

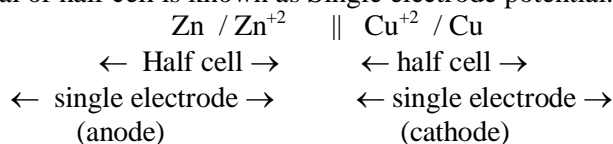
## UNIT II: ELECTROCHEMICAL CELLS AND CORROSION

[Single electrode potential, electrochemical series and uses of series, standard hydrogen electrode, calomel electrode, construction of glass electrode, batteries. (Dry cell, Li ion battery and zinc air cells), fuel cells ( $H_2-O_2$ ,  $CH_3OH-O_2$ , phosphoric acid and molten carbonate).

**Corrosion:**-Definition, theories of corrosion (chemical and electrochemical), galvanic corrosion, differential aeration corrosion, stress corrosion, galvanic series, factors influencing rate of corrosion, corrosion control (proper designing and cathodic protection), Protective coatings (surface preparation, cathodic coatings, anodic coatings, electroplating and electroless plating [nickel]), Paints (constituents, functions and special paints).]

### Q1) Write a note on Single Electrode Potential.

The Potential of half cell is known as Single electrode potential.



The total cell emf is equal to the sum of the single electrode potentials.

$$E(\text{cell}) = E(\text{anode}) + E(\text{cathode})$$

$$\text{or } E(\text{cell}) = E(\text{oxidation}) + E(\text{reduction}) \quad \text{or } E(\text{cell}) = E(\text{right}) - E(\text{left})$$

Where;  $E(\text{cell}) = \text{e.m.f of cell}$

$E(\text{right}) = \text{reduction potential of right hand side electrode.}$

$E(\text{left}) = \text{reduction potential of left hand side electrode.}$

### Q 2) What is Electrochemical Series. Give its significance.

**Definition:** The arrangement of various metals in the order of increasing values of standard reduction potential is called emf series.

**Applications of Emf Series:** [or] **Importance of Electrochemical Series:**

- 1) Relative ease of Oxidation or Reduction.
- 2) Replacement tendency.
- 3) Predicting spontaneity of the reactions.
- 4) Calculations of equilibrium constant.

#### 1) Relative ease of oxidation or reduction:

An electrode with high reduction potential easily undergoes reduction and it does not undergo easy oxidation.



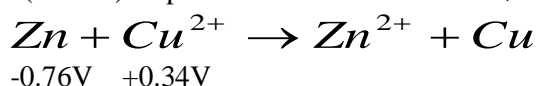
An electrode with the low reduction potential easily undergoes oxidation and it does not undergo easy reduction.



#### 2) Replacement tendency:

The electrode with lower standard electrode potential displaces the metal ions of higher standard electrode potential from its solution.

Ex: Zinc (-0.76V) displaces  $Cu^{2+}$  ions from  $CuSO_4$  solution.



#### 3) Predicting spontaneity of the reactions:

Spontaneity of the reaction can be predicted from EMF values.

A reaction with +ve EMF is spontaneous.

A reaction with -ve EMF is non spontaneous.

#### 4) Calculations of equilibrium constant:

The standard electrode potential is

$$E^{\circ} = \frac{RT}{nF} \ln K_{eq}$$

$$E^{\circ} = \frac{2.303RT}{nF} \log K_{eq}$$

$$\log K_{eq} = \frac{nFE^{\circ}}{2.303RT}$$

$$\log K_{eq} = \frac{nE^{\circ}}{0.059}$$

By measuring standard electrode potential for a cell reaction, its equilibrium can be calculated.

S.No:	Element name	Element	Electrode Reaction	Standard electrode potential ( E° ) volts
1	Lithium	Li	Li <sup>+</sup> + e <sup>-</sup> → Li	- 3.05
2	Potassium	K	K <sup>+</sup> + e <sup>-</sup> → K	- 2.925
3	Sodium	Na	Na <sup>+</sup> + e <sup>-</sup> → Na	- 2.714
4	Magnesium	Mg	Mg <sup>+2</sup> + 2e <sup>-</sup> → Mg	- 2.370
5	Aluminium	Al	Al <sup>+3</sup> + 3e <sup>-</sup> → Al	- 1.66
6	Zinc	Zn	Zn <sup>+2</sup> + 2e <sup>-</sup> → Zn	- 0.76
7	Iron	Fe	Fe <sup>+2</sup> + 2e <sup>-</sup> → Fe	- 0.44
8	Tin	Sn	Sn <sup>+2</sup> + 2e <sup>-</sup> → Sn	- 0.14
9	Lead	Pb	Pb <sup>+2</sup> + 2e <sup>-</sup> → Pb	- 0.12
10	Hydrogen	H	2H <sup>+</sup> + 2e <sup>-</sup> → H <sub>2</sub>	0.00
11	Copper	Cu	Cu <sup>+2</sup> + 2e <sup>-</sup> → Cu	+ 0.34
12	Mercury	Hg	Hg <sup>+2</sup> + 2e <sup>-</sup> → Hg	+ 0.88
13	Silver	Ag	Ag <sup>+</sup> + e <sup>-</sup> → Ag	+ 0.79
14	Platinum	Pt	Pt <sup>+2</sup> + 2e <sup>-</sup> → Pt	+ 1.2
15	Gold	Au	Au <sup>+3</sup> + 3e <sup>-</sup> → Au	+ 1.5

#### Reference Electrodes:

A Reference electrode is an electrode which has a stable and well-known electrode potential. Electrode potential is determined with respect to a reference electrode. Reference electrodes are two types:

**Primary reference electrode.** Eg: Standard Hydrogen electrode.

**Secondary reference electrode.** Eg: Calomel electrode.

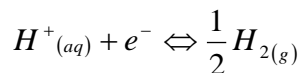
SHE or NHE is taken as the best reference electrode whose potential taken as zero.

### Q 3) Explain the construction and working of Hydrogen electrode:

#### Construction:

- A small platinum foil coated with platinum black is connected to a platinum wire is enclosed in a glass tube.
- Platinum electrode is placed in a solution of  $H^+$  ions of 1M concentration.
- $H_2$  gas with 1 atm pressure is passed over platinum electrode through the solution at  $25^\circ C$ .
- This whole assembly is considered as hydrogen reference electrode.

Using hydrogen electrode  $P^H$  of the solution can be determined.



Applying Nernst equation to the above equilibrium

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[H_2]^{1/2}}{[H^+]}$$

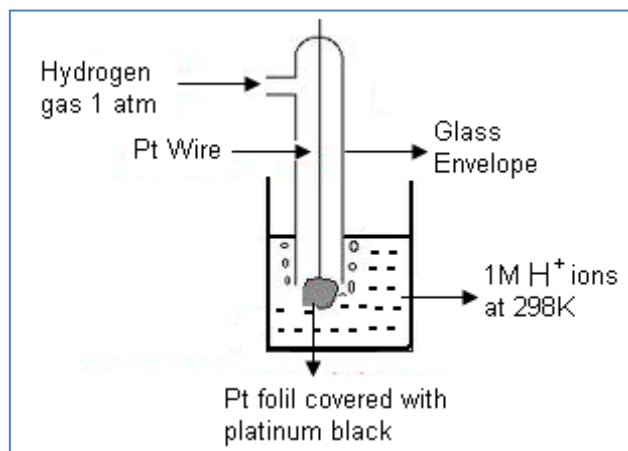
$$E = 0 - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{1}{[H^+]} (\because [H_2] = 1)$$

$$E = -\frac{0.059}{n} \log \frac{1}{[H^+]}$$

$$E = 0.059 \times \log [H^+] (\because n = 1 \text{ for } H^+ \text{ ions})$$

$$\therefore P^H = -\log [H^+]$$

$$E = -0.059 P^H$$



#### Measurement of $P^H$ using hydrogen electrode:

The above half cell (left side) placed in the solution of unknown  $P^H$  is connected to NHE through salt bridge.

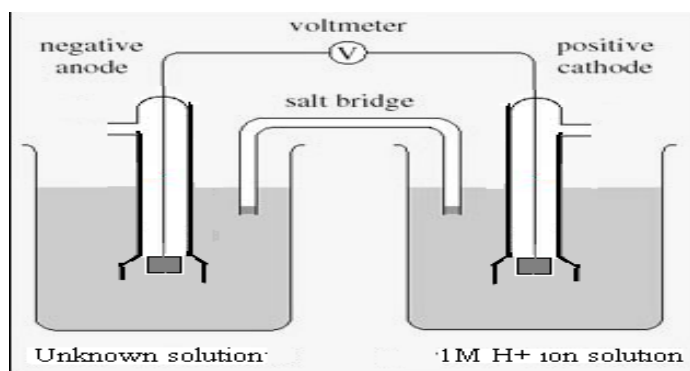
The EMF of the cell is measured by using potentiometer.

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

$$E_{cell} = 0 - (-0.059 P^H)$$

$$E_{cell} = 0.059 P^H$$

$$P^H = \frac{E_{cell}}{0.059}$$



#### Limitations:

- Hydrogen electrode can't be used in the solutions containing compounds of Hg, As, S and oxidizing agents like  $Fe^{3+}$ ,  $Cr_2O_7^{2-}$ , and  $MnO_4^-$ .
- It can't be used in the presence of ions of many metals.
- It is difficult to set up a hydrogen electrode. It cannot be used in solutions containing redox systems.

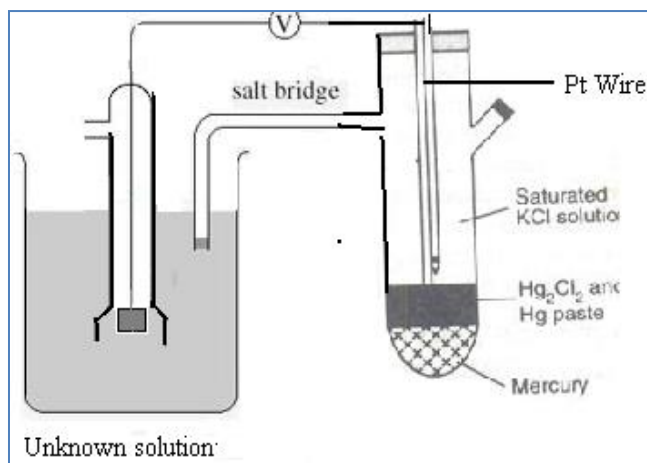
**Q 4) Explain the construction and working of Calomel electrode (Secondary reference electrode):**

- Sometimes calomel electrode is used as reference electrode instead of NHE or SHE.
- The potential of saturated calomel electrode is 0.2422V.

**Construction:**

- A glass tube is filled with a layer of mercury at the bottom.
- It is covered with a paste of Hg + Hg<sub>2</sub>Cl<sub>2</sub> and saturated KCl solution.
- A platinum wire is placed in the mercury layer for making electrical contact.

By combining calomel electrode with H<sub>2</sub> electrode, P<sup>H</sup> of unknown solution can be determined.



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

$$E_{cell} = 0.2422 - (-0.059P^H)$$

$$E_{cell} = 0.2422 + 0.059P^H$$

**Ion Selective Electrode: (ISE):**

Ion Selective Electrodes (ISE) use a membrane which is sensitive to a particular chemical species. ISE respond to certain specific ions present in a mixture while ignoring others and develop potential. The potential developed is a measure of the concentration of the species of interest.

Examples: Glass electrode and Fluoride electrode.

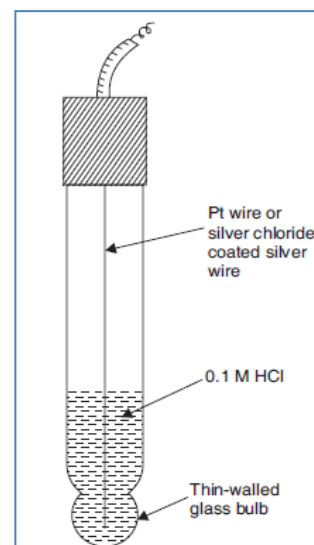
**Q 5) Explain the construction and working of Glass electrode: Principle:**

- When two solutions of different P<sup>H</sup> values are separated by a thin glass membrane, there develops a difference of potential between the two surfaces of the membrane.
- The potential difference developed is proportional to the difference in P<sup>H</sup> value.
- The glass membrane functions as ion exchange resin and set up an equilibrium between Na<sup>+</sup> ions of glass and H<sup>+</sup> ions of solution.
- Potential of glass electrode is given by the expression

$$E_G = E_G^o + 0.059VP^H \text{ at } 25^\circ\text{C}$$

➤ **Construction:**

- It consists of a thin walled glass bulb containing AgCl coated Ag electrode in 0.1M HCl.
- It is shown as  $Ag / AgCl_{(s)}; HCl(0.1M) / Glass$
- HCl in the bulb furnishes a constant H<sup>+</sup> ion concentration.
- Thus, it is a silver-silver chloride electrode, reversible w.r.t to chloride ions.



- In order to determine the P<sup>H</sup> of a solution, the glass electrode is placed in the solution and this half cell is coupled with saturated calomel electrode, the EMF of the cell is measured.

The EMF of cell is given by

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

$$E_{cell} = 0.2422V - [E_G^{\circ} + 0.059VP^H]$$

Then, 
$$P^H = \frac{0.2422V - E_{cell} - E_G^{\circ}}{0.059V}$$

Here  $E_G^{\circ}$  value of glass electrode is determined by using a solution of known  $P^H$ .

**Limitations:**

- $P^H$  beyond 12 cannot be measured because cations of solution affect the glass membrane.
- Since the resistance of glass membrane is 10 to 100 million ohms, a special potentiometer is used to measure  $P^H$ .

➤ **Advantages:**

- It can be used easily.
- Results are accurate.
- It is not easily poisoned.
- Equilibrium is rapidly achieved.

**Storage batteries:**

A device that stores chemical energy and releases it as electrical energy is called as battery or storage battery.

Cell is a device in which chemical energy is converted into electrical energy. Many cells connected in series are called battery.

Batteries are classified as follows;

- i) Primary battery.
- ii) Secondary battery.
- iii) Fuel battery or Flow battery

**1) Primary battery:**

Primary battery is a cell in which the cell reaction is not reversible. Thus, once the chemical reaction takes place to release the electrical energy, the cell gets exhausted. They are use and throw type.

Example: Dry cell, Laclanche cell etc.

**2) Secondary battery:**

Secondary battery is a cell in which the cell reaction is reversible. They are rechargeable cells. Once the battery gets exhausted, it can be recharged.

Example: Nickel-Cadmium cell, Lead-acid cell (storage cell), etc.

**3) Fuel battery or Flow battery:**

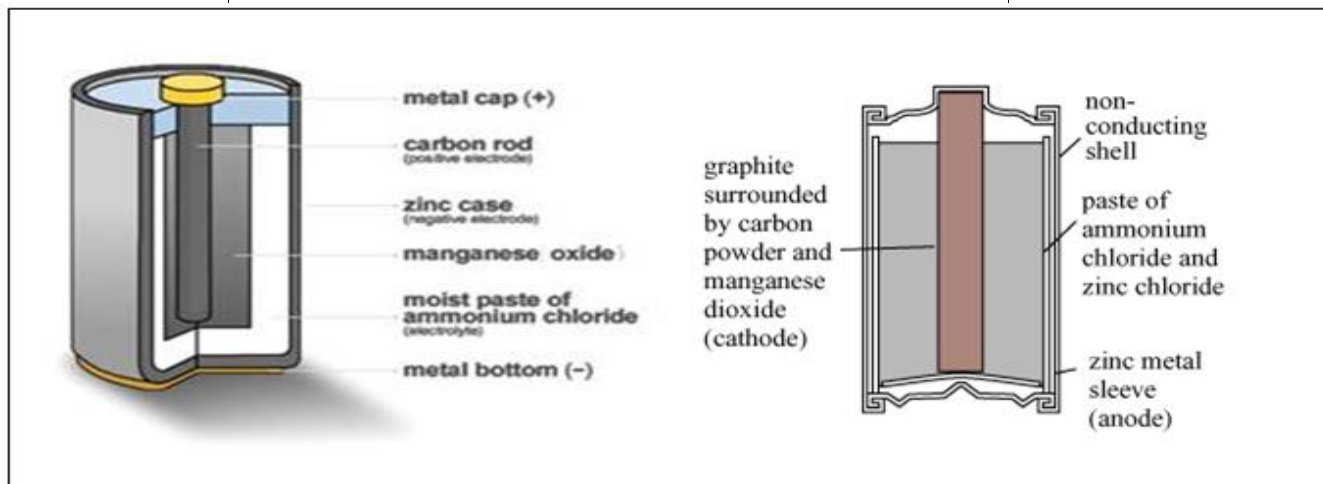
Flow battery is an electrochemical cell that converts the chemical reaction into electrical energy. When the reactants are exhausted, new chemicals replace them.

Example: Hydrogen-oxygen cell, Aluminium-air cell, etc. In Aluminium-air cell, when the cell is exhausted, a new aluminium rod is used and the solution is diluted with more water as the electrochemical reaction involves aluminium and water.

**Q 6) Explain the construction and working of Dry cell with a neat diagram.**

Dry or Leclanche cell: The dry cell is a primary cell.

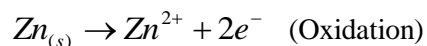
Dry cell (or) Leclanche cell	
Anode :	Zinc
Cathode :	Graphite rod (or) Carbon rod
Electrolyte :	( MnO <sub>2</sub> + NH <sub>4</sub> Cl + ZnCl <sub>2</sub> + Starch ) Paste



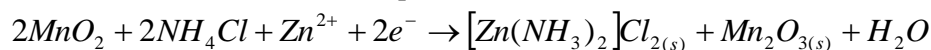
**Construction:** The anode of the cell is Zinc can contain an electrolyte consisting of NH<sub>4</sub>Cl, ZnCl<sub>2</sub> and MnO<sub>2</sub> to which starch is added to make it thick paste. A carbon rod acts as the cathode which is immersed in the electrolyte in the centre of the cell.

Cell reactions:

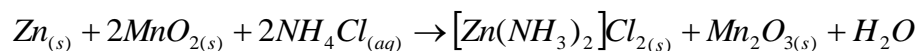
The anode half cell reaction is



At cathode, reduction of MnO<sub>2</sub> takes place



Net reaction is



The dry cell is a primary cell, since various reactions involved cannot be reversed by passing electricity into the cell. The voltage of the cell is 1.5V.

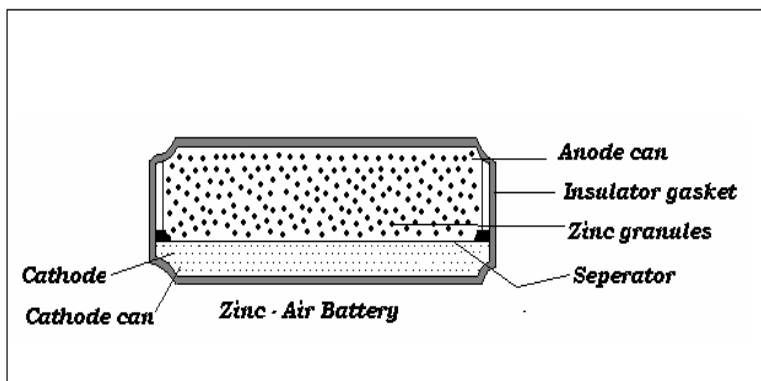
**Disadvantages:** When current is drawn immediately from it, products formed at electrodes thereby causing drop in voltage. Since the electrolytic medium is acidic, Zinc dissolves slowly thereby the cell rundown slowly even it is not in use.

**Uses:** Dry cell finds applications in flash lights, transistor radios and calculators.

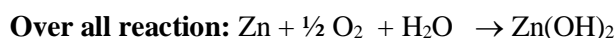
**Q 7) Explain the construction and working of Zinc air battery (or) Modern battery?**

Zinc air cell : ( Modern battery )	
Anode :	Zinc (Zn)
Cathode :	Oxygen
Electrolyte :	Potassium hydroxide (KOH)

Zinc air battery consisting of anode containing granules of zinc mixed with 20%NaOH electrolyte. Cathode can contains a porous carbon plate which provides site for the reduction reaction and do not involves in the reaction. Carbon is catalytically activated to absorb oxygen gas. The anode and cathode compartments are separated by a separator and both are encased in plastic or ebonite insulator. The reactions are as follows.



**Cell reactions:**



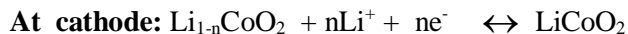
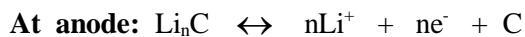
**Advantages:** 1) High energy density. 2) Low cost and compact 3) Does not produce harmful products.

**Applications:** Used in Military radio receivers, transmitters, hearing aids.

**Q 8) Write about Lithium ion battery:**

Lithium ion battery	
Anode :	Lithium doped graphite
Cathode :	Lithium Cobalt (III) Oxide
Electrolyte :	Complex Lithium compounds dissolved in organic solvents.

**Cell reactions:**



**Advantages:**

- i. They have high energy density than other rechargeable batteries.
- ii. They are light weight.
- iii. They produce high voltage out of 4 V.
- iv. They have improved safety, i.e., more resistance to overcharge.
- v. No liquid electrolyte means they are immune from leaking.
- vi. Fast charge and discharge rate.

**Disadvantages:**

1)They are expensive. 2) They are not available in standard cell types.

**Applications:**

- The Li-ion batteries are used in portable devices: these include mobile phones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights).
- Li-ion batteries are used in tools such as cordless drills, sanders, saws and a variety of garden equipment including whipper-snippers and hedge trimmers.
- Because of their light weight, Li-ion batteries are used for energy storage for many electric vehicles from electric cars to pedelec (pedelec is a bicycle where the rider's pedalling is assisted by a small electric motor), from hybrid vehicles to advanced electric wheelchairs, from radio-controlled models and model aircraft to the Mars Curiosity rover.
- They are used in cardiac pacemakers and other implantable devices.
- They are used in telecommunication equipment, instruments, portable radios and TVs, pagers.



### Q 9) Define fuel cell. How fuel cells are represented. Mention its advantages and disadvantages?

**Definition:** Fuel cells are the galvanic cells which convert chemical energy of fuels into electrical energy by the combustion of fuels.



**Fuel cell Representation:** A fuel cell essentially consists of the following arrangement:

Fuel / electrode / electrolyte / electrode / oxidant.

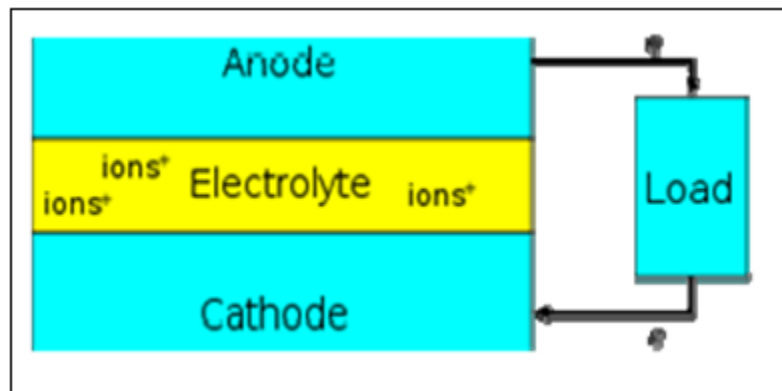
At the anode, fuel undergoes oxidation:  $\text{Fuel} \rightarrow \text{Oxidation product} + ne^-$

At the cathode, the oxidant gets reduced:  $\text{Oxidant} + ne^- \rightarrow \text{Reduction products}$ .

The electrons liberated from the oxidation process at the anode can perform useful work when they pass through the external circuit to the cathode.

#### Advantages of the Fuel cells:-

- 1) Their power efficiency is high.
- 2) The cells have high energy density.
- 3) They are ecofriendly.
- 4) Space required for fuel cell is less.
- 5) Produce harmless byproducts.
- 6) Produces direct current for a long time.
- 7) No moving parts and so elimination of wear and tear.
- 8) They operate very silently.
- 9) Absence of harmful waste products.
- 10) No need of charging.



#### Limitations of Fuel cells:-

- 1) Fuel cells produce energy only as long as fuels and oxidants are supplied.
- 2) Electrodes are very costly.
- 3) Power output is very costly.
- 4) Fuels in the form of gases and oxygen need to be stored in tanks under high pressure.
- 5) Reactions are constantly supplied and the products are constantly removed from the cell.

### Q 10) Describe the construction and working of hydrogen – Oxygen fuel cell?

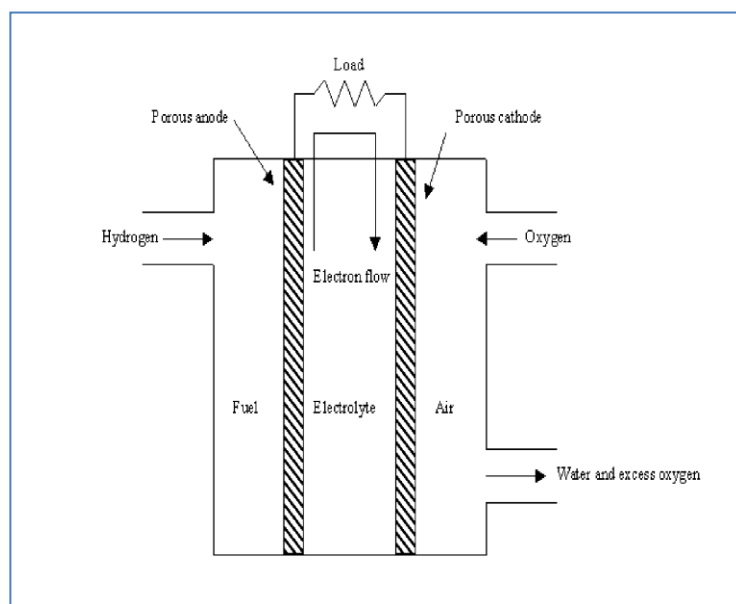
#### Hydrogen – oxygen fuel cell:

In these cells, the reactants and electrolytes are continuously supplied to the cell. It is the simplest and most successful fuel cell. The fuel-hydrogen and the oxidiser-oxygen and the liquid electrolyte are continuously supplied to the cell.

**Description:** The cell has two porous electrodes, anode and cathode. The electrodes are made of compressed carbon containing a small amount of catalyst (Pt, Pd, Ag).

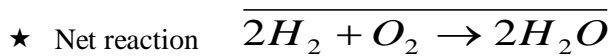
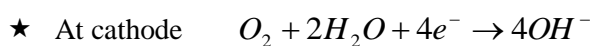
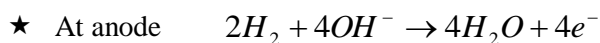
Between the two electrodes an electrolytic solution, 25% KOH is filled.

**Working:** Hydrogen passes through the anode compartment, where it is oxidised. Oxygen passes through the cathode compartment, where it is reduced.





### Cell reactions:



★ The product discharged in water and the standard EMF of the cell is  $E^\circ = 1.23V$ .

★ A number such fuel cells are stacked together in series to make a battery.

### Applications:

★ They are used as auxiliary energy source in space vehicles, submarines etc.

★ Because of light weight and pure drinking water formation, they are highly useful in space crafts.

### Advantages:

★ The efficiency is high.

★ Drinking water is produced for astronauts.

★ No noise and thermal pollution.

★ Maintenance cost is low.

### Limitations:

★ Life time of fuel cells is not known accurately.

★ Initial cost is high.

★ The distribution of  $H_2$  is not proper.

### Q 11) Describe the construction and working of Methanol-Oxygen Fuel cell ?

#### Methanol-Oxygen Fuel cell:- (DMFC)

★ Methanol is preferred as a fuel in fuel cells because of the following reasons.

★ It has low carbon content.

★ It possesses a readily oxidisable alcoholic group.

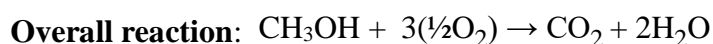
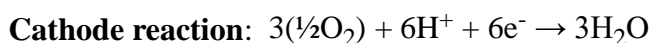
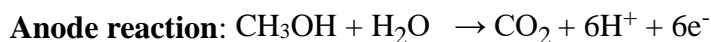
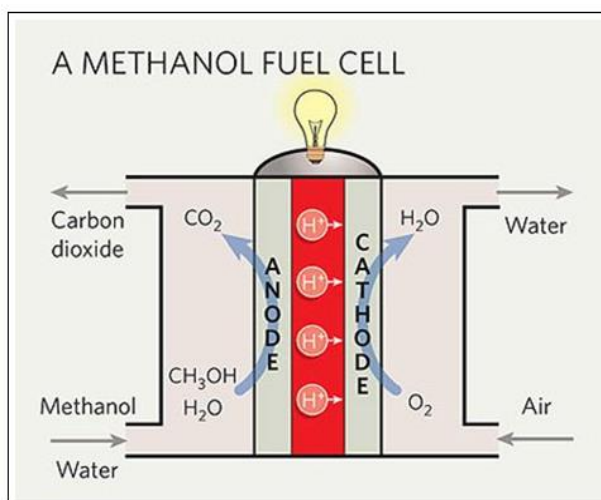
★ It has high solubility in aqueous electrolytes.

#### Construction:-

It consists of anodic and cathodic compartments and both the compartments contain platinum electrode.

Methanol containing  $H_2SO_4$  is passed through anodic compartments. Oxygen is passed through cathodic compartments. Electrolyte consists of sulphuric acid. A membrane is provided which prevents the diffusion of methanol into the cathode.

**Working:** - At anode,  $CH_3OH$  undergoes oxidation to  $CO_2$  liberates electrons, the liberated electrons taken by oxygen gets reduced into water with liberation of energy at cathode..



Fuel (methanol) and air or oxygen are fed to the electrodes. The cell potential is 1.21 V at 25 °C. The acid electrolyte offers the advantage of easy removal of  $CO_2$ , a product of the cell reaction.

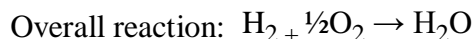
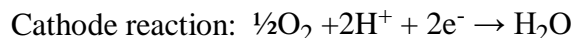
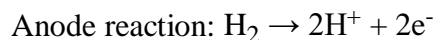
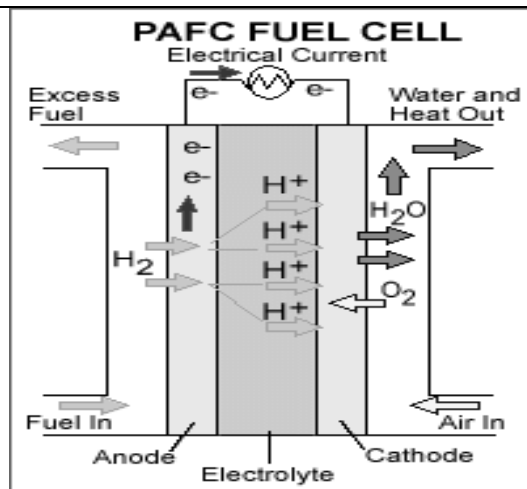
**Uses:**

- ★ In all kinds of portable, automotive and mobile applications like, Powering laptop, computers, cellular phones, digital cameras.
- ★ In Fuel cell vehicles (FCVs).
- ★ It is used in Spacecraft applications.
- ★ It is used in any consumables which require long lasting power compared to Li-ion batteries.
- ★ It is also used in Military applications.

**Q 12) Write a note on phosphoric acid fuel cells?**

**Phosphoric Acid Fuel cell:- (PAFC)**

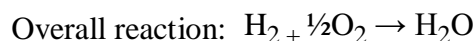
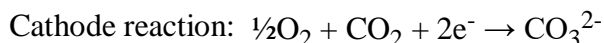
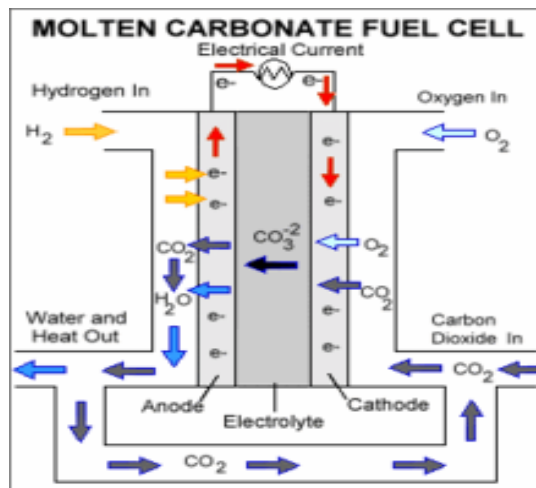
- ★ In phosphoric acid fuel cell the electrolyte is concentrated phosphoric acid.
- ★ Porous C + SiC + Teflon impregnated with Pt-catalyst acts as anode.
- ★ Porous C + SiC + Teflon impregnated with Ag-catalyst acts as cathode.
- ★ Pure H<sub>2</sub> gas is anodic fuel and pure O<sub>2</sub> gas is cathodic fuel.
- ★ These operate at a temp 190 to 200 °C . Platinum alloys such as platinum- cobalt- chromium, are used as electro catalyst.
- ★ It can produce electricity 1KW to 5KW.
- ★ **Uses:** These cells are used to provide light and heat in large buildings.



**Q 13) Write a note on molten carbonate fuel cells?**

**Molten Carbonate fuel cell:- (MCFC)**

- ★ In Molten carbonate fuel cell the electrolyte is a mixture of alkaline carbonates of sodium and potassium.
- ★ Anode is porous Ni/Ni-Cr alloy.
- ★ Cathode is porous NiO.
- ★ H<sub>2</sub> gas (or) CO gas is fuel at anode and O<sub>2</sub> gas is Fuel at cathode and operates b/w 600 °C -650 °C.
- ★ It is efficient than phosphoric acid fuel cell.
- ★ **Uses:** These are used in chemical industries such as aluminum Chloroalkali industries.



## Corrosion:

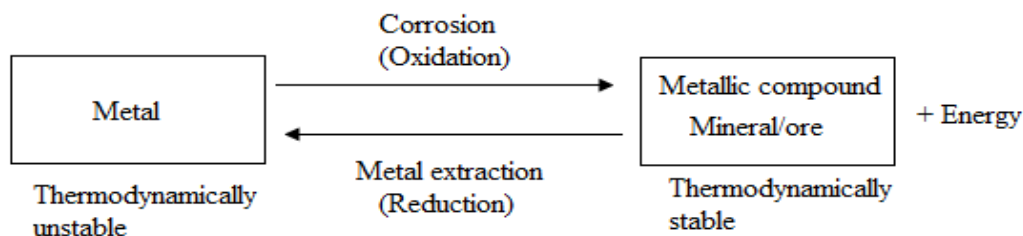
**Definition:** Corrosion is defined as the deterioration of a metal by chemical or electro chemical reactions with its environment. Due to corrosion the useful properties of a metal like malleability, ductility, electrical conductivity and also the surface appearance are lost. The most familiar example of corrosion is rusting of iron when exposed to atmospheric conditions.

✎ Examples:

- ◆ Rusting of iron: A layer of reddish brown scale ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) is formed on the surface of the iron.
- ◆ Formation of green layer of basic copper carbonate [ $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$ ] on the surface of copper.
- ◆ Tarnishing of silver: Blackening of surface of silver due to the formation of black layer of silver sulphide on it.

### Cause of corrosion:

- ▲ The metals exist in nature in the form of their minerals or ores, in the stable combined forms as oxides, chlorides, silicates, carbonates, sulphides etc.
- ▲ During the extraction of metals, these ores are reduced to metallic state by supplying considerable amounts of energy.
- ▲ Hence the isolated pure metals are regarded as excited states than their corresponding ores.
- ▲ So metals have natural tendency to go back to their combined state (minerals/ores).
- ▲ When metal is exposed to atmospheric gases, moisture, liquids etc., the metal surface reacts and forms more thermodynamically stable compounds.



### Consequences of corrosion:

- ♣ Enormous waste of machineries and different types of metallic materials
- ♣ It leads to sudden failure of machines.
- ♣ It leads to the decrease in efficiency of machine and frequent replacement of corroded equipment which is an expensive.
- ♣ It may leakage of inflammable gas from the corroded pipe lines resulting into fire accidents etc.
- ♣ It causes contamination of potable water.
- ♣ It has been estimated that 25% of annual world production of iron is wasted due to corrosion.

### Theories of corrosion :

#### Q 1) Dry corrosion (or) Chemical corrosion (or) Direct chemical attack theory (or) Mechanism of dry corrosion:

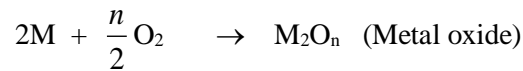
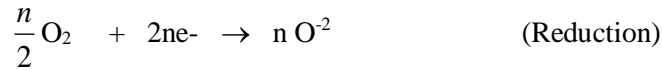
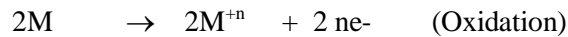
This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses like  $\text{O}_2$ , halogens,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ ,  $\text{N}_2$  or anhydrous inorganic liquid with the metal surface.

There are three types of chemical Corrosion:

- (1.) Oxidation corrosion (2.) Corrosion due to other gases (3.) Liquid metal corrosion.

#### (1.) Oxidation corrosion:

- ★ This is carried out by the direct action of oxygen at low or high temperatures on metals in absence of moisture.
- ★ This theory explains dry corrosion.
- ★ Corrosion is initiated in a metal, when it is contacted directly with oxygen.
- ★ Then the metal gets oxidized to metal ions and the electrons so released reduce oxygen to form oxide ion.
- ★ The metal ion and oxide ion combine to form metal oxide on the metal surface.

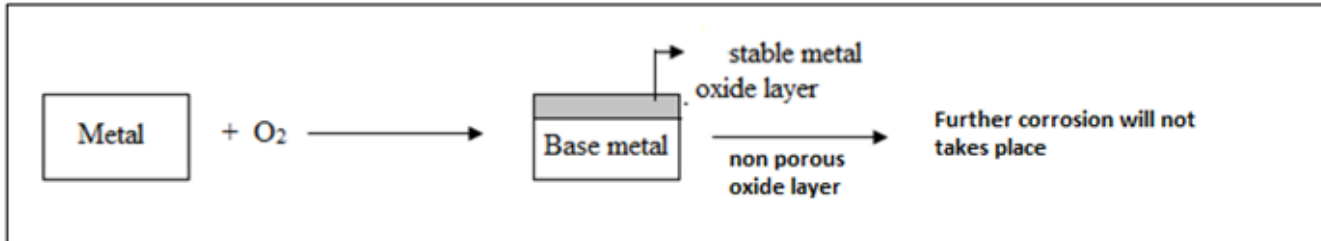


- ★ The extent of corrosion depends upon the nature of metal oxide.
- ★ The nature of metal oxide layer formed plays an important role in determining further corrosion.

**a) Stable oxide layer (or) Protective and non porous oxide film :**

If the metal oxide is stable, it behaves as a protective layer which prevents further corrosion.

E.g., The oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.

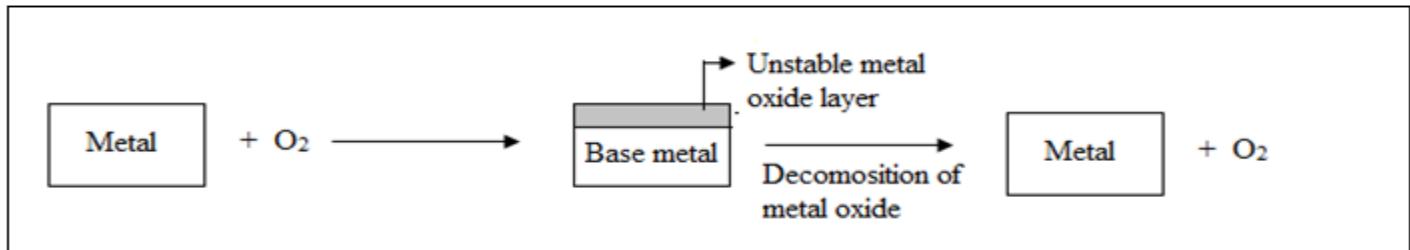


**(b) Unstable oxide layer:**

If the metal oxide layer is unstable, the oxide layer formed decomposes back into metal and oxygen.

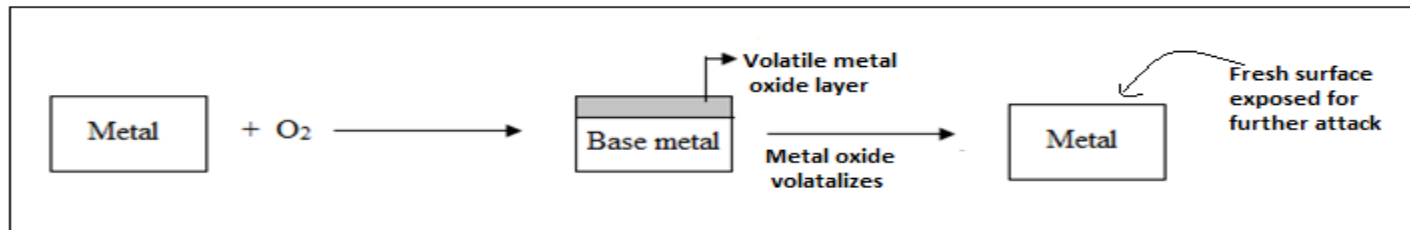
So, oxidation corrosion is not possible.

E.g., Ag, Au and Pt do not undergo oxidation corrosion.



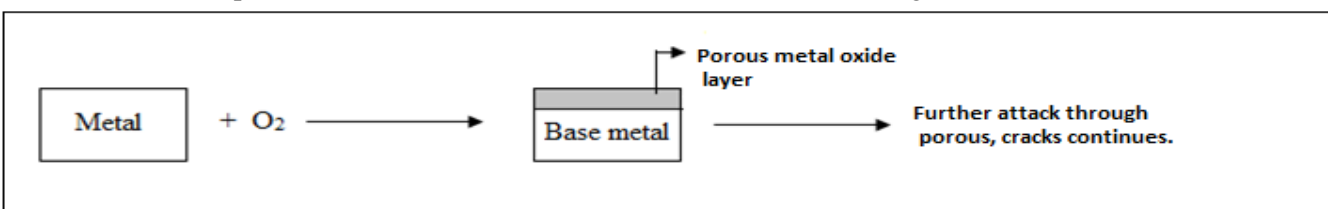
**(c) Volatile oxide layer:**

If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive in molybdenum oxide (MoO3)



**(d) Porous and non protective oxide layer:**

If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying metal surface. This causes continuous corrosion till conversion of metal into its oxide is completed. Ex: Alkali and alkaline earth metals (Li, Na, K, Mg etc.)



### Pilling-Bedworth Rule:

This rule states the extent of protection given by the corrosion layer. An oxide is protective or non – porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed.

It is the ratio of the volume of metal oxide to volume of metal.

$$\text{specific ratio} = \frac{\text{volume of metal Oxide}}{\text{Volume of Metal}}$$

The smaller the specific ratio, greater the oxide corrosion since the formed oxide film will be porous through which the oxygen can diffuse and increases the corrosion further.

- 1) If the volume of the metal oxide layer is at least as great as the volume of the metal, no corrosion occurs as the oxidation of metal reaches to zero. i.e; specific ratio  $\geq 1$   
For example, the specific volume ratios of W, Cr and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in Tungsten (W).
- 2) If the volume of metal oxide is less than the volume of the metal, the oxide film will develop cracks and pores. The atmospheric oxygen reaches the metal and increases the corrosion. In this case corrosion is continuous and rapidly increases. i.e; specific ratio  $< 1$   
For example, Li, Na and K.

### (2) Corrosion due to other gases:

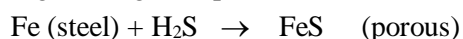
- ★ This type of corrosion is due to gases like  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{F}_2$  etc.
- ★ In this corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved.
- ★ The degree of attack depends on the formation of protective or non protective films on the metal surface which is explained on the basis of Pilling Bedworth rule.

(i) If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent, non-porous does not allow the penetration of corrosive gases. For example when Cl reacts with Ag forms AgCl film which prevents further reaction of Cl with Ag.



(ii) If the volume of the corrosion film formed is less than the underlying metal, it forms pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.

Ex. In petroleum industry,  $\text{H}_2\text{S}$  gas at high temperature reacts with steel forming a FeS scale.



### (3.) Liquid metal corrosion:

- ★ This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy.
- ★ The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal.

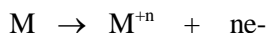
Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

### Q 2) Wet Corrosion (or) Electrochemical corrosion:

- ★ This type of Corrosion occurs where a conducting liquid is in contact with the metal.
- ★ This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution.
- ★ At anodic area, oxidation reaction occurs thereby destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

**Mechanism:** Electrochemical corrosion involves flow of electrons between anode and cathode.

The anodic reaction involves dissolution of metal liberating free electrons.

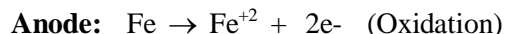


The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

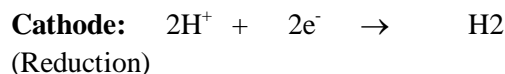
**Evolution of hydrogen :** [ Formation of Rust with evolution of H<sub>2</sub> in Wet corrosion ]:

- ★ 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.

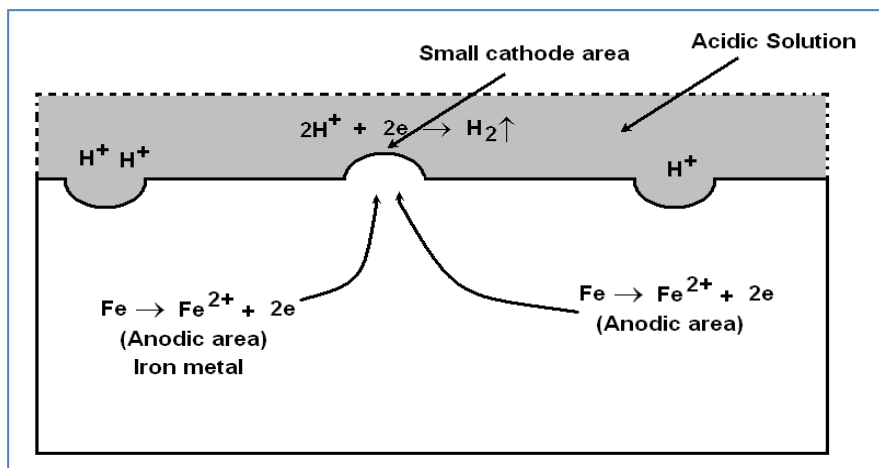


- ★ The electrons released flow through the metal from anode to cathode, whereas H<sup>+</sup> ions of acidic solution are eliminated as hydrogen gas.



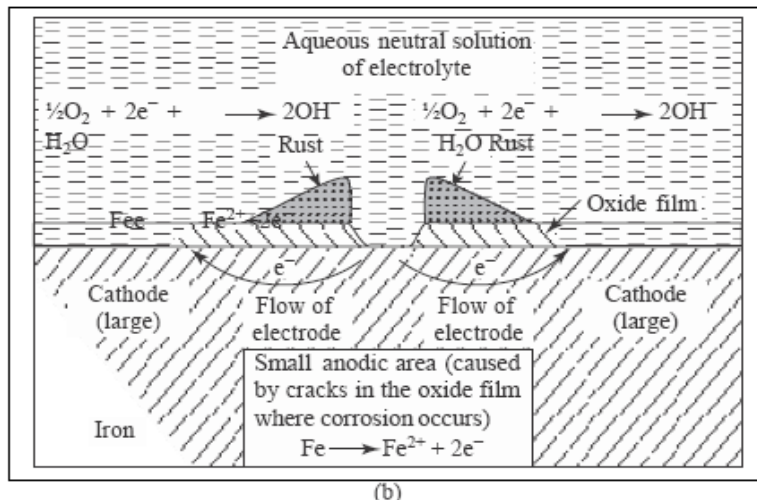
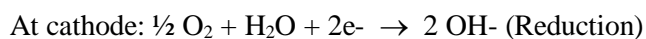
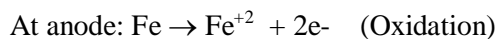
- ★ **The overall reaction** is:  $Fe + 2H^{+} \rightarrow Fe^{2+} + H_2$

- ★ 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<sub>2</sub> gas. The anodes are large areas, whereas cathodes are small areas.



**Absorption of oxygen:** [ Formation of Rust with evolution of O<sub>2</sub> in wet reaction ] :

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. It shows that anodes are small areas, while the rest metallic part forms large cathodes. The released electrons flow from anode to cathode through iron metal.

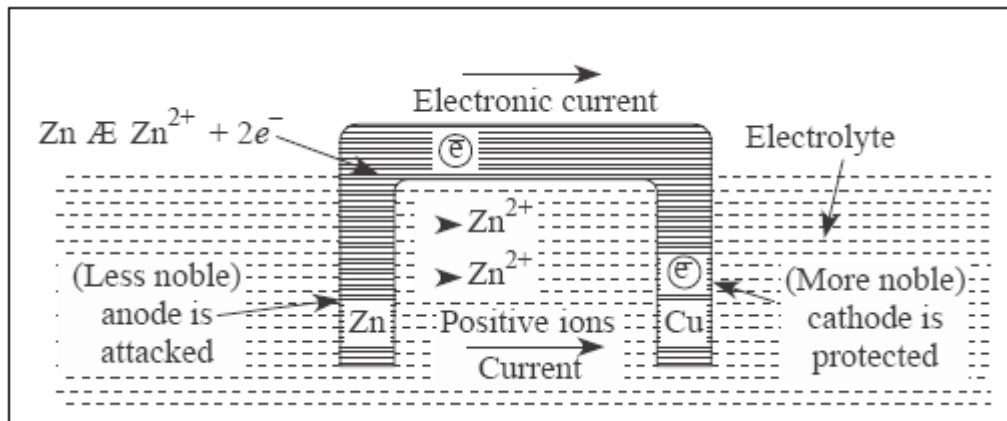


- ★ Fe<sup>2+</sup> ions and OH<sup>-</sup> ions combine to form Fe(OH)<sub>2</sub> precipitate.
- ★ If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.
 
$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$
- ★ This product called yellow rust actually corresponds to Fe<sub>2</sub>O<sub>3</sub> · H<sub>2</sub>O.
- ★ If the supply of oxygen is limited, the corrosion product may be black magnetite Fe<sub>3</sub>O<sub>4</sub>.



### Q 3) What is galvanic corrosion? How is it prevented? Give examples?

Galvanic corrosion: This type of electrochemical corrosion is also called bimetallic corrosion. When two dissimilar metals are connected and exposed to an electrolyte, they will form a galvanic cell. The anodic metal will be oxidised and it will undergo corrosion. Zinc and copper metals connected with each other in an electrolyte medium form a galvanic cell. Zinc acts as anode and undergoes corrosion while cathode will be unaffected.



**Eg:** When Zn and Cu are connected and exposed to a corroding environment, Zinc (higher in the electrochemical series) forms the anode; it undergoes oxidation and gets corroded. Cu (lower in the electrochemical series) acts as the cathode; it undergoes reduction and is protected as the electrons released by Zn flow towards Cu.

#### Prevention:

- 1) Galvanic corrosion can be avoided by coupling metals close to the electrochemical series.
- 2) Fixing insulating material between two metals.
- 3) By using larger anodic metal and smaller cathodic metal.

#### Example of galvanic corrosion:

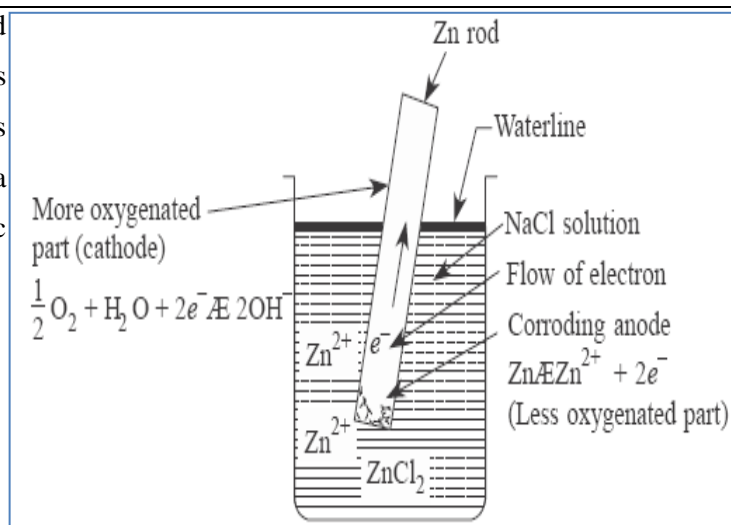
- 1) Steel screws in brass marine hardware,
- 2) steel pipe connected to copper plumbing,
- 3) steel propeller shaft in bronze bearing,
- 4) zinc coating on mild steel,
- 5) lead-tin solder around copper wires.

### Q 4) Differential aeration corrosion: or Concentration cell corrosion:

If a metal rod is dipped in an electrolyte, the portion dipped in water is poor in oxygen concentration and works as an anode which gets corroded and the portion above water acts as a cathode which is protected. The system will act as a concentration cell and the chemical reactions for zinc dipped in water are given as:

$Zn(OH)_2$  appears as corrosion products.

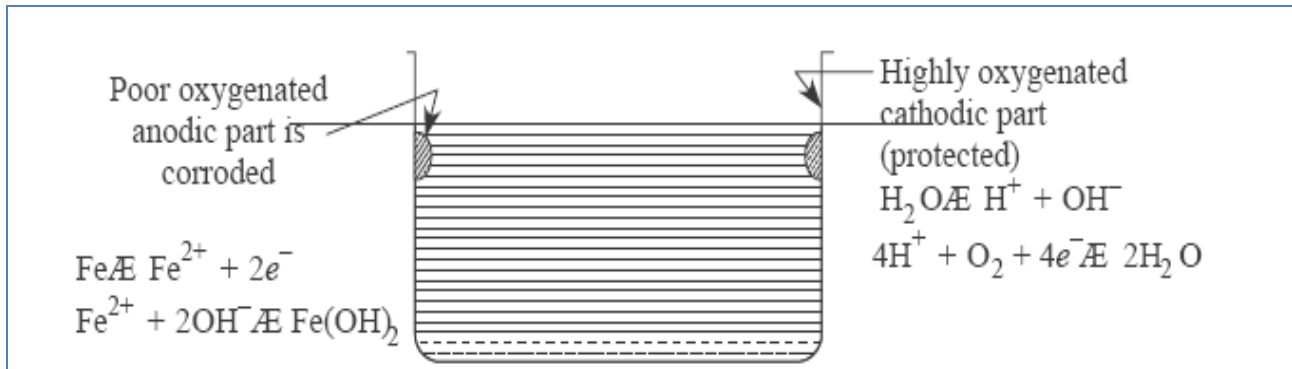
- Examples:
- 1) Water line corrosion,
  - 2) Drop corrosion.





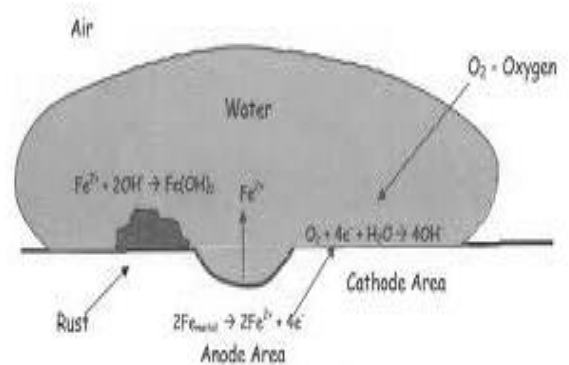
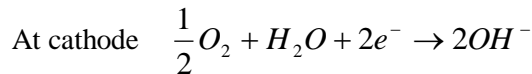
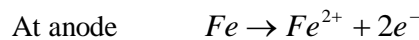
### 1) Waterline corrosion:

It has been observed in the case of an iron tank containing water, that the portion of iron tank just below the water level undergoes corrosion. It is due to the difference in oxygen concentration. Corroding portion is poor in oxygen and acts as anode.



### 2) Water Drop corrosion:-

- ★ For instance iron metal surface is covered with a drop of water.
- ★ The area covered by a drop has low oxygen concentration and thus acts as an anode and suffers corrosion, the uncovered area of the metal acts as large cathode due to high  $\text{O}_2$  concentration.



### Q 5) Write notes on Stress corrosion.

- ★ When a metal is subjected to uneven stress and exposed to corrosion environment, it undergoes stress corrosion.
- ★ The stressed portion is in thermodynamically unstable state that's why areas under stress act as the anode and other areas act as the cathode.
- ★ It is due to the combined effect of static tensile stresses and corrosive environment.
- ★ Stressed areas of alloys are chemically active and they are attacked by even mild corrosive environment, as a result cracks are developed and they propagate in a direction perpendicular to operating stress.

#### ★ Examples;

Season cracking (stress corrosion of brass):

- ▲ Season cracking is observed in brass (Copper + Zinc alloy) articles.
- ▲ Pure copper is immune to stress corrosion but presence of alloying agents such as Zn, Al etc makes it prone to corrosion.
- ▲ In the presence of  $\text{NH}_3$  or  $\text{RNH}_2$ , it undergoes corrosion due to formation of complexes like  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  and  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ .

This leads to dissolution of brass which ultimately results in the formation of cracks in the presence of stress.

**What is passivity? Explain.**

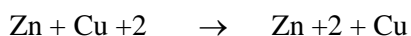
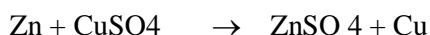
The process in which a metal exhibits higher corrosion resistance is called passivity. When a very thin, invisible and highly protective film is formed on the surface of a metal or an alloy, it is called passivity. This film is insoluble and non-passive. A metal is passive in a certain environment if its corrosion rate is very low. By the change of the environment, the passivity of a metal may change and may become active towards corrosion.

The formation of a passive film on the metal surface is determined by the Pourbaix diagram, which depends on the electrode potential and pH of the medium. Low carbon steel does not corrode in conc. HNO<sub>3</sub> due to protection effect of passive film. However, in dil. HNO<sub>3</sub> does not form a stable passive film and therefore dissolves steel. Passive film is formed on the surface of aluminium, Cr, Si, Ti in air, water and dilute acids. There is a good corrosion and oxidation resistance of stainless oxide passive layer.

A damage of passive film may cause intensive localised corrosion (pitting corrosion). Passive oxide layers are dissolved in electrolytes containing SO<sub>4</sub><sup>2-</sup> and chloride. Phosphate and chromate ions stabilise passive films, promoting the regain of its defects.

**Q 6) What is Galvanic series? Explain.**

Electrochemical reactions are predicted by electrochemical series. A metal having higher position can replace (reduce) other metals that have lower position in the series. For example, that is,



Or in other words, zinc will corrode faster than copper.

Some exceptions have been observed in this generalisation. For example, Ti is less reactive than Ag.

Galvanic series is the series of metals that is made keeping in view the process of corrosion of a metal in a particular atmosphere, i.e. sea water. In galvanic series, oxidation potential of metals is arranged in the decreasing order of activity of a series of metals. The series is towards the increasing noble nature.

More anodic: Mg, Mg alloys, Zn, Al, Cd, Fe, Pb, Sn, Ni–Mo–Fe alloys, Brasses, Cu, Ni, Cr–steel alloy, Ag, Ti, Au, Pt towards noble nature.

**Differences between electrochemical series and galvanic series:**

S.No:	Galvanic series	Electrochemical series
1	This series was developed by the study of corrosion of metals and alloys in sea	This was developed by dipping pure metals in their 1M salt solution water without their oxide film.
2	The position of the given metal may shift.	The position of the metal is fixed.
3	The corrosion of alloys can be studied.	No information regarding alloys.
4	The position of a metal is different from that of the position of the alloy which contains the same metal in it.	The position of the metal is fixed.

## Q 7) Explain about the Factors Influencing rate of Corrosion.

The rate and extent of corrosion depends upon various factors.

1. Nature of metal
2. Nature of corroding atmosphere

### Nature of the metal:

#### 1. Position in the galvanic series:

Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily. Metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion and they get protected.

#### 2. Purity of metal:

Heterogeneity is produced if impurities are present in a metal, which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded. As the extent of exposure and impurities increase, the extent of corrosion increases. For example in case of zinc metal;

% Purity	99.999	99.99	99.95	99
Corrosion rate	1	2650	5000	7200

#### 3. Relative areas of the anodic and cathodic parts:

When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the areas of the cathodic and anodic parts. i.e, the corrosion is more rapid, severe and highly localised if the anodic area is small. For example, a small pipe made of steel fitted in a large copper tank.

$$\text{In general Rate of corrosion of anodic region} \propto \frac{\text{CathodicArea}}{\text{AnodicArea}}$$

#### 4. Nature of surface film:

In aerated atmosphere, practically all metals produce a thin surface film of metal oxide. The ratio of the volumes of the metal oxide formed to the metal is called "specific volume ratio".

$$\text{specific ratio} = \frac{\text{volumeofmetalOxide}}{\text{VolumeofMetal}}$$

If the specific volume ratio is more, the rate of corrosion is less, because the surface of the metal is completely covered by the film, offering protection to the metal surface.

For example, the specific volume ratios of Ni, Cr, and W are 1.6, 2.0 and 3.6 respectively. The rate of corrosion for tungsten (W) is least even at elevated temperatures.

#### 5. Physical state of metal:

The grain size, orientation of crystals, stress etc. of the metals influence the rate of corrosion. The smaller the grain size of the metal or alloy greater will be the rate of corrosion, because of its high solubility. The areas under stress become anodic and corrosion takes place in these areas.

#### 6. Volatility of corrosion products:

If the corrosion produced volatilizes as soon as it is formed, the metal surface is exposed for further attack. This creates rapid and excessive corrosion.

For example the corrosion product of molybdenum as molybdenum oxide ( $\text{MoO}_3$ ) is volatile.

7. **Solubility of corrosion product:** If the oxide film formed as corrosion product is soluble in corroding medium, the corrosion proceeds at a faster rate. The corrosion product acts as a physical barrier between the metal and environment. For example PbSO<sub>4</sub> film formed by Pb on sulphuric acid medium.

8. **Passive character of metal:**

Metals like Ti, Al, Cr, Mg, Ni and Co are passive and they exhibit much higher corrosion resistance than expected from their position in the electrochemical series. This is because the metal forms very thin, highly protective corrosion film, by reacting with atmospheric oxygen. If the film is broken, it compensates the film by re exposure to oxidising conditions. Thus they produce "self healing film". This property is called passive character of metal.

For example the corrosion resistance of "stainless steel" is due to passivating character of chromium present in it.

**Nature of corroding environment:**

1. **Temperature:**

The rate of corrosion increases with increase of temperature.

2. **Humidity of air:**

Increase of moisture in the environment increases the rate of reaction.

3. **Presence of impurities in atmosphere:** Atmosphere is contaminated with gases like CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S; fumes of H<sub>2</sub>SO<sub>4</sub>, HCl etc. and other suspended particles in the vicinity of industrial areas. They are responsible for electrical conductivity, thereby increasing corrosion

4. **Nature of ions present in the medium :**

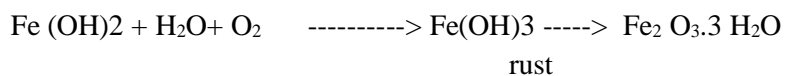
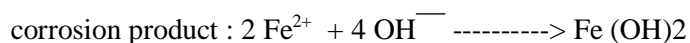
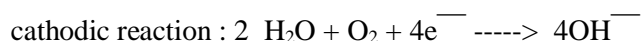
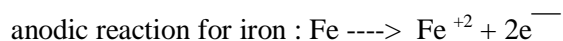
The presence of ions like silicates in the medium leads to the formation of "insoluble reaction products" like silica gel, on the metal surface which "inhibit" further corrosion. On the other hand chloride ions, if present in the medium destroys the protective film on the surface of the metal, there by exposing the metal surface for fresh corrosion attack. Presence of traces of copper in marine waters enhances the corrosion of the iron pipes or steel body of the ships.

5. **Conductance of the corroding medium:**

For the corrosion of underground or submerged structures the conductance of the corroding medium plays an important role. The conductance of dry sandy soils is lower than the conductance of clayey and mineralised soils. Hence the rate of corrosion is more in clayey and mineralized soils, causing severe damage to metallic structures buried.

6. **Amount of oxygen in atmosphere:**

As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.



7. **Velocity of ions which flow in the medium:**

As the velocity of the diffusion of ions in the medium increases, the rate of corrosion increases.

8. **pH value of the medium:**

pH value of the medium has greater effect on corrosion. When pH value is lowered, the corrosion is increases.

### Corrosion Control Methods:

As we have discussed the disadvantages and different mechanisms of corrosion so far, it is essential to know the different corrosion control methods. The following are the important control methods of corrosion.

- 1) Proper designing
- 2) Cathodic protection.
- 3) Application of protective coatings.
- 4)

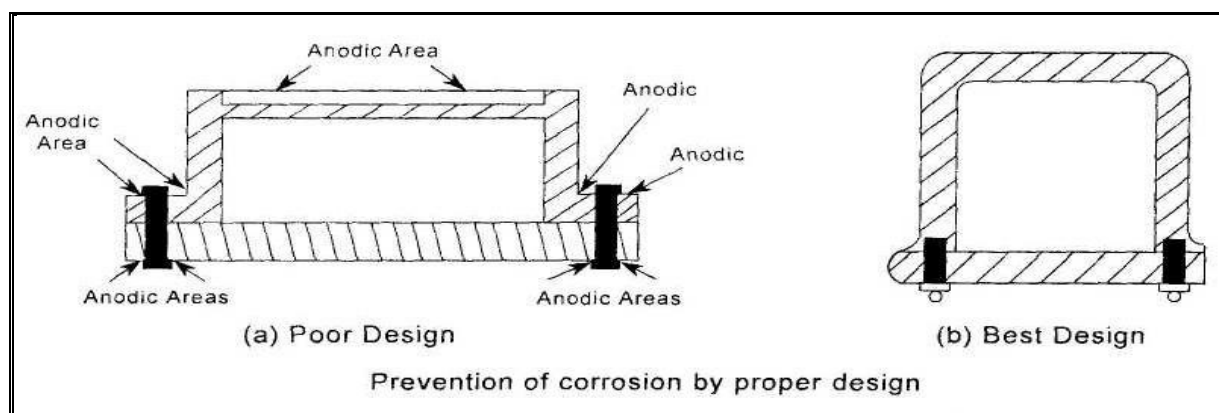
#### Q 8) Explain how proper selection and design of materials minimize corrosion.

The design of the metal under corroding atmosphere must be such that it is uniform and does not produce intense and localised corrosion, important principles of proper designing are:

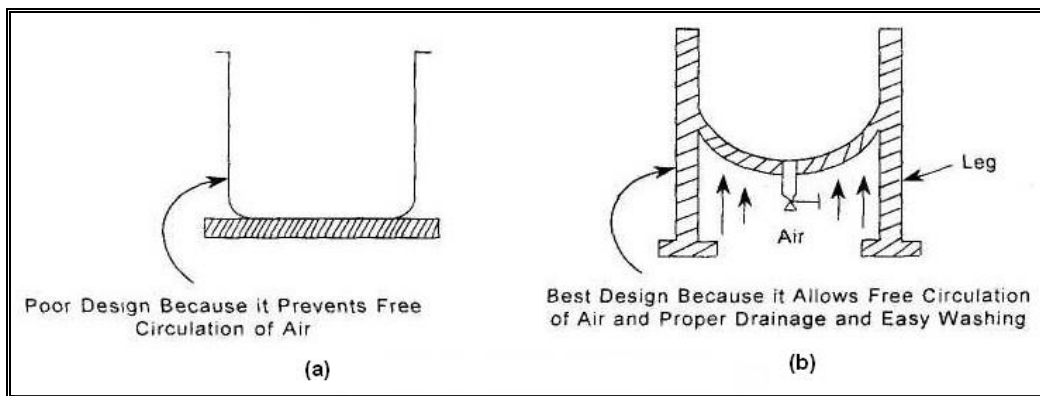
1. Avoid the contact of two dissimilar metals in the presence of corroding solution.
2. When two dissimilar metals are in contact, the anodic metal must possess large surface area, where as cathodic metal must possess smallest surface area so that the corrosion takes place is minimum.
3. If two dissimilar metals are in contact, their position in the electrochemical series must be very close, so that minimum corrosion occurs.
4. A direct metal to metal contact between two dissimilar metals must be avoided by fixing an insulating fitting in between them, so that the corrosion velocity can be minimised.
5. The anodic metal should not be painted or coated. When the anodic metal is in contact with the cathodic metal, the anodic metal should not be painted or coated, because any break in the paint would lead to rapid localisation corrosion. A proper design should avoid the presence of crevices, between the adjacent parts of the structure, even in the case of the same metal.

For example, electrical box is shown as below. The design (a) is such that rain water collects at the top and also seeps between the bolt and two housing and remains there because of capillary action producing anodic parts.

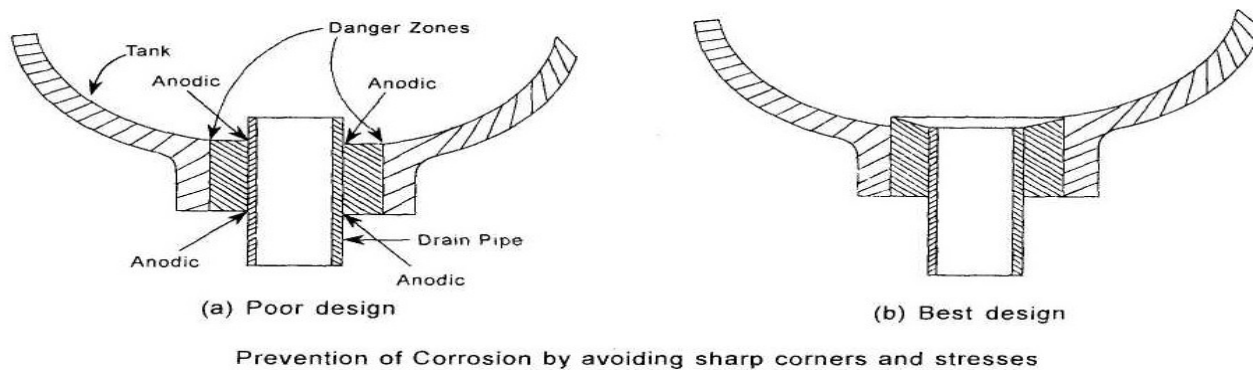
The defects can be corrected by slight modification in the designs shown in (b).



The design of the equipment should allow free circulation of air proper drainage and easy washing as shown below.



The design should eliminate sharp corners and stresses as shown in (b), along with a modification of the poor design.



**Q 9) Explain the cathodic protection method with neat diagrams and examples.**

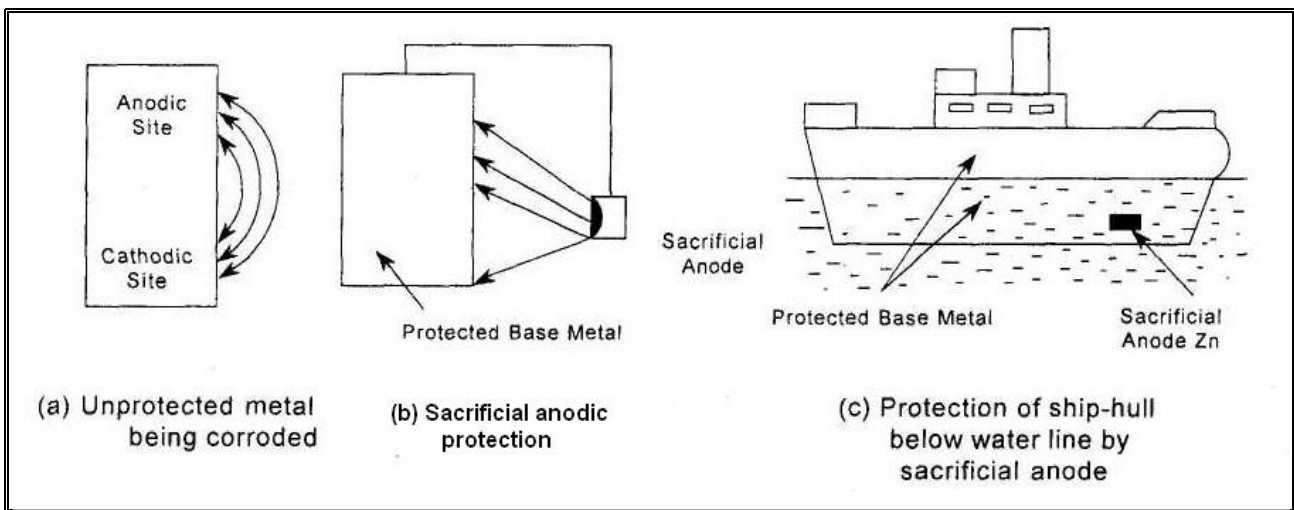
- ★ The basic principle of cathodic protection is to force the metal to behave like a cathode.
- ★ The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection.
- ★ There are two types of cathodic protection;
  - (a) Sacrificial anodic protection method.
  - (b) Impressed current cathodic protection method.

**a) Sacrificial anodic protection method :**

- ★ In this protection method, the metallic structure to be protected is called a base metal.
- ★ The base metal is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.
- ★ The more anodic metal itself gets corroded slowly, while the parent structure (cathodic) is protected.
- ★ The more active metal so employed is called sacrificial anode.
- ★ The corroded sacrificial anode is replaced by a fresh one, when consumed completely.
- ★ Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series.

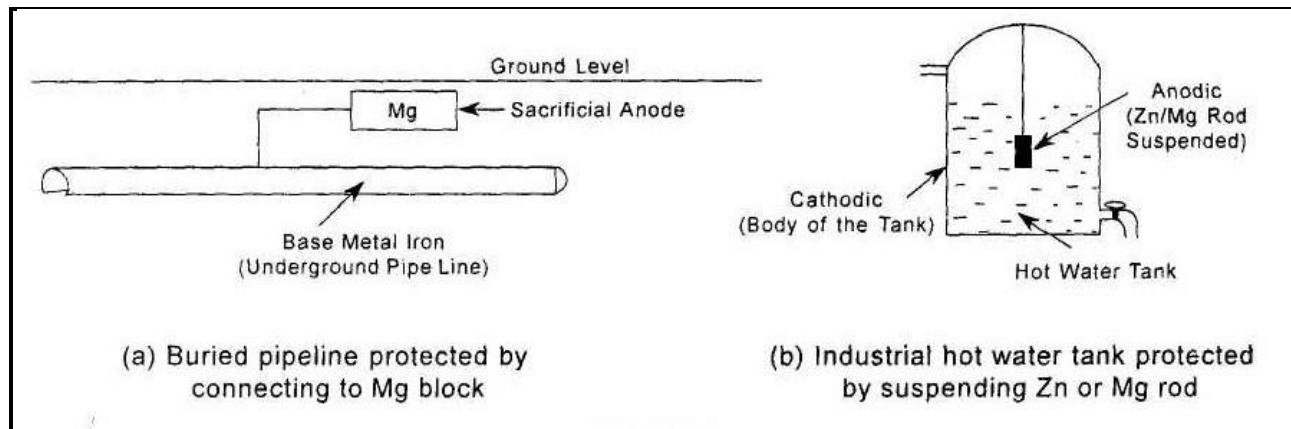
Eg 1. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.





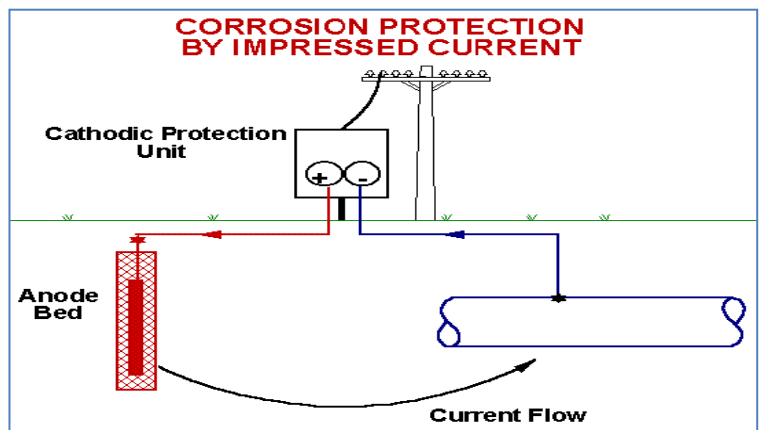
Example 2:

The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.



**(b) Impressed current cathodic protection:**

- ★ In this method an impressed current little more than corrosion current is applied in the opposite direction to nullify the corrosion current producing a reverse cell reaction.
- ★ 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 anode is usually insoluble anode like graphite, high silica iron, scrap iron, stainless steel, or platinum.
- ★ Usually a sufficient D.C. current is passed on to the insoluble anode kept in a 'back fill' composed of coke or gypsum, so as to increase the electrical contact with the surrounding soil.



- ★ This type of impressed current cathodic protection is given to
 

(1) open water box coolers	(2) water tanks	(3) buried water pipe lines or oil pipelines
(4) condensers	(5) transmission line towers	(6) marine pipes



- ★ This type of protection is more useful for large structures for long term operations.

**Disadvantages of cathodic protection:**

1. The cathodic protection may be efficient in protecting a pipeline, yet may increase the corrosion of the adjacent pipelines or metal structure because of stray currents.
2. Capital investment and maintenance costs are more.
3. Special care must be taken that the metal is not over protected, i.e., the use of much higher potential than the open circuit voltage for the metal/metal ion couple in case of impressed current method and the higher anodic metal in the series must be avoided. Otherwise problems related to cathodic reactions like evolution of H<sub>2</sub> or formation and accumulation of OH<sup>-</sup> will take place.

In spite of these disadvantages, cathodic protection has been widely used with success, when suitable precautions are taken.

**Protective coatings or Surface Coatings - Methods Of Application On Metals:**

The oldest and common method of protection of a metal from its surroundings is applying a protective coating on the surface of the metal. The coated surface isolates the metal from its corroding environment.

The coating should have the following property.

The coating applied must be chemically inert to the environment under particular conditions of temperature and pressure.

**Q 10 ) What are the methods of cleaning the metal surface before applying the surface coatings.**

Before applying any protective coating the metal surface must be thoroughly cleaned to remove dirt, old protective coatings like paints, greases, corrosion products etc.

The following are some of the methods adopted for metal cleaning .

**Solvent cleaning:**

In this method the metal surface is cleaned with organic solvents like naphtha ,carbon tetrachloride toluene, zylene or acetone. Then the metal surface is cleaned with steam and hot water containing wetting reagents this treatment is adopted for electroplating . This used method is to remove oils, greases, fatty substances.

**Alkali cleaning :**

In this method the metal surface is cleaned with alkali cleanin agents like trisodium phosphate along with wetting agents like coustic soda. It is followed by thorough rinsing with water and then immersion In 0.1% chromic acid, to remove last traces of alkalies This method is to remove old paint coatings from metal surfaces.

**Mechanical cleaning:**

In this method the metal surface is cleaned by using brushes and sand papers. Bristle brushes and metal brushes are used to remove loosely adhering impurities. Sand papers are used to remove strongly adhering scales and rust . This mehod is followed by steam or hot water treatment.

**Flame cleaning:**

This method involves heating the metal surface with a hot flame to remove loosely adhering scales, followed by wire brushing.

**Sand blasting:**

For sand blasting samples of sand of different grain size were blasted on the metal surface with a pressure of 25-100 atmospheres. It removes the scales on the metal surface . This method is used for cleaning large surface areas like large steel structures etc.

**Pickling and etching :**

In this process metals except aluminium are immersed in acid pickling solution. Aluminium is pickled in alkaline solution. Acid pickling of steel is carried out in warm dil. H<sub>2</sub>SO<sub>4</sub> solution .for cleaning copper, brass and nickl articals mixture of dilute HNO<sub>3</sub> and dil. H<sub>2</sub>SO<sub>4</sub> is used. It is followed by water and steam treatment.

**Q 11) What is meant by metallic coating? Explain anodic coating and cathodic coating with examples.**

**Metallic coatings :**

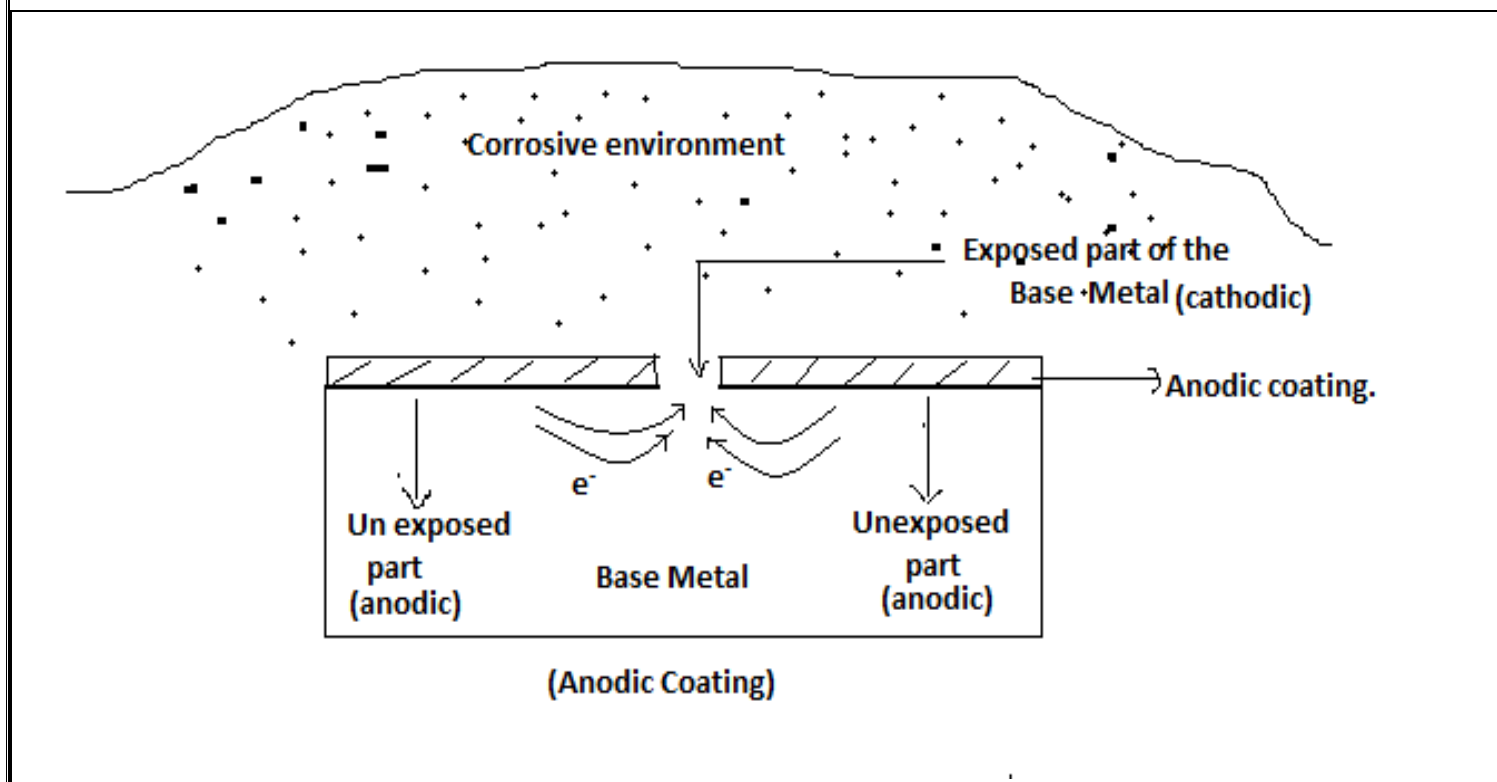
Metallic coatings are produced by coating one metal on the surface of another metal. The metal which is protected is called base metal and the metal which is coated on the surface of the base metal is called coating metal.

Metallic coating are of two types: **1. Anodic coating:**  
**2. Cathodic coating:**

**ANODIC COATINGS:**

The metal used for the surface coating is more anodic than the base metal which is to be protected.

For example, coating of Al, Cd and Zn on steel surface are anodic because their electrode potentials are lower than that of the base metal iron. Therefore, anodic coatings protect the underlying base metal sacrificially. The formation of pores and cracks over the metallic coating exposes the basemetal and a galvanic cell is formed between the base metal and coating metal. The coating metal dissolves anodically and the base metal is protected.

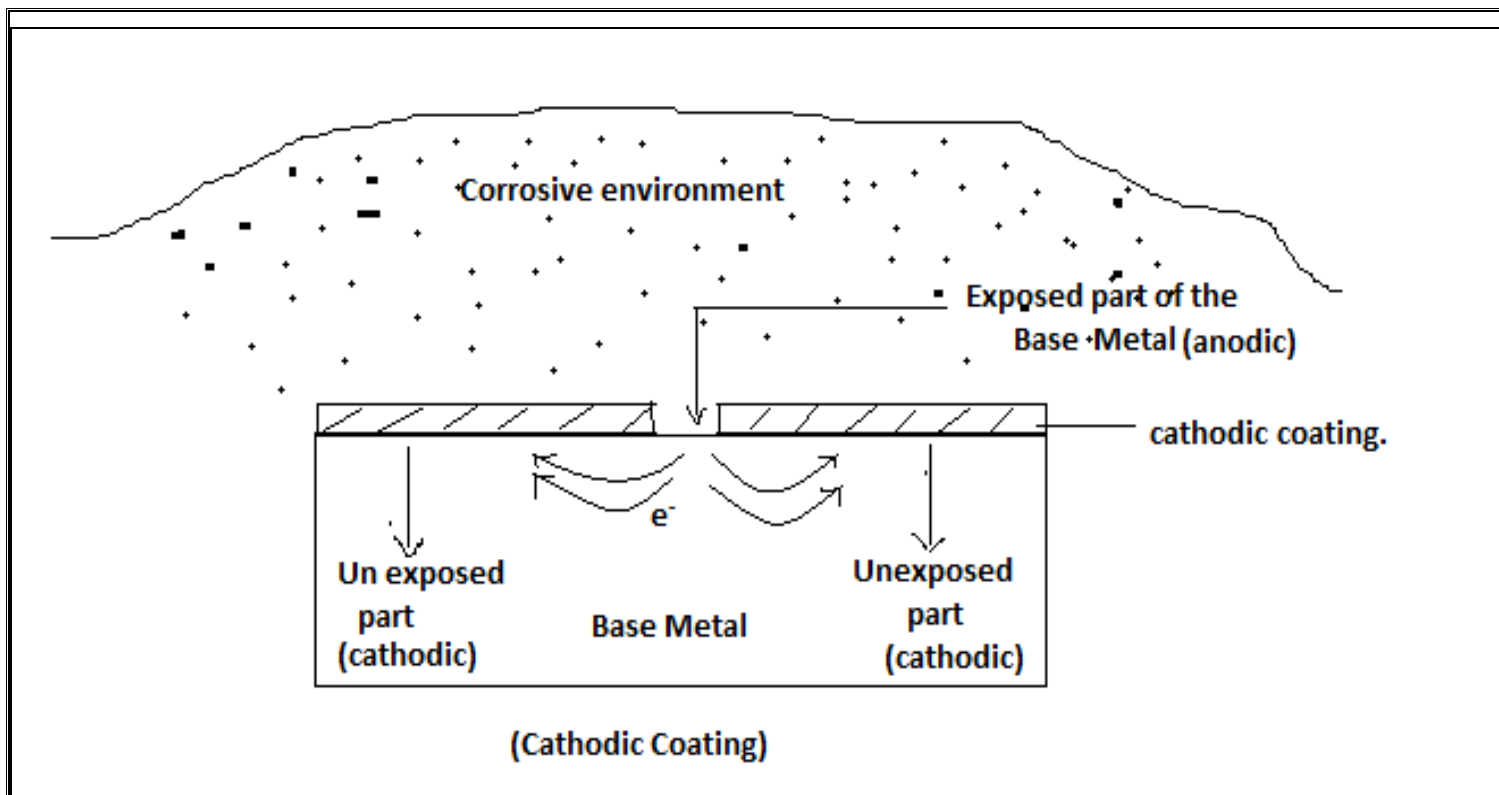


**Example: Galvanization:**

**Def:** The process of coating zinc metal on the surface of iron is called Galvanization. It is the anodic protection offered by the zinc.

**Process:** In this process, at first iron or steel is cleaned by pickling with dilute sulphuric acid solution at a temperature range of 60-90°C for 15 to 20 minutes. Therefore, it removes scale, rust and other impurities present and then washed well in a water bath and dried. Then after dipped in the bath containing molten zinc which is at 425-450 °C. To prevent it from oxide formation, the surface of bath is covered with a ammonium chloride flux. When the iron sheet is taken out it is coated with a thin layer of zinc. To remove excess zinc, it is passed through a pair of hot rollers and then it is annealed at a temperature of 450 °C followed by cooling.





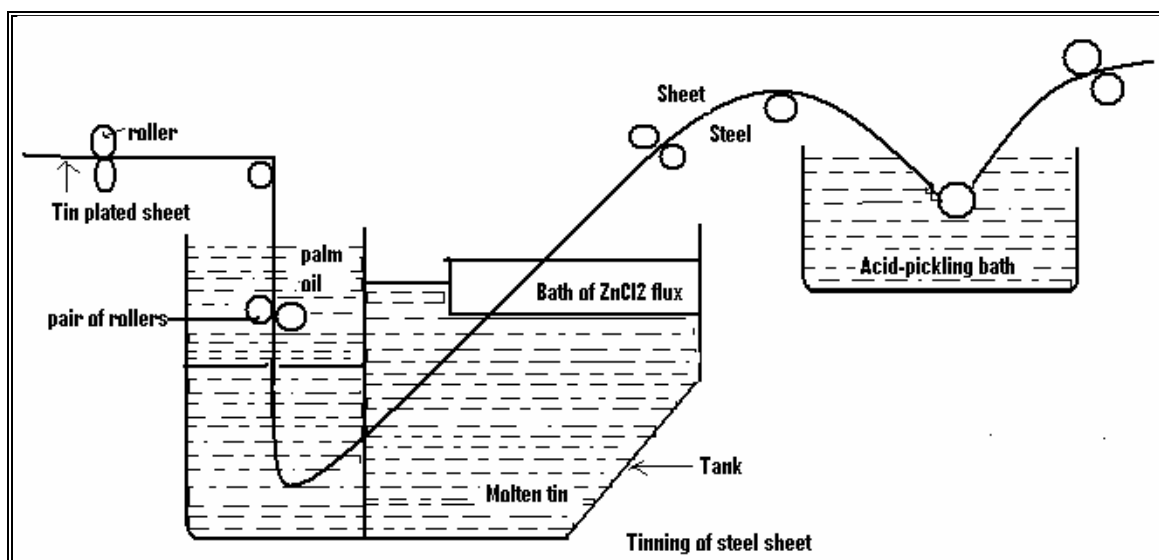
**Example: Tinning.**

**Def:** The process of coating tin metal on the surface of iron is called Tinning.

- ★ Tin is a noble metal and therefore it possess more resistance to chemical attack.
- ★ It is the cathodic protection offered by the tin.

**Process:** In this process the surface of the base metal i.e iron sheet is cleaned by acid pickling with dil  $H_2SO_4$  and passed through a bath of zinc chloride flux. The flux helps the molten metal to adhere to the metal surface.

Then the sheet is passed through molten tin bath and passed between rollers from a layer of palm oil. Palm oil helps to protect the tin coated surface against oxidation. The rollers remove excess of tin and produce a thin film of uniform concentration. An alloy of the base metal and coating metal at their junction is produced.



**Applications of tinning:**

1. Tin metal possess good resistance against atmosphere corrosion. Tin is non toxic and widely used for coating steel, copper, and brass sheet.
2. The containers coated with tin are used for storing food stuffs, ghee, oils etc., and packing food materials.
3. Tinned copper sheets are used for making cooking utensils and refrigeration equipment.

**Q 13 ) Write the differences between anodic coatings and cathodic coatings.**

<b>Anodic coatings</b>	<b>Cathodic coatings</b>
1) These coatings involve coating of an anodic metal on the surface of base metal.	1) These coatings involve coating of anoble metal on the surface of base metal
2) Protects the underlying base metals “Sacrificially”	2) Protects the base metal by theirnoble character and higher corrosion resistance.
3) The redction potential of the coating metal is lower than the base metal	3) The redction potential of the coating metal is higher than that of base metal
4) If pores, breaks or discontinues are produced in the metallic coating, the base metal is not corroded beacuae it is cathodic to coating metal. The coating metal undergo severe corrosion	4) If pores, breaks or discontinues are produced in the metallic coating, the base metalbecomes anodic and faces severe corrosion due to smaller anodic area and the protecting metal becomes cathodic and does not undergo corrosion
5) The coating metal posses lower reduction potential than base metal	5) The coating metal possess higher reduction potential than base metal
6) Ex: Galvanisation	6) Ex: Tinnings

**Q 14 ) Write the differences between galvanizing and tinning****Comparison of Galvanization with Tinning :**

<b>Galvanization</b>	<b>Tinning</b>
The process of coating Zn on the surface of iron or steel is called galvanization.	The process of coating tin on the surface of iron or steel is called tinning.
Zinc is anodic to the base metal iron or steel.	Tin is cathodic to the base metal iron or steel.
Zinc protects iron “ sacrificially”	Tin protects iron due to its noble coating.

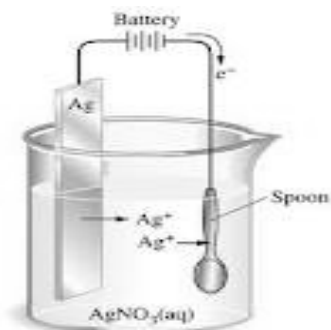
Zinc is more electropositive than iron, it does not permit iron to pass into the outside solution in other words corrosion does not occur to iron.	Tin is less electropositive than iron, it protects the iron till the coating is perfect.
Any break in the protective Zinc layer does not cause corrosion to the base metal.	Any break in the protective tin layer severe corrosion to the base metal.
Galvanised containers cannot be used for food storing.	Tin coated containers are used for food storing materials.
After galvanization, the galvanized sheet is subjected to annealing process.	No annealing process.

### Q 15 ) Describe Electroplating with suitable examples.

- ★ Electroplating is the method of electro-deposition of metal by means of electrolysis over surface of metals and alloys.
- ★ The base metal is first subjected to acid pickling to remove any scales, oxides etc.
- ★ The base metal is made as cathode of the electrolytic cell and the coating metal is made as anode.
- ★ The two electrolytes are dipped in the electrolyte solution which contains the metal ions to be deposited on the base metal.
- ★ When a direct current is passed from an external source, the coating metal ions migrate towards cathode and get deposited over the surface of base metal in the form of a thin layer.
- ★ Low temperature, medium current density, low metal ion concentration conditions are maintained for better electroplating.
- ★ It is widely used to coat the base metals with protective metallic coatings of copper, nickel, zinc, lead etc.

#### Eg: Electroplating with gold:

- Cathode: Article to be electroplated (Spoon)
- Anode: Block of gold metal
- Electrolyte: Aqueous solution of  $\text{AuCl}_3$  or Potassium auro-cyanide  $\text{K}[\text{Au}(\text{CN})_2]$



For example for electroplating of nickel on iron article, the following are maintained;

1. electrolytic bath solution : Nickel sulphate, nickel chloride and boric acid.
2. pH maintained . : 4 (by boric acid buffer)
3. Temperature maintained : 40 - 70° C
4. Current density : 20 - 30 mA/cm<sup>2</sup>
5. Additives added : Saccharin or coumarin or acetylene derivatives
6. Anode : Nickel pellets (99% pure) taken in a titanium mesh basket
7. Cathode : Base metal article

#### Factors affecting electroplating:

- Cleaning of the article is essential for strong adherent electroplating.
- Concentration of the electrolyte.
- The electrolyte selected should be highly soluble and should not undergo any chemical reactions.
- P<sup>H</sup> of the electrolytic bath.

**Q 16 ) Explain Electroless plating with suitable examples.**

Electroless plating is a technique of depositing a noble metal on a catalytically active surface of the metal to be protected by using a suitable reducing agent without using electrical energy.

**Step 1: Pretreatment and activation of the surface:**

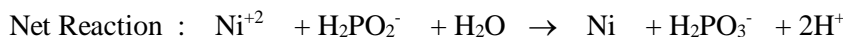
The surface to be plated is first degreased by using organic solvents or alkali, followed by acid treatment. Example: The surface of stainless steel is activated by dipping in hot solution of 50% dil.H<sub>2</sub>SO<sub>4</sub>.

**Step 2: Plating bath :**

Nature of the compound	Name of the compound	Quantity(g/l)	Function
Coating solution	NiCl <sub>2</sub>	20	Coating metal
Reducing agent	Sodium hypophosphite	20	Metal ions reduced
Complexing agent	Sodium succinate	15	Improves the quality
Buffer	Sodium acetate	10	Control the pH
Optimum pH	4.5	-----	-----
Optimum temperature	93°C	-----	-----

**Step 3: Procedure:**

The pretreated object is immersed in the plating bath for the required time.



Applications:

1. Electroless Ni plating is extensively used in electronic appliances.
2. Electroless Ni plating is used in domestic as well as automotive fields.

**Advantages of electroless plating over electro plating:**

- i) Electricity is not necessary
- ii) Complicated parts are uniformly coated
- iii) Plastics, glass etc, are easily coated
- iv) Good mechanical, chemical and magnetic properties are obtained.

**Q17 ) Define paints. What are the Constituents of Paints. Write their functions.****PAINT:**

Paint is a mechanical dispersion of one or more fine pigments in a medium (thinner + vehicle). When a paint is applied to metal surface, the thinner evaporates. The vehicle undergoes slow oxidation to form a pigmented film.

**Requirements or requisites of a good paint**

A good paint should,

- 1) have good covering power
- 2) spread easily on the surface
- 3) not crack on drying
- 4) adhere well to the surface
- 5) give a glossy film



- 6) be corrosion and water resistant
- 7) have stable colour

### **Constituents of Paints and their functions.**

- 1) Pigment
- 2) Vehicle
- 3) Thinner
- 4) Drier
- 5) Filler
- 6) Plasticizer
- 7) Anti skinning agent

**1. Pigment :** It is a solid that gives colour to the paint.

#### **Functions:**

- a) To give colour and opacity to the film.
- b) To provide strength to the film.
- c) To protect film by reflecting U.V. rays.
- d) To provide resistance to abrasion and weather.

#### **Example:**

White pigment - White lead,  $\text{TiO}_2$

Blue pigment - Prussian blue

Green pigment - Chromium oxide

Red pigment - Red lead,  $\text{Fe}_3\text{O}_4$

### **2. Vehicle (or) Drying Oil**

It is the film-forming liquid. It holds the ingredients of the paint. It is a nonvolatile high molecular weight fatty acid of vegetable or animal.

#### **Functions:**

- a) To hold the pigment on the surface.
- b) To form a protective layer by oxidation and polymerization.
- c) To impart water repellency, toughness and durability of film .
- d) To improve adhesion of film.

**Example:** Lin seed oil, Castor oil.

**3. Thinner:** It is the volatile portion of paint. It is added to reduce the viscosity of the paint for easy application on the surface. It easily evaporates after paint is applied.

#### **Functions:**

- a) To reduce viscosity of paint.
- b) To dissolve vehicle and other additives.
- c) To suspend the pigments.
- d) To increase elasticity of film.
- e) To increase penetration of vehicle.
- f) To improve drying of film.

**Example:** Turpentine, Dipentene, Xylol.

**4. Drier.** It is a substance used to speed up drying of the paint.

#### **Functions:**

- a) To act as oxygen carrier or catalyst.
- b) To provide oxygen essential for oxidation and polymerization of drying oil.

**Example:** Metallic soap, linoleate and resinate of Co, Mn etc.

**5. Extender or Filler:** These are white pigments that form bulk of the paint.

**Functions:**

- a) To reduce cost of paint
- b) To prevent shrinkage and cracking of film
- c) To modify shades of pigment
- d) To retard settling of pigments in paint.

**Example:** Talc gypsum, china-day.

**6. Plasticizer:** It is added to the paint to provide elasticity to the film and prevent its cracking.

**Example:** Triphenyl phosphate, Tricresyl phosphate etc.

**7. Antiskinning agents:** It is a chemical added to the paint to prevent gelling and peeling of the paint.

**Example:** Polyhydroxy phenols.

**Q 18) Write notes on special paints.**

In addition to the normal ingredients some special chemicals are incorporated to paints for some specific purposes. They are commonly known as special paints.

**1. Luminescent paints:**

Luminescent paints contains luminophor pigments are used for visibility in the dark. They find application in inks, advertising signboards, road marks, number plates of vehicles, watch dials, etc. The active components in luminous paint are specially prepared phosphorescent materials like CaS, ZnS, etc. They absorb light radiations and emit them in the dark. For colour effect in luminous paints, certain chemicals like copper salts (green), silver salts (blue), cerium and uranium salts (yellow), etc. are used.

**2. Heat Resistance paints:**

When the surfaces are exposed to high temperatures such as in chimneys, exhaust pipes, furnaces, oil stills, etc. Oil paints tend to decompose or get charred, they being organic in nature. Then the surfaces become liable for corrosion. To overcome this problem, a suspension of graphite or lamp black in small amounts of drying oils and more thinners can be used. But more recently, silicone paints are used for heat resistance.

**3. Fire-retardant paints:**

These are paints containing chemicals which are fire-resistant in nature. In other words, they produce gases like CO<sub>2</sub>, NH<sub>3</sub>, HCl, HBr on heating which are themselves non-combustible and do not support combustion, there by minimizing the rate of burning or extinguishing the fire.

**4. Antifouling paints:**

Oil paints are liable for attack by living organisms because of the organic content in them. So, in places where living organisms are handled or are present, such paints cannot be used. For use in breweries and biochemical laboratories, the paint is mixed with compounds having fungicidal properties. The active ingredients employed are HgO, Cu<sub>2</sub>O, Hg<sub>2</sub>Cl<sub>2</sub>, DDT, pentachlorophenol, etc. Such paints are called Antifouling paints.

**5. Cement Paint**

Cement paint is the coating, which is applied on plastered brickwork, concrete work, etc. The ingredients are

1. White cement (about 70%)
2. Hydrated lime [Ca(OH)<sub>2</sub>]
3. Pigment (a colouring agent)
4. Very fine sand (an inert filler) and
5. Water- repellent compound

Such paints of different colors are marked in powder form (eg Snowcem, Smocem). The powder is mixed with a suitable quantity of water to get a thin slurry, and applied on surfaces. For good results, a 1.5% to 2% aqueous solution of sodium silicate and Zinc sulphate is applied as primer coat.