# ELECTRO CHEMISTRY

**Introduction:**

Electrochemistry is a branch of chemistry which deals with the inter relationship between electrical and chemical energy. It is the study of process involving the transformation of electrical energy into chemical energy and chemical energy into electrical energy.

**Electrical conductors:** substances which allow electrical current to pass through them are known as electrical conductors. It is denoted by 'C'.

**Insulators:** substances which do not allow electrical current to pass through them are known as insulators.

**Current:**

- It is the flow of charged particles like electrons, protons and ions.
- The strength is denoted by the charge transferred in unit time.

$$I = Q/t \quad \text{where } Q = \text{charge}, t = \text{time } I = \text{current.}$$

**Resistance:** the tendency of a material to stop the flow of current is known as resistance. It is denoted by 'R'.

$$R = l/A$$

**Conductance:** it is the tendency of a material to allow the flow of current which is denoted by c.

$$C = 1/R$$

It depends on mobility of the ions and number of ions present in the electrolytic solution.

**Electrode:** it is a material or a metallic rod / bar / strip which conduct electrons.

**Electrolyte:** it is a water soluble substance forming ions in solution and conduct an electric current.

**Electrode potential:**

➤ When a metal rod is dipped in its salt solution (electrolyte), the metal atom tends to lose electrons (oxidation) or to accept electrons (reduction).the process of oxidation or reduction depends on the nature of metal.

➤ In this process there develops a potential between the metal atom and its corresponding ion called the electrode potential.'

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

Reduction: $M^{n+} + ne^{-} \longrightarrow M$
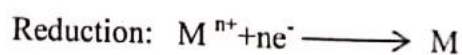
The value of electrode potential depends upon

- Nature of the metal.
- Temperature.
- Concentration of the electrolyte.

The tendency of an electrode to lose electrons is called the oxidation potential and tendency of an electrode to gain electrons is called the reduction potential.

## Standard electrode potential:

The potential of electrode at $25°C$ with 1M concentration of electrolyte is called Standard electrode potential ($E^o$).

Or

It is the measure of tendency of a metallic electrode to loose or gain electrons, when it is in contact with a solution of its own salt solution of 1M concentration at $25°C$.

Units: volts (V)

## Electro chemical cell:

➤ It is a device used for converting chemical energy into electrical energy.

➤ The EMF of such a cell is directly proportional to the intensity of chemical reactions taking place in it.

Eg: Daniel cell.

➤ Daniel cell is the typical example of the electrochemical cell.

➤ The electrode where oxidation occurs is called "anode" while the electrode where reduction occurs is called cathode.



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

$$Zn(s) \mid ZnSO_4(aq) \mid\mid CuSO_4(aq) \mid Cu(s)$$
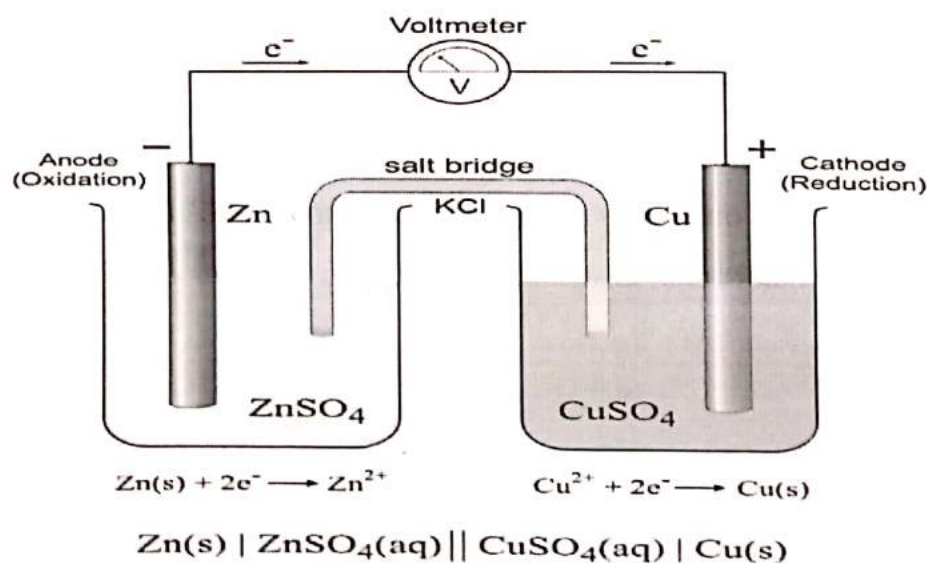
➤ The galvanic cell is made up of 2 half cells:

1. Oxidation or anodic cell.
2. Reduction or cathodic cell.

➢ It is having Zn and Cu electrodes.

➢ The first half cell consists of Zn electrode dipped in ZnSO4 solution and second half cell containing Cu electrode dipped in CuSO4 solution.

➢ Both half cells connected externally by metallic conductor and internally bent glass tube

➢ Having saturated solution of K2SO4 called salt bridge. It acts as a bridge for two half cells.

**Cell notation:**

Some rules to be taken care while representing an electrochemical cell.

➢ Cathode is on the right side and anode is on the left side.

➢ The cell is represented by the rule that metals are written first and then the metal ions that are present in the electrolyte. These two need to be separated by a verticalline

$$i.e.\ Zn/Zn^{+2}.$$

➢ The molar concentration is written within the brackets as $Zn/Zn^{+2}$ (M).

➢ Daniel cell is represented by

$$Zn/Zn^{+2}(M)//Cu^{+2}(M)/Cu$$

➢ The cell anode and cathode (half-cells) are separated by two bars (or) slashes which
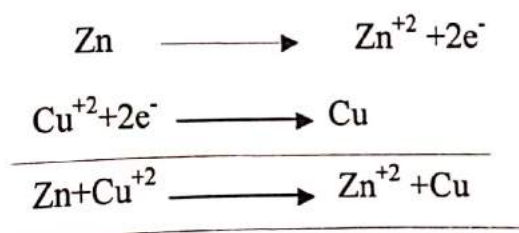
➢ Representing a salt bridge.

**Cell reaction:**

At anode oxidation reaction takes place.

$$Zn \longrightarrow Zn^{+2}+2e^- \quad (oxidation)$$
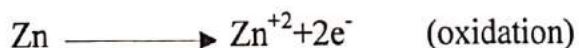
At cathode reduction reaction takes place.

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

Net reaction:

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

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

$$\overline{Zn+Cu^{+2} \longrightarrow Zn^{+2} +Cu}$$

**Reference electrode:** A reference electrode is an electrode which has a stable and well known potential. It is used as half cell to construct an electrochemical cell, to determine the potential of the other electrode. It can act both as an anode or cathode depending upon the nature of other electrode.

The Reference electrodes can be classified into two types:

I) Primary reference electrodes

   Ex: Standard Hydrogen Electrode

II) Secondary reference electrodes

   Ex: Standard Calomel Electrode

**Types of electrodes:**

**Standard Calomel Electrode: (SCE):**

➢ It is secondary standard electrode and consists of a glass tube having a side tube on each side.

➢ The mercury of high purity is placed at the bottom of the glass tube.

➢ The surface of mercury is covered with a paste of $Hg_2Cl_2$ and mercury in KCl solution.

➢ The platinum wire sealed in a glass tube which connected to the circuit.

➢ The electrolyte is a solution of KCl

➢ The electrode is connected with the help of a left side tube through a salt bridge with the other electrode.

➢ The potential of calomel electrode depends upon the concentration of the KCl solution.
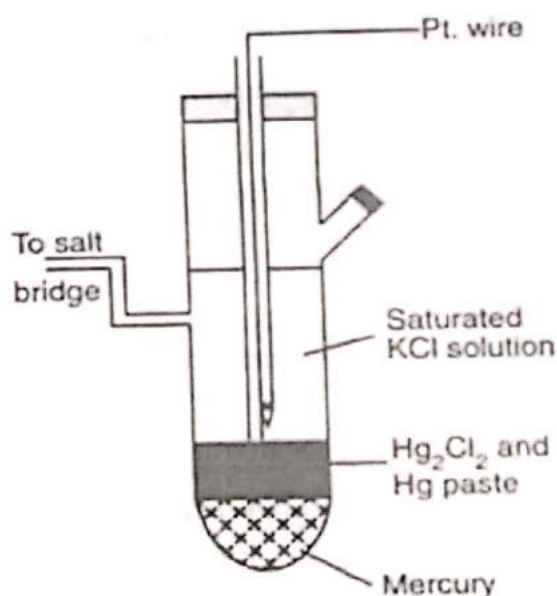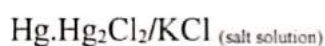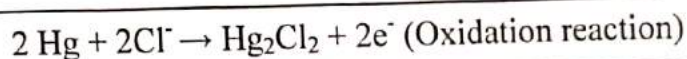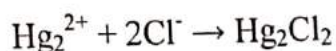
➢ The cell is represented as:

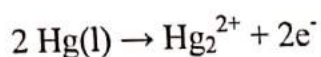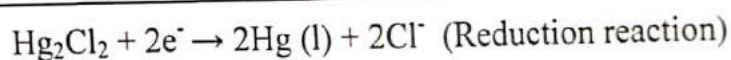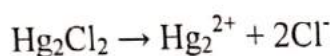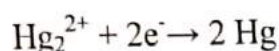$$Hg.Hg_2Cl_2/KCl \text{ (salt solution)}$$



Fig. 12.15 Calomel electrode

The calomel electrode can act as anode or cathode depending on the nature of other electrode of the cell.

When it acts as anode, the electrode reaction is

$$2 \, Hg(l) \rightarrow Hg_2^{2+} + 2e^-$$

$$Hg_2^{2+} + 2Cl^- \rightarrow Hg_2Cl_2$$

$$\overline{2 \, Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^- \text{ (Oxidation reaction)}}$$

When it acts as cathode, the electrode reaction is,

$$Hg_2^{2+} + 2e^- \rightarrow 2 \, Hg$$

$$Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2Cl^-$$

$$\overline{Hg_2Cl_2 + 2e^- \rightarrow 2Hg \, (l) + 2Cl^- \text{ (Reduction reaction)}}$$

The net reversible electrode reaction is,

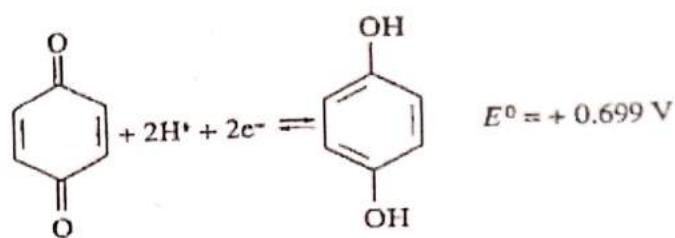$$Hg_2Cl_2(s) + 2e^- \Longleftrightarrow 2 \, Hg \, (l) + 2Cl^-$$

Electrode potential is given by

$$E = E^o - 2.303 \, RT/2F \, \log [Cl]^{-2}$$

The reduction potential for the various KCl concentrations at 25°C are:

- For saturated KCl solution electrode potential is "0.2415V".
- For 1N KCl standard reduction potential is "0.28V".
- For 0.1 KCl standard reduction potential is "0.3338V".

## Quinhydrone electrode:



$E^0 = + 0.699$ V

Quinhydrone           hydroquinone

$$Q + 2H^+ + 2e^- \rightleftharpoons QH_2$$

The potential E developed when a platinum electrode is immersed in this system is given by the Nernst equation.

$$E = E^o - \frac{2.303RT}{nF} \log \frac{[QH_2]}{[Q][H^+]^2} \longrightarrow (1)$$

$$\therefore [Q] = [QH_2]$$

From equation (1)

$$E = E^o - \frac{2.303RT}{nF} \log \frac{[Q]}{[Q][H^+]^2}$$

$$E = E^o - \frac{2.303RT}{nF} \log \frac{1}{[H^+]^2} \longrightarrow (2)$$

$n = 2e^-$, R=8.303J, T=298K at 25°C, F=96500C

Substitute above values in equation (2)

$$\therefore E = E^o + 2 \times \frac{2.303 \times 8.303 \times 298}{2 \times 96500} \log[H^+]$$

$$E = E^o + 0.0591 \log [H^+] \qquad\qquad [\because P^H = -\log [H^+]]$$

$$\boxed{E = E^o - 0.0591 P^H}$$

Since the electrode potential of the quinhydrone electrode depends upon the concentration of hydrogen ions, it can be used for the determination of $P^H$ value.

The standard oxidation potential of quinhydrone electrode at 25°C is 0.6994V.

## Construction of electrode:

Add a pinch of quinhydrone to the solution under examination and immersed a clean platinum electrode in it.

Advantages of quinhydrone electrode with limitations.

- The electrode is very easy to setup.
- The ph value obtained is very accurate.
- Very small quantity of the solutions is sufficient for the measurement.

Standard electrode potential of quinhydrone electrode is $E^\circ_Q$ 0.6994V

$$E_Q = 0.6994V - 0.00591VP^H \qquad \text{(from above equation)}$$

## Determination of $P^H$ of a solution:

To determine $P^H$ of a solution, quinhydrone electrode is connected to reference electrode like calomel electrode whose electrode potential is known. Quinhydrone electrode is known as indicator (or) working electrode. These two electrodes are connected through potentiometer and emf is determined.

Cell notation: $Pt/Hg_{(l)},Hg_2Cl_{2(s)}, KCl_{(sat)}//H^+(Q),QH_2/Pt$

Cell reaction: $2\ Hg_{(l)}+2Cl^-+Q+ 2H^+ \longrightarrow Hg_2Cl_{2(s)}+QH_2$

$$\therefore E_{cell} = E_R - E_L$$

$$= E_Q - E_{SCE}$$

$$= (0.6994-0.0591P^H) - 0.2422$$

## Nernst equation:

Consider the following redox reaction

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

For such a redox reversible reaction, the free energy change ($\Delta G$) and its equilibrium constant (k) are related as;

$$\Delta G = -RT \ln k + RT \ln \frac{[product]}{[Reactant]}$$

$$= \Delta G^0 + RT\ln \frac{[product]}{[Reactant]} \qquad \text{——— Eq- (1)}$$

Where, $\Delta G^0$ = standard free energy change

The above equation is known as Van't Hoff Isotherm.

The decrease in free energy in the reversible reaction will produce electrical energy i.e.

$$- \Delta G = nEF \text{ and}$$

$$\Delta G^0 = -nE^0F \text{ ——————— Eq-(2)}$$

Where, E = Electrode potential
$E^0$ = Standard electrode potential
F = Faraday (96,500 coulombs)

Comparing equation 1 & 2

$$-nEF = -nE^0F + RT \ln \frac{[M]}{[M^{n+}]}$$

$$= -nE^0F + RT \ln \frac{1}{[M^{n+}]}$$

Where, concentration of the metal is unity i.e. [M] = 1

$$-nEF = -nE^0F - RT \ln [M^{n+}]$$

Dividing the equation by '=nF'

$$E = E^0 + RT \ln \frac{[M^{n+}]}{nF}$$

$$E = E^0 + 2.303RT \log \frac{[M^{n+}]}{nF}$$

$$E = E^0 + 0.0591 \log \frac{[M^{n+}]}{n} \text{ ——————— Eq-(3)}$$

This equation is known as "Nernst Equation" for electrode potential.

**Applications of Nernst Equation:**

- One of the major applications of Nernst equation is in determining ion concentration.
- It is used in oxygen and the aquatic environment.
- It is also used in solubility products and potentio-metric titrations.
- It is also used in pH measurements.

## Batteries:

- A battery is an arrangement of several electrochemical cells connected in series that can be used as a source of direct electric current.
- A cell contains only one anode and one cathode.
- A battery contains several anode and cathodes.
- Battery is an electrochemical cell, which converts chemical energy into electrical energy is called battery.

Batteries are classified into two categories depending on their recharging capabilities.

I. Primary batteries
II. Secondary Batteries

## I. Primary batteries:

In which the cell reaction is irreversible. Once the reactants are converted into products no more electricity is produced and the battery becomes dead so it must be discarded after use and it can't be recharged and it cannot be used as storage device.

Ex: Lithium cells

## Lithium cells:

Lithium cells belong to primary cells. The cells having lithium anodes are called lithium cells, Lithium cells are two types

a) Lithium cells with solid cathodes

b) Lithium cells with liquid cathodes

### a) Lithium cells with solid cathode:

Anode: lithium

Cathode: $MnO_2$

Electrolyte: mixture of propylene carbonate and 1,2-dimethoxyethane.

Cathode $MnO_2$ should be heated to >300o C to remove water before incorporating it in cathode.

Anodic reaction: $Li \longrightarrow Li^+ + e^-$ (oxidation)

Cathodic reaction: $Li^+ + e^- + MnO_2 \longrightarrow LiMnO_2$ (reduction)

Net reaction: $Li + MnO_2 \longrightarrow LiMnO_2$

## Applications:

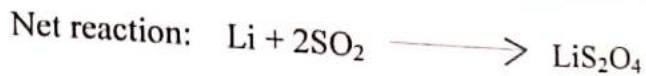Cylindrical cells are used in fully automatic cameras.
Coin cells are widely used in electronic devices such as calculators and watches.

## b) Lithium cells with liquid cathode:

In this first type cell is

Anode: lithium

Cathode: $SO_2$ Electrolyte: Either acrylonitrile or propylene carbonate or mixture of these two

Net reaction: $Li + 2SO_2 \longrightarrow LiS_2O_4$

Second type cell is

Anode: lithium

Cathode: $SOCl_2$ (thionyl chloride)

Thionyl chloride acts as an electrolyte and an active cathode

Net reaction: $4\ Li + 2\ SOCl_2 \longrightarrow 4\ LiCl + SO_2 + S$

## Applications:

These cells are used for military and space applications
These cells are used in medical devices such as neuro-stimulators and drug delivery systems.
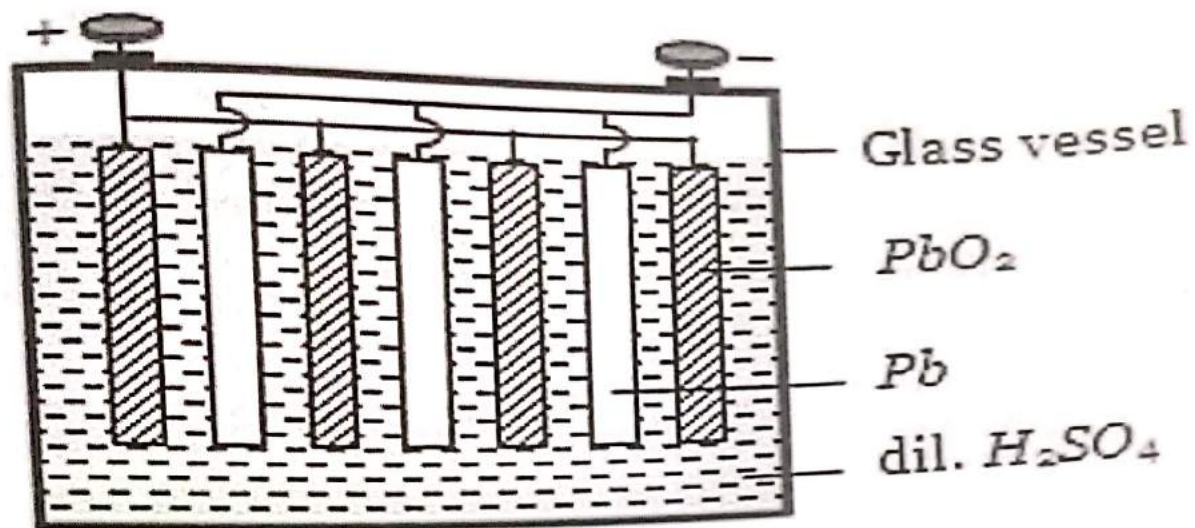
## II. Secondary battery:

The cells in which the cell reaction is reversed by passing direct current in opposite direction. These batteries have very large capacitance and long periods of low current rate discharge. They can be used as energy storage devices and can be recharged.

Ex: Lead-acid cell, lithium ion cell
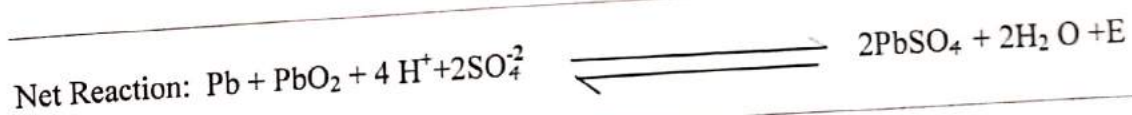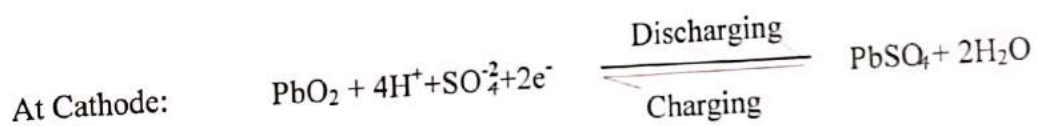
## Lead-acid battery:

## Construction:

- The lead acid storage cell contains of lead anode and lead dioxide cathode.
- A number of lead plates (- ve plates) are connected in parallel and a number of lead dioxide plates (+ve plates) are also connected in parallel.
- The lead plates are fit in between the lead dioxide plates.
- The plates are separated from adjacent plates by insulators like wood strips, rubber or glass fiber.
- The entire combination is immersed in 20 – 21 % dil.$H_2SO_4$.

Glass vessel

$PbO_2$

$Pb$

dil. $H_2SO_4$

**Working:**

**Discharging:**

At anode:  $Pb + SO_4^{-2}$  $\underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}}$  $PbSO_4 + 2e^-$

At Cathode:  $PbO_2 + 4H^+ + SO_4^{-2} + 2e^-$  $\underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}}$  $PbSO_4 + 2H_2O$

Net Reaction:  $Pb + PbO_2 + 4H^+ + 2SO_4^{-2}$  $\rightleftharpoons$  $2PbSO_4 + 2H_2O + E$

# Charging:

At anode: $PbSO_4 + 2e^-$ $\xrightarrow[\text{Discharging}]{\text{Charging}}$ $Pb + SO_4^{2-}$

At Cathode: $PbSO_4 + 2H_2O$ $\xrightarrow[\text{Discharging}]{\text{Charging}}$ $PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

Net reaction: $2\ PbSO_4 + 2H_2O + E$ $\xrightarrow{\hspace{3cm}}$ $Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$

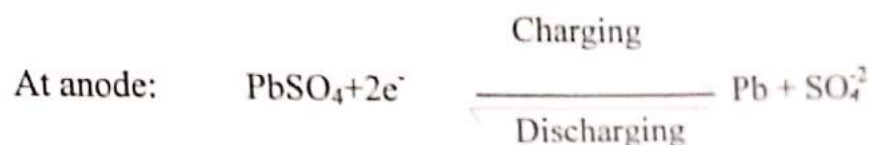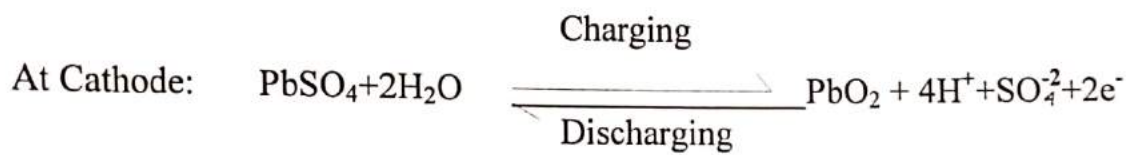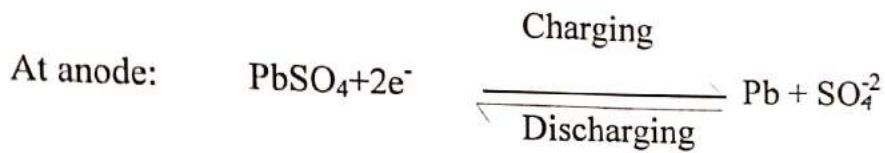## Applications of Lead-acid battery:

➢ Lad acid battery is used for starting motors.

➢ Automobile and construction equipment.

➢ Used mainly for engine batteries.

➢ Standby / backup system.

## Lithium ion battery:

➢ A lithium ion battery is a rechargeable portable battery in which lithium ions move from negative electrode to positive electrode.

➢ The primary components of lithium ion battery are the negative electrode made from carbon (graphite), positive electrode made from a metal oxide like lithium cobalt oxide or lithium manganese oxide and the electrolyte is either non aqueous lithium hexa fluro phosphate ($LiPF_6$) or lithium perchlorate ($LiClO_4$).

**Charging:**

At anode: $PbSO_4 + 2e^- \xrightleftharpoons[\text{Discharging}]{\text{Charging}} Pb + SO_4^{-2}$

At Cathode: $PbSO_4 + 2H_2O \xrightleftharpoons[\text{Discharging}]{\text{Charging}} PbO_2 + 4H^+ + SO_4^{-2} + 2e^-$

Net reaction: $2\,PbSO_4 + 2H_2O + E \xrightarrow{\hspace{3cm}} Pb + PbO_2 + 4H^+ + 2SO_4^{-2}$
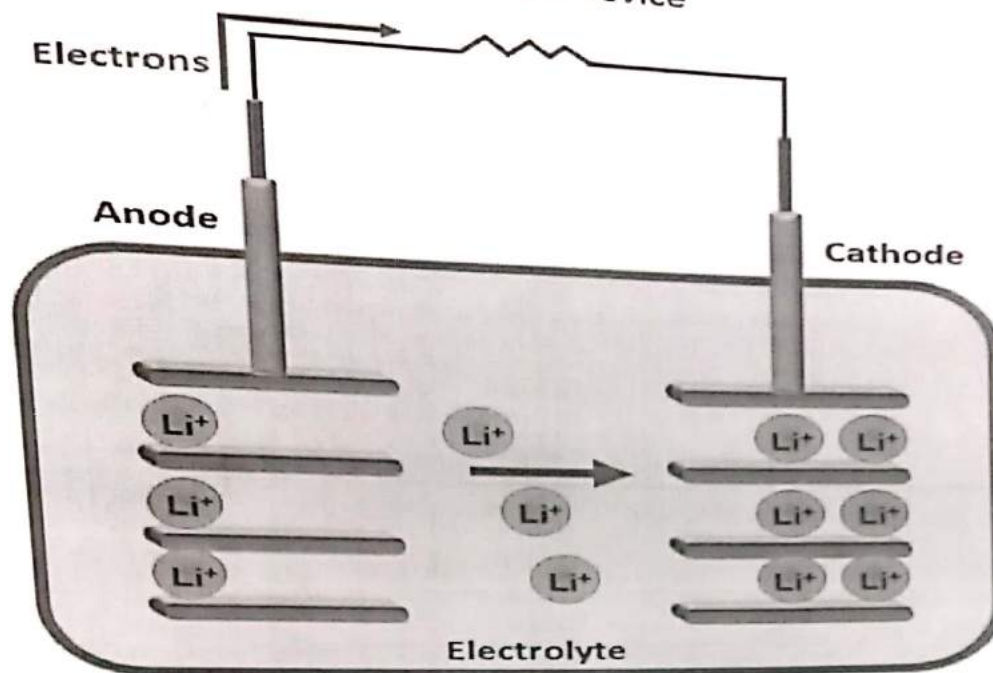
**Applications of Lead-acid battery:**

➤ Lad acid battery is used for starting motors.

➤ Automobile and construction equipment.

➤ Used mainly for engine batteries.

➤ Standby / backup system.

**Lithium ion battery:**

➤ A lithium ion battery is a rechargeable portable battery in which lithium ions move from negative electrode to positive electrode.

➤ The primary components of lithium ion battery are the negative electrode made from carbon (graphite), positive electrode made from a metal oxide like lithium cobalt oxide or lithium manganese oxide and the electrolyte is either non aqueous lithium hexa fluro phosphate ($LiPF_6$) or lithium perchlorate ($LiClO_4$).

## Lithium-ion Battery: Powering a device

Electrons

Anode

Cathode

Li⁺ ... Electrolyte

Working:

Discharging:

At anode:    $x\,LiC \longrightarrow x\,Li^+ + xe^{\ominus} + xC$

At cathode:  $LiMnO_2 + xLi^{\oplus} + xe^{\ominus} \longrightarrow Li_{(x+1)}MnO_2$

Net reaction:  $x\,LiC + LiMnO_2 \longrightarrow xC + Li_{(x+1)}MnO_2 + E$

Charging:

At anode:    $x\,Li^+ + xe^{\ominus} + xC \longrightarrow x\,LiC$

At cathode:  $Li_{(x+1)}MnO_2 \longrightarrow LiMnO_2 + xLi^+ + xe^{\ominus}$

Net reaction:  $xC + Li_{(x+1)}MnO_2 + E \longrightarrow LiMnO_2 + x\,LiC$
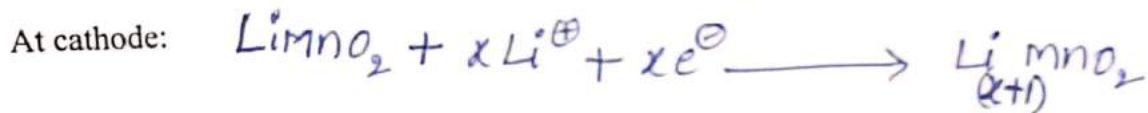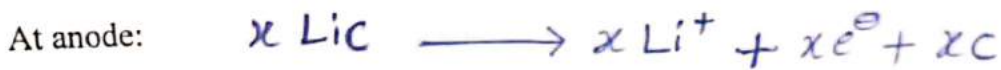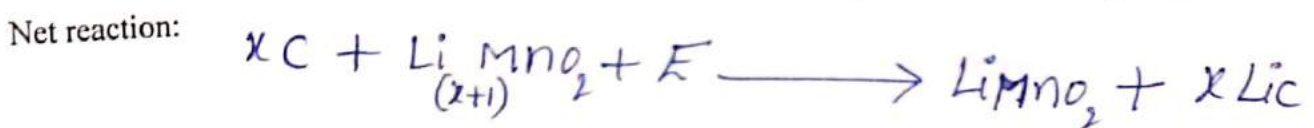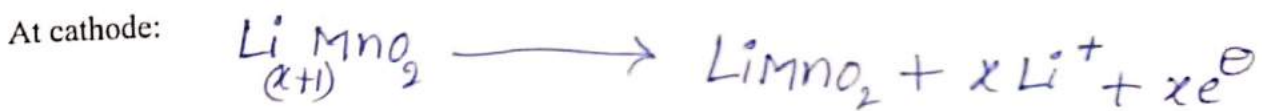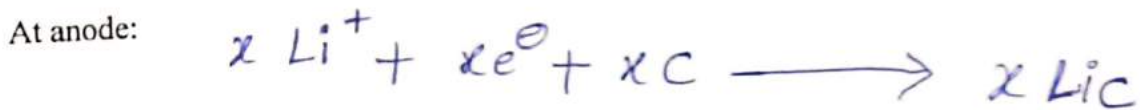
## Applications:

- Lithium-ion batteries are used in Laptops, Tablets, Smart phones, electrical vehicles.
- Lithium metal batteries have some safety disadvantages, Lithium ion batteries overcomes that problem.

## Fuel cell:

In a fuel cell electrical energy is obtained from oxygen and a fuel that can be oxidized. The essential process in a fuel cell is

$$\text{Fuel + Oxygen} \longrightarrow \text{Oxidation product + Electricity}$$

## Methanol- oxygen fuel cell:

- It consists of two electrodes made up of platinum in between the electrodes $H_2SO_4$ is placed as a electrolyte.
- Methanol and $H_2O$ is supplied at the anode and pure oxygen gas is supplied at the cathode.

In this $H^+$ ions moved from anode to cathode.

- The Methanol is oxidized to $CO_2$ & $H_2O$ with the liberation of electrical energy.
- The cell delivers an emf of 1.20v.

The cell reactions are as follows.

At anode:    $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

At cathode: $3/2\ O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$

___

Net reaction: $CH_3OH + 3/2O_2 \longrightarrow CO_2 + 2H_2O$

___
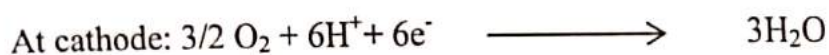
**Uses:**

Used in Military applications.
Used for large scale power production station

**Corrosion:**

The surface of almost all metals begins to decay more or less rapidly. When the metal is exposed to environmental condition like gases, water. Corrosion may be defined as "the destruction of a metallic material by chemical, electrochemical, or metallurgical interaction between the environment and the material".
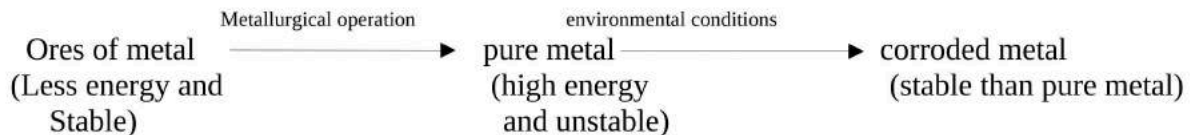
**Causes of corrosion:**

Metals exist in nature in the form of oxides, sulphides, sulphates and carbonates are called as ores.

Ore has low energy and stable. So a considerable amount of energy is required during metallurgy (extraction of metals) the extracted metal has high energy and unstable.

Metals have natural tendency to go back to their combine states (ores), when the metal is exposed to environmental conditions like dry gases, moisture, and liquids etc. the metal surface reacts and forms the more stable compounds of metals like oxides and carbonates.

The corrosion can be considered as the reversible process of metal extraction.

<div align="center">

Metallurgical operation      environmental conditions

Ores of metal  ————————▶  pure metal ————————▶ corroded metal

(Less energy and       (high energy     (stable than pure metal)

Stable)         and unstable)

</div>

**Disadvantages of corrosion or Effects:**
* The valuable metallic properties like conductivity, ductility and malleability are lost due to corrosion.
* Loss of efficiency of metals.
* The process of corrosion is very harmful and responsible for wastage of metals in the form of compounds.
* Life span of the metallic parts of the machineries is reduced.
* The failure of the machinery takes place due to loss of useful properties of metals.

<u>**Theories of corrosion:**</u>

    I) **Chemical (or) Dry corrosion**
    II) **Electrochemical (or) Wet corrosion**

**Dry (or) Chemical Corrosion:**

This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses ($O_2$, halogen, $H_2S$, $SO_2$.$N_2$ or anhydrous inorganic liquid) with metal surface.
Three types of chemical Corrosion are

**1. Oxidation Corrosion:** This is carried out by the direct action of oxygen at low or high temperatures on metals in absence of moisture at ordinary temperature metals are very slightly

attacked. The Exceptions are alkali metals and alkaline earth metals. At high temperature all metals are oxidized. The exception is Ag, Au and Pt.
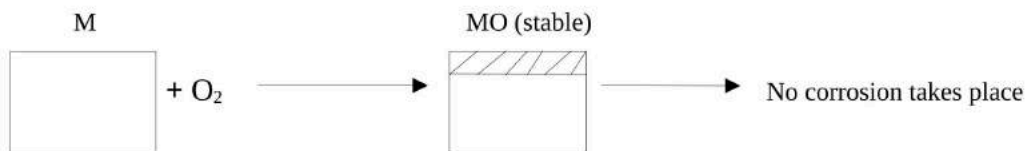
$$M \longrightarrow M^{2+} + 2e^-$$
(Metal ion)

$$1/2O_2 + 2e^- \longrightarrow O^{2-}$$
(Oxide ion)

$$M + 1/2O_2 \longrightarrow M^{2+} + O^{2-} = MO \text{ (Metal oxide)}$$

**Mechanism:** At the surface of metal oxidation occurs and the resulting metal oxide scale forms a barrier which restricts further oxidation. For oxidation to continue either the metal must diffused outwards through the scale to the surface or the oxygen must defuse inwards through the scale to the underlying metal. Both the cases are possible.
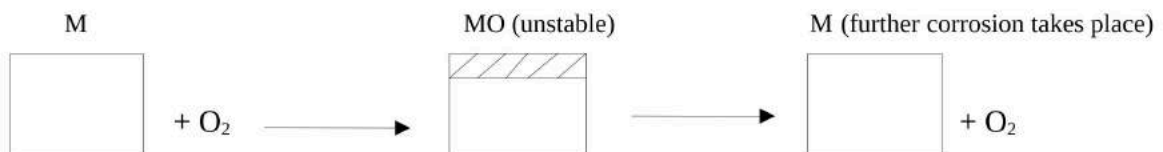
$$\text{Metal + Oxygen} \longrightarrow \text{Metal oxide}$$

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides further action. If the film is,

**a) Stable:** it behaves a protective coating in nature e.g., the oxide films on Al, Pb, Cu, Pt etc. are stable and therefore further oxidation corrosion is not possible.



**b) Unstable:** The oxide layer formed decomposes back into metal and oxygen. So, further oxidation corrosion is possible.



**c) Volatile:** The oxide layer volatilizes after formation and as such leaves the underlying metal surface. So, further oxidation corrosion is possible.

**d) Porous:** A porous layer of metal oxide contains pores; cracks provide access of oxygen to reach the surface of the metal. In this case the Atmospheric oxygen passes through the pores or cracks of the underlying metal surface. This causes continuous corrosion till complete conversion of metal into its oxide.



**Pilling- bed worth rule:**

According to this rule, if the volume of oxide layer formed is greater than the volume of the metal, the oxide layer is protective and non-porous. However if the volume of the oxide layer lesser than that of the underlying metal then the oxide layer is porous and non-protective.

**Wet Corrosion (or) Electro-chemical:**

This type of Corrosion occurs where a conducting liquid is in contact with the metal or when two dissimilar metals or alloys are dipped partially in a solution.
This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution.
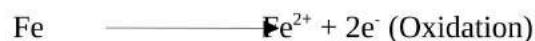
**Mechanism:**

Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.

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

The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

**Evolution of hydrogen:** This type of corrosion occurs in acidic medium e.g., considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.

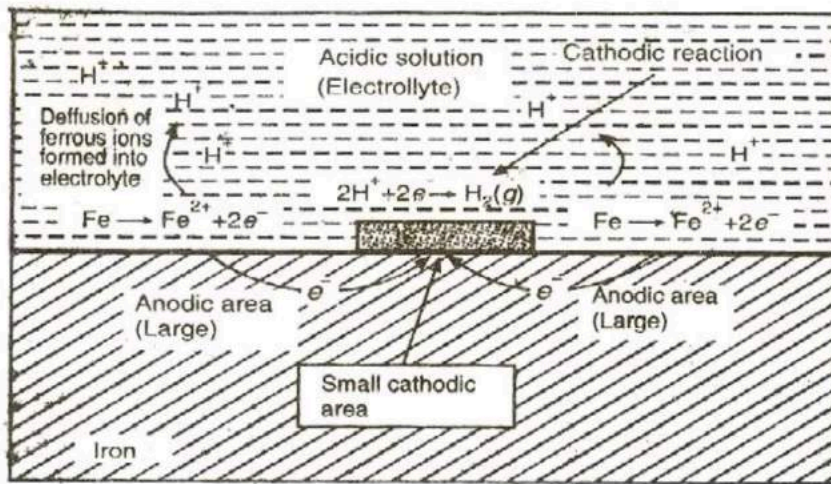$$Fe \longrightarrow Fe^{2+} + 2e^{-} \text{ (Oxidation)}$$

The electrons released flow through the metal from anode to cathode, whereas $H^+$ ions of acidic solution are eliminated as hydrogen gas.

$$2H^{+} + 2e^{-} \longrightarrow H_2 \text{ (reduction)}$$

The overall reaction is
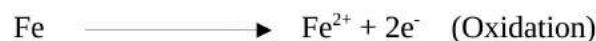
$$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$$

This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of $H_2$ gas. The anodes are large areas, whereas cathodes are small areas.



## Absorption of oxygen:

For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes.

**At anode:**

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad \text{(Oxidation)}$$

The released electrons flow from anode to cathode through iron metal.

**At cathode:**

$$\tfrac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^- \quad \text{(Reduction)}$$

Overall reaction:

$$Fe + \tfrac{1}{2} O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^- = Fe(OH)_2$$

If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.

$$4Fe\,(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe\,(OH)_3$$

Ferric hydroxide undergoes further oxidation and forms the product called yellow rust corresponds to $Fe_2O_3 \cdot xH_2O$.



**Factors affecting the rate of corrosion:**

       The rate and extent of corrosion depends on the nature of the metal and nature of the environment.

**Nature of the metal:**

1) **Position in galvanic series:**
   - The galvanic series in which the metals are arranged to their tendency to corrode in a specific environment.
   - The metals present at the top of the series are very active and have a high tendency to corrode.
   - When two metals or alloys are in electrical contact in presence of an electrolyte the more active metal having higher position in the galvanic series undergoes corrosion.

2) **Purity of the metal:** Impurities present in the metal result in heterogeneity and thereby help in the development of anodic and cathodic areas. The result is corrosion of the metal.

∴The rate and severity of corrosion increases with increase in impurities.

**3) Nature of the corrosion product:**

- If the corrosion product is soluble in the corroding medium, the corrosion rate will be faster.
- Similarly if the corrosion product is volatile, the corrosion rate will be faster.

**Nature of environment:**

1) **Temperature:** The rate of diffusion increases by rise in temperature; hence the rate of corrosion is also increased. At higher temperature, passive metals also become active and undergo corrosion.
   ∴ The rate of corrosion increases, with rise in temperature.

2) **Effect of pH:** pH value of the medium as greater effect on corrosion. When ph value is lowered the corrosion will be increased in general acidic medium i.e. pH < 7 is more corrosive than basic or neutral medium.

3) **Humidity / moisture content:** most of the metals corrode faster in humid atmosphere than in dry air.

**Corrosion control methods:**

**Cathodic protection:** it is a technique used to control the corrosion of a metal surface by making it cathode of an electro chemical cell.
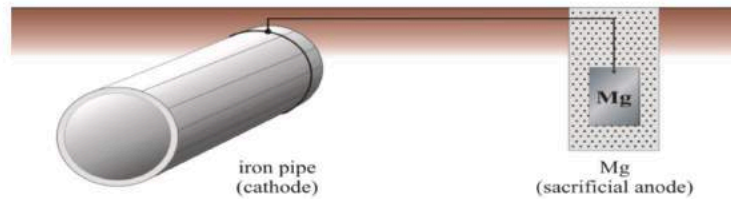
Types of cathodic protection: There are two types:

1) Sacrificial Anodic Protection (SAP)
2) Impressed Current Cathodic Protection (ICCP)

**1) Sacrificial Anodic Protection (SAP):**

- The metal structure can be protected from corrosion is called base metal, by connecting to anodic metal (more active than base metal) through a wire.
- The anodic metal undergoes corrosion slowly while the base metal is protected. Hence, it is known as sacrificial anode.
- Sacrificial anodes are highly active metals than base metals that are used to prevent a less active material surface from corroding.

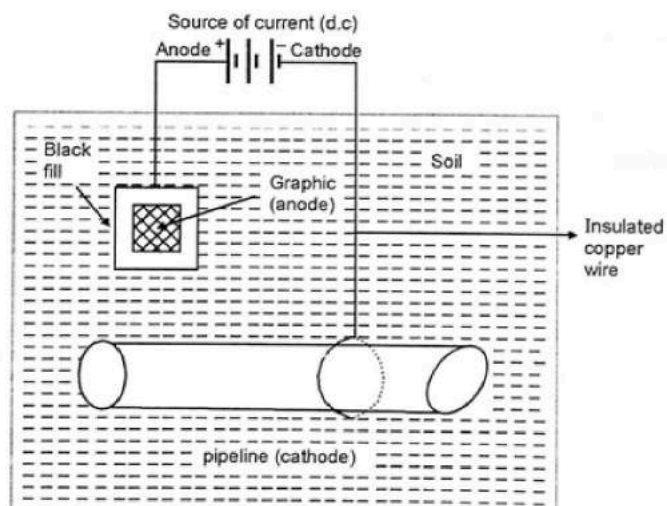   Eg. Zn, Al, Mg. (Sacrificial anodes)

iron pipe
(cathode)

Mg
(sacrificial anode)

**Applications:**

- Protection of underground cables and pipelines from soil corrosion.
- Protection of ships and boats from marine corrosion which are made of steel connected to a sacrificial anode which undergoes corrosion and leaving the base metal.

## 2) Impressed Current Cathodic Protection (ICCP):

- In this method an impressed direct current is sent in the opposite direction of the corrosion current to nullify it.
- Usually a battery is at one terminal connected with an insoluble anode (graphite electrode) immersed in a 'back fill.' And other terminal of the battery is connected to the metallic structure to be protected.
- The back fill provides a surrounding for good electrical conductivity of anode.
- This is done to convert corroding metal from anode to cathode. Once the metal becomes cathode it can be protected from corrosion.
- The commonly used anodic materials are graphite, carbon, stainless steel and platinum.
- This type of corrosion control is usually applied to underground water pipeline, oil pipelines, ships and tanks.

**Protective coatings:**

**Metallic coatings:**
- These are produced by coating of one metal on the surface of another metal.
- The metal which is protected is called base metal and the metal which is coated on the surface of the base metal is called coating metal.

These are of two types:

1) Anodic coatings
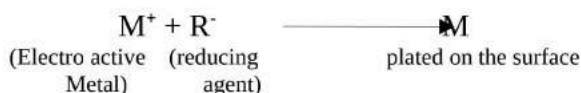2) Cathodic coatings

**Anodic coatings:**

- These types of coatings are produced by an anodic coating metal on the surface of the base metal.
- In this type of coatings, the metal used for coating is more anodic in nature than base metal.
- Eg: coatings of Zn, Al, Cd or Fe are anodic, because their oxidation potentials are higher than that of the base metal.

**Cathodic coatings:**

- These are produced by coating a more noble metal than the base metal.
- These coating metals have higher reduction potentials than that of base metal.
- Eg: coating of Sn on the surface of iron.

**Electroless plating:**

The method of deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy is called electroless plating. In this process the metallic ions ($M^+$) are reduced to the metal in the presence of reducing agent. When the metal (M) is formed it gets plated over a catalytic surface.

$$M^+ + R^- \longrightarrow M$$

(Electro active Metal)   (reducing agent)          plated on the surface

**Electroless plating of Ni:**

- The base object a plastic material like acrylonitrile – butadiene styrene can be coated with Ni.
- The base metal surface is activated by stannous chloride followed by palladium chloride to get a layer of palladium and the surface is dried.
- The base is dipped in a solution of nickel chloride, sodium hypophosphite (reducing agent) and temperature maintained at 93°C.

- The following reaction takes place and Ni gets plated on the surface of the base metal (object).

$$Ni^{+2} + H_2PO_2^- + H_2O \longrightarrow Ni + H_2PO_3 + 2H^+$$

**Corrosion:**

The surface of almost all metals begins to decay more or less rapidly. When the metal is exposed to environmental condition like gases, water. Corrosion may be defined as "the destruction of a metallic material by chemical, electrochemical, or metallurgical interaction between the environment and the material".
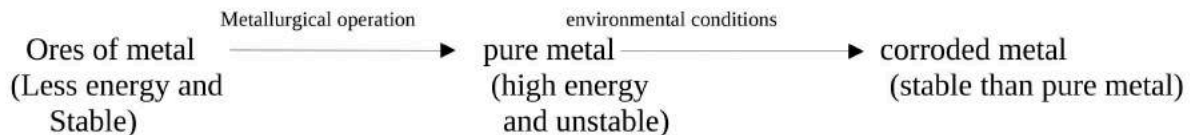
**Causes of corrosion:**

Metals exist in nature in the form of oxides, sulphides, sulphates and carbonates are called as ores.

Ore has low energy and stable. So a considerable amount of energy is required during metallurgy (extraction of metals) the extracted metal has high energy and unstable.

Metals have natural tendency to go back to their combine states (ores), when the metal is exposed to environmental conditions like dry gases, moisture, and liquids etc. the metal surface reacts and forms the more stable compounds of metals like oxides and carbonates.

The corrosion can be considered as the reversible process of metal extraction.

|  | Metallurgical operation | | environmental conditions | |
|---|---|---|---|---|
| Ores of metal | ────────────► | pure metal | ────────────► | corroded metal |
| (Less energy and Stable) | | (high energy and unstable) | | (stable than pure metal) |

**Disadvantages of corrosion or Effects:**
- The valuable metallic properties like conductivity, ductility and malleability are lost due to corrosion.
- Loss of efficiency of metals.
- The process of corrosion is very harmful and responsible for wastage of metals in the form of compounds.
- Life span of the metallic parts of the machineries is reduced.
- The failure of the machinery takes place due to loss of useful properties of metals.

**Theories of corrosion:**

I) Chemical (or) Dry corrosion
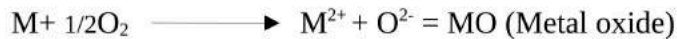II) Electrochemical (or) Wet corrosion

**Dry (or) Chemical Corrosion:**

This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses ($O_2$, halogen, $H_2S$, $SO_2.N_2$ or anhydrous inorganic liquid) with metal surface.
Three types of chemical Corrosion are

**1. Oxidation Corrosion:** This is carried out by the direct action of oxygen at low or high temperatures on metals in absence of moisture at ordinary temperature metals are very slightly

attacked. The Exceptions are alkali metals and alkaline earth metals. At high temperature all metals are oxidized. The exception is Ag, Au and Pt.
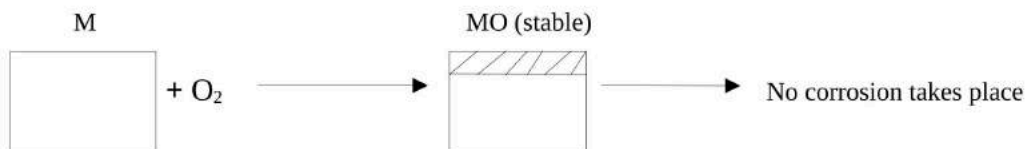
$$M \longrightarrow M^{2+} + 2e^-$$
(Metal ion)

$$1/2 O_2 + 2e^- \longrightarrow O^{2-}$$
(Oxide ion)

$$M + 1/2 O_2 \longrightarrow M^{2+} + O^{2-} = MO \text{ (Metal oxide)}$$

**Mechanism:** At the surface of metal oxidation occurs and the resulting metal oxide scale forms a barrier which restricts further oxidation. For oxidation to continue either the metal must diffused outwards through the scale to the surface or the oxygen must defuse inwards through the scale to the underlying metal. Both the cases are possible.
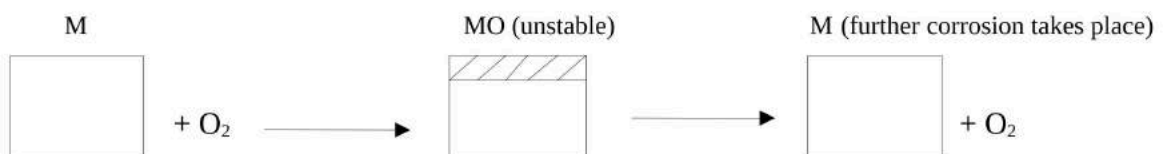
$$\text{Metal} + \text{Oxygen} \longrightarrow \text{Metal oxide}$$

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides further action. If the film is,
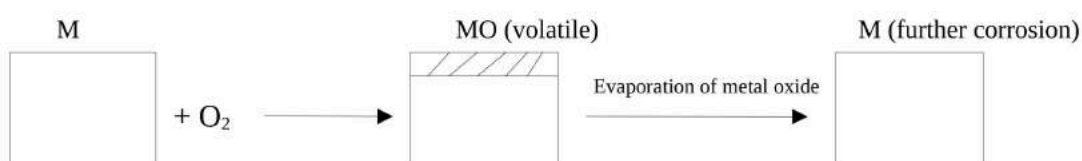
**a) Stable:** it behaves a protective coating in nature e.g., the oxide films on Al, Pb, Cu, Pt etc. are stable and therefore further oxidation corrosion is not possible.

M          MO (stable)

[ ] + O₂ → [///] → No corrosion takes place

**b) Unstable:** The oxide layer formed decomposes back into metal and oxygen. So, further oxidation corrosion is possible.

M     MO (unstable)     M (further corrosion takes place)

[ ] + O₂ → [///] → [ ] + O₂

**c) Volatile:** The oxide layer volatilizes after formation and as such leaves the underlying metal surface. So, further oxidation corrosion is possible.

M     MO (volatile)     M (further corrosion)

[ ] + O₂ → [///] → Evaporation of metal oxide → [ ]

**d) Porous:** A porous layer of metal oxide contains pores; cracks provide access of oxygen to reach the surface of the metal. In this case the Atmospheric oxygen passes through the pores or cracks of the underlying metal surface. This causes continuous corrosion till complete conversion of metal into its oxide.



**Pilling- bed worth rule:**

According to this rule, if the volume of oxide layer formed is greater than the volume of the metal, the oxide layer is protective and non-porous. However if the volume of the oxide layer lesser than that of the underlying metal then the oxide layer is porous and non-protective.

**Wet Corrosion (or) Electro-chemical:**

This type of Corrosion occurs where a conducting liquid is in contact with the metal or when two dissimilar metals or alloys are dipped partially in a solution.
This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution.
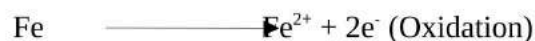
**Mechanism:**

Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.

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

The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

**Evolution of hydrogen:** This type of corrosion occurs in acidic medium e.g., considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.
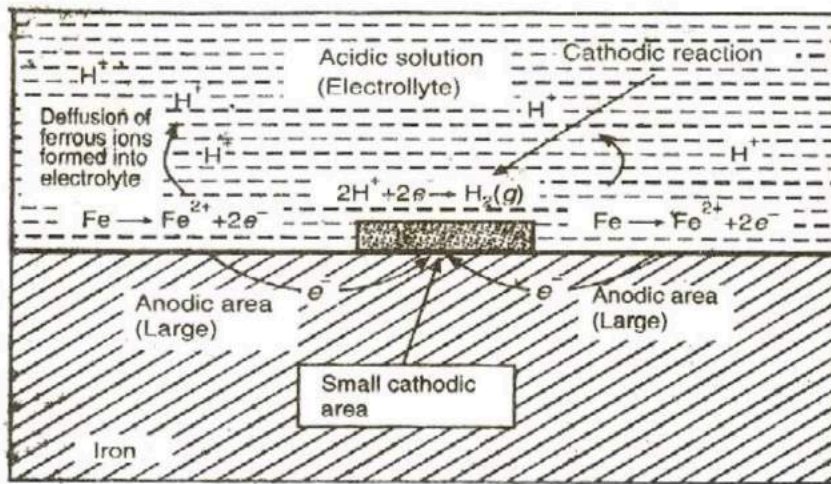
$$Fe \longrightarrow Fe^{2+} + 2e^- \text{ (Oxidation)}$$

The electrons released flow through the metal from anode to cathode, whereas $H^+$ ions of acidic solution are eliminated as hydrogen gas.

$$2H^+ + 2e^- \longrightarrow H_2 \text{ (reduction)}$$

The overall reaction is
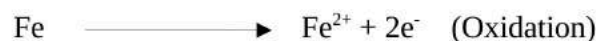
$$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$$

This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of $H_2$ gas. The anodes are large areas, whereas cathodes are small areas.



## Absorption of oxygen:

For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes.

## At anode:

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad (Oxidation)$$

The released electrons flow from anode to cathode through iron metal.

## At cathode:

$$½ O_2 + H_2O + 2e^- \longrightarrow 2OH^- \quad (Reduction)$$

Overall reaction:

$$Fe + ½ O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^- = Fe(OH)_2$$

If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.

$$4Fe\ (OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe\ (OH)_3$$

Ferric hydroxide undergoes further oxidation and forms the product called yellow rust corresponds to $Fe_2O_3 \cdot xH_2O$.



**Factors affecting the rate of corrosion:**

The rate and extent of corrosion depends on the nature of the metal and nature of the environment.

**Nature of the metal:**

1) **Position in galvanic series:**
   - The galvanic series in which the metals are arranged to their tendency to corrode in a specific environment.
   - The metals present at the top of the series are very active and have a high tendency to corrode.
   - When two metals or alloys are in electrical contact in presence of an electrolyte the more active metal having higher position in the galvanic series undergoes corrosion.

2) **Purity of the metal:** Impurities present in the metal result in heterogeneity and thereby help in the development of anodic and cathodic areas. The result is corrosion of the metal.

∴The rate and severity of corrosion increases with increase in impurities.

### 3) Nature of the corrosion product:

- If the corrosion product is soluble in the corroding medium, the corrosion rate will be faster.
- Similarly if the corrosion product is volatile, the corrosion rate will be faster.

## Nature of environment:

1) **Temperature:** The rate of diffusion increases by rise in temperature; hence the rate of corrosion is also increased. At higher temperature, passive metals also become active and undergo corrosion.
   ∴ The rate of corrosion increases, with rise in temperature.

2) **Effect of pH:** pH value of the medium as greater effect on corrosion. When ph value is lowered the corrosion will be increased in general acidic medium i.e. pH < 7 is more corrosive than basic or neutral medium.

3) **Humidity / moisture content:** most of the metals corrode faster in humid atmosphere than in dry air.

## Corrosion control methods:

**Cathodic protection:** it is a technique used to control the corrosion of a metal surface by making it cathode of an electro chemical cell.
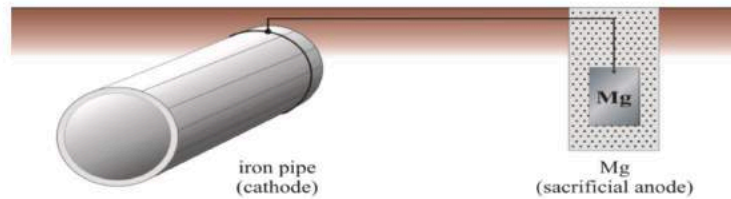
Types of cathodic protection: There are two types:

> 1) Sacrificial Anodic Protection (SAP)
> 2) Impressed Current Cathodic Protection (ICCP)

## 1) Sacrificial Anodic Protection (SAP):

- The metal structure can be protected from corrosion is called base metal, by connecting to anodic metal (more active than base metal) through a wire.
- The anodic metal undergoes corrosion slowly while the base metal is protected. Hence, it is known as sacrificial anode.
- Sacrificial anodes are highly active metals than base metals that are used to prevent a less active material surface from corroding.

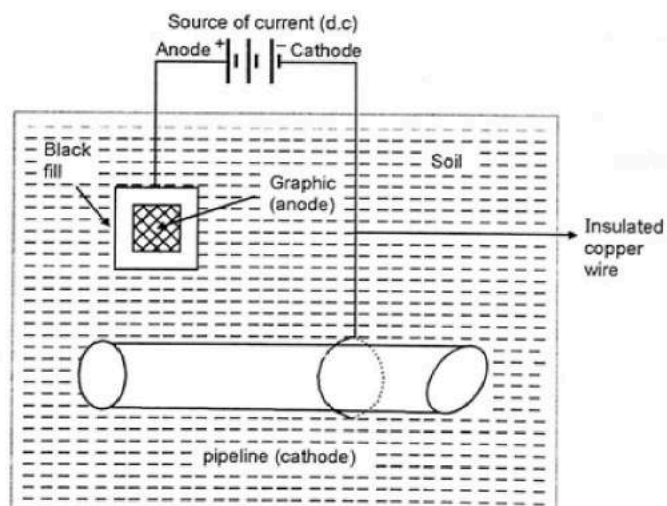    Eg. Zn, Al, Mg. (Sacrificial anodes)

iron pipe
(cathode)

Mg
(sacrificial anode)

**Applications:**

- Protection of underground cables and pipelines from soil corrosion.
- Protection of ships and boats from marine corrosion which are made of steel connected to a sacrificial anode which undergoes corrosion and leaving the base metal.

**2) Impressed Current Cathodic Protection (ICCP):**

- In this method an impressed direct current is sent in the opposite direction of the corrosion current to nullify it.
- Usually a battery is at one terminal connected with an insoluble anode (graphite electrode) immersed in a 'back fill.' And other terminal of the battery is connected to the metallic structure to be protected.
- The back fill provides a surrounding for good electrical conductivity of anode.
- This is done to convert corroding metal from anode to cathode. Once the metal becomes cathode it can be protected from corrosion.
- The commonly used anodic materials are graphite, carbon, stainless steel and platinum.
- This type of corrosion control is usually applied to underground water pipeline, oil pipelines, ships and tanks.

**Protective coatings:**

**Metallic coatings:**
- These are produced by coating of one metal on the surface of another metal.
- The metal which is protected is called base metal and the metal which is coated on the surface of the base metal is called coating metal.

These are of two types:

1) Anodic coatings
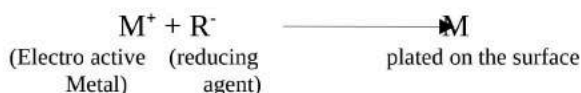2) Cathodic coatings

**Anodic coatings:**

- These types of coatings are produced by an anodic coating metal on the surface of the base metal.
- In this type of coatings, the metal used for coating is more anodic in nature than base metal.
- Eg: coatings of Zn, Al, Cd or Fe are anodic, because their oxidation potentials are higher than that of the base metal.

**Cathodic coatings:**

- These are produced by coating a more noble metal than the base metal.
- These coating metals have higher reduction potentials than that of base metal.
- Eg: coating of Sn on the surface of iron.

**Electroless plating:**

The method of deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy is called electroless plating. In this process the metallic ions ($M^+$) are reduced to the metal in the presence of reducing agent. When the metal (M) is formed it gets plated over a catalytic surface.

$$M^+ + R^- \longrightarrow M$$

(Electro active Metal)  (reducing agent)      plated on the surface

**Electroless plating of Ni:**

- The base object a plastic material like acrylonitrile – butadiene styrene can be coated with Ni.
- The base metal surface is activated by stannous chloride followed by palladium chloride to get a layer of palladium and the surface is dried.
- The base is dipped in a solution of nickel chloride, sodium hypophosphite (reducing agent) and temperature maintained at 93°C.

- The following reaction takes place and Ni gets plated on the surface of the base metal (object).

$$Ni^{+2} + H_2PO_2^- + H_2O \longrightarrow Ni + H_2PO_3 + 2H^+$$