

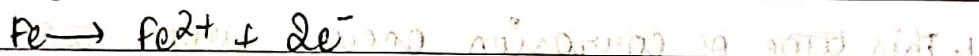
X:X Define corrosion. Explain the electrochemical theory of corrosion taking iron as example. (9 marks) → I

Test → (7 marks)

1. The process of destruction or degradation or loss of metal on its surface through a chemical or electrochemical attack by the environment in a conducting medium is called as corrosion.

2. In electrochemical theory of corrosion there is a formation of galvanic cell on the surface of metal when it is connected to different metal or when it is exposed to different oxygen concentration.

3. Taking iron as an example the anode reaction is:

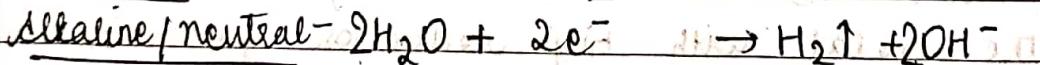
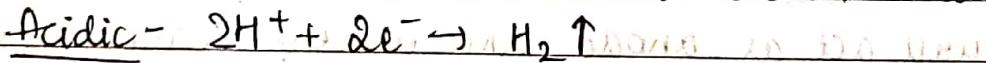


Cathode reaction: depends on the nature of the environment

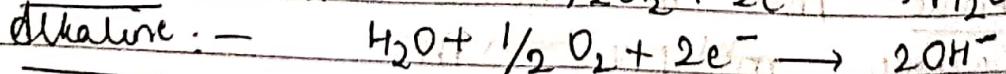
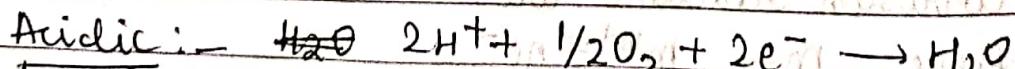


① Liberation of hydrogen in the absence of oxygen.

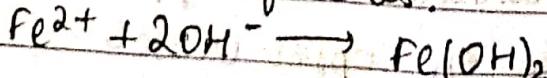
The cathodic reaction in acidic and alkaline medium are:



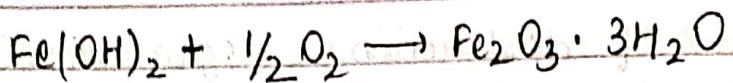
② Absorption of oxygen: (in the presence)



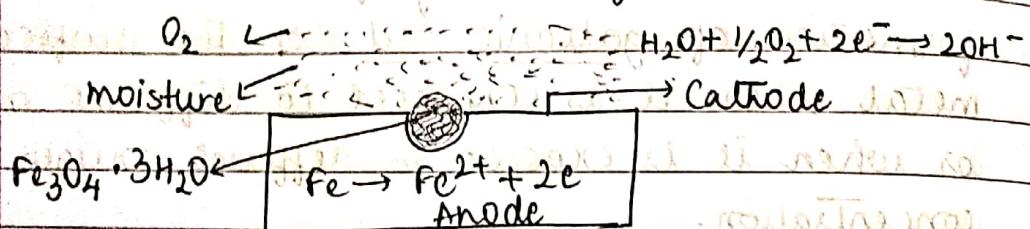
4. The product from the anode and cathode reaction on the metal surface is.



5. The first layer of the rust formed on the metal surface when exposed to less oxygen hydrated ferric oxide is formed.



6. High oxygen concentration  $\text{Fe(OH)}_2 + \text{H}_2\text{O} + \text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 \cdot 3\text{H}_2\text{O}$  magnetite (Black rust).

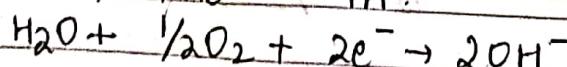
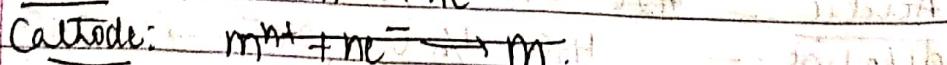
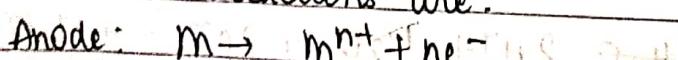


Write a note on differential metal corrosion: [6marks]

1. This type of corrosion occurs when two different metals comes in contact with each other in a conducting medium.

2. The metal with low reduction potential value will act as anode and undergo corrosion whereas the metal with high reduction potential value is free from corrosion or will not undergo.

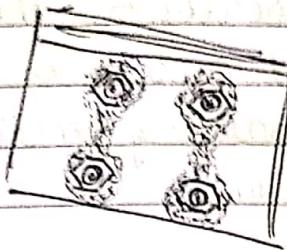
3. Corrosion reactions are:



Ex: Steel pipe connected to copper

Tin coating on copper vessel

Zinc coating on mild steel



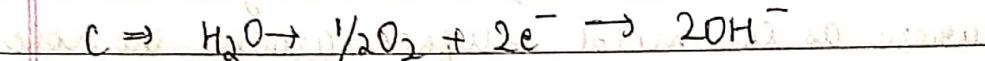
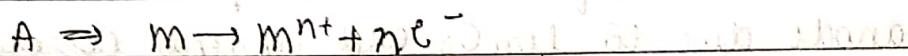
## Rust -

Write a note on differential aeration corrosion.

In this type of corrosion metal surface is exposed to different oxygen concentration in the conducting medium is called as differential aeration corrosion.

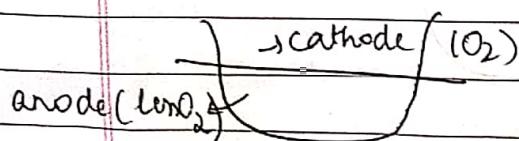
The metal surface exposed to less oxygen concentration will act as anode and undergo corrosion whereas the metal surface exposed to more oxygen concentration are free from corrosion which acts as cathode.

### Corrosion reactions:



Ex: Ocean going ship

Partially water filled boiler.

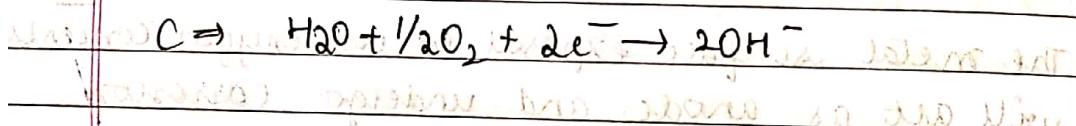
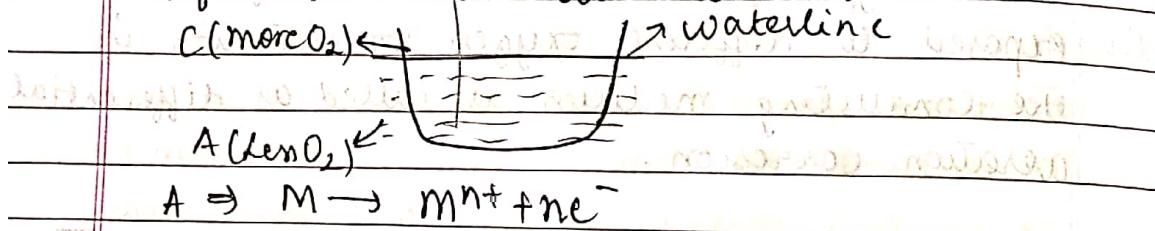


Write a note on waterline corrosion:

- It is a type of differential aeration corrosion.

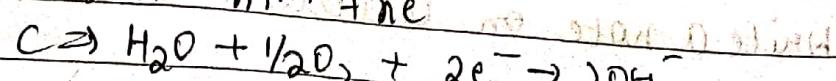
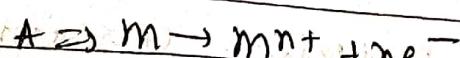
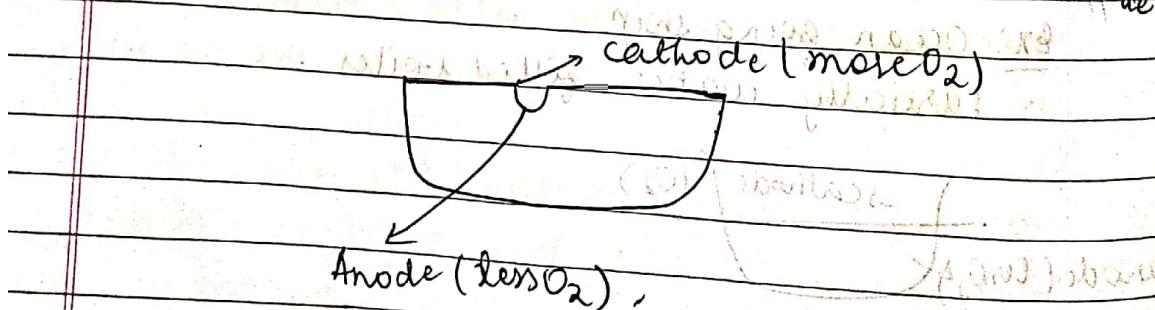
2. In this type of differential corrosion - the metal is in contact with water and exposed to different oxygen concentration in conducting medium is called as waterline corrosion.

3. The metal surface below the water line is exposed to less oxygen concentration act as anode and undergoes corrosion whereas the metal surface above the waterline will act as cathode.



It is a type of corrosion where the formation of pit due to the deposition of dust, water droplet etc and metal surface is exposed to different oxygen concentration is called pitting corrosion.

The metal surface below the pit will act as anode due to less  $O_2$  and undergo corrosion whereas the metal surface around the hole is exposed to more  $[O_2]$  and act as cathode.



Ex: Ocean going ship

Explain the factors affecting the nature of corrosion.

1. Nature of metal - The metal with low reduction potential value i.e. rate of corrosion will be more.

High reduction potential value i.e. rate of corrosion will be less.

Ex: Zinc, magnesium, iron etc. [LRPV].

Al, Tin, Silver [HRPV]

2. Nature of Corrosion product - (Non porous)

Corrosion product itself act as a protective layer to prevent the corrosion of the further metal if it is non porous, insoluble, stable and uniform.

Ex: Oxides of Al, Tin, silver etc.

If the corrosion product is porous, soluble and non-uniform and unstable it will not act as a protective layer and allows the corrosion of the further metal.

Ex: Oxides of iron, magnesium etc.

3. Ratio of anodic to cathodic area:

(1) Smaller the anodic area, larger the cathodic area the rate of corrosion is more. Since, liberation of electrons is continuously accepted by cathodic area resulting in the formation of rust.

Ex: Broken coating of tin on steel.

(2) Larger the anodic area and smaller the cathodic area, the rate of corrosion is less.

Ex: 1. broken coating of zinc on steel.

4. Nature of the medium: Higher the temperature,

higher is the conductivity of the medium,

higher is the diffusion rate where liberation of hydrogen takes place and the rate of corrosion is higher.

As the temperature decreases, conductivity of the medium decreases, diffusion rate decreases and the rate of corrosion will be less.

5. pH: pH decides the nature of cathodic reaction.

Lower the pH, the rate of corrosion is high leading to the liberation of hydrogen.

Higher the pH the rate of corrosion is low leading to the liberation of

6. Conductivity of the medium:

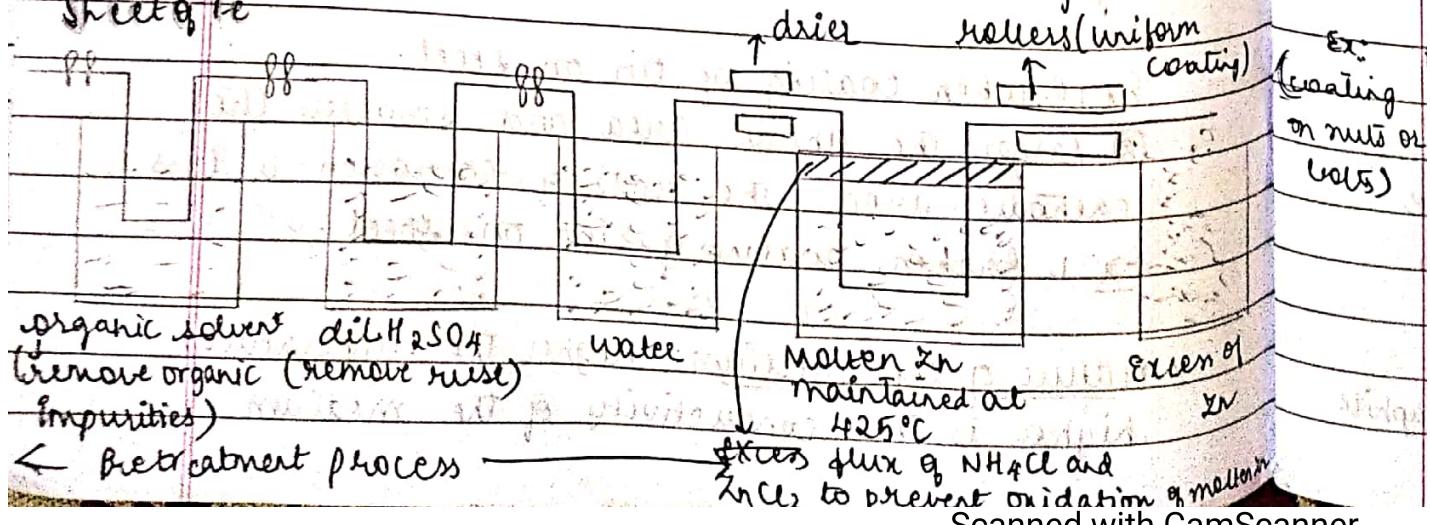
Higher the conductivity of the medium, higher is the movement of ions between anodic and cathodic area, higher is the diffusion rate and higher will be the rate of corrosion.

Low the conductivity medium, lower is the corrosion rate. Ex: metal corrode faster in soil than in clay.

Corrosion control:

i) Define metal coating and explain the galvanizing process with the neat diagram.

Sheet of Fe



metal coating: The process of coating a protective metal over a base metal where protective metal can be anodic or cathodic to the base metal to prevent the corrosion of the base metal.

Ex: Galvanizing

Definition of Galvanizing:

The process of coating a zinc over the base metal to prevent the corrosion of the base metal where zinc is anode to the base metal.

Hot dipping process: (Refer diagram under corrosion control)

The sheet of iron is first dipped in organic solvent to remove organic impurities and then it is dipped into dil  $H_2SO_4$  to remove dust and then dipped in water and dried.

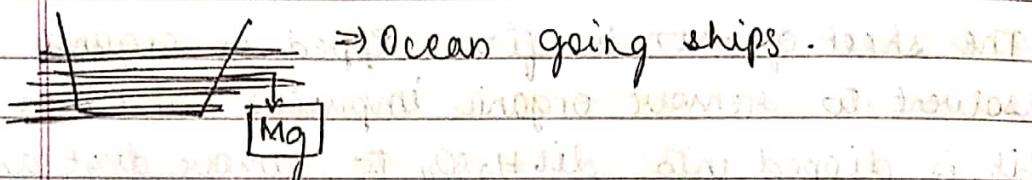
Then the dried iron sheet is dipped in molten Zn maintained at temp  $425^\circ C$  which is closed by flux of ammonium chloride and zinc chloride in order to prevent the oxidation of zinc.

Define cathodic protection? Explain the process with diagram. [sacrificial anode and impressed current technique].

In this method, the base metal is prevented from corrosion by converting the base metal into cathode and no part of the base metal should act as anode. It is called as cathodic protection.

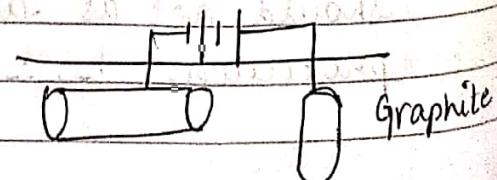
## 1. Sacrificial anode technique:

- It is one of the techniques of cathodic protection.
- In this technique the more active metal which acts as anode is connected to the base metal where it sacrifices its life to prevent the corrosion of the base metal and whole surface of the base metal act as cathode.
- Ex: Ocean going ships connected to magnesium rod.
- Simple and low cost method. but once the magnesium is corroded completely, it has to be replaced.



## 2. Impressed Current technique:

- It is one of the techniques of cathodic protection.
- In this technique the base metal is connected to the external source where negative terminal of the external source is connected to base metal and positive terminal is connected to graphite where the base metal will act as cathode.
- Buried oil pipelines are connected to the external source to prevent the corrosion of the base metal.
- One installation can prevent larger surface area of the base metal [but maintain uniform current flow].



Explain anodizing of aluminium and define anodizing.

Anodizing is a process of converting the metal into its own oxides which prevent the corrosion of the metal itself by passing current.

In anodizing of aluminium, the aluminium is made anode and inert metal as cathode.

Electrolytic solution:

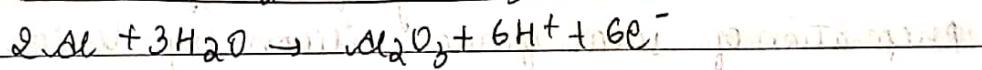
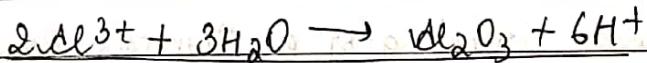
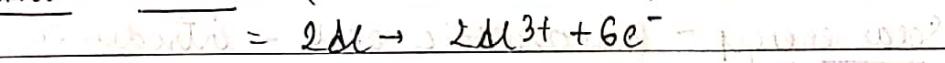
Temperature is 30 to 40°C

pH = 3-4 (min) (max) 8-10 (for aluminium)

current density = 10 to 20 mA per cm<sup>2</sup>

Reaction:

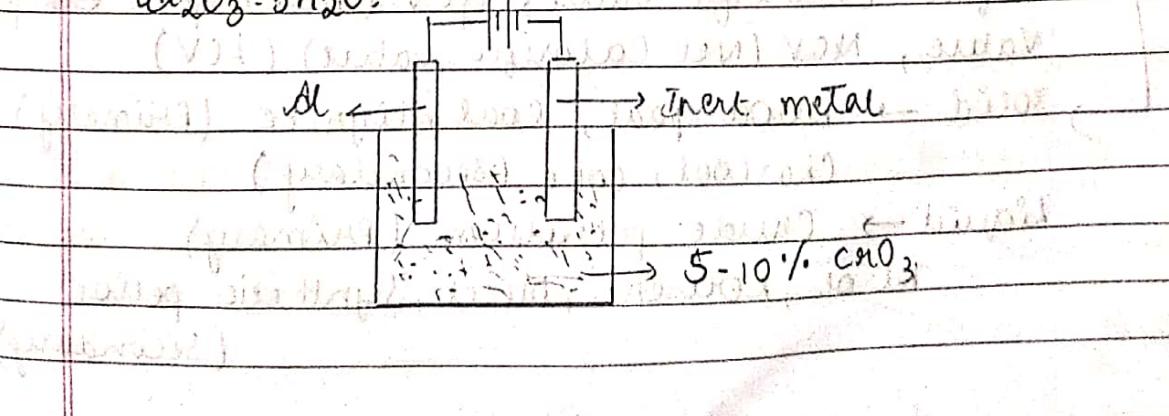
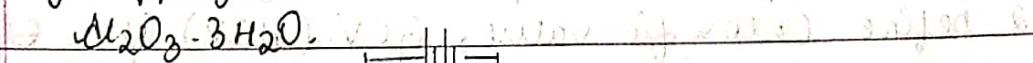
Anode reaction:  $(Al \rightarrow Al^{3+} + 3e^-) \times 2$



Cathode reaction:  $6H^+ + 6e^- \rightarrow 3H_2$

Net cell reaction:  $2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$

$Al_2O_3$  is always porous in nature, we can fill the dice. You can fill the dice and seal the pore by dipping in hot water. Product formed is



## Electroplating of Chromium

Cr Plating	Decorative Cr Plating	Hard Cr.
Anode	Insoluble anode like, $Pb - 6\% Sb, Pb - 7\% Sn$ Coated with $PbO_2$	Insoluble anode like, $Pb - 6\% Sb, Pb - 7\% Sn$ Coated with $PbO_2$
Cathode	Object to be plated	Object to be plated
Bath composition	250g chromic acid + 2.5g $H_2SO_4$	250g chromic acid + 2.5g $H_2SO_4$
current density	100 - 200mA/cm <sup>2</sup>	215 - 430mA/cm <sup>2</sup>
Temperature	415 - 55°C	45 - 66°C
pH	3 - 4	3 - 4
Applications	Provides durable and good decorative finish on automobile and surgical instruments etc.	Used in industries in electric motors and generators.

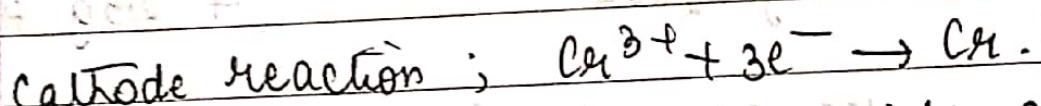
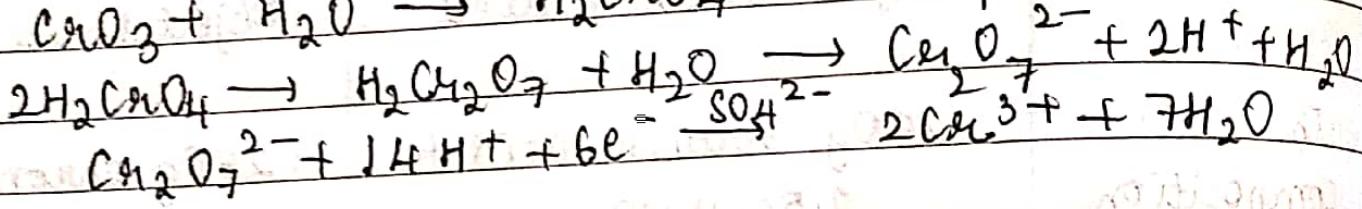
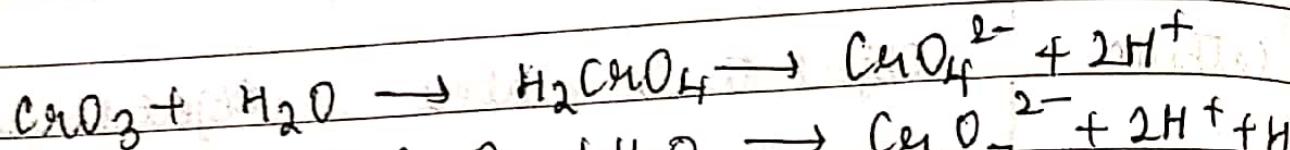
In the case of chromium plating inert anodes are used:

Reason:

1. The metal going into the solution is five times of the metal getting deposited, resulting in the building up of excessive chromic acid (Cr(III)) concentration.

2. This leads to imbalance of bath composition and black deposit is formed on the cathode.

3. In the plating bath sulphate ion from sulphuric acid act as catalyst. Cr is in hexavalent state as chromic acid in bath solution. In the presence of sulphate Cr(VI) is converted to Cr(III) by complex Anodic reaction.



$\text{PbO}_2$  is coated on anode to - oxide Cr(III) to Cr(VI) and thus controls concentration of Cr(III) ions and thus controls concentration of Cr(III) ions because large excess of Cr(III); a black deposit is obtained.

## Metal Finishing:

Factors governing electroplating process.

1. Polarization
2. Decomposition Potential
3. Over Voltage

### Polarization:

The process where there is variation of electrode potential takes place due to inadequate supply of metal ions from bulk of the solution to electrode surface is called polarization.

It is also called conc. polarization because depletion of concentration of ions near the electrode is not compensated by diffusion of ions from bulk of solution therefore a cell requires excess voltage over theoretical voltage for process of electrolysis which can be minimised by stirring the solution.

Polarisation depends on:

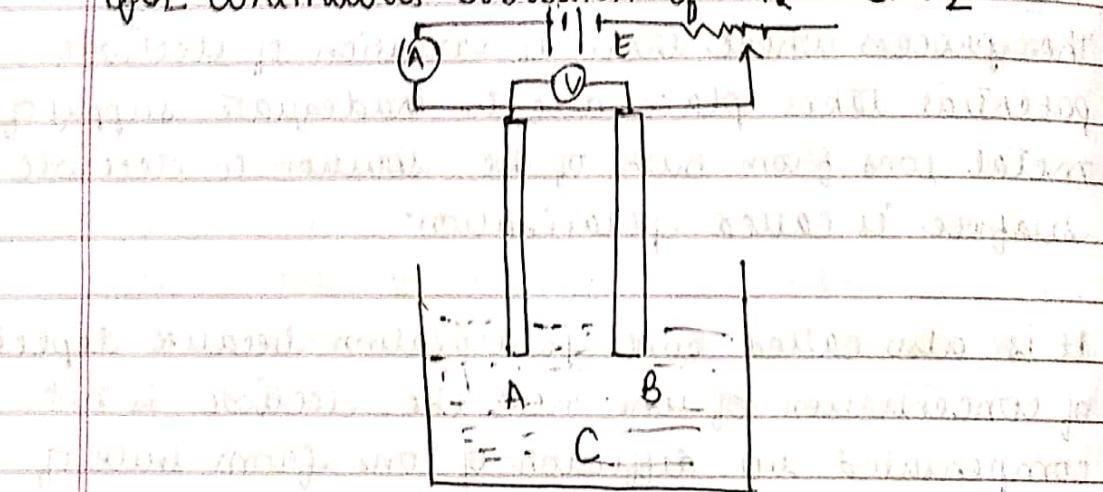
1. Nature of electrode
  2. Temperature
  3. Rate of stirring
- A. Electrolytic solution and its conductivity.

### Decomposition Potential ( $E_0$ ):

1. The minimum voltage or potential required for the continuous electrolysis of an electrolyte in an electrolytic cell.

2. For example  $E_0$  of  $\text{K}^+$  =  $-0.76\text{ V}$   
 $E_0$  of  $\text{Cu}^+$  =  $+0.34\text{ V}$ .

3. First  $E_0$  was determined for  $\text{H}_2\text{O}$ . In the electrolysis of water, a pair of Pt electrode is immersed in a solution of an acid or base with water. It is found experimentally that a potential of about  $1.7\text{ V}$  must be applied to cell for continuous evolution of  $\text{H}_2$  and  $\text{O}_2$ .



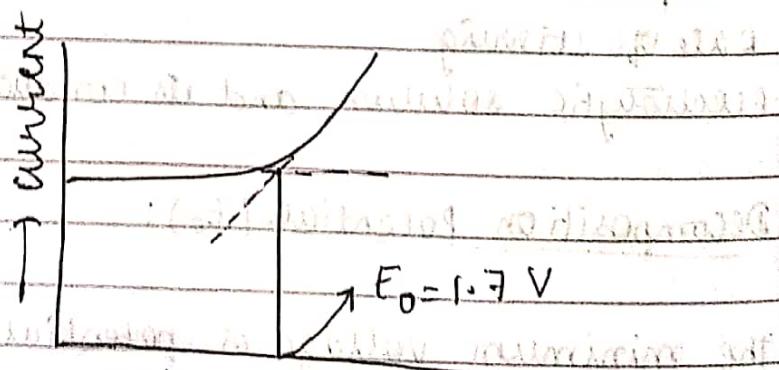
A and B = platinum electrodes

C = electrolytic solution

A = Ammeter

E = Battery

V = Voltmeter



4. From the above graph, it is clearly seen that by keeping current constant, in beginning

There is no vary in current but at 1.7V there is abrupt increase in current where evolution of gases take place, but theoretically it was told that evolution of gas takes place at 1.23V.

5. If a solution (electrolytic) solution contain mixture of ion the one with high reduction potential value gets discharged first -

### Over voltage:

1. Over voltage is the difference between the actual applied emf to bring about continuous electrolysis and the theoretical emf needed for such electrolysis.
2. For instance the reversible potential of oxygen gas with smooth Pt electrode is 1.23V. But actual gas evolution takes place at a potential of 1.7V. The excess 0.43V is the over voltage of oxygen on smooth Pt surface.

### factors Affecting Over Voltage:

1. Electrode surface.

2. Nature of the electrolyte.

3. Temperature.

4. Current density.

## Electroless plating:

It is a method of depositing a noble metal or alloy over a catalytic active surface of a substrate (conductor or non-conductor) by controlled chemical reduction of the metal ions by a suitable reducing agent without using electrical energy.

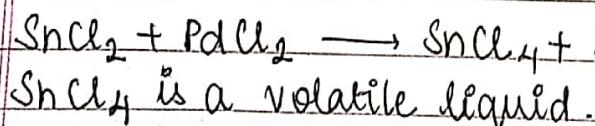
It is also termed as autocatalytic plating.

The surface to be plated be catalytically active. The catalytic metals like Ni, Co, Steel, Pd, etc., do not require any surface preparation. Non-catalytic like such as Cu, brass, Ag etc need activation.

This can be done by dipping in palladium chloride and  $\text{SnCl}_2$  solution.

Non conductors like glass, plastics, etc, are first activated in a solution of  $\text{SnCl}_2$  and  $\text{PdCl}_2$  solution.

This treatment yields a thin layer of Pd on the treated surface.



### Advantages of electroless plating:

1. NO electrical energy is required.

2. Better throwing power.
3. Plating on articles made of insulators and semiconductors.
4. Electroless plated coatings possesses unique mechanical, chemical properties.

### 1. Electroplating (plating)

1. Electrical power is needed.

2. Less throwing power

3. Driving force is electrolysis by electricity.

4. Reduction is brought by electrons

5. Applicable only to conductors.

6. The coating is less harder.

### 2. Electroless plating

No electrical is needed.

Better throwing power

Driving force is autocatalytic redox reaction over active surface and reducing agent.

Reduction is brought by reducing agent on a catalytic active surface

Applicable to conductors and semiconductors and non conductors.

The coating is more harder.

## Electroless plating of Cu:

Composition of bath solution:

Coating solution -  $\text{CuSO}_4$  solution (12 g/l)

Reducing agent -  $\text{HCHO}$  (8 g/l)

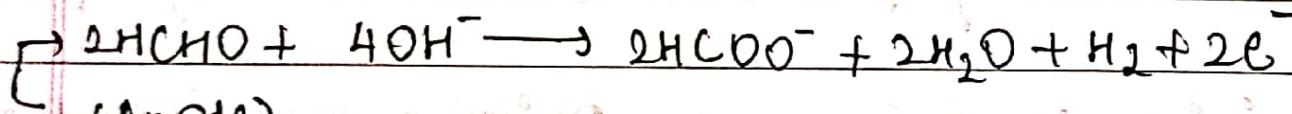
Buffer -  $\text{NaOH}$  (16 g/l)

Complexing agent - EDTA di sodium salt (20 g/l)

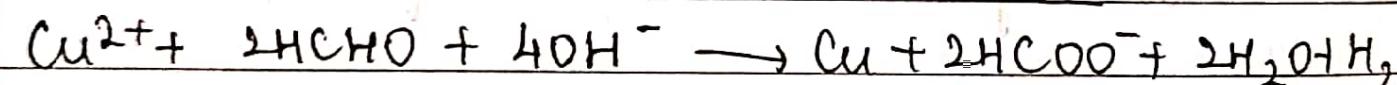
Optimum pH - 11

Optimum temperature -  $25^\circ\text{C}$

### Reactions:



(Anode)



### Applications of electroless plating of Cu:

1. Used for metalising printed circuit boards
2. It is used on instrumentation and industrial components.
3. For plating on non conductors.

## Electroless plating of Ni:

Composition of bath

		Acid	Alkaline -
reducing agent	sodium hypophosphite	20g/dm <sup>3</sup>	10g/dm <sup>3</sup>
Cathode	Object to be plated.		
Electrolytic or coating solution	NiCl <sub>2</sub> / NiSO <sub>4</sub>	20g/dm <sup>3</sup>	30g/dm <sup>3</sup>
Competing agents and brightness	EDTA (25g/dm <sup>3</sup> )		
Temperature	93°C		90°C
pH/buffer	4-5/ carboxylic acid (15g/dm <sup>3</sup> )		8-10/ ammonium chloride (5g/dm <sup>3</sup> )
Applications	Used on instruments and computers in view of its magnetic properties. Coat on steel PCB, Used on industrial components such as pumps, valves, pistons etc.		

## Electroless plating of Ni:

