

Questions

1. Define corrosion. Why do metals undergo corrosion?

Corrosion also can be defined as a chemical or electrochemical reaction between the material usually a metal and its environment that produces a deterioration of the material and its properties.

Most metals except noble metals occur in nature in the form of their compounds such as oxides, sulphides, carbonates and chlorides etc. The metals are extracted from these ores. The extraction of metals from these ores are endothermic process. Therefore when metals are put in use of other forms, they combine with the constituents of the environment and get converted into compounds(corrosion)

2. Explain electrochemical theory of corrosion with an example

Anodic reaction



The number of electrons produced is equal to the valency of the ion.

There are several cathodic reactions, which are frequently encountered, in metallic corrosion.

Cathodic reaction

Liberation of hydrogen in the **absence of oxygen**

i) In acidic medium



ii) In neutral or basic medium



Cathodic reaction

Absorption of oxygen in the presence of oxygen

i) In acidic medium



ii) In neutral or basic medium



Example: Corrosion of Iron



3. Explain the effect of following factors on corrosion rate

Factors affecting Corrosion rate

Nature of metal

Difference in potential between anodic and cathodic region

The ratio of anodic to cathodic area

pH

Hydrogen overvoltage

Temperature

1. Nature of metal

- The metals with lower electrode potential (reduction potential) values are more reactive than the metals with higher electrode potential values.
- The active metals like Na, K, Mg, Zn with lower electrode potential values are highly susceptible for corrosion.
- The noble metals such as silver, gold, platinum etc with higher electrode potential values are less susceptible for corrosion.

2. Difference in potential between anodic and cathodic region

- Larger the potential difference between the anodic and cathodic region of the corrosion cell, higher is the corrosion rate.
- When two different metals with large difference in their electrode potentials are in contact with each other, the more reactive metal undergoes corrosion very fast.

Example: Cu & Zn

3. Ratio of anodic to cathodic area

- The rate of corrosion is more with the combination of a large cathodic region and a small anodic region.

Reason:

The greater demand for electrons at the larger cathodic region has to get a greater current density which is supplied by the smaller anodic region.

Why Iron bolts or nuts are not used in copper boilers?

4. pH

- Lower the pH, higher is the corrosion rate.

Exceptional:

Al, Zn & Pb undergo fast corrosion in highly alkaline solution

5. Hydrogen over voltage

- The difference between the actual potential at which the hydrogen evolution takes place at the electrode and the theoretical potential for the same process is called Hydrogen overvoltage.
- Higher the hydrogen overvoltage, more difficult is the liberation of hydrogen on the metal surface.
- With lower hydrogen overvoltage, hydrogen gas is liberated easily and thus the cathodic reaction rate is faster.
- When the hydrogen overvoltage on the metal is high, cathodic reaction is slower and the corrosion of the metal also becomes slower.

6. Temperature

The increase in temperature increases the corrosion rate

4. Explain the galvanic corrosion

2. Galvanic Corrosion

Definition

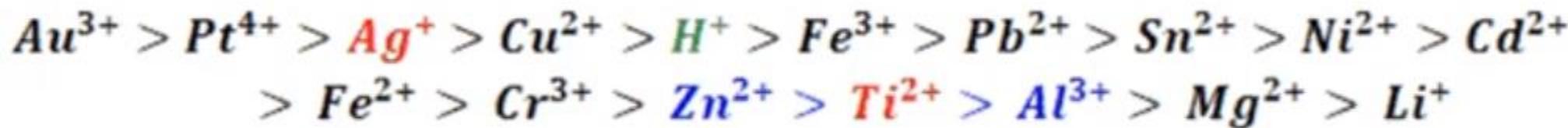
When two dissimilar metals are in contact with each other in the presence of a corrosive medium (electrolyte), the more active metal acts as an anode and undergoes corrosion.

The metal with low standard reduction potential (high std. oxidation potential), acts as anode and undergoes corrosion and the metal with high standard reduction potential acts as cathode and is protected. (electrochemical series)



ELECTROCHEMICAL SERIES

Arrangement of the standard reduction potential or standard oxidation potential of all metals *on hydrogen scale* in an *increasing or decreasing order* is known as electrochemical series.



Metal combination

$\text{Cu}^{2+} - \text{Zn}^{2+}$

$\text{Pb}^{2+} - \text{Ni}^{2+}$

$\text{Fe}^{2+} - \text{Zn}^{2+}$

$\text{Sn}^{2+} - \text{Fe}^{2+}$

$\text{Ag}^+ - \text{Ti}^{2+}$

$\text{Zn}^{2+} - \text{Al}^{3+}$

Anode

Zn

Ni

Zn

Fe

Ti

Al

Cathode

Cu

Pb

Fe

Sn

Ag

Zn

Magnesium (Mg)

Aluminium (Al)

Zinc (Zn)

Iron (Fe)

Nickel (Ni)

Tin (Sn)

Lead (Pb)

Hydrogen (H)

Copper (Cu)

Silver (Ag)

Gold (Au)

$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$

$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$

$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$

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

$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$

$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$

$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$

$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

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

$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$

$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$

-2.37

-1.66

-0.76

-0.44

-0.25

-0.14

-0.13

0.00

+0.34

+0.80

+1.50

EXAMPLES OF GALVANIC CORROSION

1.



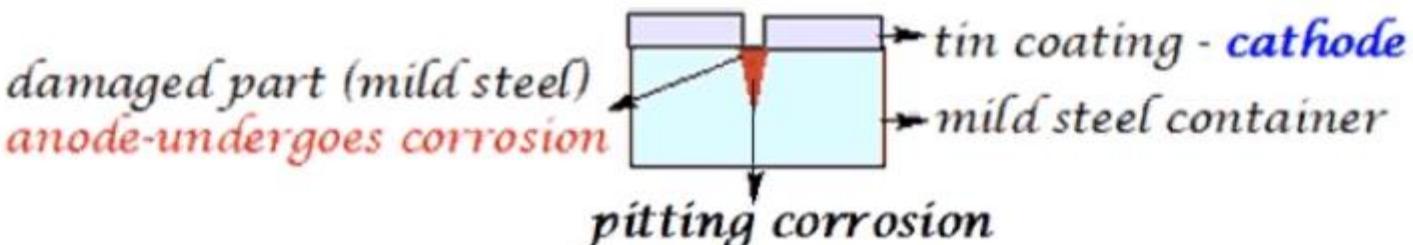
Brass screw (Cu)

Mild steel nut (Fe)

Cathode-protected Anode - undergoes corrosion

2. Mild steel pipe connected to copper plumbing
(anode - undergoes corrosion) (cathode)

- ### **3. Damaged tin coated mild steel container left out in rain**



PREVENTION

- ❖ Avoid contact of two dissimilar metals.
- ❖ For unavoidable situations
 - Anodic area should be larger than the cathodic area.
 - The two metals should be as close as possible in the electrochemical series/galvanic series.
 - An insulator may be fitted between the two metals
 - Anodic area should never be painted.
 - Avoid threaded joints between the metals.

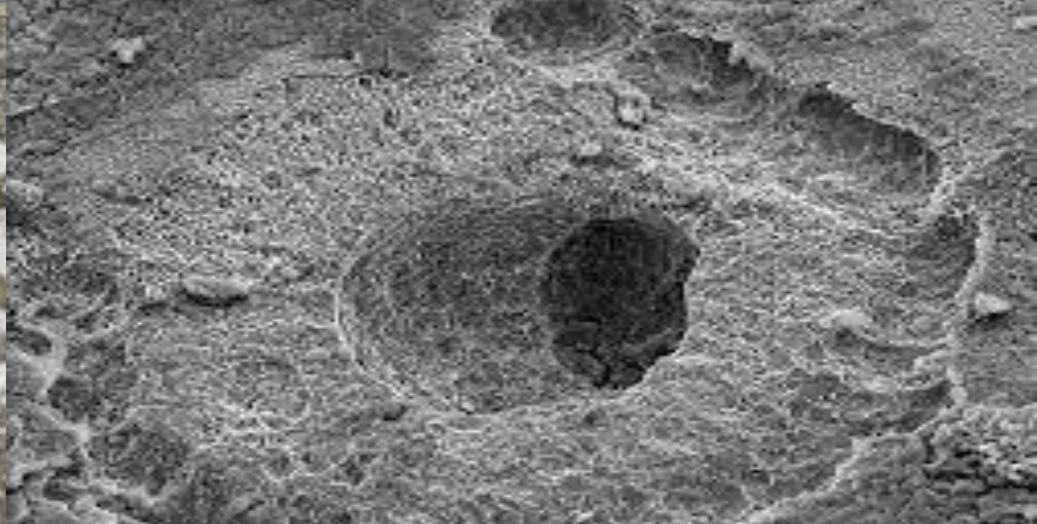
4. Write a note on Pitting corrosion

PITTING CORROSION

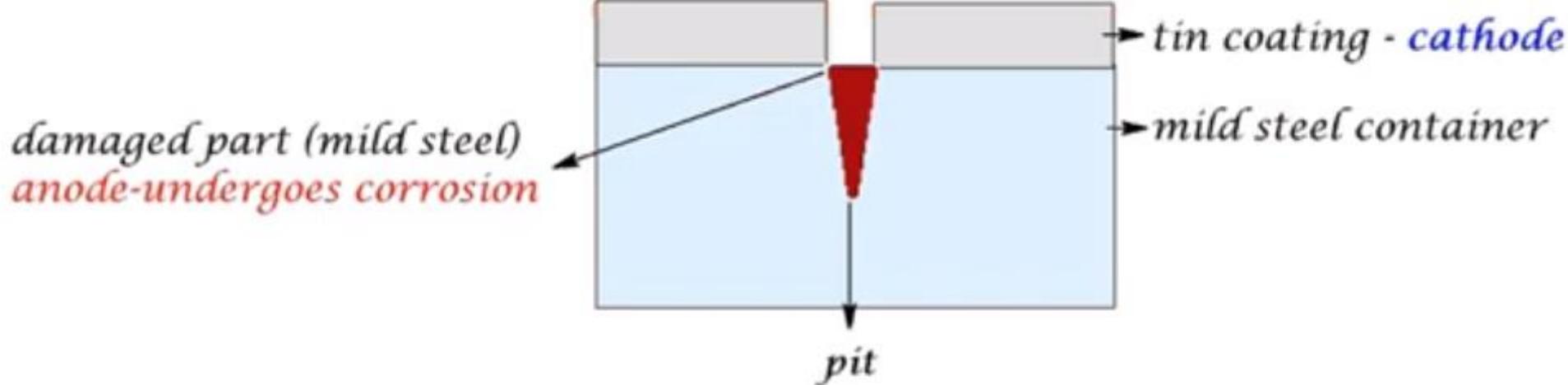
It is a localized and accelerated corrosion resulting in the formation of pits

Pitting corrosion is characterised by small anodic area and large cathodic area resulting in accelerated corrosion in the anodic area.

It is an autocatalytic process, initially formed pit produces conditions that are stimulating.



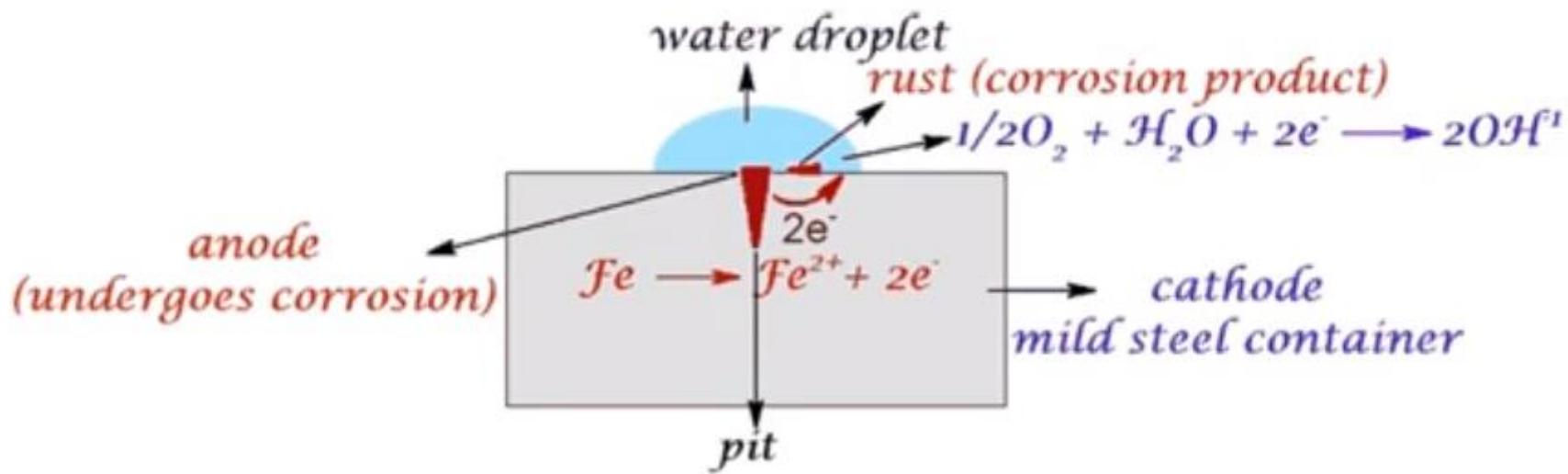
Pitting corrosion/ Galvanic corrosion



Damaged tin coated mild steel container left out in rain

Note: The same effect occurs when the protective metal oxide layer over the metal gets damaged.

Pitting corrosion/ Differential aeration corrosion

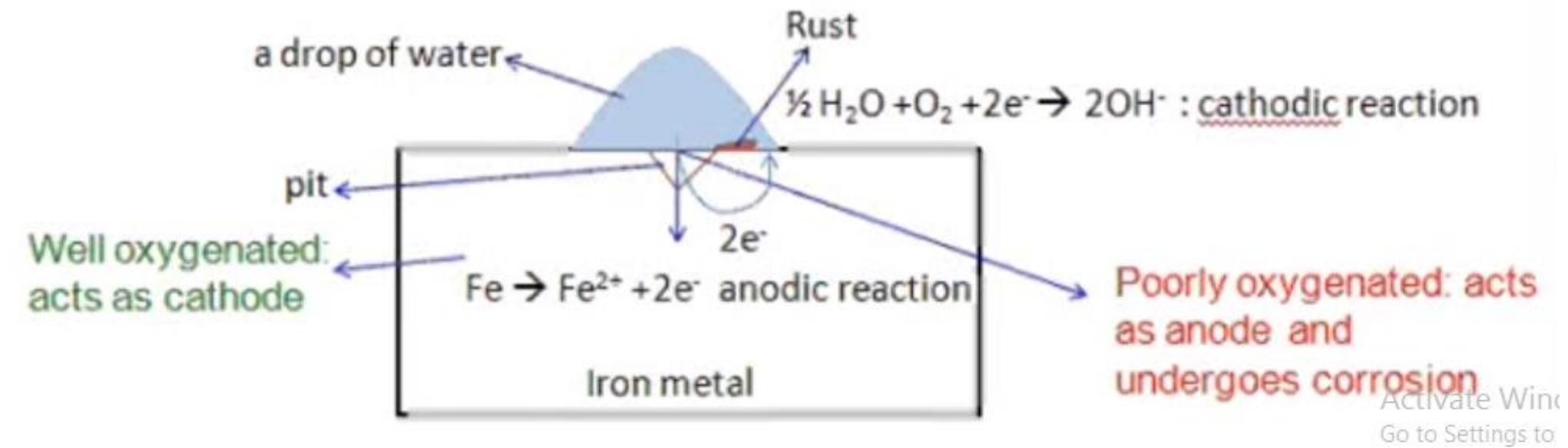


4. Explain the Differential aeration corrosion

- Differential aeration corrosion is a type of corrosion that occurs when oxygen concentrations vary across a metal's surface.
- The varying concentration of oxygen creates an anode and a cathode on the metal's surface.
- The part of the metal exposed to lower oxygen concentration acts as anodic region, higher oxygen concentration as cathodic region.

Differential Aeration Corrosion

Definition: When a part of a metal is exposed to a different aeration condition than the other part of the same metal, the part of the metal which is **poorly oxygenated** acts as an **anode** and **undergoes corrosion**.



Reaction Mechanism



(Yellow rust)



(black rust)

Some of the examples are

- i. Part of the nail inside the wall, being exposed to lower oxygen concentration than the exposed part, undergoes corrosion
- ii. Window rods inside the frame suffers corrosion but not the exposed region
- iii. Paper pins inside the paper gets corroded and exposed part is free of corrosion
- iv. Metal under dirt, dust, scale or water undergoes corrosion
- v. Partially buried pipeline
- vi. Ocean going ship

5. Write a note on the following
Caustic embrittlement

Caustic embrittlement

It is a form of stress corrosion takes place in boilers operating at high temperature and pressure. Caustic embrittlement focus at stressed part of boilers such as cracks, rivets, bents, joints etc.

The boiler fed water usually contains some residual sodium carbonate (used for softening process). At high temperature and pressure it undergoes hydrolysis to form sodium hydroxide.



The alkali water sweeps through the minute cracks, crevices between the rivets and joints by capillary action. Inside the cracks water gets evaporated leaving behind NaOH. The concentrations of the NaOH gradually increase on these sites due to poor circulation of water.



6. Explain the following methods of controlling corrosion?

- i) Electroplating
- ii) metal coating

1. Electroplating

ELECTROPLATING OF COPPER

Anode

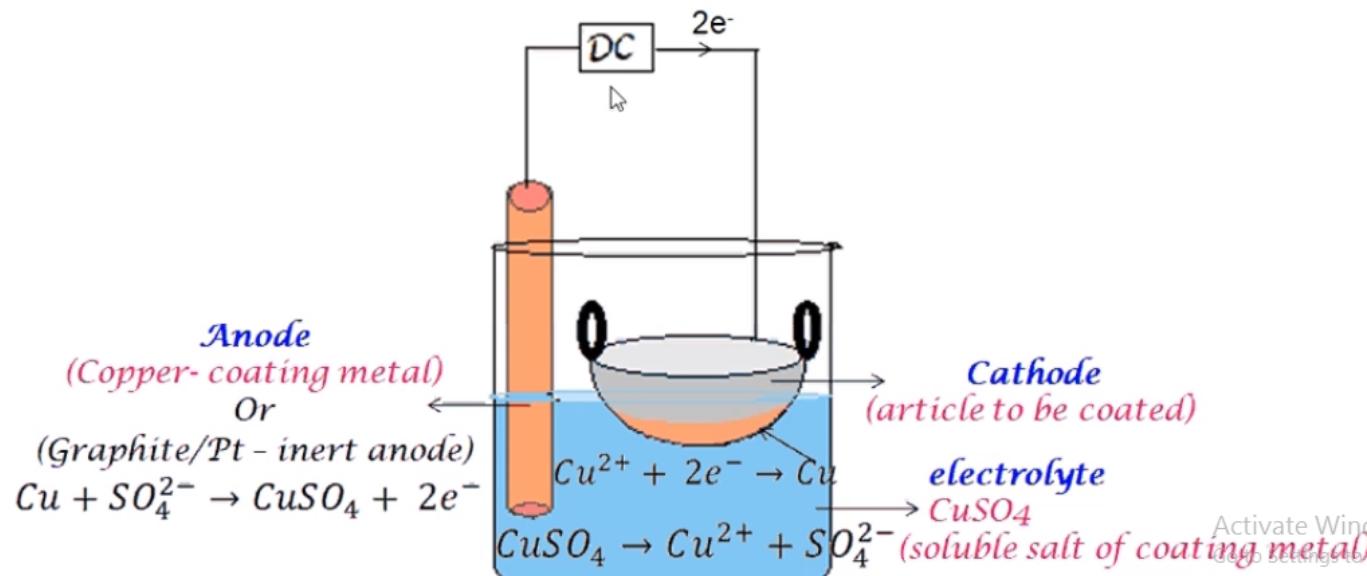
Coating metal (Cu) or inert metal

Cathode

Article to be coated

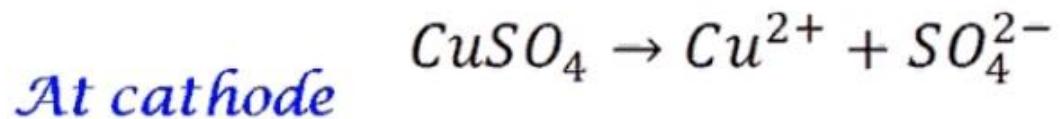
Electrolyte

$CuSO_4$ (solution with soluble salt of coating metal)

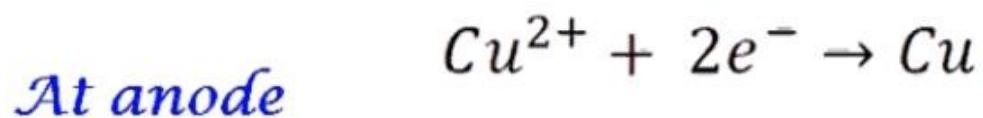


PROCESS (ELECTROPLATING OF COPPER)

When direct current is passed through $CuSO_4$ (electrolyte), it decomposes to its ions

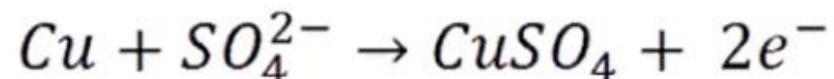


Cu^{2+} ions gets reduced to Cu and gets deposited on the article



Case-I - Anode is the coating metal (Copper)

Copper gets oxidised to form Cu^{2+} ions and reacts with SO_4^{2-}



Case-II - Anode is the inert metal (Pt, Graphite etc.)

Electrolyte has to be added to maintain the concentration of $CuSO_4$.

Metal coatings

2 types

- Anodic coating
- Cathodic coating

1. Anodic Coating

Anodic coatings are produced by coating a base metal with more active metals which are anodic to the base metal.

Example : Iron is coated with anodic and more active metals such as zinc, magnesium and aluminium.



Advantages of Anodic Coating:

Even if the coating is ruptured, the base metal does not undergo corrosion.

The exposed surface of the metal is cathodic with respect to the coating metal and the coating metal preferentially undergoes corrosion.

Galvanisation is an example of anodic coating.

What is Galvanisation???????

Galvanisation is a process of coating a base metal surface with zinc metal

Galvanised steel is not used to store foods??

Zinc dissolves in dil acids to produce toxic zinc compounds

2. Cathodic coating

- Cathodic coatings are produced by coating a base metal with a more noble metal which is cathodic.
- The metals such as copper, nickel, tin, silver are commonly used as cathodic coatings on steel.
- These coating metals are less reactive than the base metal & are less susceptible for corrosion.

Disadvantages of cathodic coating.....

When coating is damaged, an intense localised corrosion occurs due to setting up of a galvanic cell that consists of large cathodic area & a small anodic area.

Tinning is an example

What is tinning????

Coating a base metal with tin.

Tinning involves following steps

- 1.The sheet is first washed with organic solvents to remove rust and scale deposits
- 2.Then treated with dilute sulphuric acid to remove rust and scale deposits. Finally washed with water and air dried.
- 3.The clean & dry sheet is passed through molten stannous chloride flux. The flux helps molten metal to adhere on the metal surface
- 4.It is then passed through a tank that contains molten tin.
- 5.Finally passed through a series of rollers immersed in palm oil. The oil prevents the oxidation of tin coated surface.

12 Account for the following

- i. Zinc in contact with silver undergoes corrosion faster than zinc in contact with copper-**Galvanic series**
- ii. Though aluminium is with lower electrode potential than iron, it has higher corrosion resistance than iron in oxidizing environments-**Passivity**
- iii. Iron bolt in copper vessel are undesirable- **Ratio becomes small**
- iv. Ruptured tin coating on iron is more disastrous than not having the coating at all- **Ratio becomes small**
- v. Even if zinc coating on iron is discontinuous, iron is free from corrosion- **Ratio becomes Large**
- vi. Part of nail inside the frame undergoes corrosion but the exposed part does not-**Differential aeration corrosion**
- vii. Ocean going ships undergo differential aeration corrosion but ships sunk under sea do not- **water line corrosion**
- viii. Metal under water drop undergo accelerated corrosion- **presence of Chlorine**
- ix. Anodic coatings are sacrificial coatings
- x. Use of insufficient quantity of anodic inhibitors is more disastrous than not using at all.-**Ratio effect**