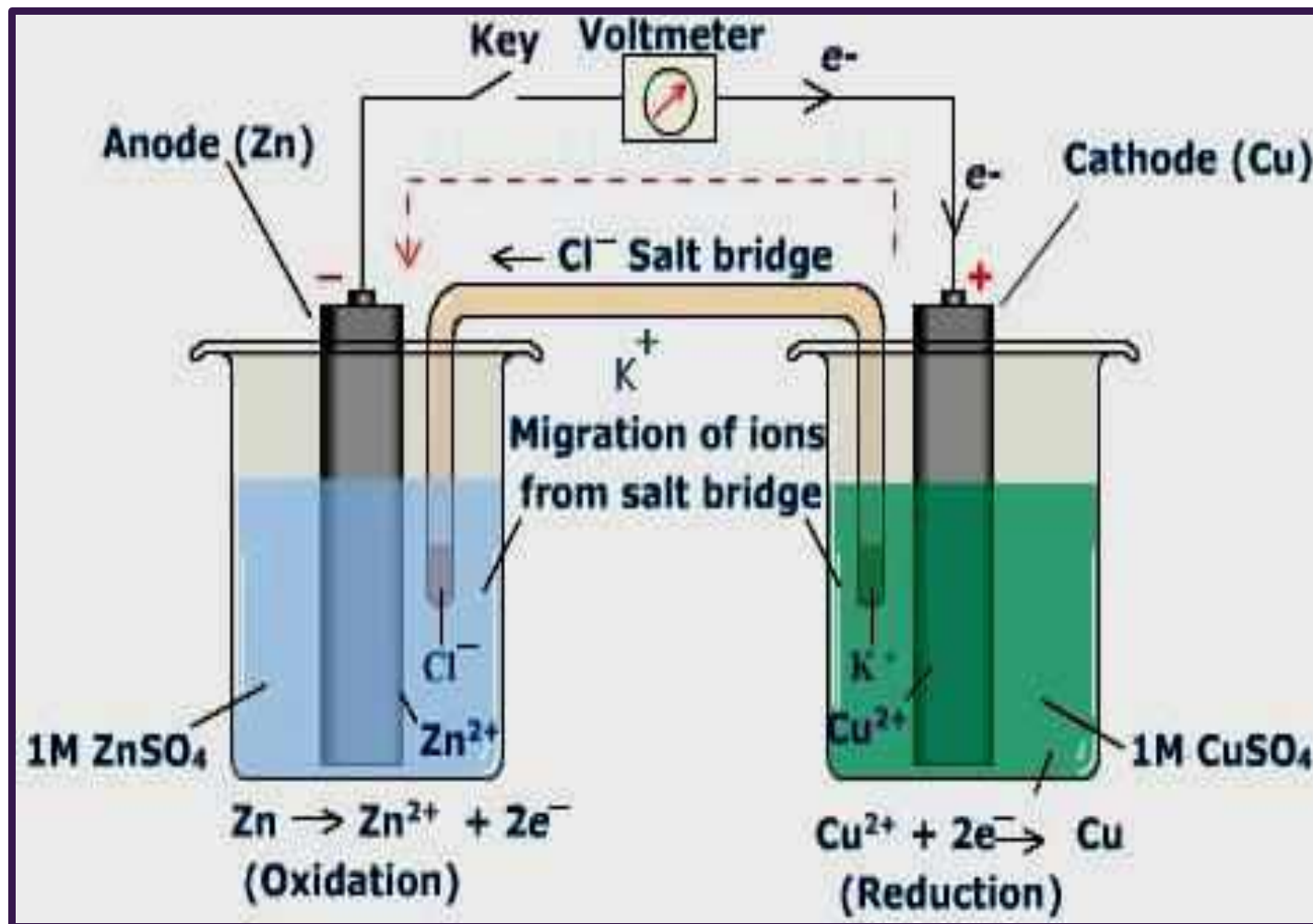
Galvanic cell	Electrolytic cell
Cell which converts chemical energy to electrical energy.	Cell which converts electrical energy to chemical energy.
Redox reaction takes place which is spontaneous and it is responsible for the production of electrical energy.	Redox reaction is non spontaneous and electrical energy is supplied so that the reaction may take place.
Electrodes used are of dissimilar material.	Electrodes used may be of similar or different material.



Galvanic cell	Electrolytic cell
Each electrode is dipped in its own electrolytic solution .	Both electrodes are dipped in same electrolytic solution.
Salt bridge is used.	Salt bridge is not used.
Anode is negative and cathode is positive.	Anode is positive and cathode is negative.
Electrons move from anode to cathode in external circuit.	Electrons are supplied by battery and enter through cathode and come out through anode .
e.g.: Daniel cell.	e.g.: Lead acid storage battery.



GALVANIC CELL or VOLTAIC CELL

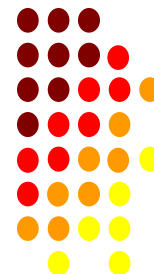


Working Of Galvanic Cell

Following reactions occur at anode and cathode respectively:



Cell Representation:



Working Of Galvanic Cell

The Redox Process allow the electrons to flow **from Zn electrode** to the electron-deficient **Cu electrode** due to which a minute amount of Zn from Zn electrode can go into the solution as Zn^{2+} ions leaving a **negative charge** on the anode and a positive charge in the solution.



Similarly, on the Cu electrode a few Cu^{2+} ions from the solution may be deposited as Cu atoms on the Cu electrode.

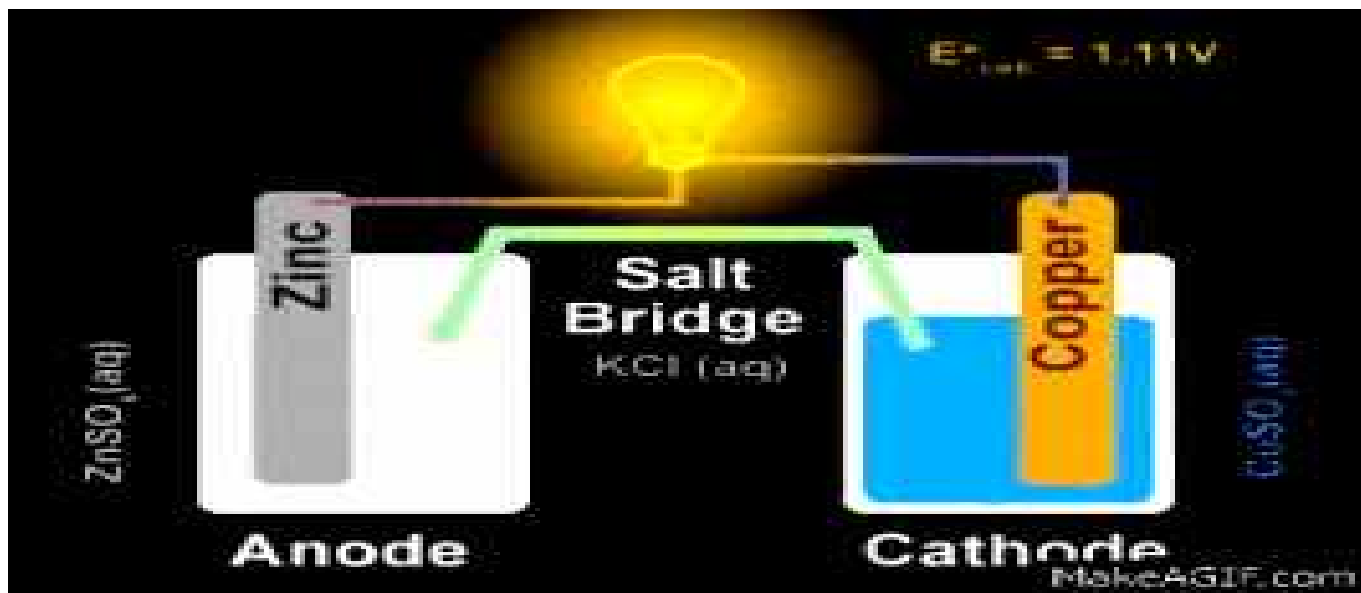


Salt bridge

It is an inverted U shaped tube containing a saturated solution of strong electrolyte (KCl).

Function of Salt Bridge

- It connects the solution of two half cells to complete the inner circuit.
- It maintains the electrical neutrality of the solution to give a continuous flow of current.



Representation of Full Cell

Ways for the Representation of Full Cell are :

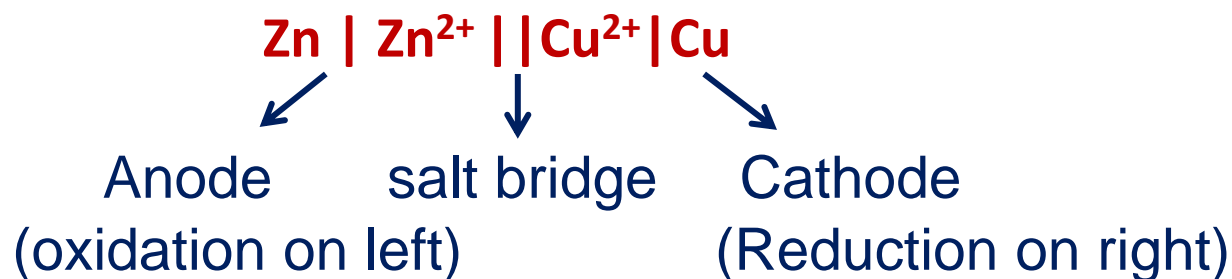
E.g. Daniel Cell can be represented in any of the following ways :



OR



(single Line)	For representing different phase
(Double Line)	For representing Salt Bridge



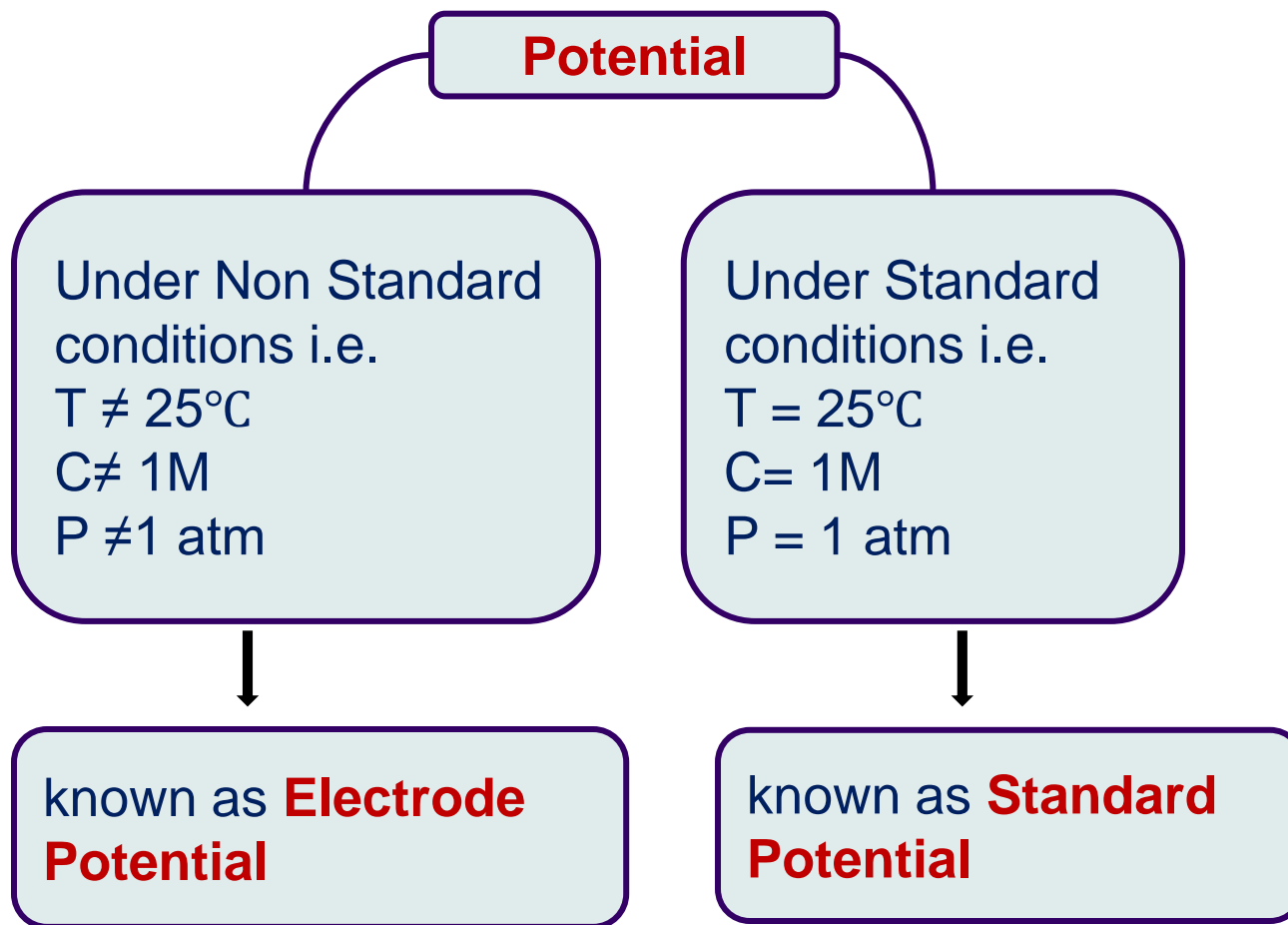
[

RRCP= Right, Reduction, Cathode, Positive

LOAN= left, Oxidation, Anode, Negative

]





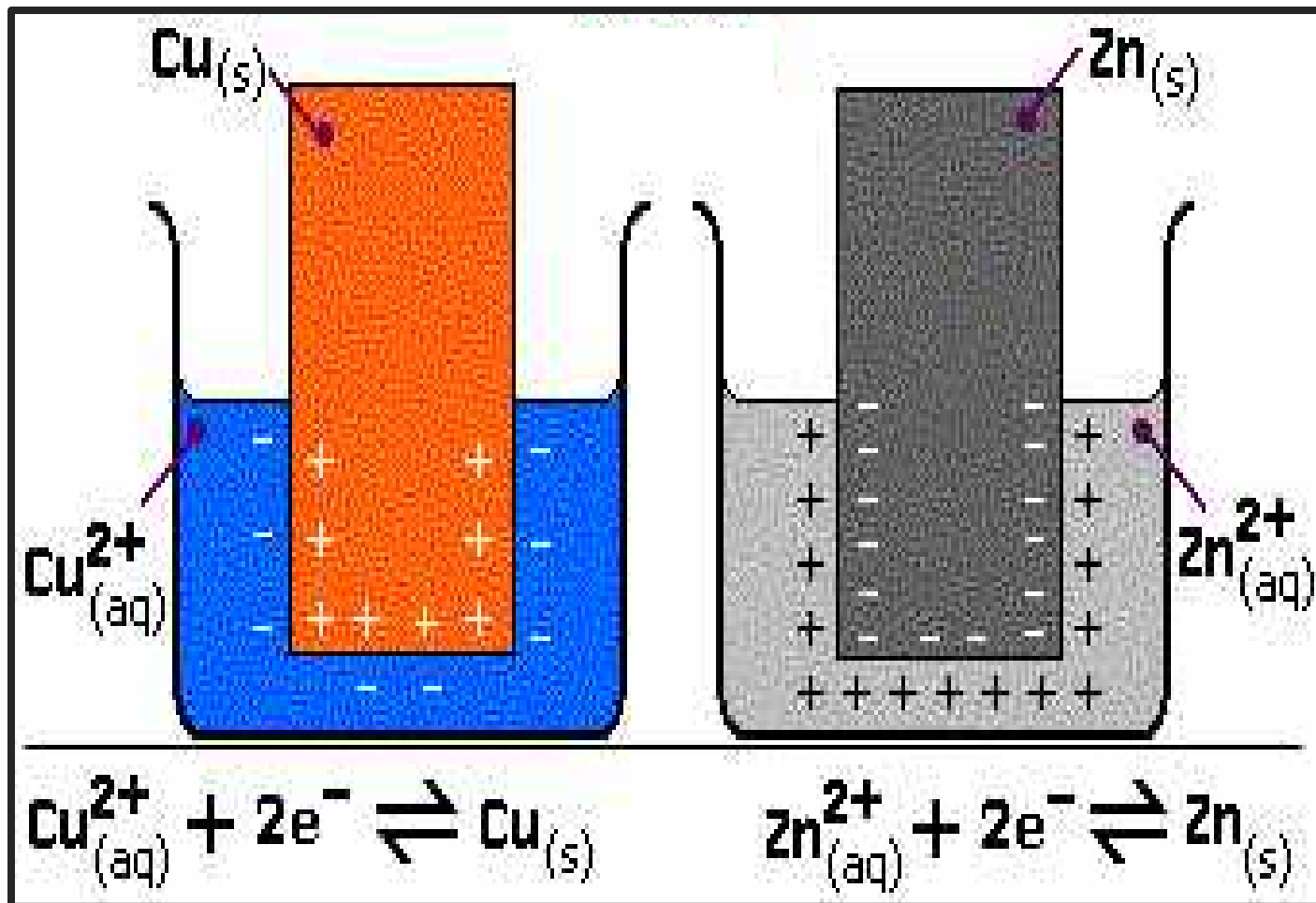
Electrode Potential (E):

It is the measure of the tendency of metallic electrode to lose or gain electrons, when it is in contact with its own salt solution.”

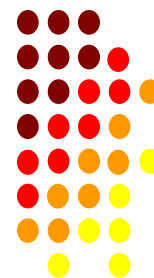
Electrode potential depends on:

- Nature of metal and its ions
- Temperature
- Concentration of ions in the solution





Electrode Potential



Depending on the “*Nature of metal*”,
Electrode potential is of two types:

Oxidation potential: It is the measure of tendency of an electrode *to lose electrons or to get oxidised*.



Represented as: $E^{\circ}_{\text{M} | \text{M}^{n+}} = \mathbf{x}$

eg. $E^{\circ}_{\text{Zn} | \text{Zn}^{2+}} = \mathbf{0.76V}$



Reduction potential: It is the measure of tendency of an electrode to **gain electrons** or to **get reduced**.



Represented as: $E^{\circ}_{M^{n+} | M} = -x$

eg. $E^{\circ}_{Zn^{2+} | Zn} = -0.76V$



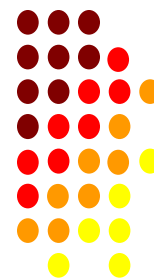
Cell Potential (E_{cell}) or Electro Motive Force (EMF)

It is the difference in electrode potential (RP) of cathode and anode when no current is allowed to flow in the circuit.

$$E_{\text{cell}} = \text{R.P. of cathode} - \text{R.P. of anode}$$

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

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$



Standard Electrode Potential (E°):

It is the Potential difference developed between Electrode and its Electrolyte of unit Molarity (1M) at 25°C .

Standard cell Potential (E°_{cell}):

$$E^\circ_{\text{cell}} = \text{R.P. of cathode} - \text{R.P. of anode}$$

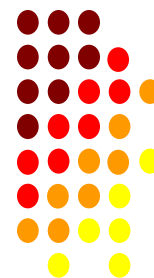
$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$



Measurement of Electrode Potential:

The electrode whose potential is known called as ***REFERENCE ELECTRODE***.

To determine the electrode potential of a half cell, the electrode is connected to a reference electrode whose potential is fixed to 0.0 V. This reference electrode is known as ***SHE/NHE*** (Standard or Normal hydrogen electrode)



Measurement of Electrode Potential:

The *standard hydrogen electrode* consists of a *platinum electrode* coated with *platinum black*.

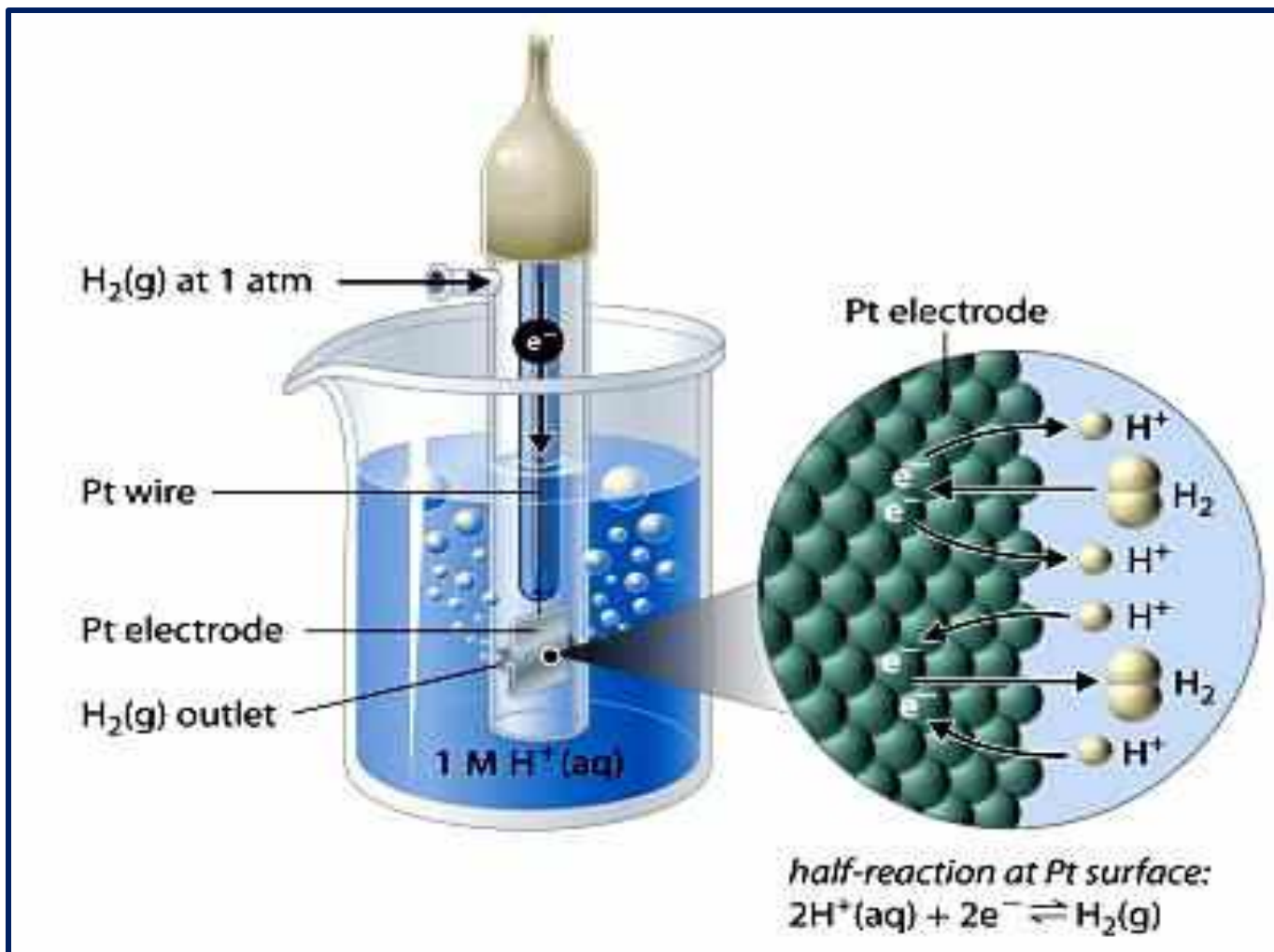
The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it.

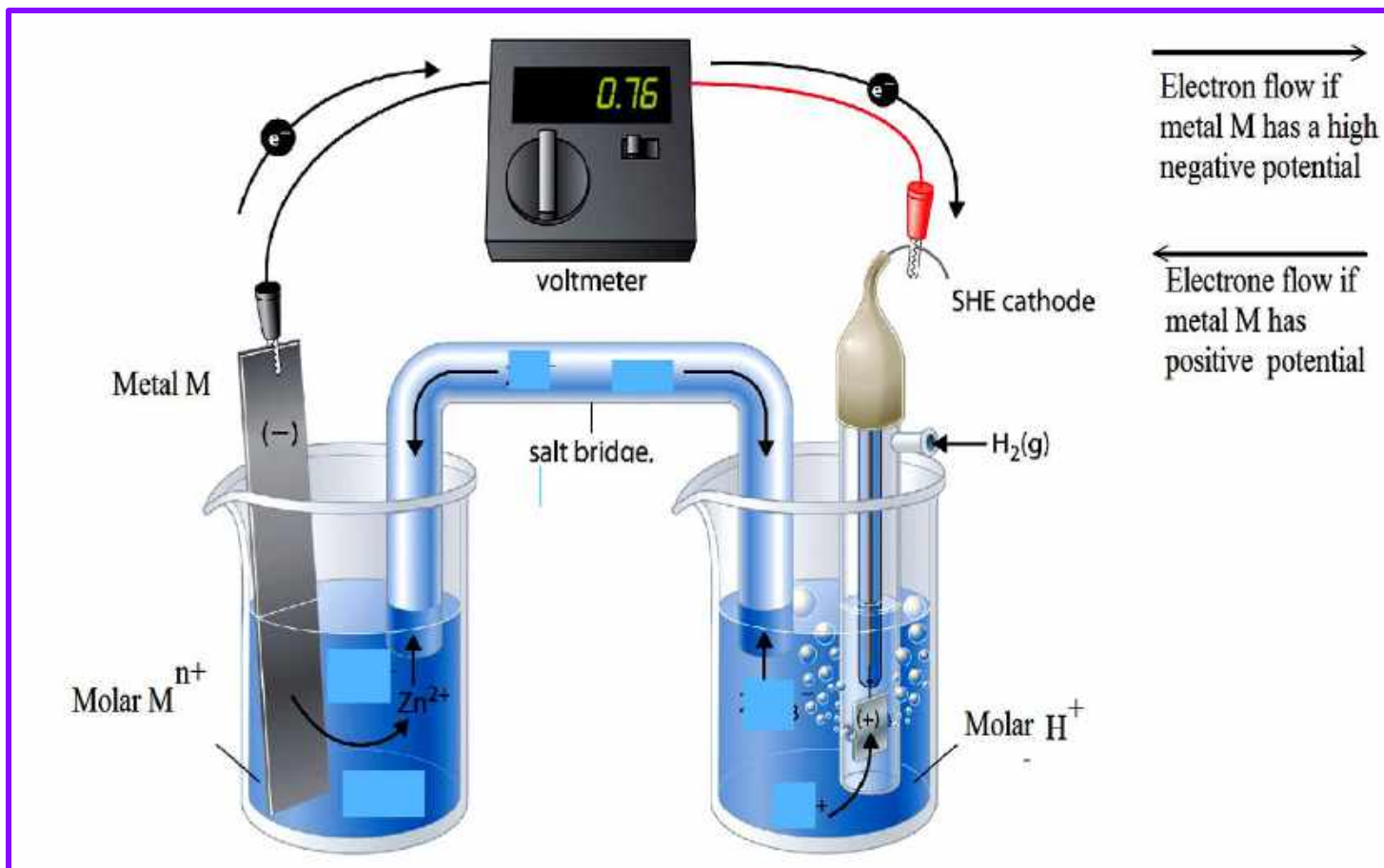
The pressure of hydrogen gas is *1atm* and the concentration of hydrogen ion in the solution is *1 molar*.

Hydrogen electrode can act as anode as well as cathode depending on the potential of the second half cell.



Standard Hydrogen Electrode



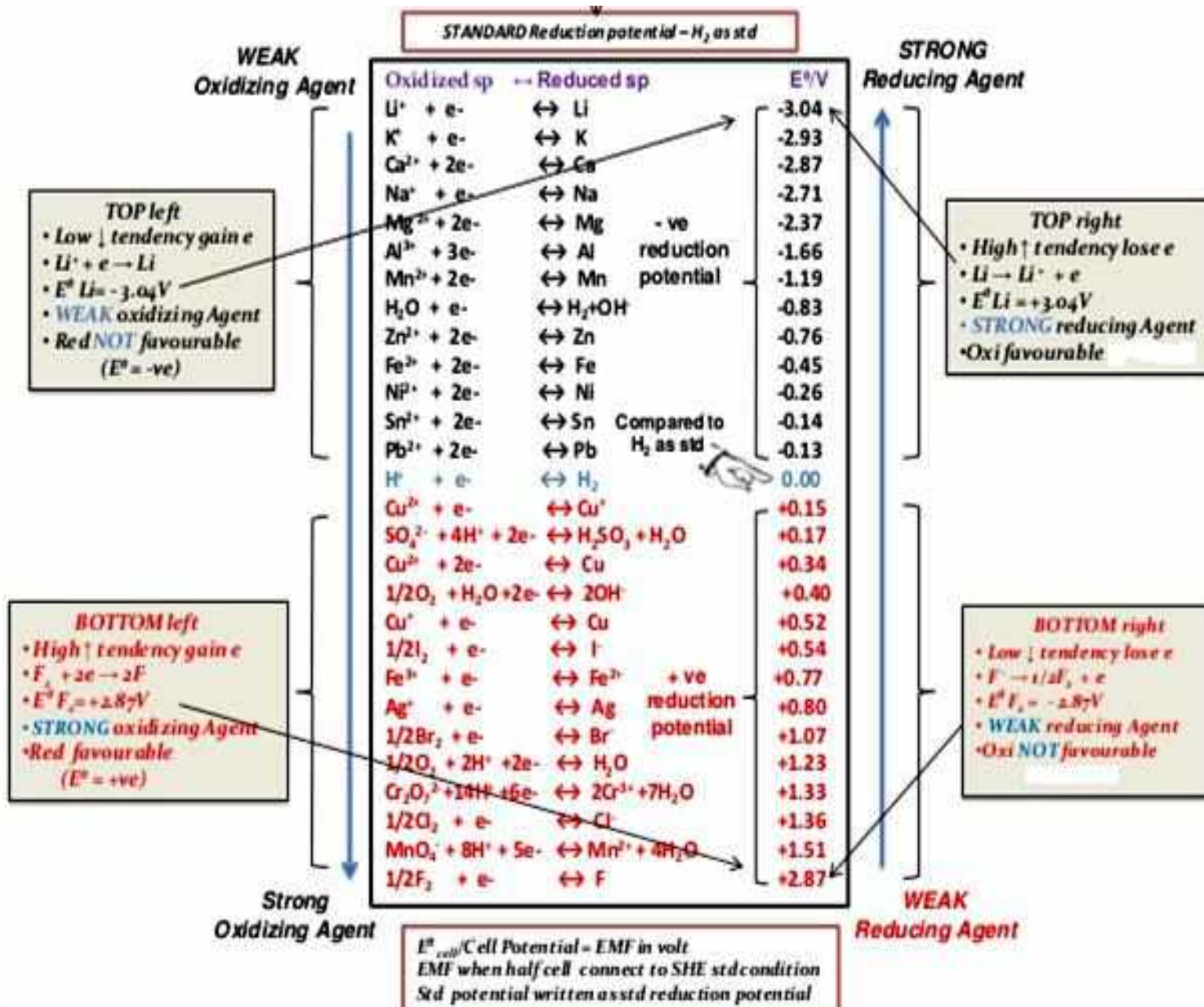


Cell notation: $\text{Pt}|\text{H}_2(\text{g})|\text{H}^+(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu}(\text{s})$

$\text{Zn}(\text{s})|\text{Zn}^{2+}(\text{aq})||\text{H}^+(\text{aq})|\text{H}_2(\text{g})|\text{Pt}$



ELECTROCHEMICAL SERIES



ELECTROCHEMICAL SERIES

- Arranged in the order of increasing reduction potential. These values are said to be on Hydrogen scale since H is use as a reference at 0V.
- The most negative E° values are placed at the top of the electrochemical series, and the most positive at the bottom.
- The standard reduction potential of hydrogen electrode is zero.
- More negative E° values, therefore will loose electrons. Hence stronger reducing agent.
- More positive E° values, therefore will gain electrons. Hence stronger oxidising agent.



How to find E° of any cell:

The E° for any cell can be calculated using the formula:

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

For example:

For a given cell: **Zn | Zn²⁺ || Cu²⁺ | Cu**

$E^\circ_{\text{Zn}^{2+} | \text{Zn}} = -0.76 \text{ V}$ and $E^\circ_{\text{Cu} | \text{Cu}^{2+}} = -0.34 \text{ V}$.

Find E° of the cell.



$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= 0.34 - (-0.76) \end{aligned}$$

$$E^{\circ} = 1.10 \text{ V}$$

Cathode: copper

$$E^{\circ} \text{ Cu} | \text{Cu}^{2+} = -0.34 \text{ V (oxidation pot)}$$

$$E^{\circ} \text{ Cu}^{2+} | \text{Cu} = 0.34 \text{ V (Reduction pot)}$$

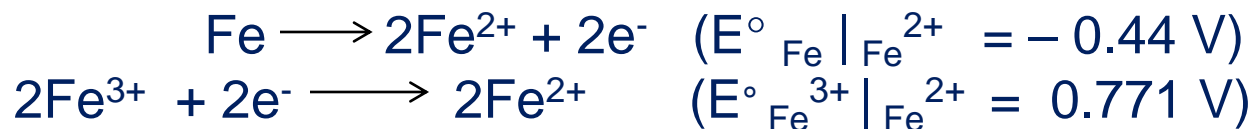
Anode: Zinc

$$\text{Zn}^{2+} | \text{Zn} = -0.76 \text{ V (Reduction pot)}$$



Ques: Find E° of the cell: $\text{Fe} + 2\text{Fe}^{3+} \longrightarrow 3\text{Fe}^{2+} + \text{Fe}^{2+}$
Given that : $E^\circ_{\text{Fe} | \text{Fe}^{2+}} = -0.44 \text{ V}$ and
 $E^\circ_{\text{Fe}^{3+} | \text{Fe}^{2+}} = 0.771 \text{ V}.$

Sol. As it is a complete cell so we can do it directly.



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= 0.771 \text{ V} - 0.44 \text{ V} \\ &= 0.331 \text{ V} \end{aligned}$$



APPLICATIONS:

- ***To predict the relative strengths of oxidising or reducing agents-*** elements at the bottom of the series have maximum tendency to get reduced and will act as good oxidizing agents while the elements which have lower reduction potential are stronger reducing agents
- ***To predict whether the electrode will act as a anode or cathode-*** the electrodes which lies above in the series will act as a anode and the one which lies below in the series will act as a cathode.



- ***To predict the feasibility of the reaction:*** If E_{cell} is positive, reaction is feasible and vice versa.
- ***To predict whether the metal can liberate hydrogen from an acid or not:*** Only those metals which lie above hydrogen in series can liberate hydrogen from an acid.



- ***To predict relative replacement tendency:***

Metal having lower value of reduction potential can replace the metal with higher reduction potential from the solution.

E.g. i) zinc will displace copper from its solution.

ii) Aluminium can displace Zn from zinc sulphate solution, Cu from copper sulphate solution and Fe from ferrous sulphate solution.

$$E^{\circ}_{\text{Zn}^{+2}/\text{Zn}} = -0.76 \text{ V}, E^{\circ}_{\text{Fe}^{+2}/\text{Fe}} = -0.44 \text{ V}$$

$$E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} = +0.15 \text{ V}, E^{\circ}_{\text{Al}^{+3}/\text{Al}} = -1.66 \text{ V}$$



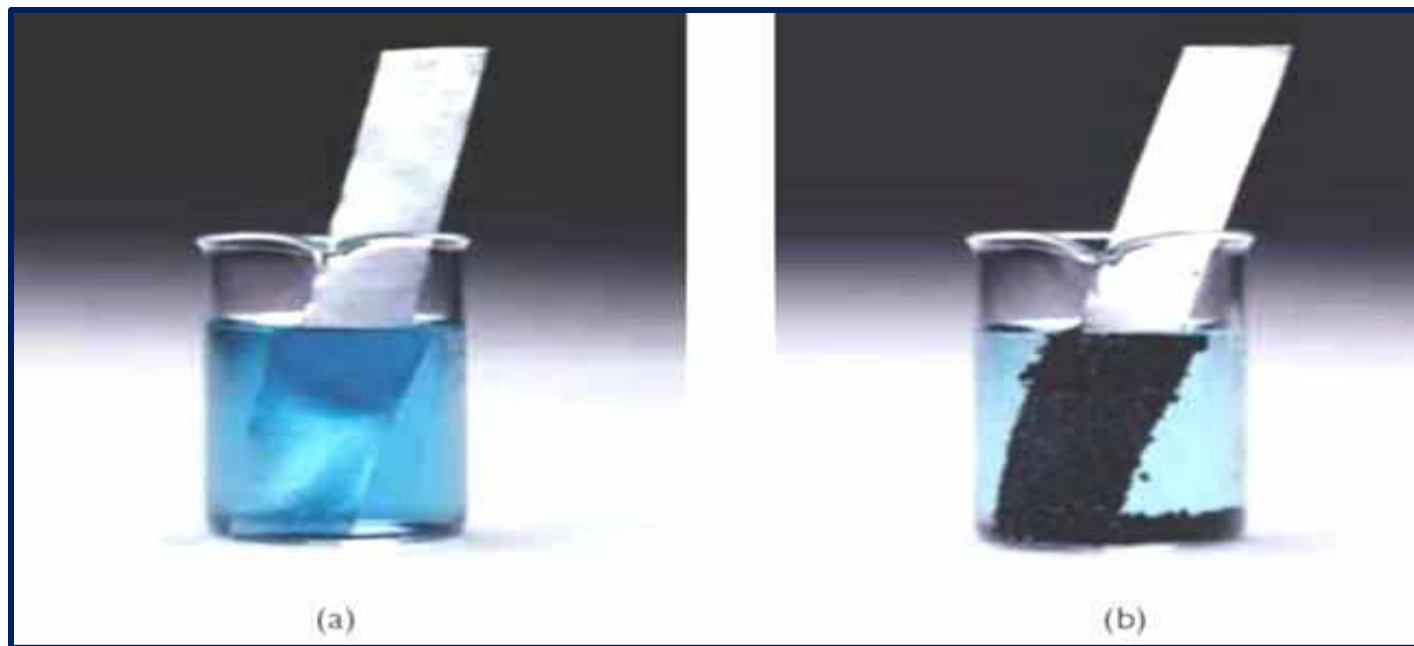
zinc will displace copper from its solution, (CuSO₄) as well as iron displaces copper from copper sulphate.

Explanation: because a metal having lower reduction potential acts as anode and the metal with higher reduction potential acts as cathode. So, metal acting as anode can displace metal acting as cathode.

Red. Pot: $E^{\circ}_{\text{Zn}^{+2} | \text{Zn}} = -0.76 \text{ V} < E^{\circ}_{\text{Cu}^{+2} | \text{Cu}} = +0.15 \text{ V}$

(A metal with higher reduction potential deposits as a solid on its electrode)





When a zinc rod is placed in a copper sulfate solution, (a) **zinc replaces the copper in solution**, and (b) elemental copper forms.



Same is the case with Fe and CuSO_4

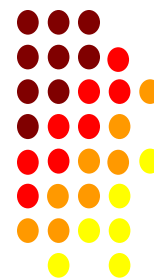
Iron displaces copper from copper (II) sulfate:



Similarly Al (acts as anode) can displace zinc from zinc sulphate, copper from copper sulphate as well as iron from iron sulphate.

$$E^\circ_{\text{Al}^{+3}|\text{Al}} = -1.66 \text{ V} < E^\circ_{\text{Zn}^{+2}|\text{Zn}} = -0.76 \text{ V},$$

$$E^\circ_{\text{Fe}^{+2}|\text{Fe}} = -0.44 \text{ V}, E^\circ_{\text{Cu}^{+2}|\text{Cu}} = +0.15 \text{ V}$$



Some Conceptual Questions

Ques. $\text{Al}_2(\text{SO}_4)_3$ solution (or Al^{3+}) should not be stored in magnesium vessel. Why?

$$E^\circ_{\text{Mg}^{+2}/\text{Mg}} = -2.37 \text{ V}, \quad E^\circ_{\text{Al}^{+3}/\text{Al}} = -1.66 \text{ V}$$

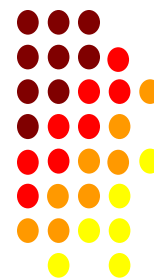
Ans. Since reduction potential of Al is more than that of Mg (Mg is placed above in the reactivity series or electrochemical series), it will be more reactive than Al. Therefore aluminium sulphate solution should not be stored in the magnesium vessel.



Ques. The standard reduction potential of three metallic cations X,Y,Z are 0.52, -3.03 and 1.18 V respectively, arrange them in decreasing order in their reducing power.

Ans. *The reducing power of metals \propto Reduction potential* (More is the reduction potential, more will be its reducing power)

So, decreasing order of reducing power of metallic cations X,Y and Z will be: **Z > X > Y**



Ques. Construct the cell from the given data: $E^{\circ}_{\text{Mg}^{+2} | \text{Mg}} = -2.37 \text{ V}$, $E^{\circ}_{\text{Ni}^{+2} | \text{Ni}} = +0.28 \text{ V}$

Ans. For a cell reaction to be feasible or for a cell to be working its E°_{cell} should be positive, i.e. The electrode with higher reduction potential should be acting as cathode.

Hence, in the given situation Nickel should act as cathode and Magnesium as anode.

So, the cell will be written as: $\text{Mg} | \text{Mg}^{2+} || \text{Ni}^{2+} | \text{Ni}$

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= 0.28 - (-2.37) \\ &= 2.65 \text{ V} \end{aligned}$$

Since E°_{cell} is positive , so the construction of cell is correct.



Ques. From the given data

$E^{\circ}_{\text{Mg}^{+2}/\text{Mg}} = -2.37 \text{ V}$, $E^{\circ}_{\text{Zn}^{+2}/\text{Zn}} = -0.76 \text{ V}$,
 $E^{\circ}_{\text{Cu}^{+2}/\text{Cu}} = +0.34\text{V}$. **Predict strongest reducing agent
and strongest oxidising agent.**

Ans. In the above data we are provided with the reduction potential of Mg, Zn and Cu. And we know that more be the reduction potential better is the tendency to get reduced and it acts as a good oxidising agent and vice-versa.



Since here Mg has smallest reduction potential, so it acts as strongest reducing agent. At the same time Cu has highest reduction potential, so it acts as strongest oxidising agent.

[**Oxidising agent**: one which oxidises other and reduces itself i.e. It undergoes reduction. It has high reduction potential, i.e. It has high tendency to get reduced.

Whereas **Reducing agent**: one which reduces others and itself undergoes oxidation. It has low reduction potential, which means it has low tendency to get reduced and high tendency to get oxidised].



Nernst Equation

The effect of concentration (activity or Pressure) and temperature on the E_{cell} for a chemical reaction was studied by Nernst and the equation known as Nernst equation.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 RT}{nF} \log_{10} \frac{[\text{Product}]}{[\text{Reactant}]}$$



Derivation of Nernst Equation

We know that, $\Delta G = - nFE_{\text{cell}}$

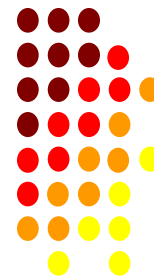
Under standard conditions: $\Delta G^{\circ} = - nFE_{\text{cell}}^{\circ}$

(n = No. of e⁻ transferred)

Also, $\Delta G = \Delta G^{\circ} + 2.303 RT \log Q$

R = Universal Gas Constant = 8.314 JK⁻¹ mol⁻¹,

F = Faraday Constant = 96500 Cmol⁻¹



So, $-nFE_{\text{cell}} = -nFE_{\text{cell}}^{\circ} + 2.303 + RT \log Q$,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 RT}{nF} \log_{10} \frac{[\text{Product}]}{[\text{Reactant}]}$$

Eq.1

At standard temperature $T = 25^{\circ}\text{C}$ or 298 K ,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log_{10} \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\{\because \text{at } 298\text{K} ; \frac{2.303 RT}{F} = 0.059\}$$



Ques. a) Construct a cell from the given data at 25 °C

Given: $E^\circ_{\text{Zn}^{+2}/\text{Zn}} = - 0.76 \text{ V}$; $E^\circ_{\text{Cu}^{+2}/\text{Cu}} = + 0.34\text{V}$

b) Also find E°

Sol. a) It is clear from the given data that Zn will act as anode as its has lower reduction potential and Cu will act as cathode.

So, cell will be represented as : $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$

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

$$E^\circ_{\text{cell}} = 0.34 - (- 0.76) = 1.10 \text{ V}$$



Difference Between Q and K_{eq}

Q (Reaction Quotient): It is defined at any stage of Reaction **other than equilibrium.**

For a cell reaction: $aA + bB \rightarrow cC + dD$

The reaction quotient will be:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$



K_{eq} (Equilibrium Constant): It is defined for the reaction only **at the stage of equilibrium.**

For a cell reaction: $aA + bB \rightleftharpoons cC + dD$

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

**Ques. For a cell reaction: $2A + 3B \rightarrow 4C + 5D$
Find Q ?**

Ans: $Q = \frac{[C]^4[D]^5}{[A]^2[B]^3}$



Ques. Calculate the EMF of the following cell and also write the cell reactions: Zn / Zn⁺⁺ (0.001M) // Ag⁺ (0.1M) / Ag. The standard potential of Ag / Ag⁺ half-cell is 0.80 V and Zn / Zn⁺⁺ is -0.76 V. (2017-18)

Ans. Anode: Zn \longrightarrow Zn²⁺ + 2e⁻ (oxidation)
Cathode: 2 (Ag⁺ + e⁻ \longrightarrow Ag) (Reduction)



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}, E^\circ_{\text{cell}} = -0.80 - (-0.76) = -1.56 \text{ V}$$

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0592}{n} \log_{10} \frac{\text{Product}}{\text{Reactant}} \\ &= -1.56 - \frac{0.0592}{2} \log_{10} \frac{0.001}{(0.1)^2} = -1.56 - \frac{0.0592}{2} \log_{10} \frac{1}{10} \\ &= -1.53 \text{ V} \end{aligned}$$



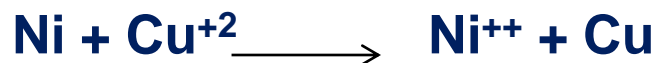
Ques. Calculate the cell potential the given cell at 25°C

(R= 8.31 JL⁻¹mol⁻¹, F= 96500C mol⁻¹)

Ni_(s) / Ni⁺²(0.01 mol) // Cu⁺² (0.1 mol) /Cu_(s) ;

Given: E°_{Cu⁺²/Cu} = 0.34 V; E°_{Ni⁺²/Ni} = - 0.25 V (2018-19)

Ans. Anode: Ni $\xrightarrow{\quad}$ Ni⁺² +2e⁻ (oxidation)
Cathode: Cu⁺² +2e⁻ \rightarrow Cu (Reduction)



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0.34 - (-0.25) = 0.59 \text{ V}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{.059}{n} \log_{10} \frac{[\text{Ni}^{+2}]}{[\text{Cu}^{+2}]} = 0.59 - \frac{.059}{2} \log_{10} \frac{[.01]}{[0.1]}$$

$$= 0.59 - \frac{0.059}{10} \log_{10} \frac{1}{2} = 0.59 + \frac{0.059}{2} = .619 \text{ V}$$



**Ques. Calculate the cell potential at 298 K for cell reaction: $\text{Al}^{+3} + \text{Fe} \longrightarrow \text{Fe}^{+3} + \text{Al}$; $E^\circ_{\text{Cell}} = -1.62$
The concentration of Al^{+3} and Fe^{+3} are 1.2 and 2.5 M respectively. (2018-19)**

Ans. $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{.059}{n} \log_{10} \frac{[\text{Product}]}{[\text{Reactant}]}$

$$= -1.62 - \frac{.059}{3} \log_{10} \frac{[2.5]}{[1.2]}$$

$$= -1.62 - .017 (0.397 - .0791)$$

$$= -1.6254 \text{ V}$$



LECTURE - 21

- **Gibb's Helmholtz Equation**
- **Relation between ΔH and ΔS and with E_{cell} and Numerical**

Gibbs-Helmholtz Equation

$$G = G(T, P)$$

$$dG = -S dT + V dP$$

$$\Delta G = G_f - G_i = \int_i^f dG = \int_i^f (-S dT + V dP)$$

$$\text{if } dT = 0, \Delta G = \int_{P_i}^{P_f} V dP$$

$$PV = nRT \quad V = \frac{nRT}{P} \quad \bar{G} = \frac{G}{n} \quad \bar{V} = \frac{V}{n}$$

$$\Delta \bar{G} = \int_{P_i}^{P_f} \bar{V} dP = \int_{P_i}^{P_f} \frac{RT}{P} dP = RT (\ln P_f - \ln P_i)$$

$$\Delta \bar{G} = RT \ln \left(\frac{P_f}{P_i} \right)$$

$\Delta \bar{H} \rightarrow$ independent of P for ideal gases

$$\Delta \bar{G} = -T \Delta \bar{S}$$

$$\Delta \bar{S} = -R \ln \left(\frac{P_f}{P_i} \right) \quad \left(\frac{\partial \bar{G}}{\partial T} \right)_P = -\bar{S}$$

$$G(T) = H(T) - TS(T)$$

$$\frac{G(T)}{T} = \frac{H(T)}{T} - S(T)$$

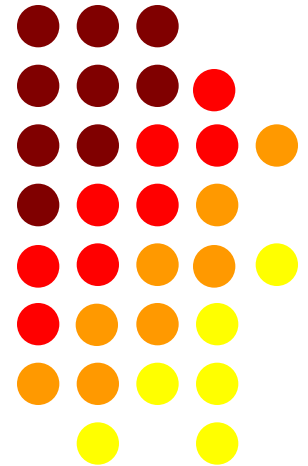
$$\left(\frac{\partial (G(T)/T)}{\partial T} \right)_P = -\frac{H(T)}{T^2} + \frac{1}{T} \left(\frac{\partial H(T)}{\partial T} \right)_P - \left(\frac{\partial S(T)}{\partial T} \right)_P$$

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_p(T)}{T} = \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P$$

$$C_p(T) = \left(\frac{\partial H}{\partial T} \right)_P$$

$$\left(\frac{\partial (G/T)}{\partial T} \right)_P = -\frac{H}{T^2}$$

$$\left(\frac{\partial (\Delta G/T)}{\partial T} \right)_P = -\frac{\Delta H}{T^2}$$



Thermodynamics of Galvanic Cell: Relation between ΔH and ΔS with E_{cell}

From Gibbs-Helmholtz equation, we have:

$$\Delta G = \Delta H + T \left[\frac{\delta(\Delta G)}{\delta T} \right]_P \text{ ————— (1)}$$

Also, $\Delta G = - nFE$ ————— (2)

differentiating eq. 2 with temperature at constant pressure gives:

$$\left[\frac{\delta(\Delta G)}{\delta T} \right]_P = - nF \left[\frac{\delta E}{\delta T} \right]_P \text{ ————— (3)}$$



Putting the value of 2 and 3 in 1 we get:

$$- nFE = \Delta H + T \left[- nF \left(\frac{\delta E}{\delta T} \right)_P \right] \quad \text{———— (4)}$$

$$\Delta H = nF \left[T \left(\frac{\partial E}{\partial T} \right)_P - E \right]$$

ΔH = Enthalpy change (Joules)

$\left[\frac{\delta E}{\delta T} \right]_P$ = Temperature coefficient (V/K)

F = Faraday constant = 96500 Coulomb/ mole

n = no. of electrons transferred

T = Temperature in Kelvin

E = EMF of cell in volts



Relation ΔS with E_{cell}

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = \Delta H + T \left[-nF \left(\frac{\delta E}{\delta T} \right)_P \right] \quad (\text{from equation 4})$$

On comparing the above two equations we get:

$$\Delta S = nF \left[\frac{\delta E}{\delta T} \right]_P$$

Here,

ΔS = Entropy change (Joules/ K)

$\left[\frac{\delta E}{\delta T} \right]_P$ = Temperature coefficient (V/K)

F = Faraday constant = 96500 Coulomb/ mole

n = no. of electrons transferred

E = EMF of cell in volts



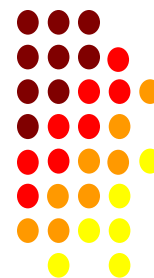
Types of questions on ΔH and ΔS and ΔG s in which

Type 1: Directly formula based.

Type 2: Questions in which Temperature coefficient is given in $V\ C^{-1}$, then the same value is used in $V\ K^{-1}$
Without any conversions as $\Delta T = ^\circ C = K$

Type 3: At temp. $T_1 \rightarrow E_1$ is given
At temp. $T_2 \rightarrow E_2$ is given
Then find $\left[\frac{\delta E}{\delta T} \right]_P$ (Temperature coefficient)

$$\left[\frac{\delta E}{\delta T} \right]_P = \frac{(E_2 - E_1)}{(T_2 - T_1)} \quad V/K$$



Numericals on Gibb's Helmholtz Equation

Ques. For the following cell



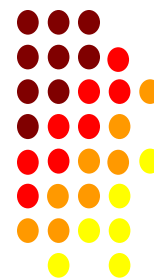
the potential at 298 K is 0.490 V and the variation of emf with temperature is given by

$$E = a - (1.86 \times 10^{-4} \text{ V K}^{-1}) (T - 25 \text{ K})$$

Write the equation for the cell reaction and calculate ΔG , ΔH and ΔS for the reaction at 298 K.

Sol. For the given cell, we have

<i>Electrode</i>	<i>Reduction reaction</i>	
Right	$2\text{AgCl}(\text{s}) + 2\text{e}^- \rightarrow 2\text{Ag}(\text{s}) + 2\text{Cl}^-(\text{aq})$	(i)
Left	$\text{PbCl}_2(\text{s}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s}) + 2\text{Cl}^-(\text{aq})$	(ii)



Subtracting Eq. (ii) from Eq. (i), we get



Now since $E = a - (1.86 \times 10^{-4} \text{ V K}^{-1})(T - 25 \text{ K})$, therefore

$$\left(\frac{\partial E}{\partial T}\right)_p = -1.86 \times 10^{-4} \text{ V K}^{-1}$$

Hence $\Delta G = -nFE = -2(96\,500 \text{ C mol}^{-1})(0.490 \text{ V})$
 $= -94\,570 \text{ J mol}^{-1}$

$$\Delta H = -nF \left[E - T \left(\frac{\partial E}{\partial T}\right)_p \right]$$

$$= -2(96\,500 \text{ C mol}^{-1}) [(0.490 \text{ V}) - (298 \text{ K})(-1.86 \times 10^{-4} \text{ V K}^{-1})]$$

$$= -105\,267.6 \text{ J mol}^{-1}$$

$$\Delta S = nF \left(\frac{\partial E}{\partial T}\right)_p = 2(96\,500 \text{ C mol}^{-1})(-1.86 \times 10^{-4} \text{ V K}^{-1})$$

$$= -35.9 \text{ J K}^{-1} \text{ mol}^{-1}$$



Ques. The emf of the cell



is 0.045 5 V at 298 K and the temperature coefficient is $3.38 \times 10^{-4} \text{ V K}^{-1}$. What is the reaction taking place in the cell and what are free energy, enthalpy and entropy changes at 298 K?

Sol. For the given cell, we have

<i>Electrode</i>	<i>Reduction reaction</i>	
Right	$\text{Hg}_2\text{Cl}_2\text{(s)} + 2\text{e}^- \rightarrow 2\text{Hg(l)} + 2\text{Cl}^-\text{(aq)}$	(i)
Left	$2\text{AgCl(s)} + 2\text{e}^- \rightarrow 2\text{Ag(s)} + 2\text{Cl}^-\text{(aq)}$	(ii)

Subtracting Eq. (ii) from Eq. (i), we get



The number of electrons involved at the electrode reactions is 2.

Thus $\Delta G = -nFE$

$$= -2(96\,500 \text{ C mol}^{-1})(0.045\,5 \text{ V}) = -8\,782 \text{ J mol}^{-1}$$

$$\Delta H = -nF \left[E - T \left(\frac{\partial E}{\partial T} \right)_p \right]$$

$$= -2(96\,500 \text{ C mol}^{-1}) [0.045\,5 \text{ V} - (298 \text{ K})(3.38 \times 10^{-4} \text{ V K}^{-1})]$$

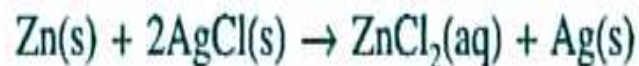
$$= 2(96\,500 \text{ C mol}^{-1})(0.055\,2 \text{ V}) = 10\,650 \text{ J mol}^{-1}$$

and $\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_p = 2(96\,500 \text{ C mol}^{-1})(3.38 \times 10^{-4} \text{ V K}^{-1})$

$$= 65.23 \text{ J K}^{-1} \text{ mol}^{-1}$$



Ques. At 273 K, the calorimetric determination of ΔH for the reaction

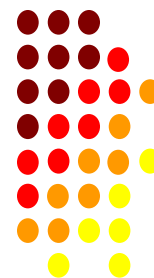


yielded $-217.78 \text{ kJ mol}^{-1}$, while the emf of the corresponding cell was 1.015 V. What was $(\partial E/\partial T)_p$ of the cell?

Sol. From the expression

$$\Delta H = -nF \left[E - T \left(\frac{\partial E}{\partial T} \right)_p \right]$$

we get
$$\left(\frac{\partial E}{\partial T} \right)_p = \frac{1}{T} \left[E + \frac{\Delta H}{nF} \right]$$

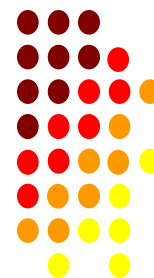


we get

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{1}{T} \left[E + \frac{\Delta H}{nF} \right]$$

Substituting the given data, we get

$$\begin{aligned} \left(\frac{\partial E}{\partial T}\right)_p &= \frac{1}{(273 \text{ K})} \left[(1.015 \text{ V}) + \frac{(-217\,780 \text{ J mol}^{-1})}{2(96\,500 \text{ C mol}^{-1})} \right] \\ &= -4.154 \times 10^{-4} \text{ V K}^{-1} \end{aligned}$$



Ques. The EMF of the cell $\text{Cd} , \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}_{(\text{saturated})} // \text{AgCl}_{(\text{s})} , \text{Ag}$ is 0.6915 V at 0°C and 0.6753 V at 25°C , in which the cell reaction is:



Calculate the free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) of the cell at 25°C .

Sol. $E_1 = 0.6915$ at $T_1 = 0^\circ \text{C} = 273 \text{ K}$

$E_2 = 0.6753$ at $T_2 = 25^\circ \text{C} = 298 \text{ K}$

$$\left[\frac{\delta E}{\delta T} \right]_P = \frac{(E_2 - E_1)}{(T_2 - T_1)} = \frac{(0.6753 - 0.6915)}{(298 - 273)}$$

$$= - 0.0006 \text{V/K}$$



$$\begin{aligned}\Delta G &= -nFE_{\text{cell}} \quad (E_{\text{cell}} \text{ is asked for } 25^\circ \text{ C}) \\ &= 2 \times 96500 \times 0.6753 \\ &= -130332.9 \text{ Joules}\end{aligned}$$

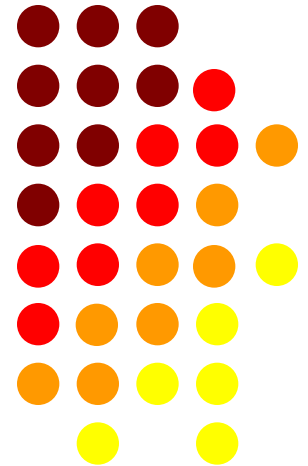
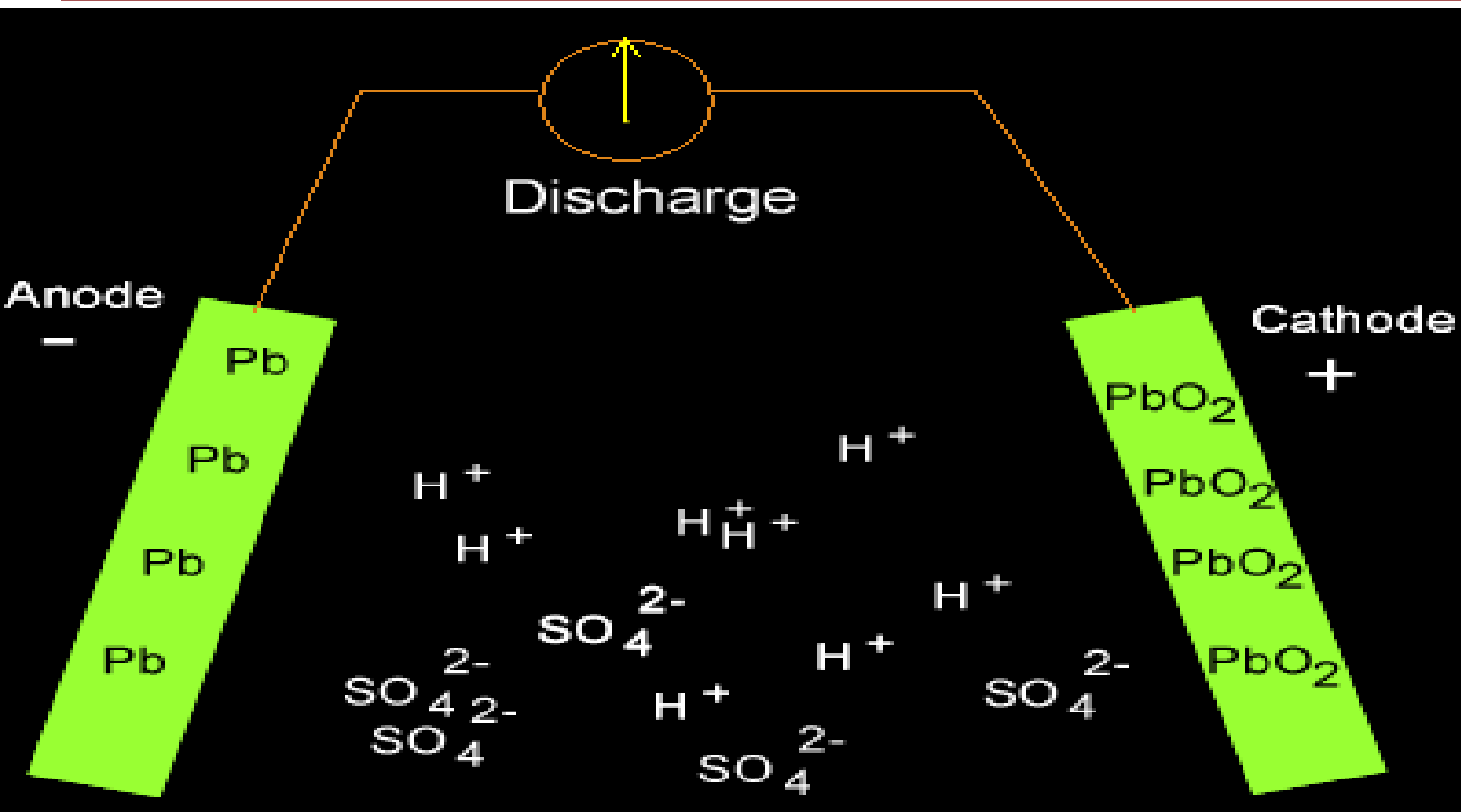
$$\begin{aligned}\Delta H &= nF \left[T \left(\frac{\partial E}{\partial T} \right)_P - E \right] \\ &= 2 \times 96500 \left[298 (-0.00065) - 0.6753 \right] \\ &= -167717 \text{ Joules}\end{aligned}$$

$$\begin{aligned}\Delta S &= -nF \left[\frac{\delta E}{\delta T} \right]_P \\ &= 2 \times 96500 (-0.00065) \\ &= -125.45 \text{ J/ K}\end{aligned}$$



LECTURE - 22

- Batteries and their types
- Lead acid storage battery



Introduction

Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at constant voltages. A device which converts chemical energy to electrical energy is called battery cells, connected together electrically in series. Batteries are commercial electrochemical cells.



BATTERY

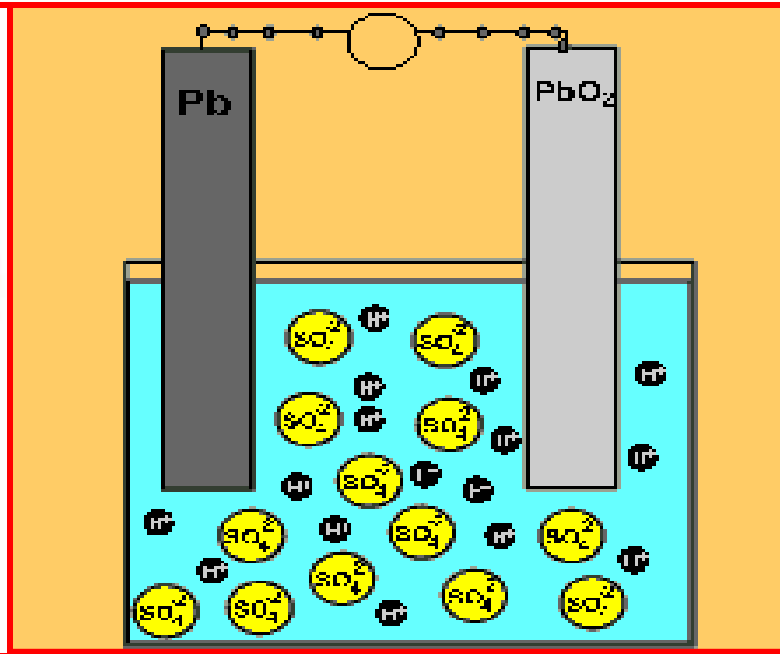
- Battery is a combination of more than one galvanic cells in series.
- Batteries are of two types:
 1. **Primary Battery:** This type of battery can not be recharged and hence can not be reused (use and throw). Eg. Batteries used in remotes, dry cell, button cell etc.



2. Secondary Batteries: These are rechargeable batteries and hence can be reused. eg. Lead acid storage battery, Li-ion battery, invertors battery, car battery etc.



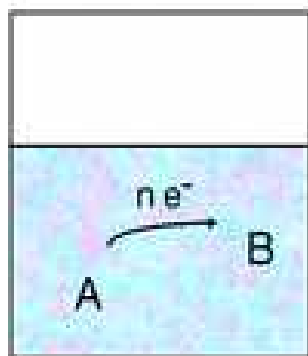
Car Battery



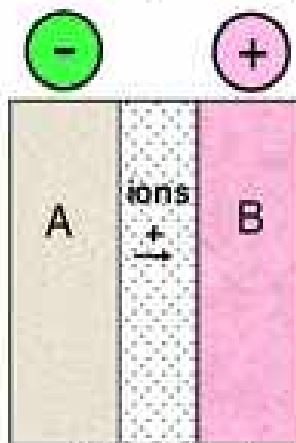
Lead Acid Battery



(a)
Redox reaction



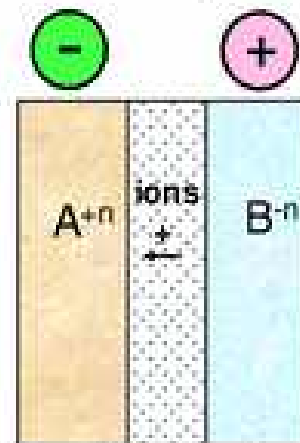
(b)
Primary Battery



discharge



(c)
Secondary Battery



charge



ADVANTAGES OF BATTERIES:

- Batteries act as a portable source of electrochemical energy.
- The portability of electronic equipment in the form of handsets has been made possible by batteries.
- A variety of electronic gadgets have been made more useful and popular with the introduction of rechargeable storage batteries having reliability, better shelf life and tolerance to service.
- For all commercial applications, batteries are constructed for their service. For example batteries for automobiles and aircrafts, stand by batteries etc.



Requirements of Battery:

- It should be light and compact for easy transport.
- It should have long life both when it is being used and when it is not used.
- The voltage of the battery should not vary appreciably during its use



Differences between Primary, Secondary and Fuel cells

Primary cell	Secondary cells
It acts as a simple galvanic cell.	It acts as a galvanic cell while discharging and electrolytic cell while charging.
Cell reaction is not reversible.	Cell reaction can be reversed.
Cannot be recharged.	Can be recharged
Can be used as long as the materials are active in their composition. E.g: Leclanche or dry cell. Zn/NH_4Cl (20%), $ZnCl_2/MnO_2/C$. emf = 1.5V. Applications: Radios, torches, transistors, hearing aids.	Can be used again and again by recharging the cell E.g: 1. Lead storage cell 2. Nicol or Nickel cadmium battery emf = 1.4 Applications: Electronic calculators, electronic flash units & cordless electronic shavers etc.



PRIMARY CELLS:

- **Lithium cells:**

Lithium cells are primary cells in which lithium acts as anode and the cathode may differ. Lithium metal **is** used as anode because of its light weight, high standard oxidation potential ($\geq 3V$) and good conductivity. As the reactivity of lithium in aqueous solution is more, lithium cells use non-aqueous solvents as electrolyte.

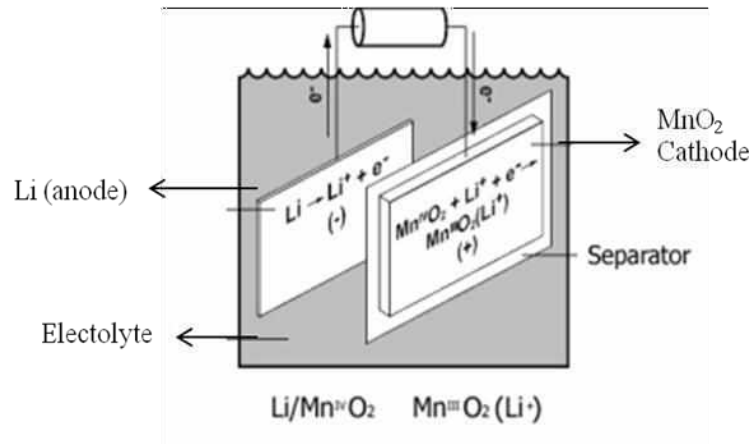
Lithium cells are classified into two categories:

- Lithium cells with solid cathode
- Lithium cells with liquid cathode



Lithium cells with solid cathode

- The electrolyte in this system is a solid electrolyte. The most widely used cell is lithium
- Manganese dioxide cell (3V). MnO_2 should be heated to over 300°C to remove water before keeping it in the cathode, thereby increasing the efficiency of the cell.



- **Anode:** Lithium Metal,
- **Cathode:** MnO_2 as an active material.
- **Electrolyte:** LiBF_4 salt in a solution of propylene carbonate and dimethoxy ethane.
- **Reactions:**
 - ❑ **At anode:** $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$
 - ❑ **At cathode:** $\text{e}^- + \text{MnO}_2 \rightarrow \text{MnO}_2^-$

 - ❑ **Net reaction:** $\text{Li} + \text{MnO}_2 \rightarrow \text{LiMnO}_2$

Applications

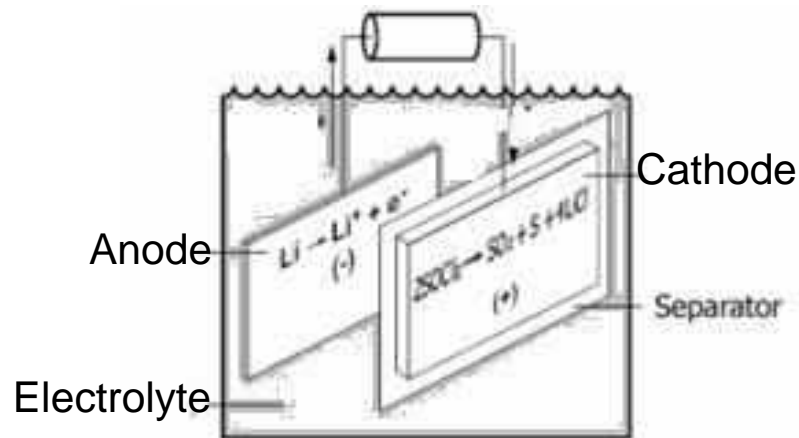
- The coin type cells are used in watches and calculators.
- Cylindrical cells are used in fully automatic cameras.



Lithium cells with liquid cathode

- Lithium–sulphur dioxide cell is an example of liquid cathode. The co-solvents used are acrylonitrile or propylene carbonate (or) mixture of the two with SO_2 in 50% by volume.
- **Cell reaction:** $2\text{Li} + 2\text{SO}_2 \rightarrow \text{Li}_2\text{S}_2\text{O}_4$.
- Lithium thionyl chloride cell is another example of liquid cathode. It consists of high surface area carbon cathode, a non – woven glass separator. Thionyl chloride acts as an electrolyte and as a cathode.





■ Cell reaction:

- **At anode:** $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$
- **At cathode:** $4\text{Li} + 4\text{e}^- + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{SO}_2 + \text{S}$
- **Net reaction:** $4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{SO}_2 + \text{S}$

In this cell no co-solvent is required as SOCl_2 is a liquid with moderate vapor pressure. The discharging voltage is 3.3 -3.5V.



USES

- They are used for military and space applications.
- In medicinal devices such as neuro-stimulators, drug delivery system, lithium batteries are widely used.
- They are also used in electric circuit boards for supplying fixed voltage for memory protection and standby functions.



Advantages:

- The energy output of a lithium cell is 2-4 times better than that of conventional zinc anode batteries.
- Lithium batteries can work over temperature range of 40-70⁰C.
- They have higher voltages of about 4V when compared to other primary cells with 1.5 V only.



Leclanche's cell

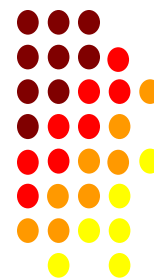
■ (A) Principle:

Leclanche's cell is a primary voltaic cell. It doesn't contain mobile liquid electrolyte but contains moist viscous aqueous paste of the electrolytes. It is an irreversible voltaic cell which can't be recharged.

■ (B) Construction:

(i) It consists of a small zinc vessel which serves as an anode (negative electrode).

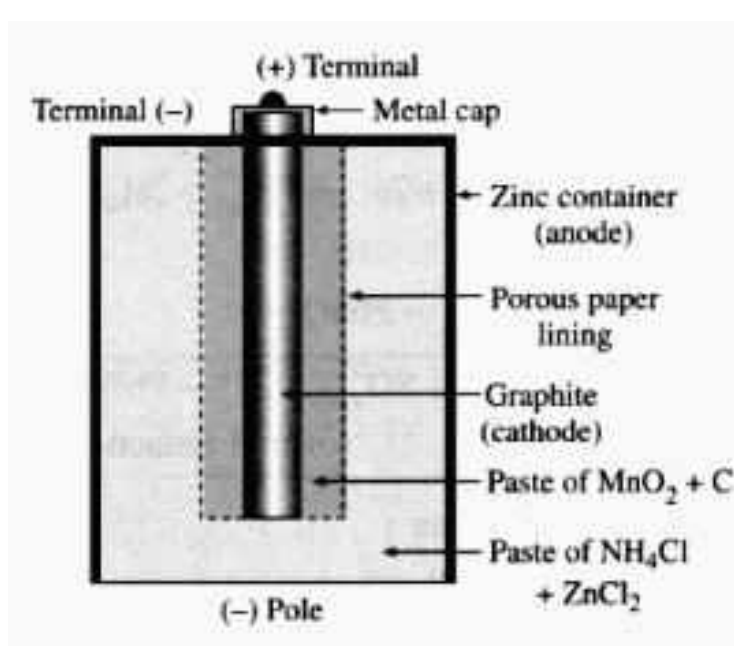
(ii) The zinc vessel contains a porous paper bag containing an inert graphite electrode which serves as cathode, immersed in a paste of MnO_2 and carbon black. This paper bag divides the dry cell into two compartments, namely anode and cathode compartments.



(B) Construction:

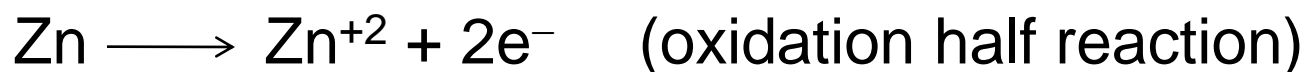
(iii) The rest of the cell is filled with a moist paste of NH_4Cl and ZnCl_2 which acts as an electrolyte for zinc anode.

(iv) The graphite rod is fitted with a metal cap and the cell is sealed to prevent the drying of moist paste by evaporation.



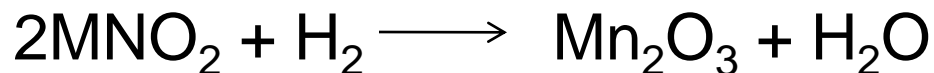
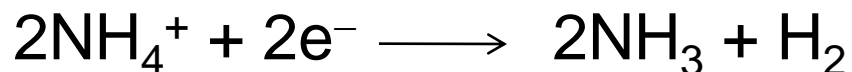
(C) Reactions in the dry cell

(i) Oxidation at zinc anode:



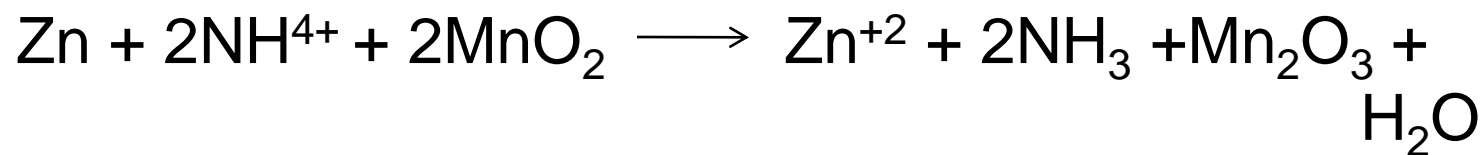
(ii) Reduction at graphite (C) cathode:

The electrons released in the oxidation reaction at anode, flow to cathode through external circuit. Hydrogen in NH_4^+ ion is reduced to molecular hydrogen which reduces MnO_2 to Mn_2O_3 .

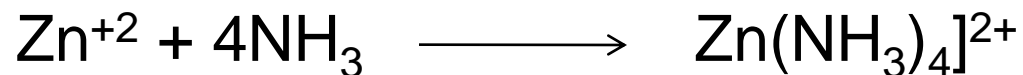


(C) Reactions in the dry cell

The overall cell reaction



(iii) Zn^{2+} react with NH_3 and form a complex.



Since Zn^{2+} ions are removed, the overall cell reaction can't be reversed.



(D) Uses:

- Dry cell is used as a source of electric power in radios, flashlights, torches, clocks, etc.
- Since they are available in small size and portable, they can be used conveniently.



LEAD ACID STORAGE BATTERY

- It is a combination of both voltaic cell and an electrolytic cell used in invertors, car batteries.
- It is a secondary storage battery, as it can be recharged.
- It is called lead acid battery because it contains acid as an electrolyte and plates are made up of lead.



Construction:

- **Anode** : Made of lead.
- **Cathode**: Made of a lead coated with PbO_2
- **Electrolyte**: 28-30% solution of H_2SO_4 ($d=1.31 \text{ g/cm}^3$; 38% by mass) in a hard rubber or plastic container (ebonite case).
- The battery consists of *6 such cells connected in series*. Since each cell has an emf of about 2V, the overall *emf of the battery is 12V*.
- The cathode and anode plates are arranged alternatively, separated by thin perforated plastic or fibre glass.



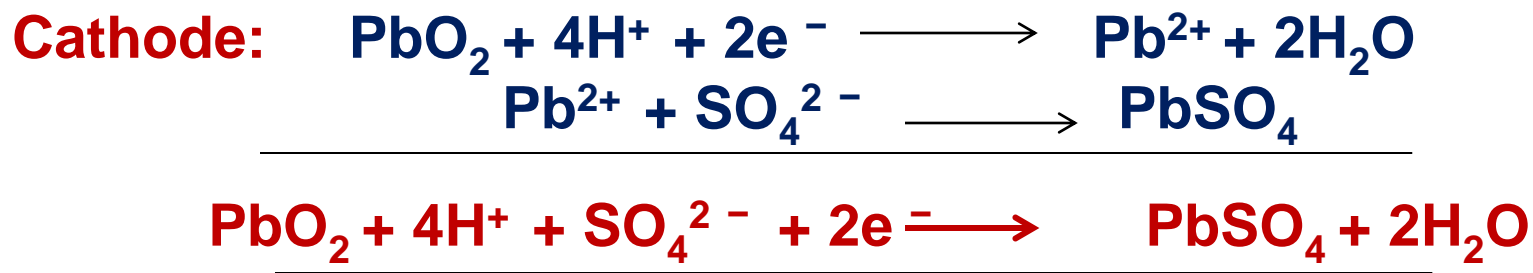
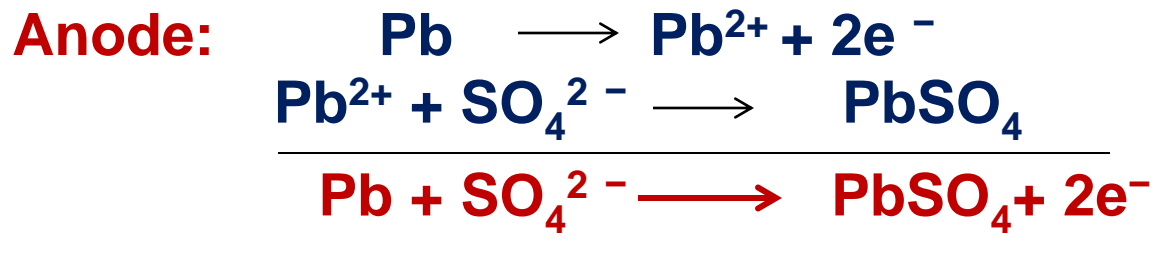
Working:

H_2SO_4 is used up during discharging so level of acid falls. When the density falls below $1.20g/cm^3$ the battery needs recharging.

Also precipitate of lead sulphate is formed during discharging which completely covers both anode & cathode. As a result, cell stops working, Then, it needs to be recharged.

During Discharging: Works as electrochemical cell when the battery supplies current or electrical energy.

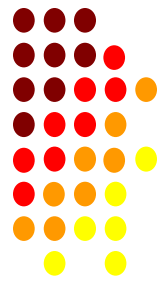
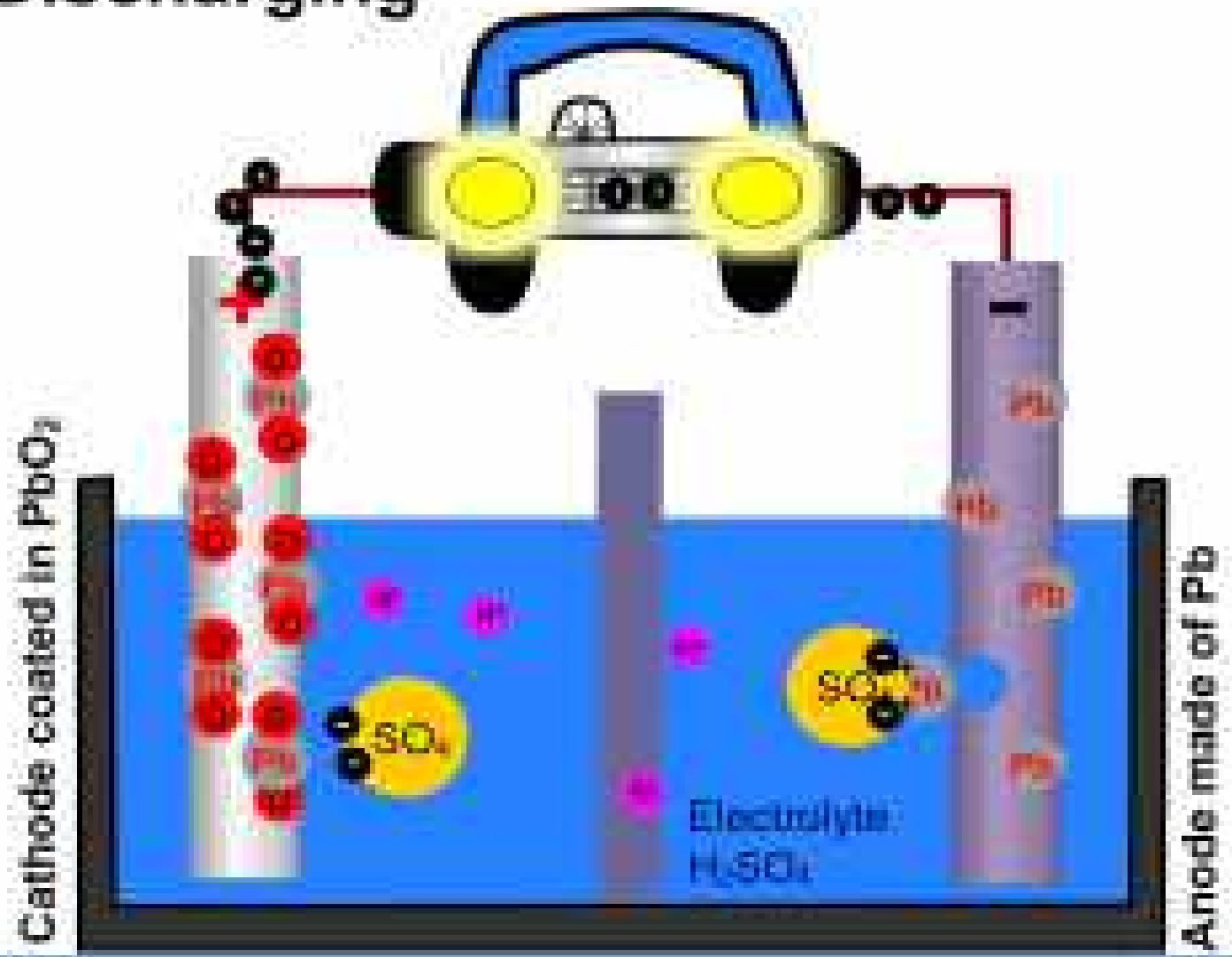




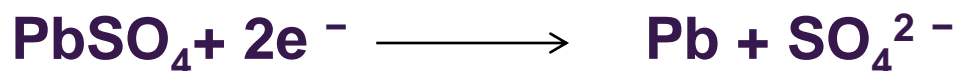
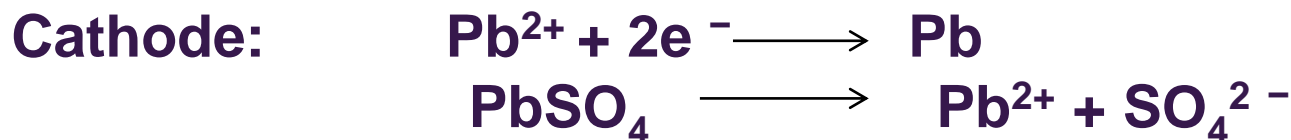
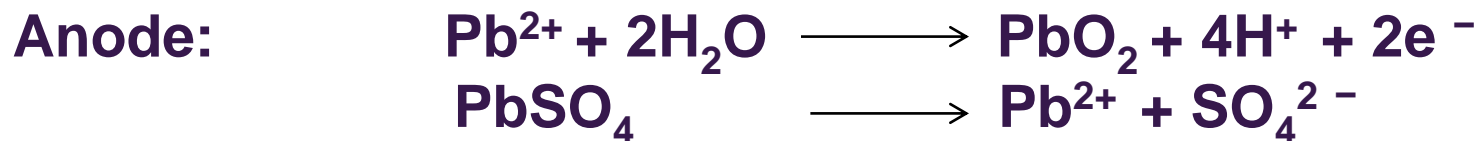
Net reaction during discharging :



Discharging



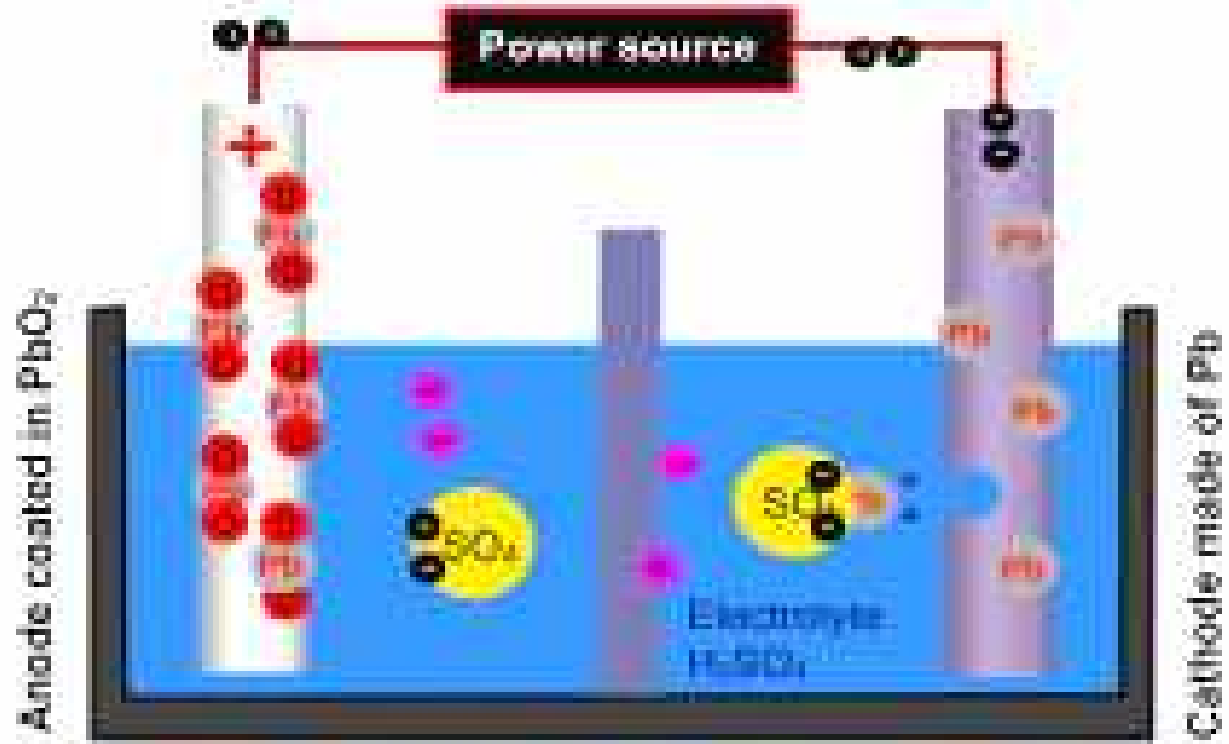
During charging: Acts as electrolytic cell.



Net reaction during recharging :



Charging



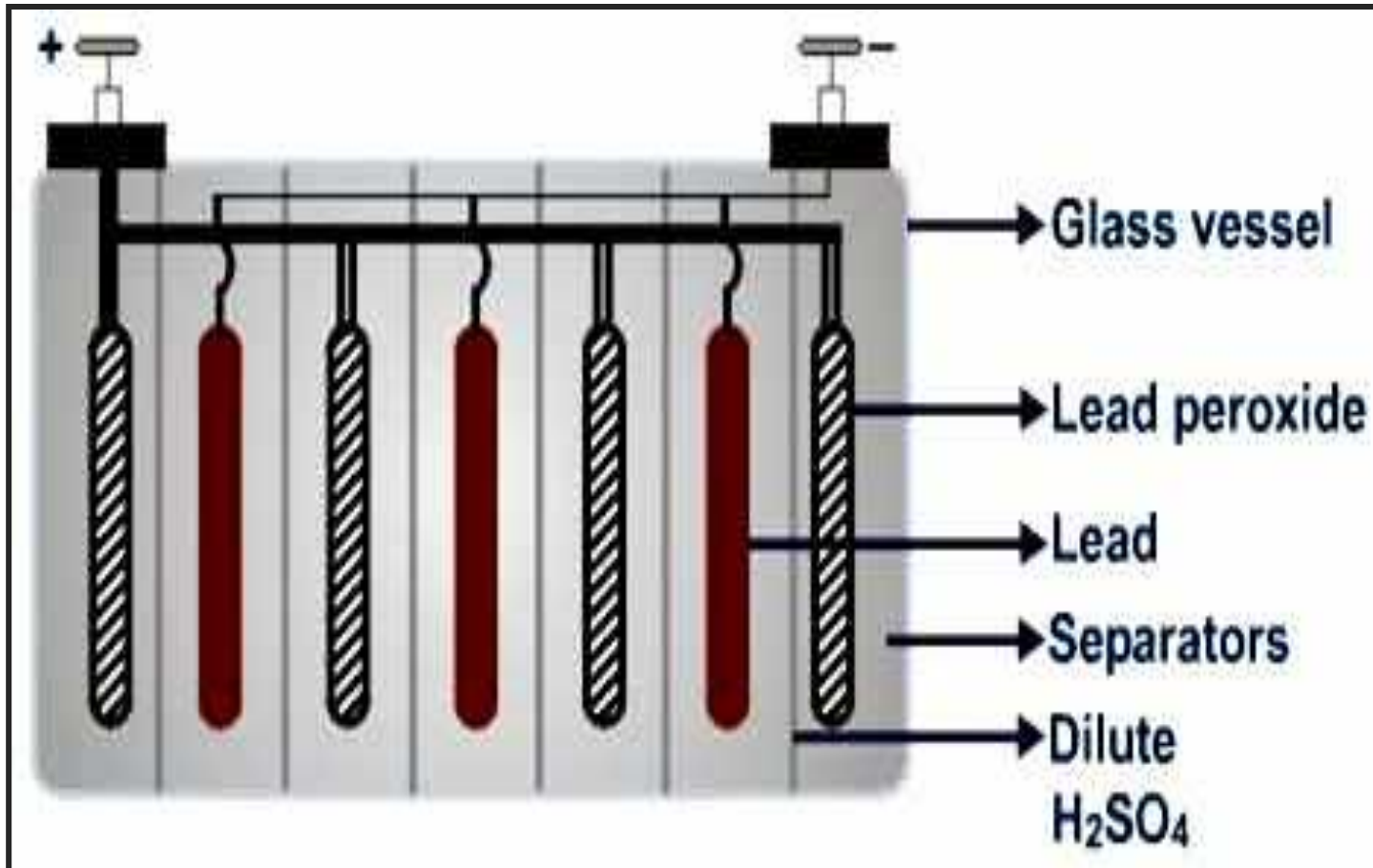
During recharging cell operates like an electrolytic cell. Lead sulphate formed is used up during recharging.

Recharging is done by passing an external emf greater than 2V. Electrode reactions are reverse of those during discharging.

The cell could be recharged because solid lead sulphate is formed during discharging which acts as a reactant in recharging.

The net cell reaction during charging and discharging process for a cycle:



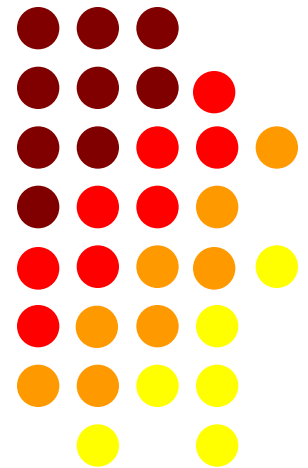


LEAD ACID STORAGE CELL



Lecture - 23

- Definition and cause of corrosion
- Factors affecting Corrosion
- Electrochemical theory of corrosion.



Anodic

Cathodic

CORROSION

Corrosion is a process of gradual destruction or deterioration of metals by chemical or electrochemical attack of environment. Ex: Rusting of iron, tarnishing of silver etc.



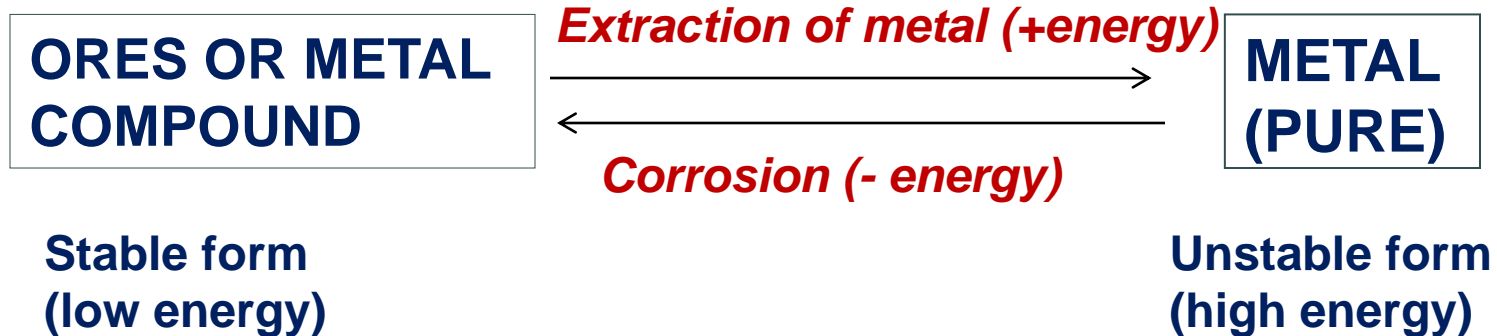
Units of Corrosion:

Mils per year (MPY)

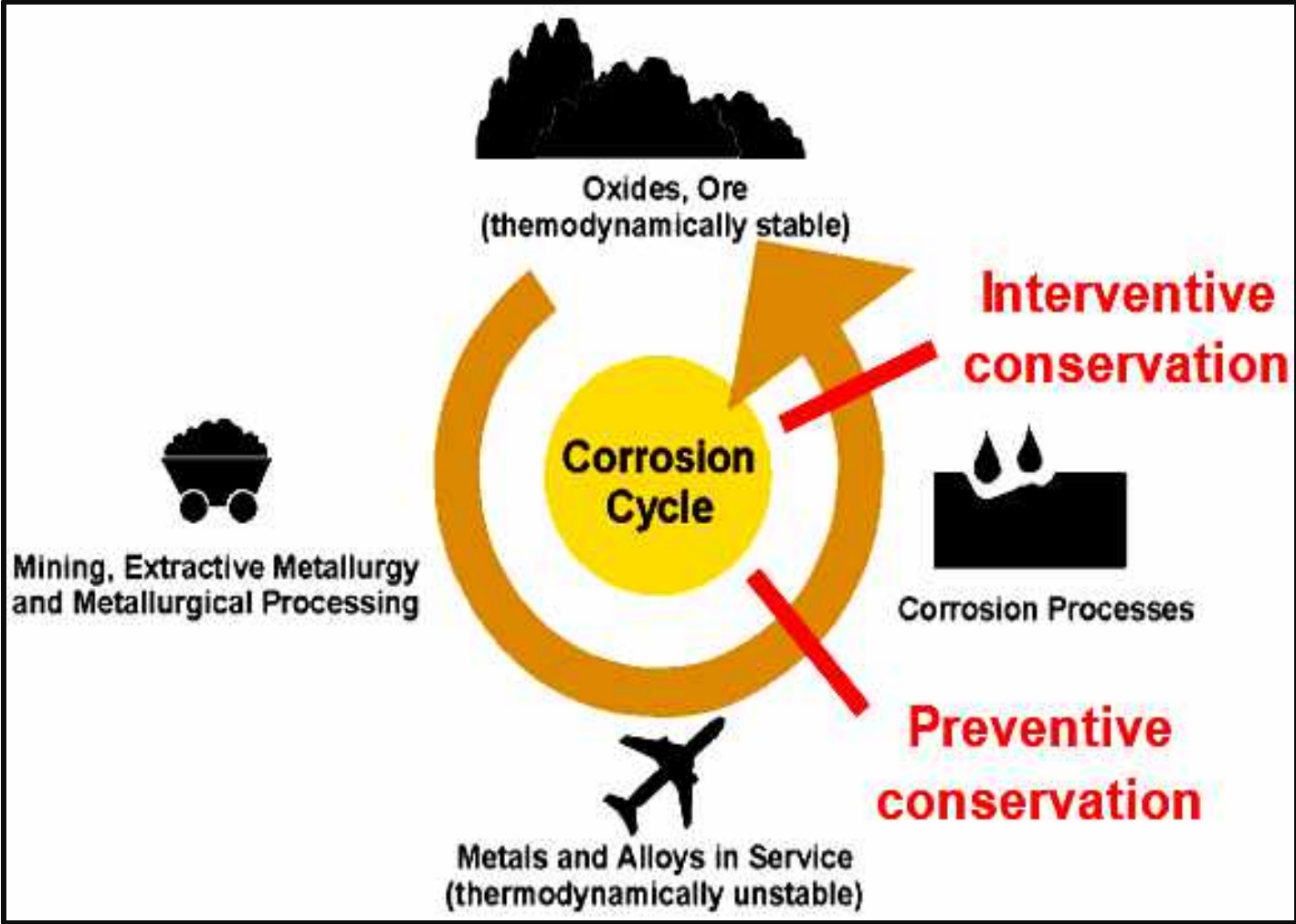
Milligram per decimeter square per day (MDD)

1 mil = 1/1000 inch

Reason / Causes of corrosion



REASON / CAUSES OF CORROSION



Galvanic Series:

It says that the "anodic" or "less noble" metals at the negative end of the series such as magnesium, zinc and aluminium - are more likely to be attacked than those at the "cathodic" or "noble" end of the series such as gold and graphite.

The most noble metal lower in the Galvanic Series, will be the cathode while the less noble, higher in the Galvanic Series, will act as an anode and it will corrode.



The Galvanic Series Chart



Factors affecting corrosion:

Rate and extent of corrosion depends upon :

- Nature of metal
- Nature of environment

1. Nature of metal :

1. Position of metals in galvanic series:

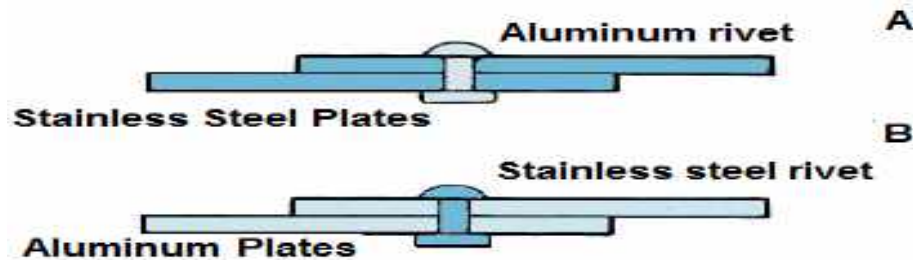
a) If two metals are in electrical contact, then the metal placed higher in galvanic series acts as anode and get corroded.

b) More is the difference in the position of the metals in the galvanic series, faster is the rate of corrosion.



ii. Relative areas of anode and cathode

Rate of corrosion \propto Cathodic area/ Anodic area



The cathode-to-anode area ratio, C/A , is illustrated in above figure for riveted plates. In both couples A and B, aluminum is the anode, and stainless steel is the cathode. In couple A, the aluminum rivet is comparatively small, and the C/A ratio is large. In couple B, the situation is reversed: the stainless steel rivet is small, and the C/A ratio is also small. Corrosion of the aluminum rivet in couple A will be severe. However, corrosion of the large aluminum plate in couple B will be much less, even though the potential difference is the same in each case.



iii. Purity of metal: The impurities present in metal results in setting up small electrochemical cells leading to corrosion.



iv. Physical state of metal: Rate of corrosion $\propto 1/\text{grain size of metal}$.

Smaller the size of the metal, more the area under stress and greater is the corrosion.



v. Nature of oxide film:

Explained by: **PILING BED-WORTH RULE:**

Specific volume ratio = $\frac{\text{volume of metal oxide}}{\text{volume of metal}}$

If, volume of the oxide < volume of metal
Oxide film is porous and non protective. Corrosion continues due to penetration of oxygen through pores. Eg. Metals such as Mg, Ca, Ba.

If volume of oxide > volume of metal
Oxide film is non porous and protective. No further corrosion occurs. Eg. Metals such as Al, Cr, Ni etc.



2. NATURE OF CORRODING ENVIRONMENT:

i. Temperature: Rate of corrosion \propto Temperature

ii. Moisture: Moisture acts as solvent for corrosion.

So, *Rate of corrosion \propto Moisture*

iii. pH: Generally acidic medium leads to more corrosion.

iv. Nature of corroding medium: Nature of anions, cations and their conducting nature affects the rate of corrosion.

v. Presence of impurities and suspended particles in atmosphere: Corrosive gases, fumes of sulphuric acid and hydrochloric acid, suspended particles like NaCl, charcoal, etc. increases the rate of corrosion.



Types of corrosion

There occurs two types of corrosion processes:

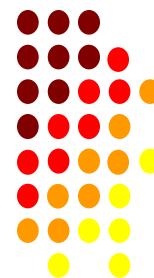
1) *Wet corrosion or Electrochemical corrosion:*

when corrosion takes place by the transfer of electrons from anodic parts of metal to cathode part through a conducting solution . It is known as wet corrosion.

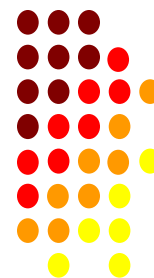
2) *Dry corrosion or Chemical corrosion:* Occurs due to direct chemical action of an oxidising gas eg – O_2 ,S ,Halogens, H_2S , etc in the absence of moisture. Increase with increase in temperature



CHEMICAL (DRY) CORROSION	ELECTROCHEMICAL (WET) CORROSION
Takes place in dry condition. Gases and vapours are corrodants.	Takes place in presence of water or an electrolyte .
It involves direct chemical attack on the metal by environment.	It involves setting up of large number of galvanic cells on metal surface.
It is explained by absorption mechanism.	It is explained by mechanism of electrochemical reaction.
Corrosion is uniform.	Corrosion is not uniform.



CHEMICAL (DRY) CORROSION	ELECTROCHEMICAL (WET) CORROSION
It occurs on both homogeneous and heterogeneous surfaces.	It occurs only on heterogeneous surfaces.
Also known as high temperature corrosion.	Also known as low temperature corrosion.
It is a slow process.	It is a fast process.
Corrosion products accumulate at the same place where corrosion occurs.	Corrosion occurs at the anode but products accumulated near cathode.



Electrochemical / wet theory of corrosion

Electrochemical corrosion involves flow of electrons between anode and cathode.

For Ex: Rusting of iron.

Electrochemical theory of corrosion is explained by two mechanisms:

- Oxygen absorption mechanism (in neutral and alkaline medium).
- Hydrogen evolution mechanism (in acidic medium).



Mechanisms:

Oxygen absorption mechanism (in basic or neutral medium)

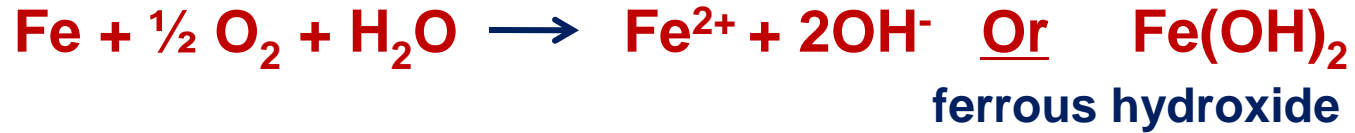
Reaction at anode (OXIDATION)



Reaction at cathode (REDUCTION)



OVERALL REACTION



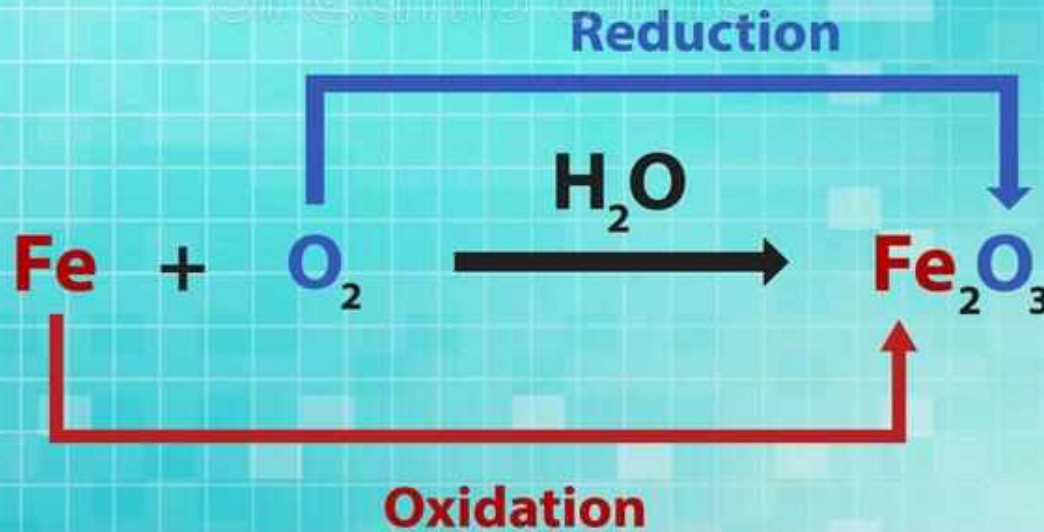
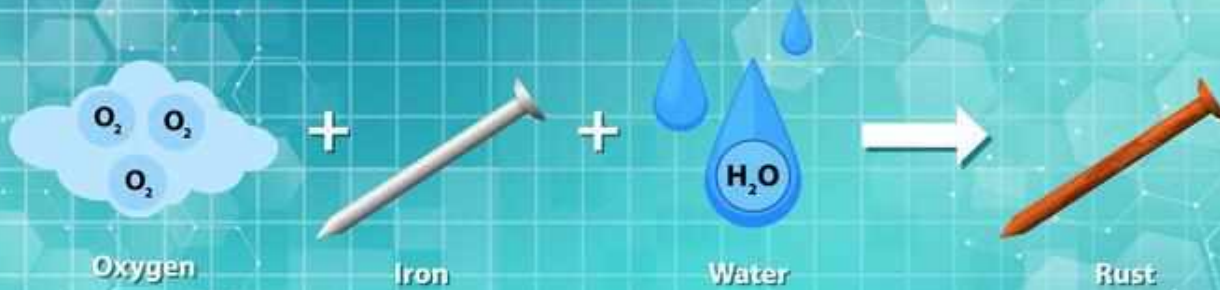
i) If enough O_2 is present: $\text{Fe}(\text{OH})_2$ is oxidised to rust:

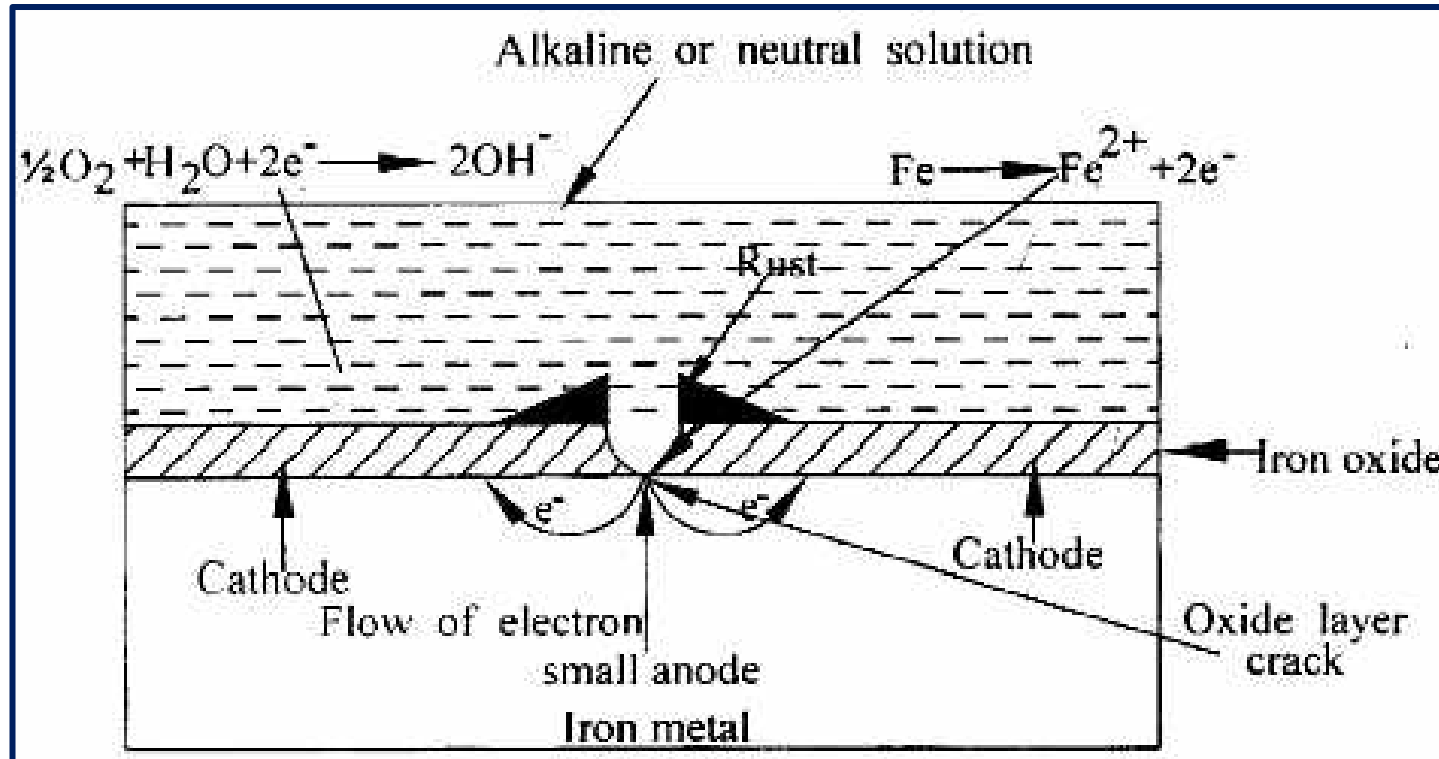


ii) In limited supply of oxygen Black Magnetite is formed:



PROCESS OF RUSTING





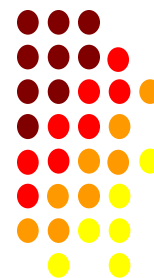
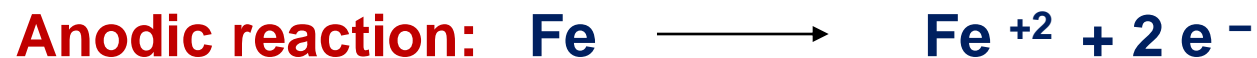
Mechanism of wet corrosion by oxygen absorption mechanism

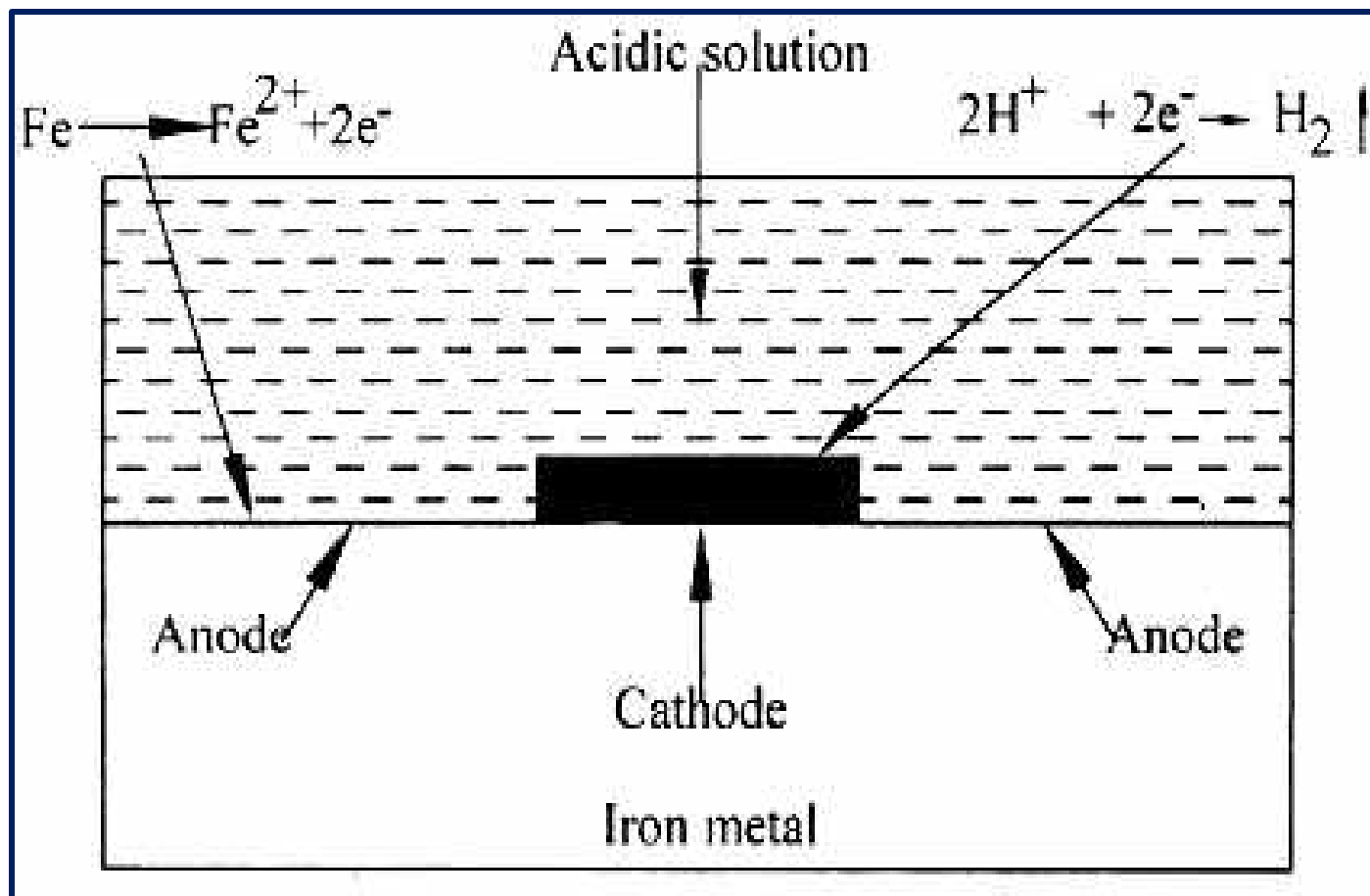
(Small anodic area and large cathodic area, so higher rate of corrosion)



Hydrogen evolution mechanism (in acidic medium)

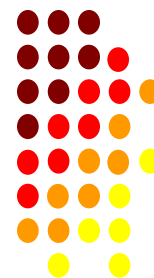
All the metals placed above H_2 in electrochemical series, corrodes in acidic solution by hydrogen evolution mechanism.





Mechanism of wet corrosion by hydrogen evolution mechanism

(Small cathodic area and large anodic area, so higher rate of corrosion)



CHEMICAL CORROSION OR DRY CORROSION

Corrosion that takes place in the absence of electrolyte, due to direct attack of gases on metals is called dry corrosion.

This type of corrosion takes place at elevated temperature and corrosion is uniform over metal surface. E.g. attack of oxygen on iron.

Mechanism:

At anode (oxidation): $2M \longrightarrow 2M^{n+} + 2ne^{-}$

At cathode (Reduction): $O_2 + 2ne^{-} \longrightarrow nO^{2-}$

Overall Reaction: $2M + O_2 \longrightarrow 2M^{n+} + nO^{2-}$



Oxidation occurs first at the surface of the metal and a scale of metal oxide is formed and it tends to act as a barrier for further oxidation.

Nature of the oxide formed:

It plays an important role in further oxidation corrosion process. When the oxide film formed is:

i) Stable layer: - It get adhered tightly to the parent metal surface. It is impervious in nature and hence behaves as protective coating, thereby shielding the metal surface. Consequently further oxidation corrosion is prevented. E.g.: Al, Sn. Pb, Cu, etc. form stable oxide layers on surface thus preventing further oxidation.

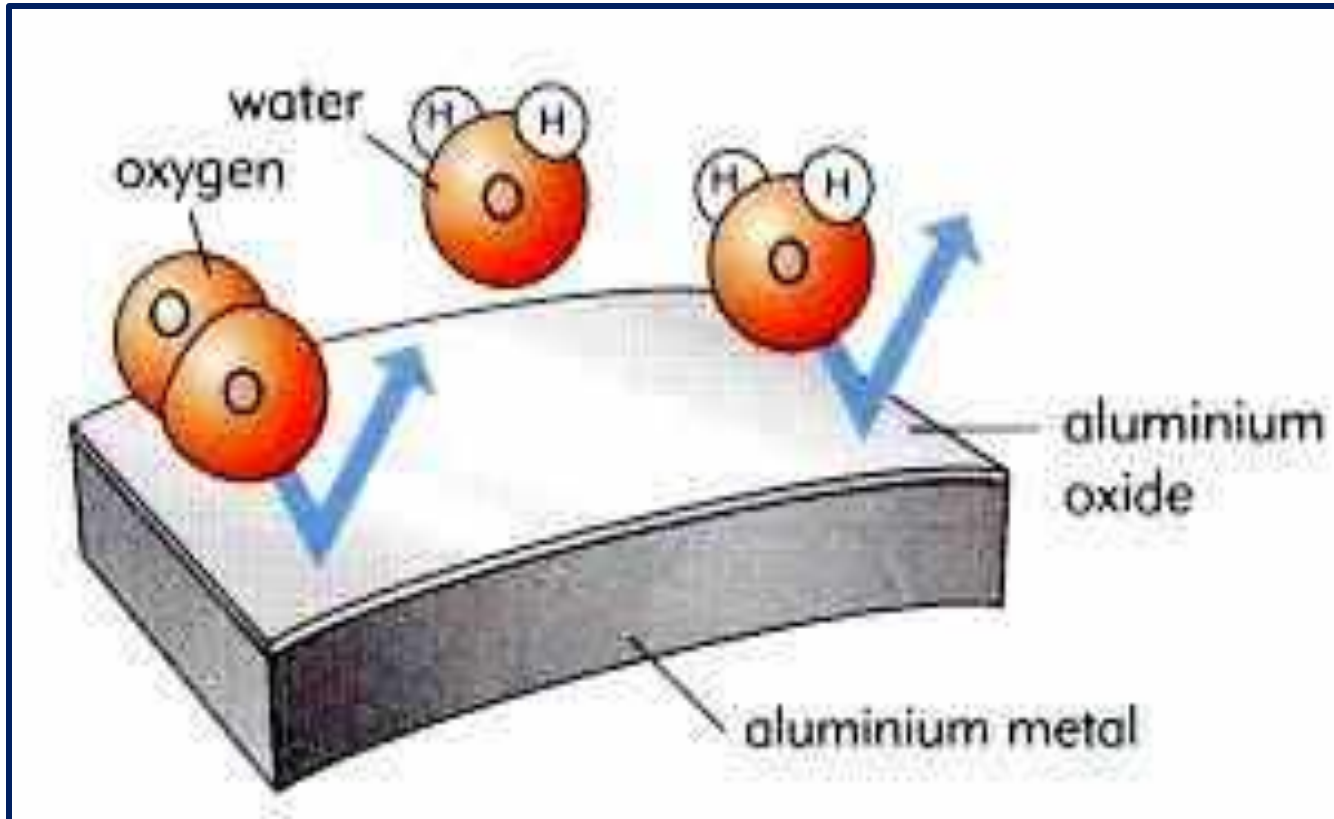


Passivity:

Some metals do not corrode according to their position in galvanic series and resist corrosion. This property of metals is called passivity and such metals are called passive metals.

This happens because they form a protective, self-healing and strong metal oxide layer on their surface which protects them from further corrosion.

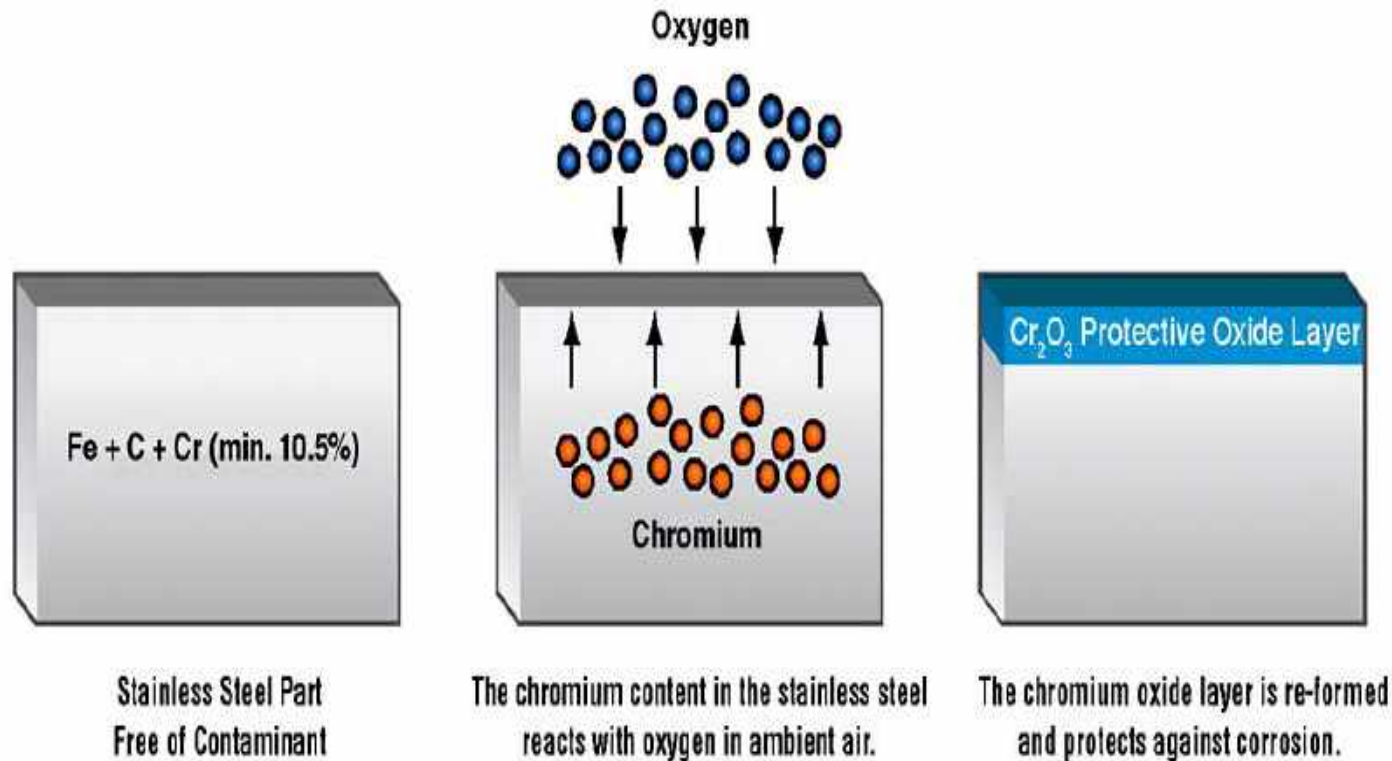




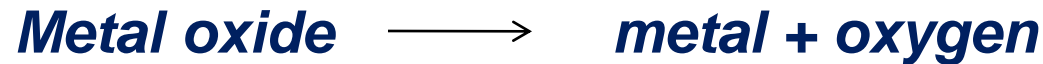
Aluminium is protected due to formation of Aluminium Oxide layer on its surface which acts as a protective layer.



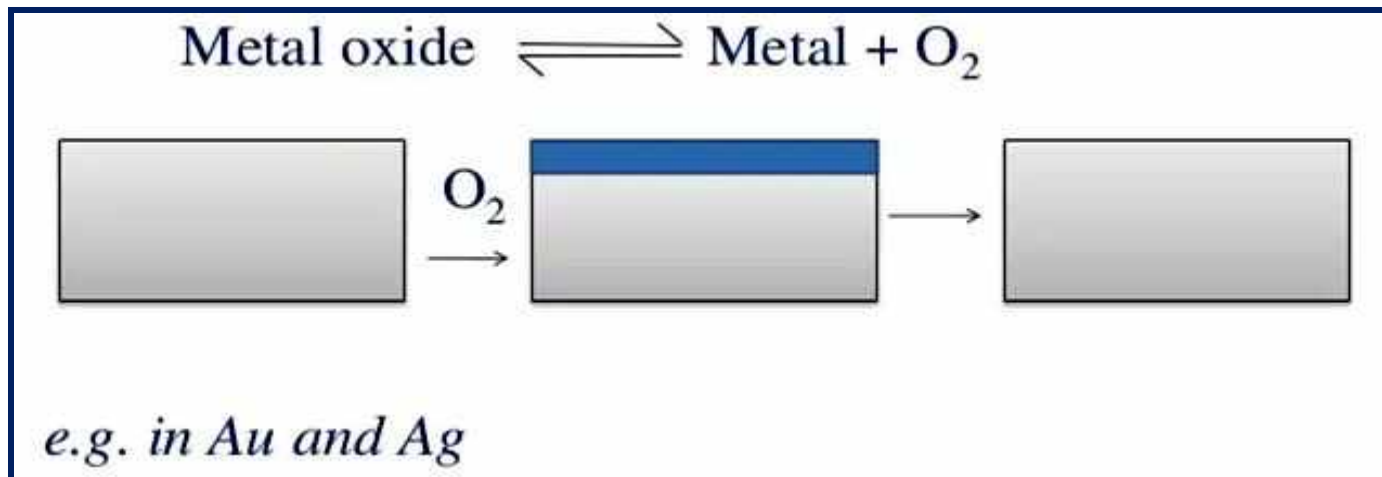
Passivation Process



ii) **Unstable Layer:** The oxide layer formed decomposes back into metal and O₂.



Consequently oxidation corrosion is not possible in such cases. Eg: Ag, Au and Pt do not undergo oxidation corrosion.



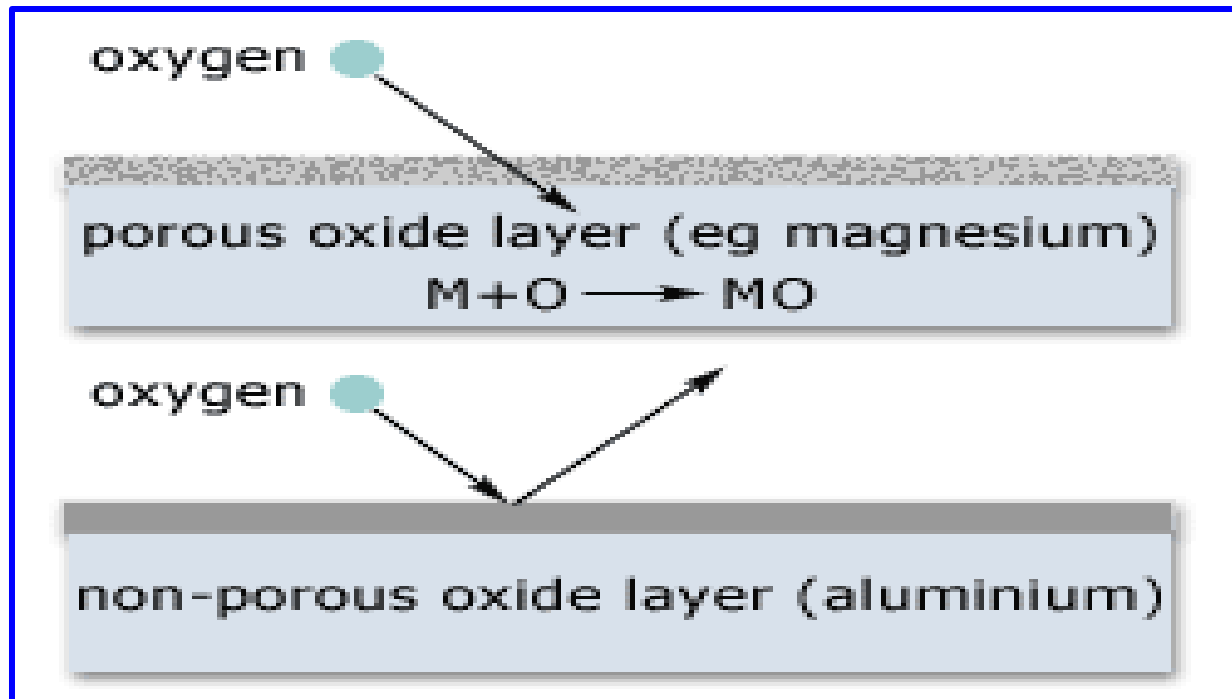
iii) Volatile Layer: The oxide layer formed is volatile in nature and evaporates as soon as it is formed. There by leaving the under lying metal surface exposed for further attack. This causes rapid continuous corrosion, leading to excessive corrosion eg: Mo- molybdenum forms volatile MoO_3 layer.

E.g. molybdenum oxide (MoO_3) is volatile.



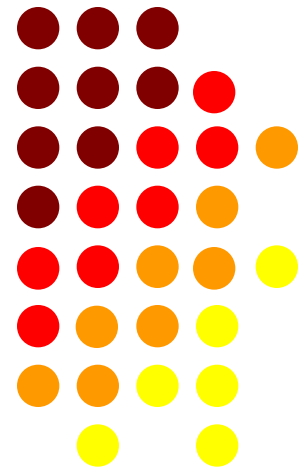
iv) Porous Layer: Contains pores and cracks. In such a case the atmospheric oxygen has access to the underlying surface of the metal through the pores or cracks of the layer, there by corrosion continues until the entire metal is converted to its oxide.

Eg: Iron when attacked by H_2S at high temperature forms porous FeS layer.



LECTURE - 24

- **Prevention of corrosion**
- **Types of corrosion**



FeOH

FeOH

FeOH

Also known as RUST.

Prevention of corrosion

Corrosion can be prevented by the following methods:

1. Proper design

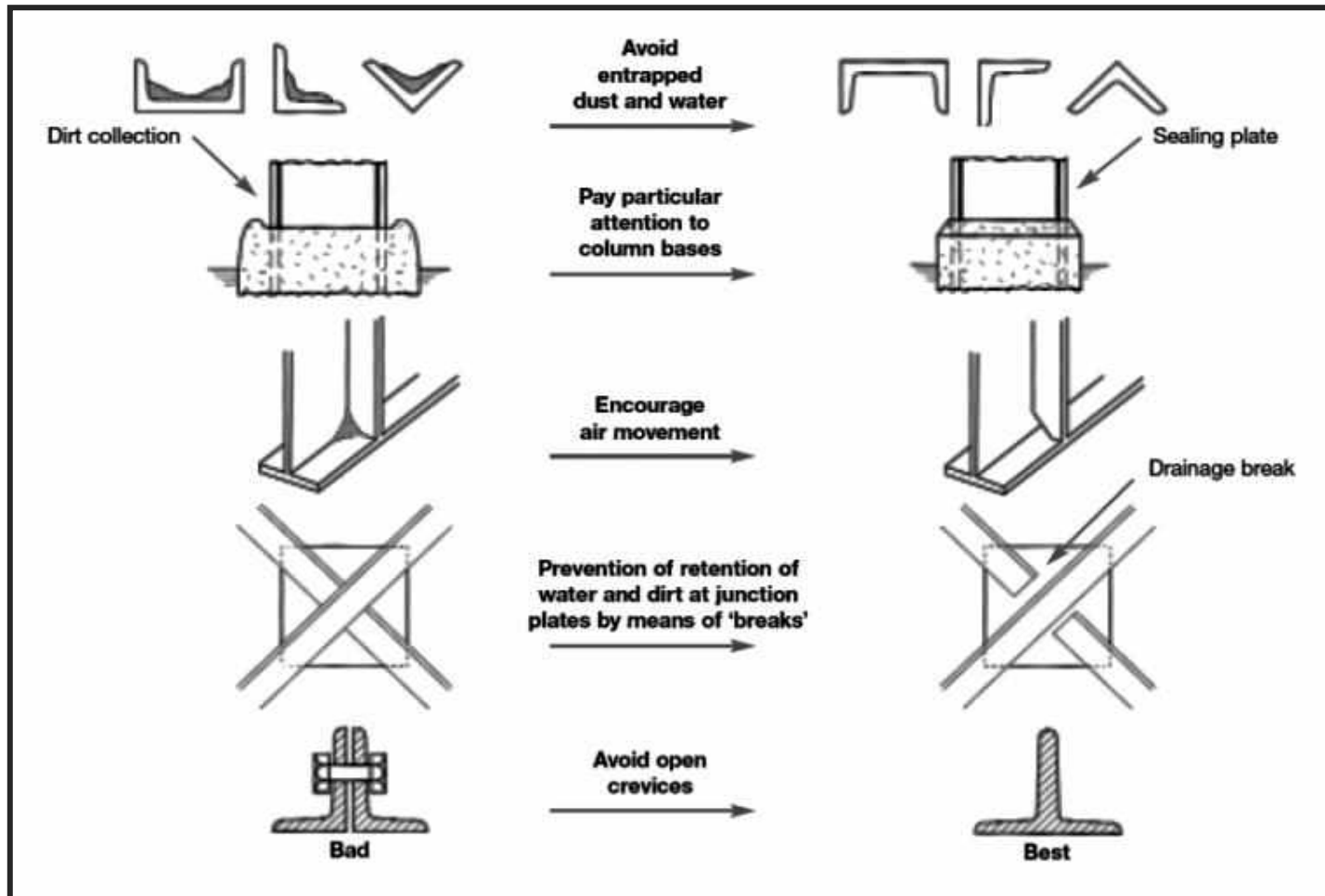
- Avoid sharp bends and sharp corners.
- Avoid contact of dissimilar metals in presence of corroding medium.
- There should be proper drainage.
- When the two dissimilar metals are to be used in contact, anodic area should be large and cathodic area should be small.
- If two dissimilar metals have to be used in contact, their position in electrochemical series should be as close as possible.
- If two metals have to be coupled use insulation between them.

2. Modification of environment

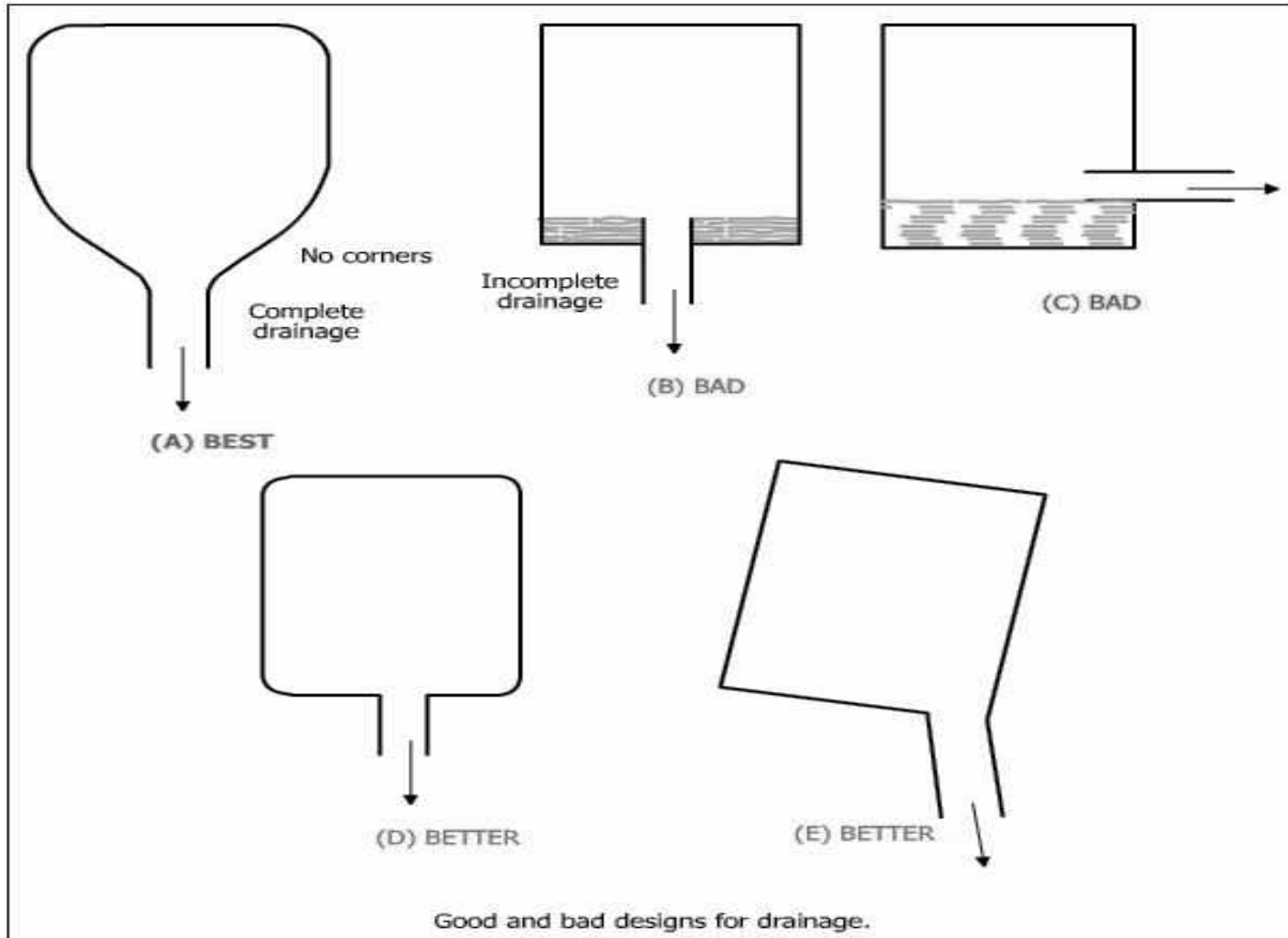
- Removing moisture by using silica gel.
- Removing oxygen by adding oxygen scavengers like hydrazine



Prevention of Corrosion by Proper Designing



Prevention of Corrosion by Proper Designing

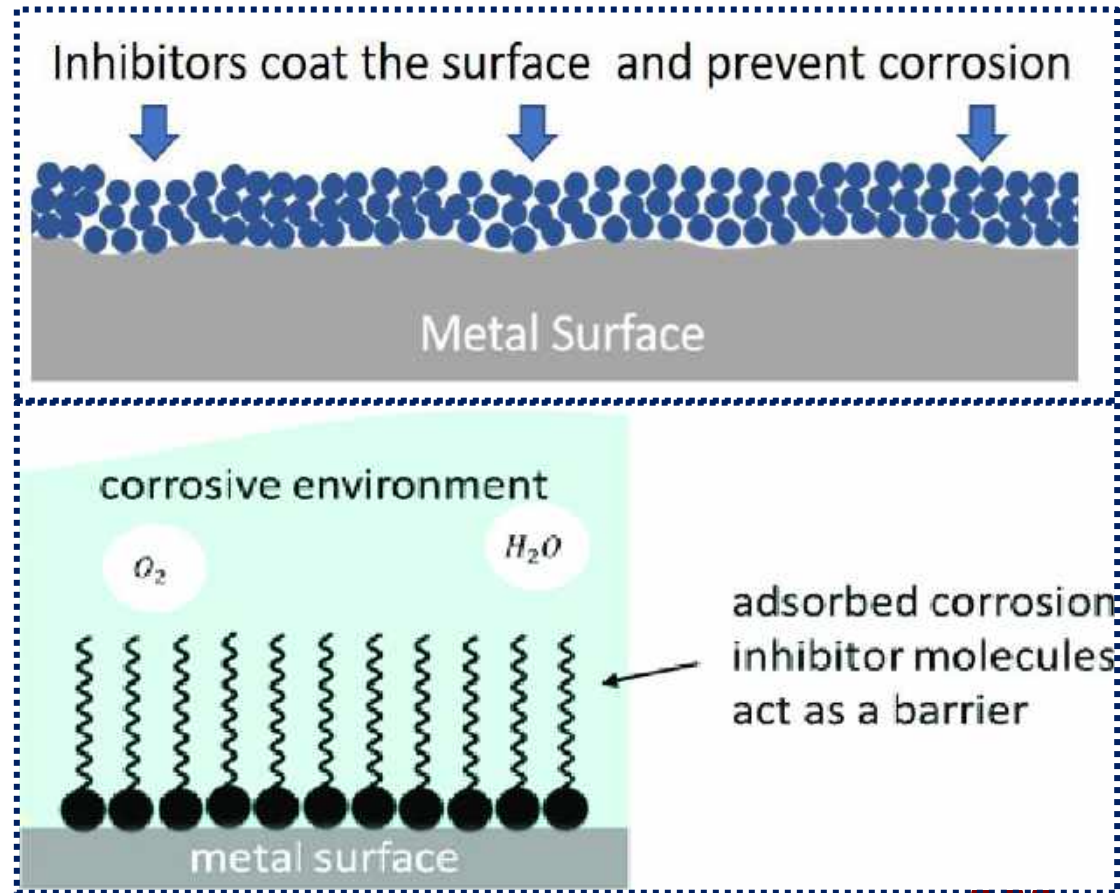


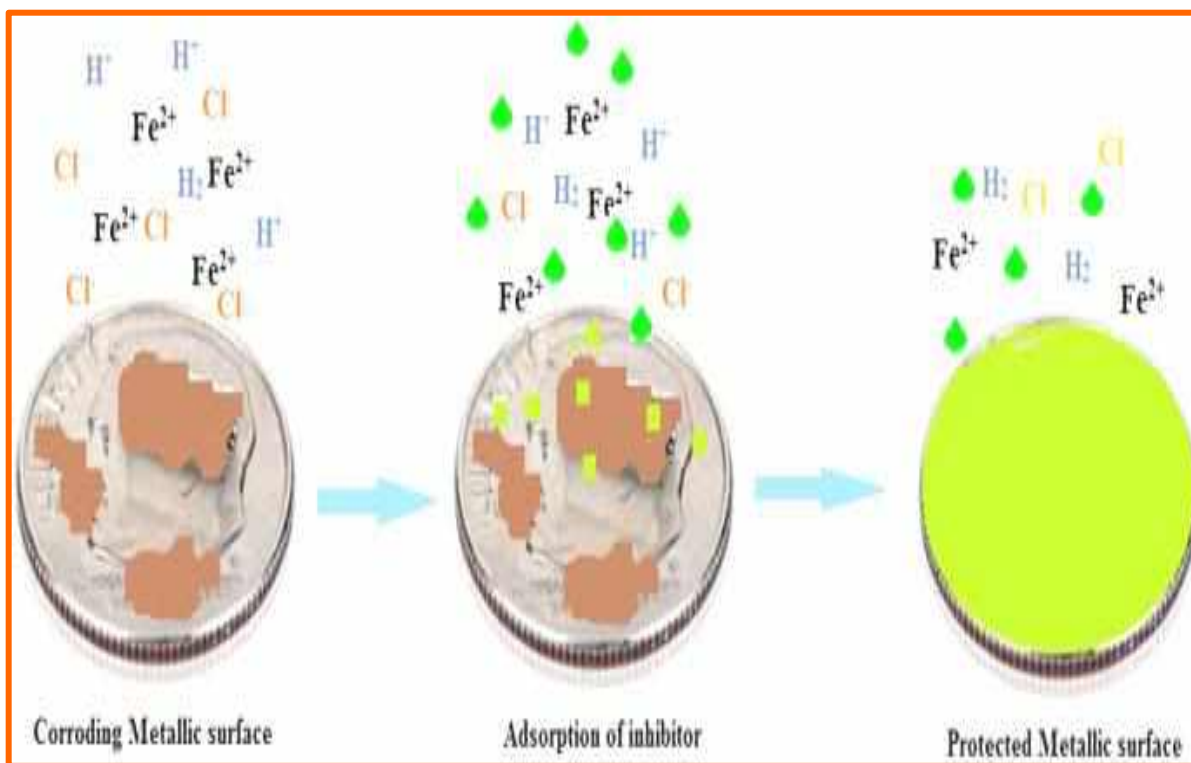
3. **By using inhibitors:** The substances which are added from outside to inhibit the corrosion are known as inhibitors.

There are two types of inhibitors: Anodic Inhibitors and Cathodic Inhibitors.

a) Anodic inhibitors

They react with the metallic ions of anode and form insoluble precipitate which is adsorbed on metal surface forming a protective film/barrier. Ex: alkalis, phosphates, chromates, etc.





b) CATHODIC INHIBITORS

They decrease the rate of reaction thereby reducing rate of overall corrosion.

i) In acidic medium

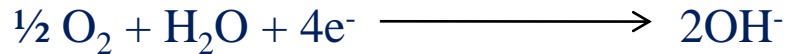


Cathodic inhibitors slow down the diffusion of H^+ ions through cathode and thus reduces corrosion rate.

Ex – Amines, Mercaptans, ureas, thioureas, etc.

ii) In neutral/alkaline medium

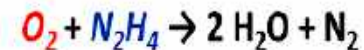
Cathodic reaction:



Cathodic inhibitors remove O_2 that is being used at cathode, thereby reducing corrosion.

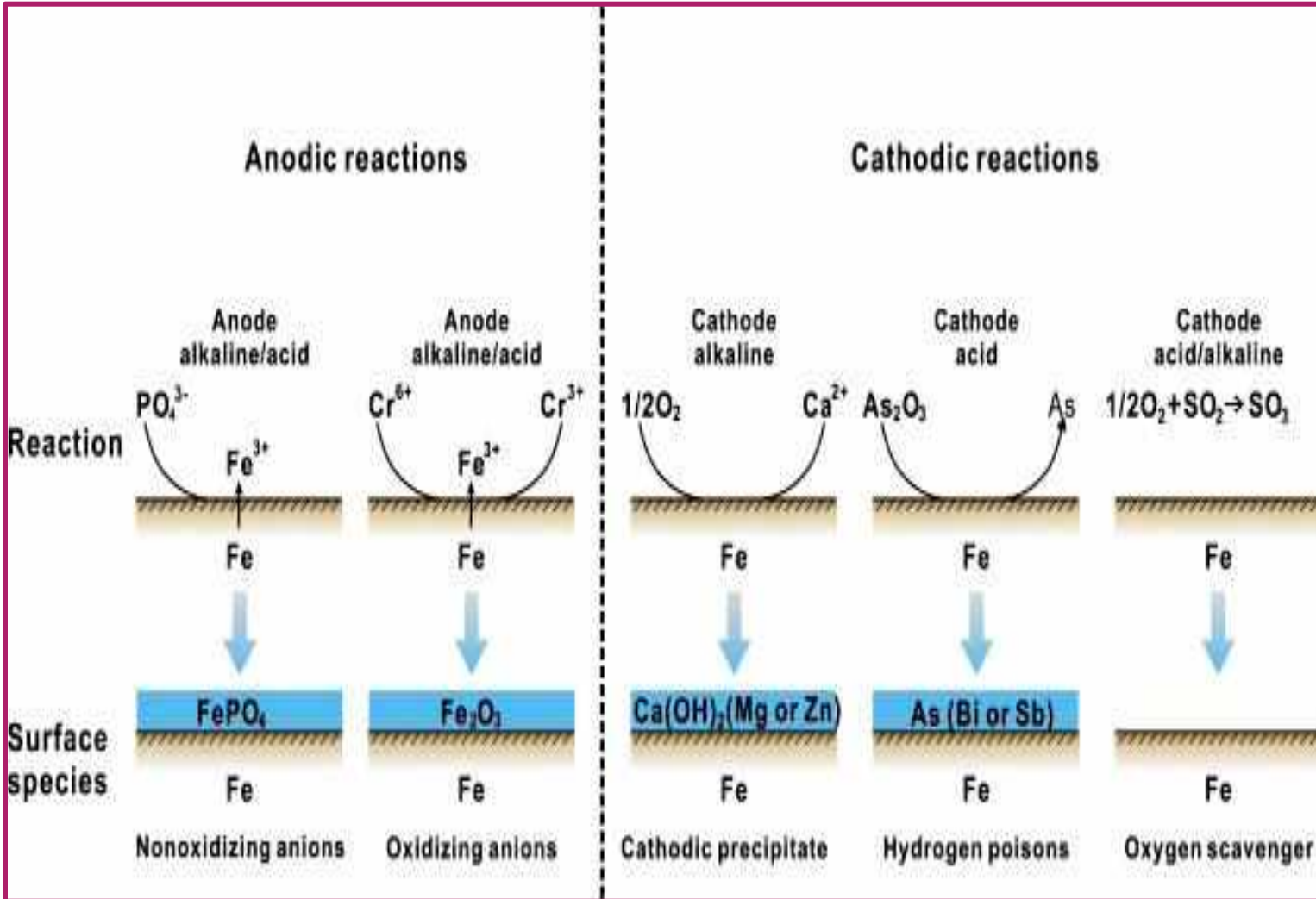
O_2 scavengers like Na_2SO_3 , N_2H_4 , etc. are used.

– Hydrazines



– Sodium Sulfite





Anodic and Cathodic inhibitors



4. Changing the operating variables: lowering the temperature, selecting suitable pH.

5. Protective coatings: Protective coatings are of three types:

- **Organic coating:** includes use of paints, varnishes, etc. which acts as organic barrier between metal and environment.
- **Inorganic coating:** inorganic surface barriers produced by chemical/ electrochemical reactions at the surface of base metal coatings are used for paints. Ex – phosphates, chromates , etc.



Inorganic coating to prevent corrosion



Corrosion resistant paint



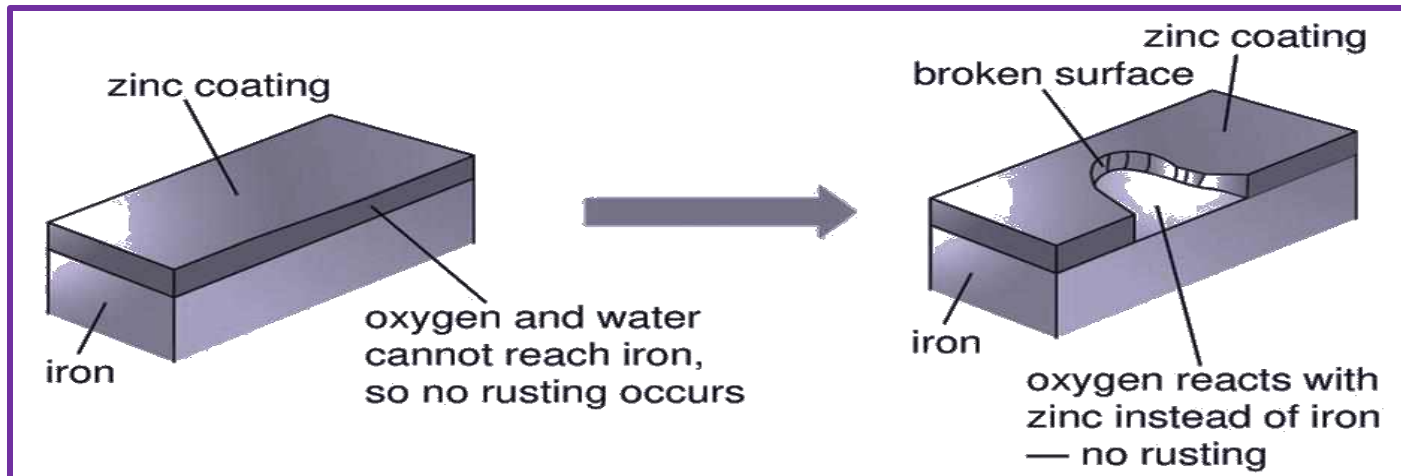
Metallic coatings: In metallic coatings one metal is coated over another metal. There are two types of metallic coatings: i) anodic coating and ii) cathodic coating.

i) ANODIC COATING or SACRIFICIAL COATING

- Base metal is coated with a metal which is more reactive.
- Protects the underlying base metal sacrificially.
- Known as anodic coating as the reduction potential of coated metal is less than that of base metal.



- If there are pores, cracks, or breaks in such a coating base metal is not corroded till all the coated metal is consumed.
- Zn, Cd, Al are generally used as sacrificial coatings.
- Ex: galvanised iron (coating of Zn on Fe)



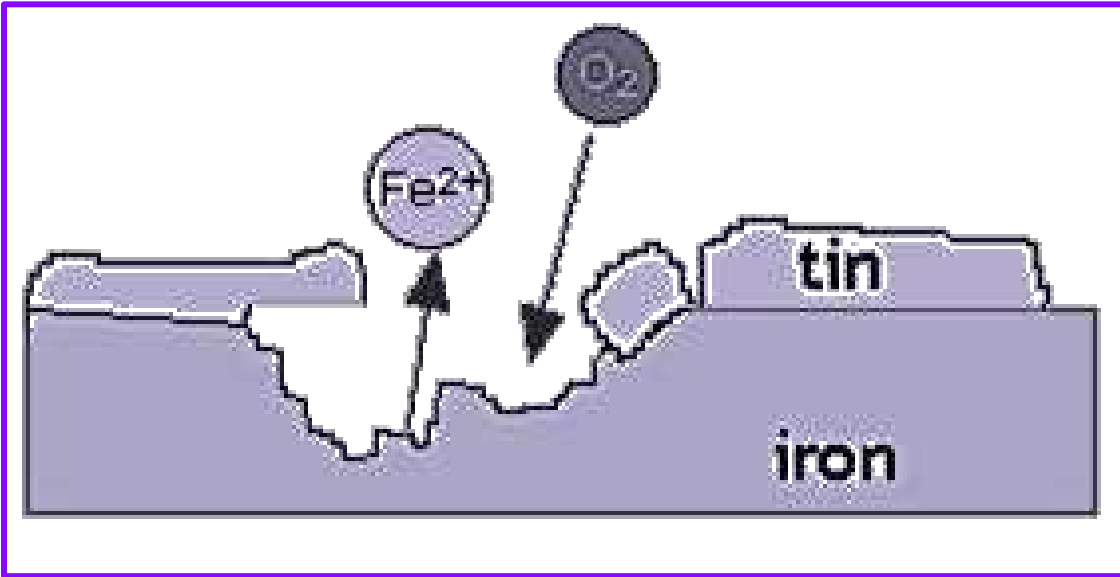
SACRIFICIAL PROTECTION OF IRON BY ZINC



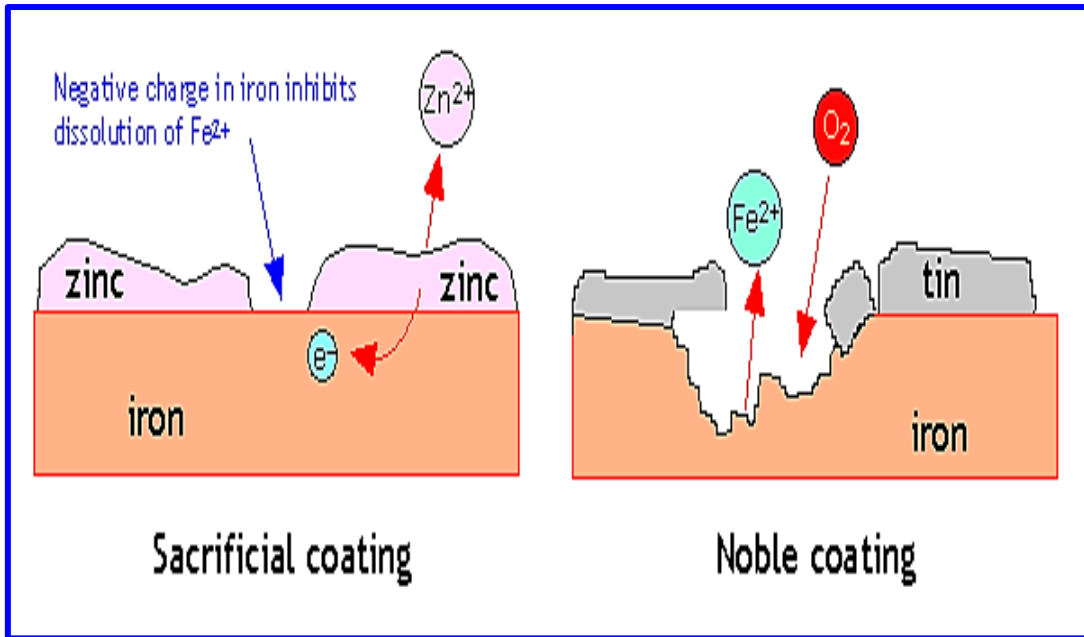
ii) CATHODIC COATING or NOBLE COATING

- Base metal is coated with a metal which is less reactive (more noble) in its comparison.
- Protects the base metal due to its noble character.
- Also known as Cathodic coating as reduction potential of coated metal is more than that of base metal.
- If there are pores, break, etc. corrosion takes place because of small anodic area and large cathodic area.
- Ni, Ag, Cr, Pb, etc. are used generally for noble coating. Ex: coating of Sn on Fe.





CATHODIC COATING or NOBLE COATING



6. MODIFICATION OF METAL

Metal can be modified by annealing, refining and alloying.

- **Annealing** is the heat treatment process that changes the physical and sometimes also the chemical properties of a material. It is used mostly to increase the ductility, reduce the hardness and to help to eliminate the internal stress of a material .
- **Refining** consists of purifying an impure metal.
- **Alloying** is a process in which two or more metal elements are melted together in a precise combination to form a specific material or alloy.

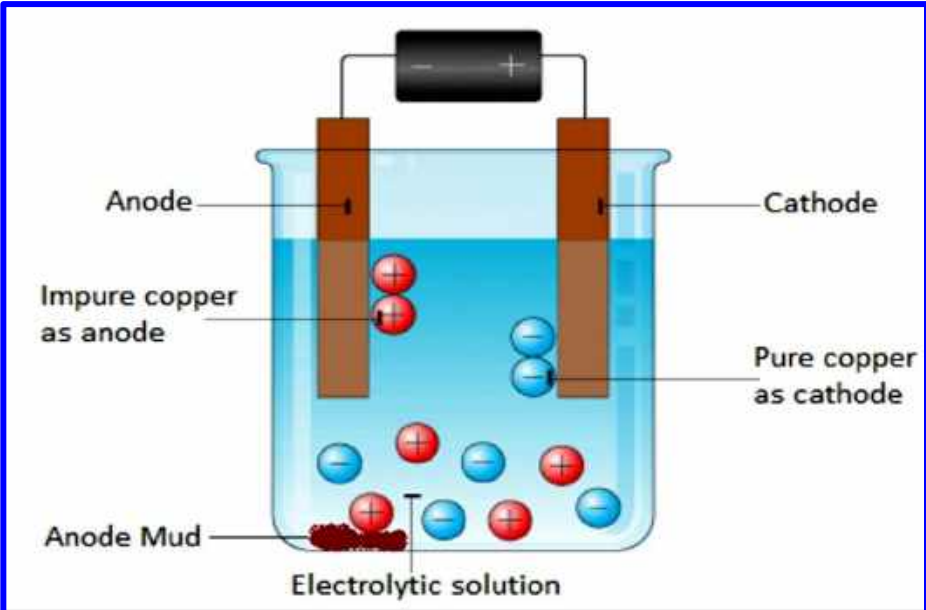


Metal Refining

Annealing



Alloying



 Bronze copper (78-95%) tin (5-22%)	 18K Gold gold (75%) copper (12.5%) silver (12.5%)	 Brass copper (60-90%) zinc (10-35%)
 Cast Iron iron (96-98%) carbon (2-4%)	 Sterling Silver silver (92.5%) copper (7.5%)	



7. Cathodic protection

The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection.

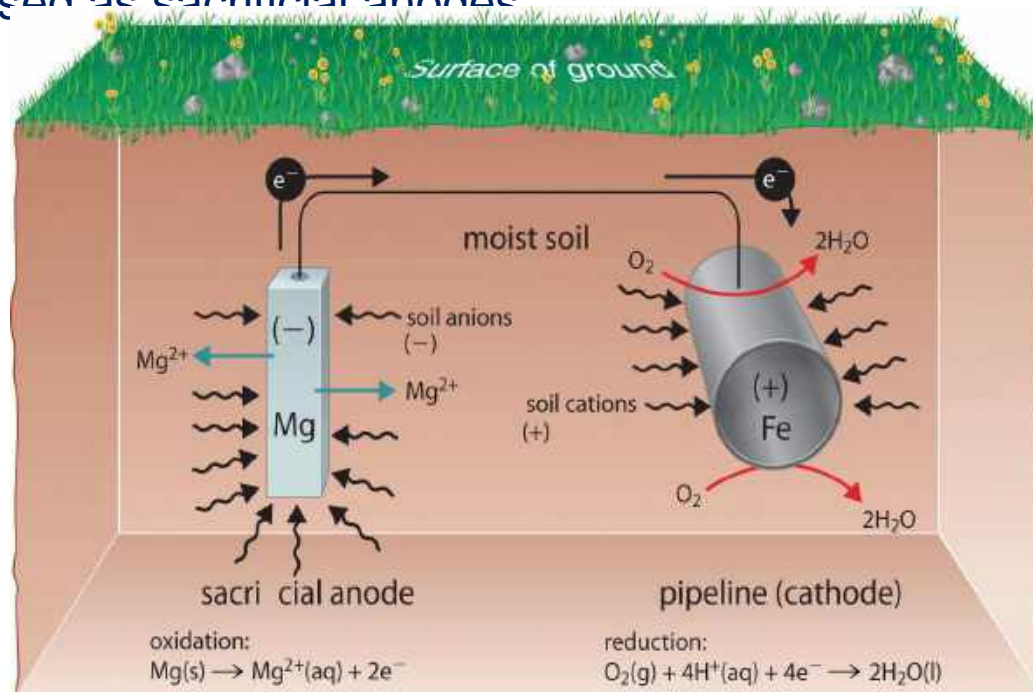
There are two types of cathodic protection:

- Sacrificial anodic protection.
- Impressed current method.



a) Sacrificial anodic protection

- Base metal is connected by a wire to a more reactive metal so that the base metal becomes cathode and more reactive metal becomes anode.
- The anodic metal gets corroded slowly, while the base metal (cathodic) is protected. The more active metal is called sacrificial anode and is replaced by a fresh one, when it is completely consumed. Mg, Zn, Al and their alloys are generally used as sacrificial anodes.

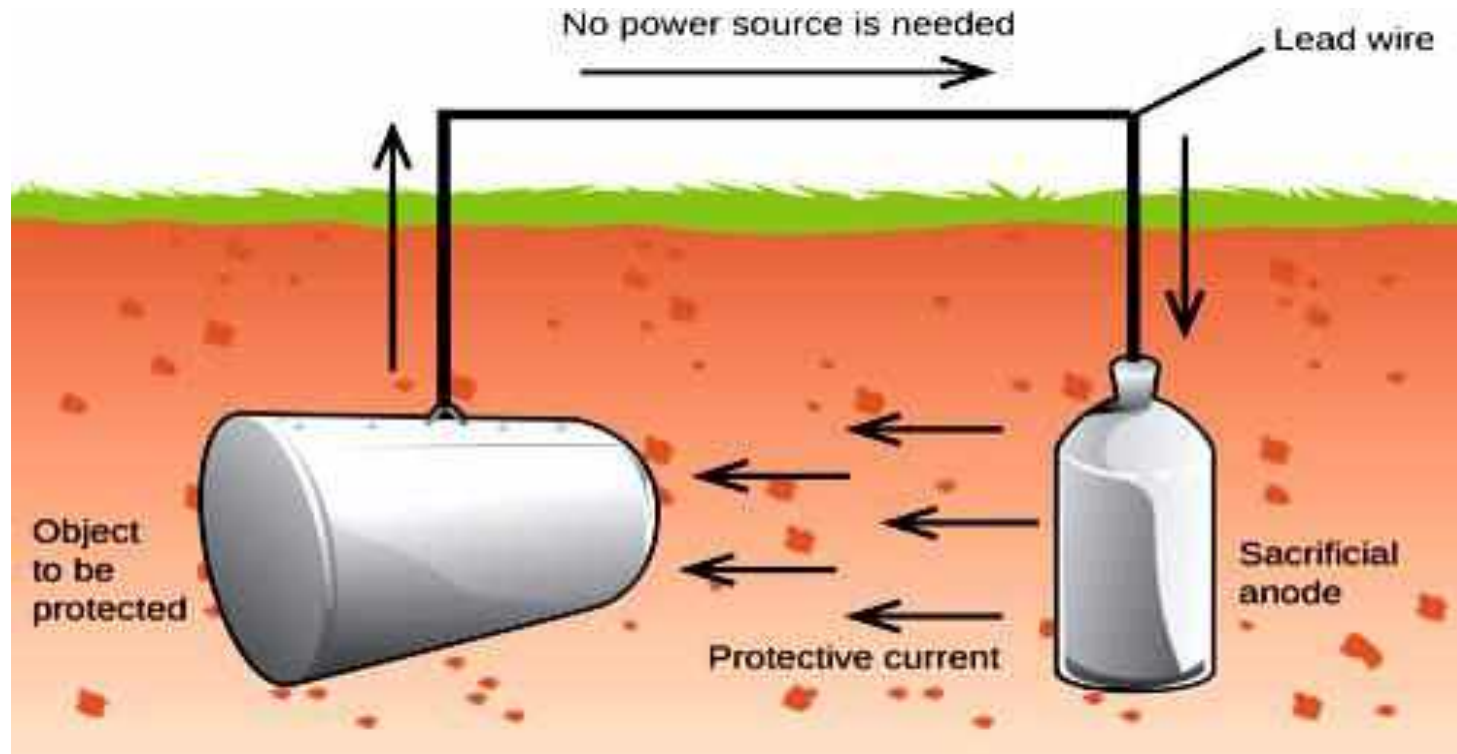


SACRIFICIAL ANODIC PROTECTION



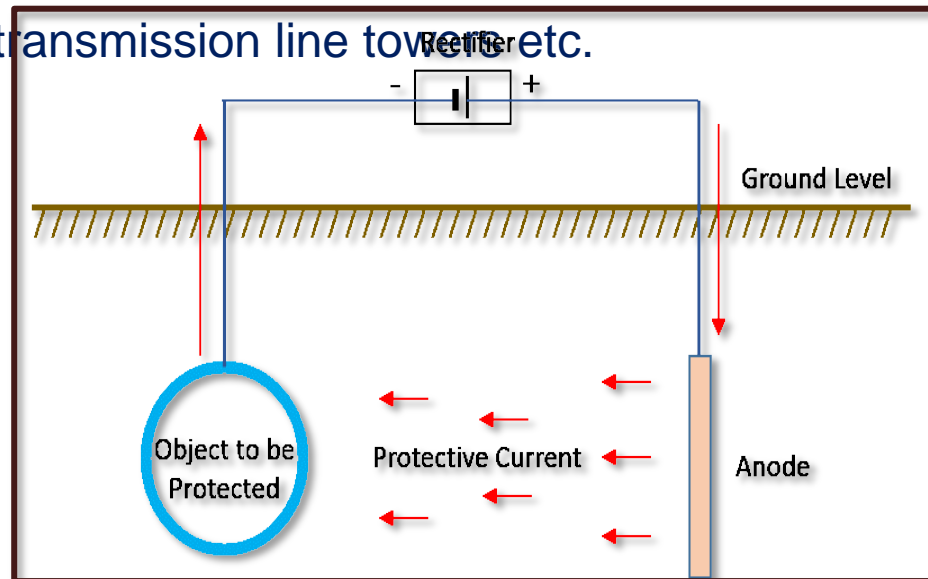
Ex: 1. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

2. The underground water pipelines and water tanks are also protected by sacrificial anode method.



b) Impressed current cathodic protection

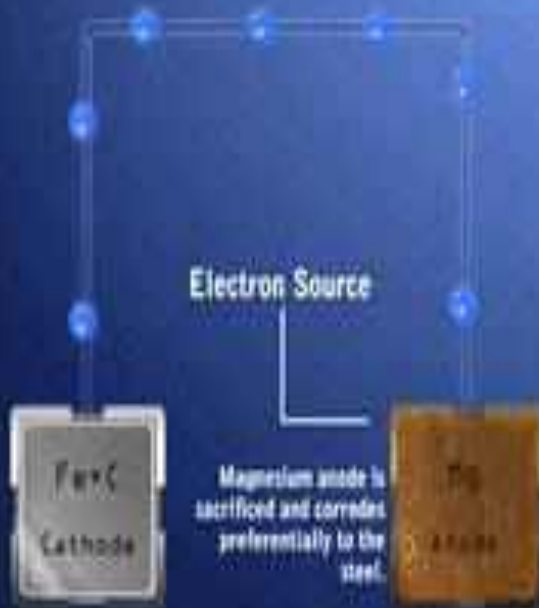
- In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.
- The impressed current is slightly higher than the corrosion current. Thus, the anodic corroding metal becomes cathodic and protected from corrosion.
- The impressed current is taken from a battery or rectified on A.C. line. The impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers etc.



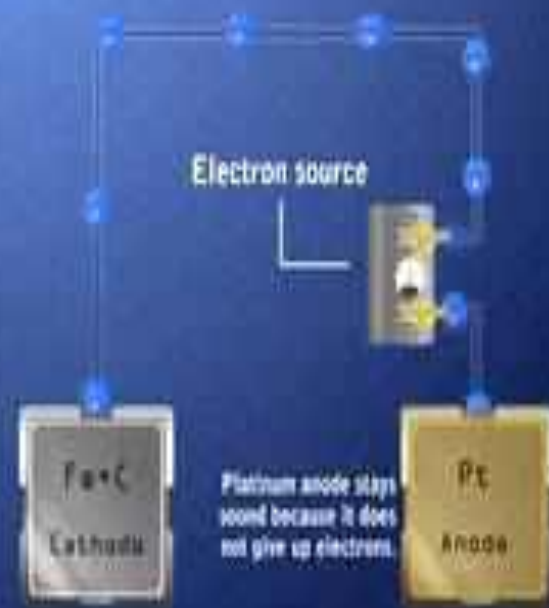
IMPRESSED CURRENT CATHODIC PROTECTION



Galvanic (sacrificial) Cell

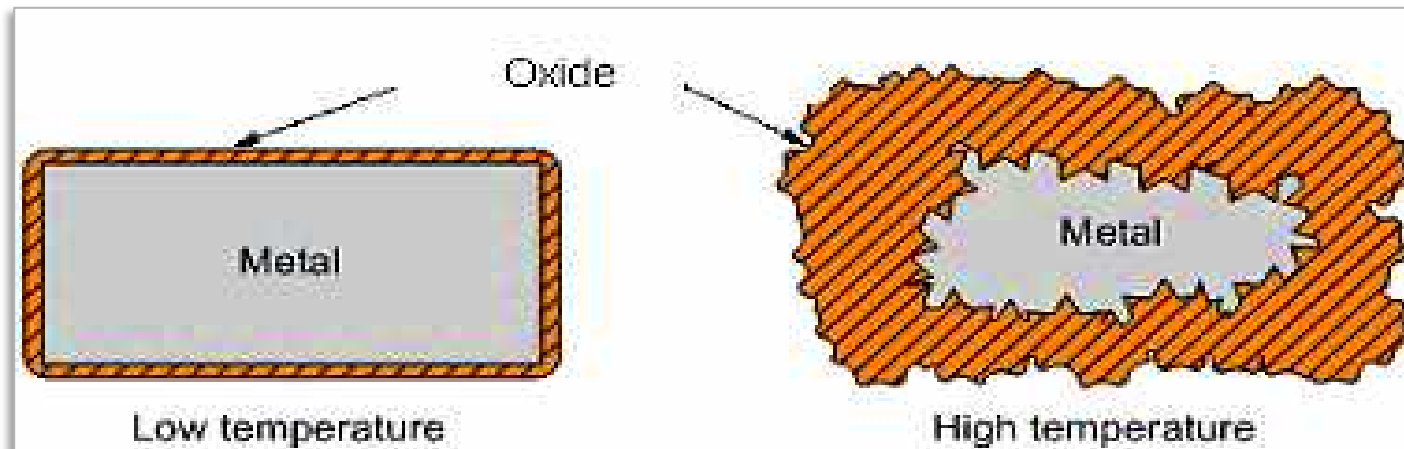


Impressed Current Cell



DIFFERENT TYPES OF CORROSION

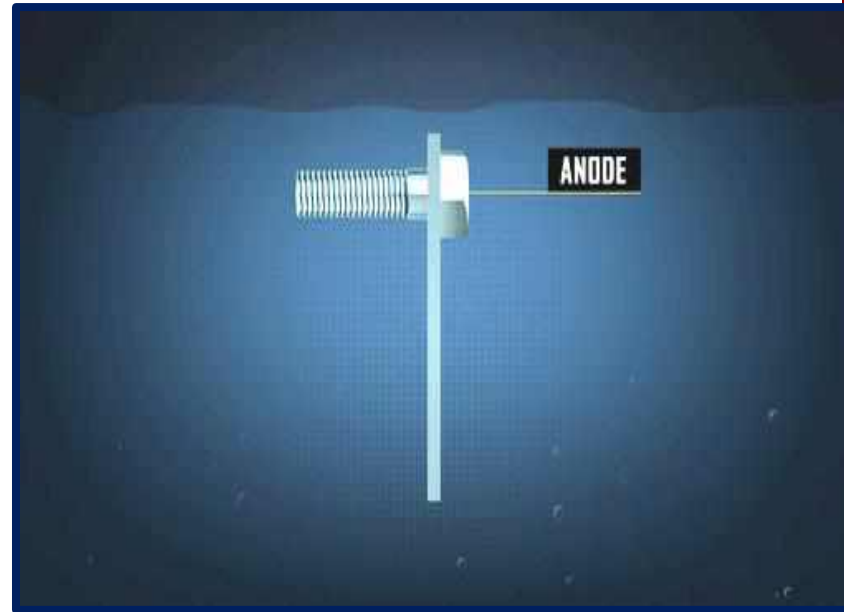
Corrosion due to difference in temperature: Usually, a **temperature** or pressure **increase** directly leads to a higher **corrosion** rate because electrochemical reactions generally occur faster at higher **temperatures**. **Temperature** increases add energy to the reactions, which increases the **corrosion** rate.



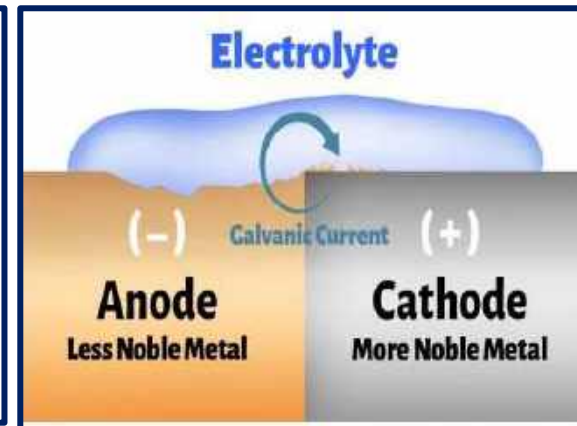
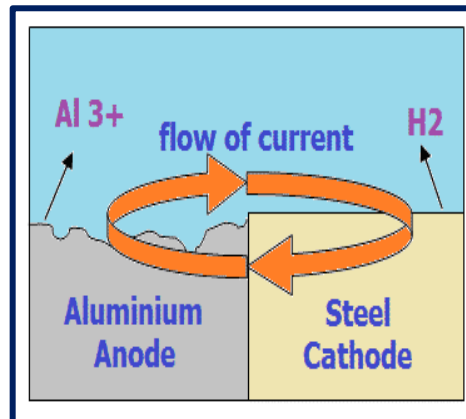
Galvanic corrosion (bimetallic corrosion):

It is an electrochemical process whereby one metal corrodes in preference to another metal that it is in contact with through an electrolyte.

Galvanic corrosion occurs when two dissimilar metals are immersed in a conductive solution and are electrically connected.

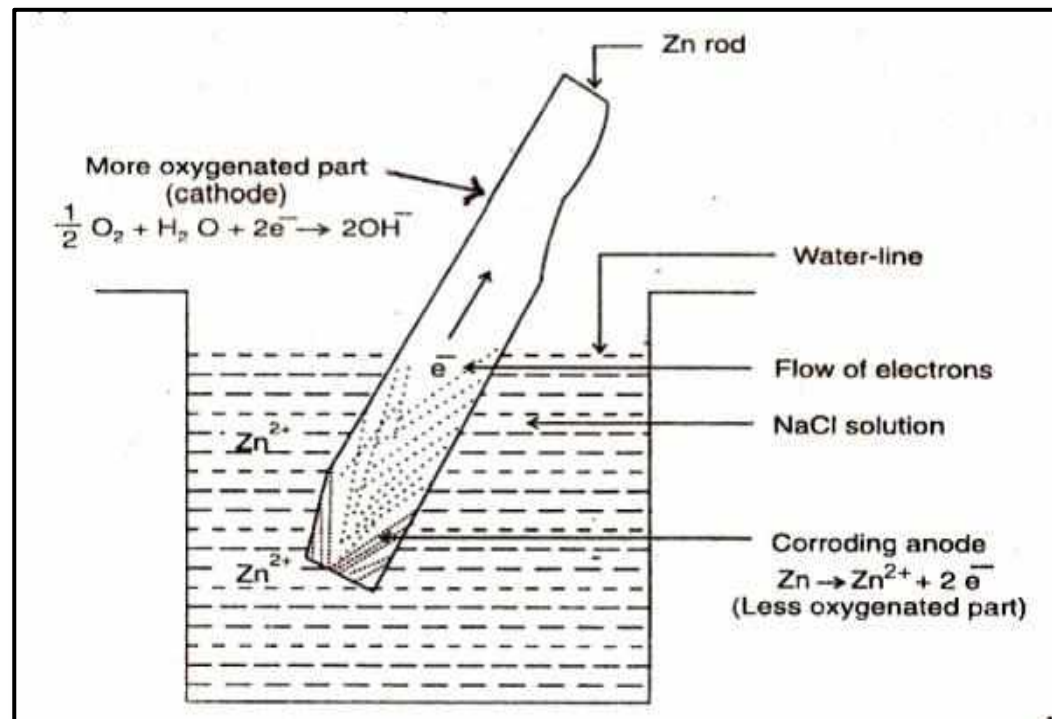


Galvanic corrosion



Concentration cell corrosion:

- Occurs when two or more areas of the same metal surface are in contact with electrolytic solutions of different concentrations.
- The area of metal surface in contact with the higher concentration of metal ions will become anodic and eventually corrode.
- It may also occur when a significant difference in metal ion concentration exists over a metal surface.

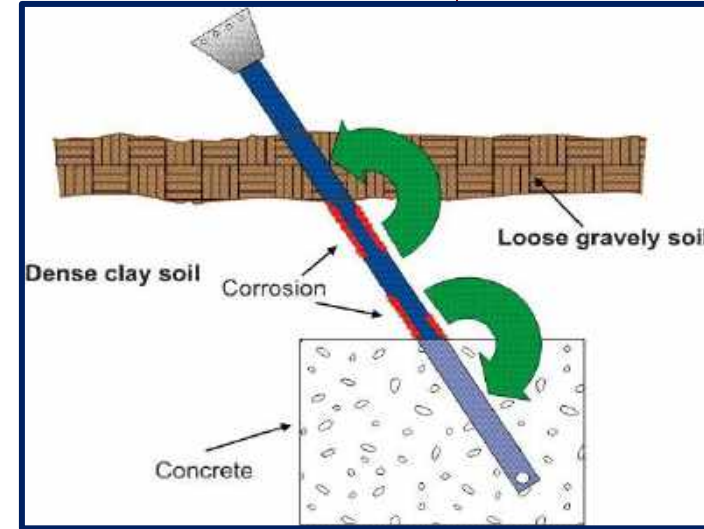


Concentration cell corrosion

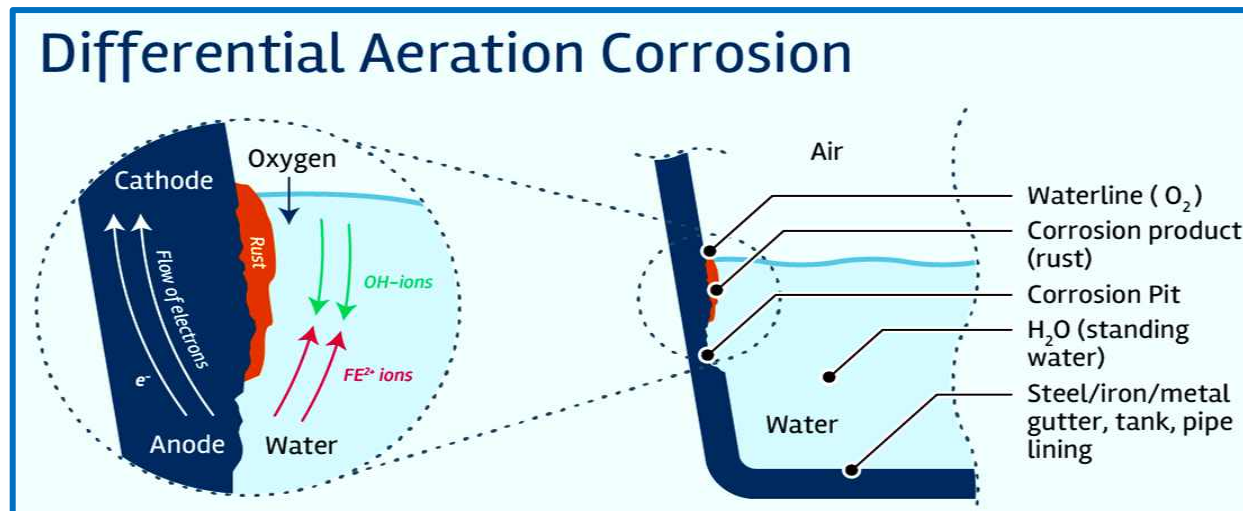


Differential aeration corrosion:

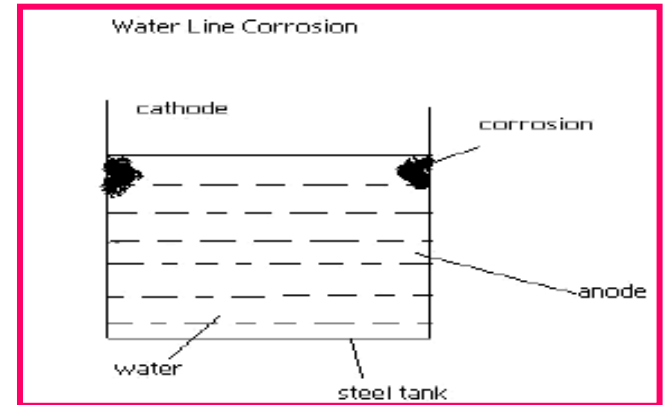
It is a type of corrosion that occurs when oxygen concentrations vary across a metal's surface. The area with the higher oxygen concentration becomes the cathode. The area with the lower oxygen concentration becomes the anode. Consequently, the portion of the metal that has the lower oxygen concentration is the portion subject to corrosion.



Differential aeration corrosion



Waterline corrosion: occurs when one portion of a base material is submersed in the water and another portion is in contact with the air. This creates a differential of the amount of oxygen in contact with the material's surface above and below the **waterline** and results in a **corrosive** reaction.



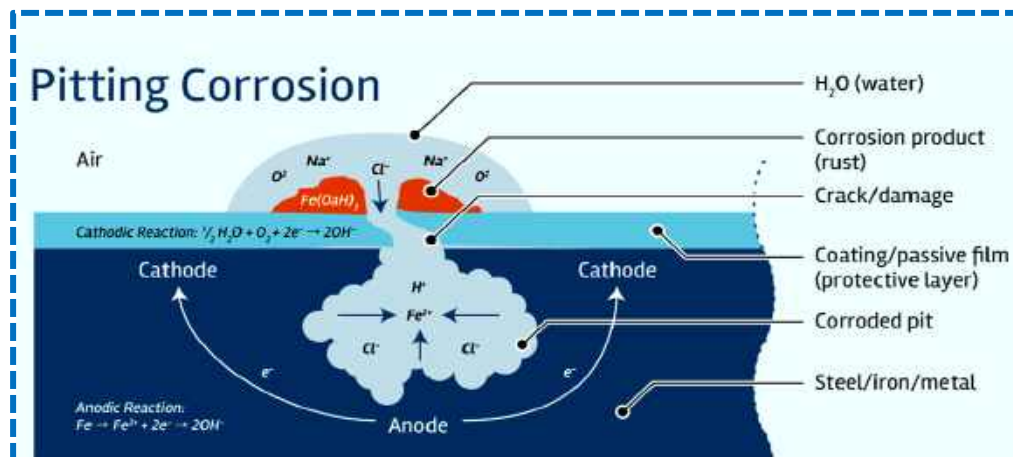
Images to show waterline corrosion



Pitting corrosion is a localized form of **corrosion** by which cavities or "holes" are produced in the material. **Pitting** is considered to be more dangerous than uniform **corrosion** damage because it is more difficult to detect, predict. **Corrosion** products often cover the pits.

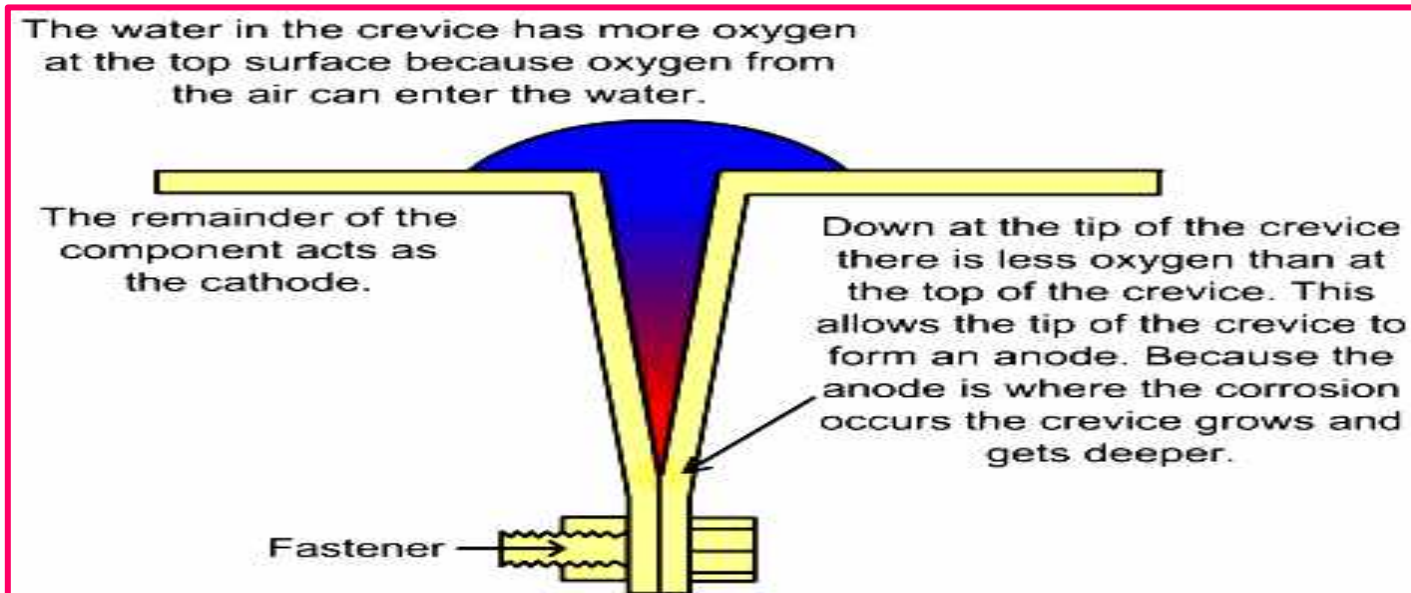


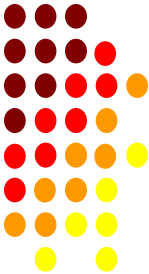
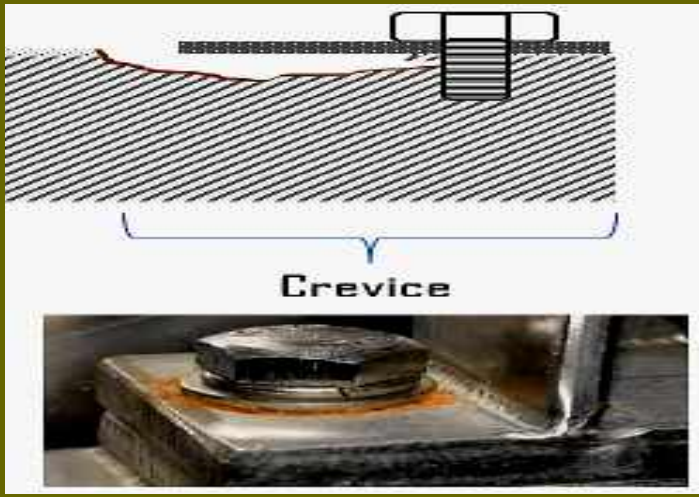
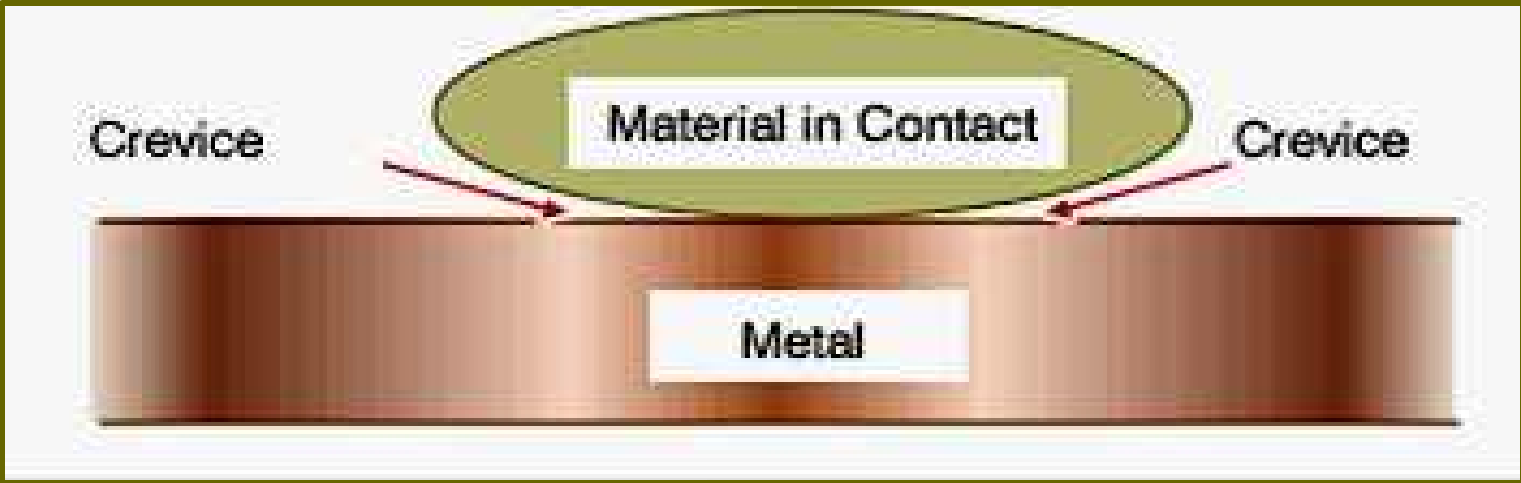
Images to show Pitting corrosion



Crevice corrosion

Crevice corrosion is also a localized form of corrosion and usually results from a stagnant microenvironment in which there is a **difference** in the **concentration** of ions between two areas of a metal. Crevice corrosion **occurs** in shielded areas such as those under washers, bolt heads, gaskets, etc.





Corrosion issues



Power Industry



Chemical Industry



Oil and gas Industry



Paper and pulp Industry



**Q1. Calculate the amount of rust ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) formed by complete rusting of 1 Kg of iron.
(2016-17)**

Ans.



Atomic weight of iron = 55.85

Molecular weight of rust formed = $2 \times 55.85 + 3 \times 16 + 3 \times 18 = 213.7$

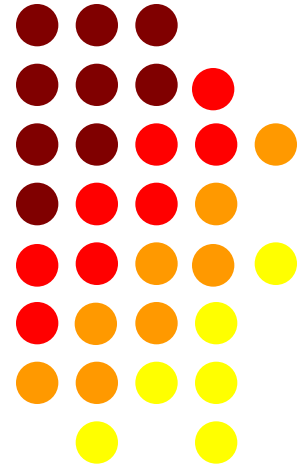
As, 2×55.85 Kg of iron forms 213.7 Kg rust

Hence 1 Kg iron forms $1 \times 213.7 / 2 \times 55.85 = 1.94$ Kg rust.



Cement and POP

- Introduction
- Portland cement
- Manufacture of Portland Cement
- Preparation
- use



Introduction

Concrete is widely used as a non-metallic material in construction of buildings, dams, bridges, high ways etc. In concrete, cement is a building material that possesses cohesive and adhesive properties and capable of bonding with stones, bricks, building blocks etc.

Portland Cement

The name Portland cement is used because this powder on mixing with water gives a hard, stone like mass which resembles Portland rock (Leeds city UK). It is widely used as a non-metallic material in construction. It is a composition of calcium silicates, calcium aluminates and small amount of gypsum.



Composition of Portland Cement

A sample of Portland cement contain following composition:

i) Calcium Oxide or lime (CaO)	: 60-70%
ii) Silica (SiO ₂)	: 20-24%
iii) Alumina (Al ₂ O ₃)	: 5-7.5%
iv) Magnesia (MgO)	: 2-3%
v) Ferric Oxide (Fe ₂ O ₃)	: 1-2.5%
vi) Sulphur trioxide (SO ₃)	: 1-1.5%
vii) Sulphur Oxide (Na ₂ O)	: 1%
viii) Potassium Oxide (K ₂ O)	: 1%



Manufacture of Portland Cement

The steps involve in the manufacturing process are as follows:

- ❖ **Crushing**
- ❖ **Mixing**
- ❖ **Burning**
- ❖ **Grinding**

Crushing:

In this step raw material of Portland cement lime, Silica, Alumina, Magnesia, Ferric Oxide, Sulphur trioxide, Sulphur Oxide, Potassium Oxide are crushed and ground to fine powder through ball mill.

Mixing:

In this step raw ingredients or fine powder are mixed in presence (wet process) or absence (dry process) of water to form slurry, then slurry is stored in storage tank.



Burning:

The burning process is done in Rotary Kiln. The Rotary Kiln possesses three different temperature zone like drying zone, calcinations zone and Clinkering zone.

- **Drying zone:**

It is the upper part of Rotary Kiln having temperature around 250°C where the water from the slurry evaporates.

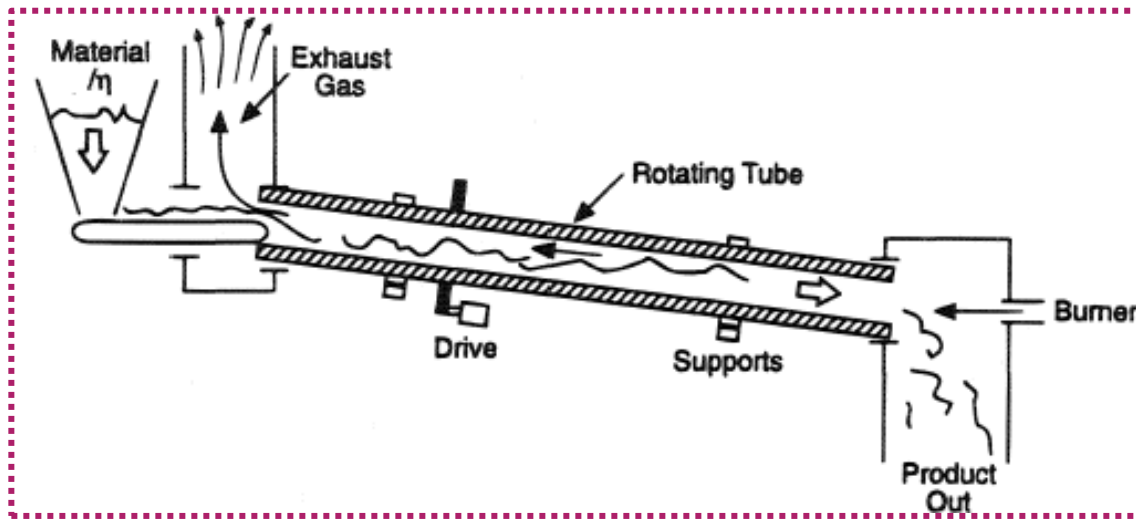
- **Calcinations zone:**

It is middle portion of Rotary Kiln where temperature ranges from 700°-1200°C in this region limestone undergoes decomposition to form quick lime and carbon dioxide (escape out).

- **Clinkering zone:**

It is the lower part of Rotary Kiln where quick lime with clay to form calcium silicate, aluminates and ferrite





- $2\text{CaO} + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4$ (Ca_2S)
Dicalcium silicate
- $3\text{CaO} + \text{SiO}_2 \rightarrow \text{Ca}_3\text{SiO}_5$ (Ca_3S)
Tricalcium silicate
- $3\text{CaO} + \text{Al}_2\text{O}_3 \rightarrow \text{Ca}_3\text{Al}_2\text{O}_6$ (Ca_3A)
Tricalcium aluminate
- $4\text{CaO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \rightarrow 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ (Ca_4AF)
Tetracalcium alumino ferrite

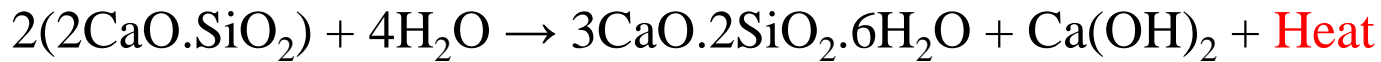
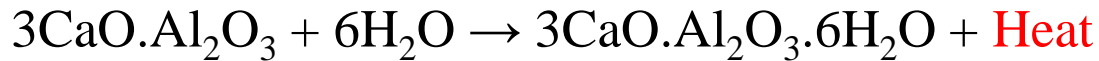
Grinding:

The cooled clinkers are ground to a fine powder in ball mill. At this time 2-3% of gypsum is added to prevent the early setting of cement.

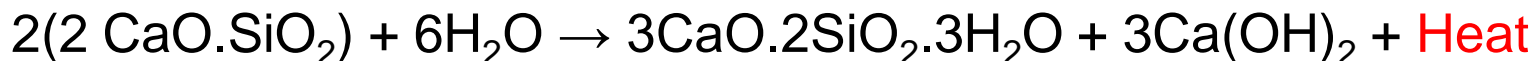


Setting and hardening of cement

- ❖ When water mixed with Cement, form a plastic paste. The paste is subjected to hydration and gel and finally crystalline products are formed.

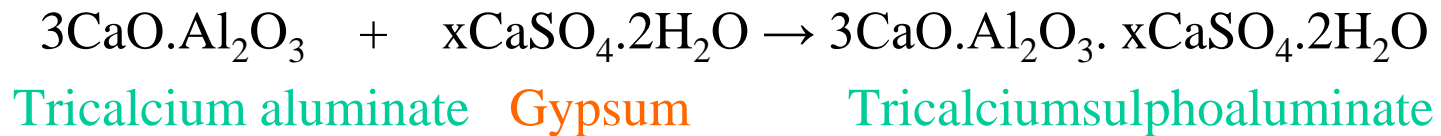


- ❖ Tobermonite gel, calcium hydroxide crystallization and hydrated tricalcium aluminate are responsible for final setting and hardening of cement.



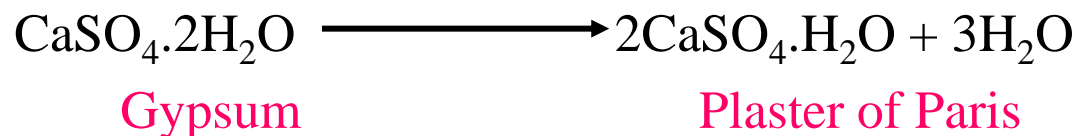
Role of Gypsum??

➔ 2-3% of gypsum is added to prevent the early setting of cement.



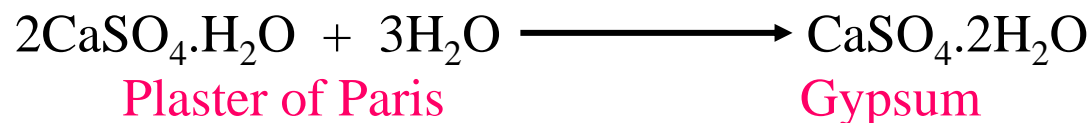
Preparation

When gypsum is heated about at 150°C then plaster of Paris is formed.



Properties of Plaster of Paris:

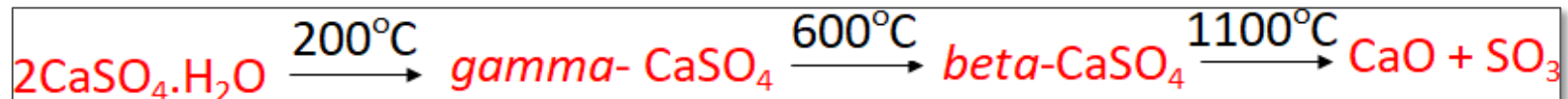
1. When plaster of Paris reacts with water, large amount of heat is released. It absorbs water and converts into gypsum. This process is known as setting of plaster of Paris



Properties of Plaster of Paris:

2. Plaster of Paris is a fine white powder.

- When heated at 200°C it first convert into gamma- CaSO₄,
- On further heating at 600°C it changes into beta-CaSO₄
- When beta-CaSO₄ is heated about 1100°C, then it converted into quick lime (CaO) and SO₃.
- The quick lime is used in formation of cement.



Uses of Plaster of Paris:

- It is used in making casting and in surgical bandage.
- Used in making plaster wall and for making plaster boards.
- Used in making statue, toy, models etc.
- Used in formation of gypsum and cement.
- Used in the formation of calcium sulphate.





THANK YOU

