

Corrosion

The destruction of a metal by chemical or electrochemical reaction with its environment is called corrosion.

e.g:- Rusting of iron, Tarnishing of silver, Green deposition on copper

Consequences of Corrosion

- Enormous wastage of machine and machinery parts.
- Machinery failure (leads to a dangerous situation)
Accidental
- Contamination of drinking water due to corrosion
- Corrosion causes leakage of inflammable gases from conoidal pipelines.
- Metals and alloy due to corrosion lose their strength, ductility and lustre.
- Economic loss to the country-(roughly estimated so that \$300 Bn per annum loss due to corrosion in the form of wastage iron and coins)

Types of corrosion

→
Dry corrosion
Direct chemical
corrosion

(i) Dry corrosion occurs due to a direct chemical attack of gases like O_2 ,

→
wet corrosion

electrochemical

or
Immersed corrosion,

(i) Electrochemical corrosion takes place in an aq.

~~H₂, N₂, SO₂, H₂S, Cl₂ etc.~~ medium and is electrochemical in nature.
on the metal surfaces
but in absence of
moisture.

Day Chemical corrosion

Oxidation
corrosion

Corrosion
by other gases

Liquid
metal corrosion

Wet corrosion

H₂ Evolution
mechanism
(or)

Delocalized
corrosion mechanism

O₂ Absorption
mechanism
(localized mechanism)

oxidation corrosion:- This type of corrosion occurs by the direct chemical attack of oxygen on the metal surface at low or high Temp.

e.g:- All alkali and alkaline earth metals all are attacked by corrosion.

Corrosion by other gases:- This type of corrosion occurs by the direct attack of gases like SO₂, CO₂, Cl₂, H₂S, F₂ etc. on the metal surface.

The extent of corrosion will depend upon the chemical affinity of the metal and the gas involved.

e.g.: Hydrogen sulphide gas attacks on steel forming FeS .

Liquid metal! In this type of metal corrosion there is an effect of flowing liquid on the solid metal surface

e.g.: Liq. sodium which is used in Nuclear reactors as heat transfer media causes corrosion of metal carrier tubes.

Factors Affecting Rate of corrosion :-

1) Position of a metal in a galvanic series :-

- metal placed higher in galvanic series more easily it will be corroded.
- Two metals should be chosen such that they should be very near to relative to each other

2) Purity of metal :-

The rate of corrosion increases with increase in Impurities, because due to the difference in purity (Heterogeneity) an electrochemical cells are formed and the anodic part gets corroded.

3) Temperature :-

Higher the Temp. Higher will be the electrochemical rxn, Hence higher will be the Rate of corrosion.

4) Nature of oxide film :-

The rate of corrosion depends upon the protective and Non protective nature of oxide layer.

If oxide layer is protective \rightarrow lower rate of corrosion.

If oxide layer is Non protective \rightarrow Higher rate of corrosion.

5) Humidity :-

Corrosion increases with Humidity.

6) Presence of Impurities in the surrounding environment :-

More polluted is the air higher is the rate of corrosion.

7) Effect of PH:-

Lower is the pH higher will be the rate of corrosion.

Pilling Bedworth Rule:-

According to this rule the oxide layer formed on a metal surface can be protective or Non-protective, depends upon the ratio of Vol. of oxide layer formed to the vol. of metal consumed.

$$\text{Pilling Bedworth Ratio} = \frac{\text{Vol. of metal oxide layer formed}}{\text{Vol. of metal consumed.}}$$

There are 2 cond^{ns}. Acc. to this piling Ratio:-

- If the vol. of metal oxide layer formed is less than the vol. of metal consumed i.e. if the piling Bedworth Ratio is less than (1) then the oxide layer will be Non protective or porous in nature.
- If the vol. of oxide layer formed is either equal or greater than the vol. of metal consumed i.e. If the piling ratio is greater than unity (1). Then the oxide layer will be protective or Non porous in nature.

Different types of metal oxide layers:-

1) Stable oxide film or Layer:-

A stable oxide layer is fine grain and adheres tightly to the metal surface, preventing any entry of further oxygen to the metal.

e.g:- oxide film on Al, Cr, Cu, Pb, Sr, Sn

2) Unstable oxide film or layer

If the oxide film formed on the metal surface decomposes back to metal and oxygen
(metal oxide \rightleftharpoons metal + oxygen)

e.g:- oxide layer on Au, Ag, Pt

3) Volatile oxide layer or film:-

If the metal oxide layer volatilizes or evaporates from the metal surface as soon as it is formed.

e.g:- oxide layer on Mo \rightarrow MoO_3

4) Porous layer:-

If the oxide layer formed develops cracks or pores through which diffusion of oxygen takes place.

e.g:- oxide layer on Alkali and Alkaline earth metals.

Mechanism of Electrochemical or wet corrosion

This type of metal corrosion mechanism takes place in aq. medium and is electrochemical in Nature.

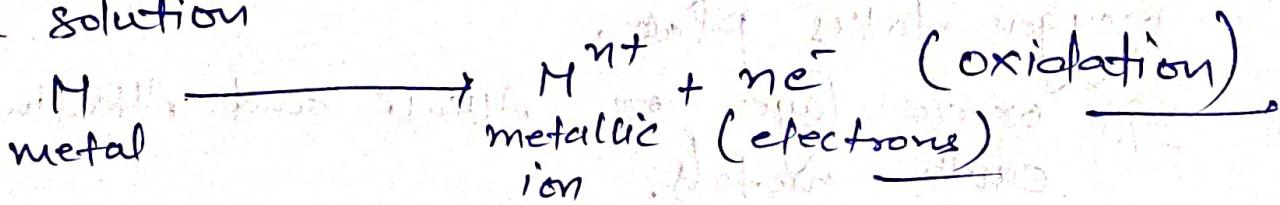
It generally takes place under following conditions:-

- i) The metal should be in contact with either moist layer or any liq. medium.
- ii) There must be a Cathode and Anode.
- iii) There must be an electrode potential develop b/w an ad anode and cathode.
- iv) The anode and cathode must be emerged in any electrical conducting medium.
- v) A metallic pathway should be formed b/w the anode and cathode.

If following above conditions are satisfied then corrosion will takes place by this mechanism and is mentioned below.

i) Anodic reaction:

At anode oxidation rxn takes place the metal loses the e^- and changes to metallic ions and these e^- passes into the solution



ii) Cathodic Rxn:-

Depending upon the nature of corrosive medium and the presence and absence of oxygen cathodic reaction can be divided into 2 types:-

a) Hydrogen evolution Rxn.

b) Oxygen Absorption Rxn.

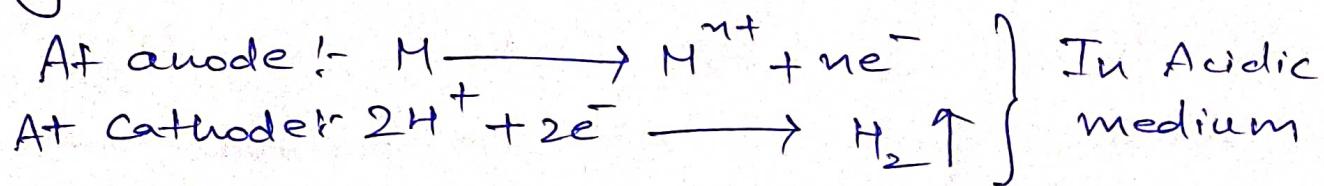
(a) Hydrogen evolution corrosion Mechanism:-

Delocalized corrosion mechanism:-

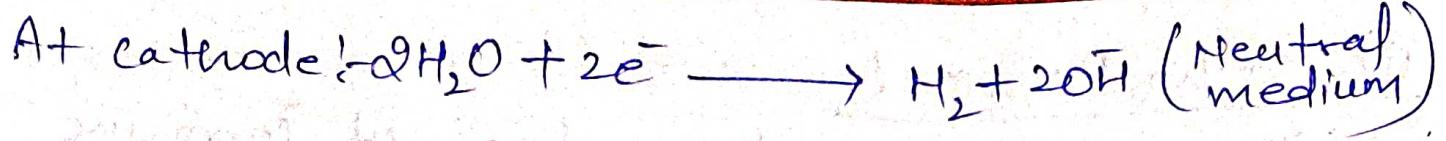
→ (Anodic area should be Large)

In absence of O_2 and in Acidic medium evolution of H_2 takes place in the corrosion mechanism.

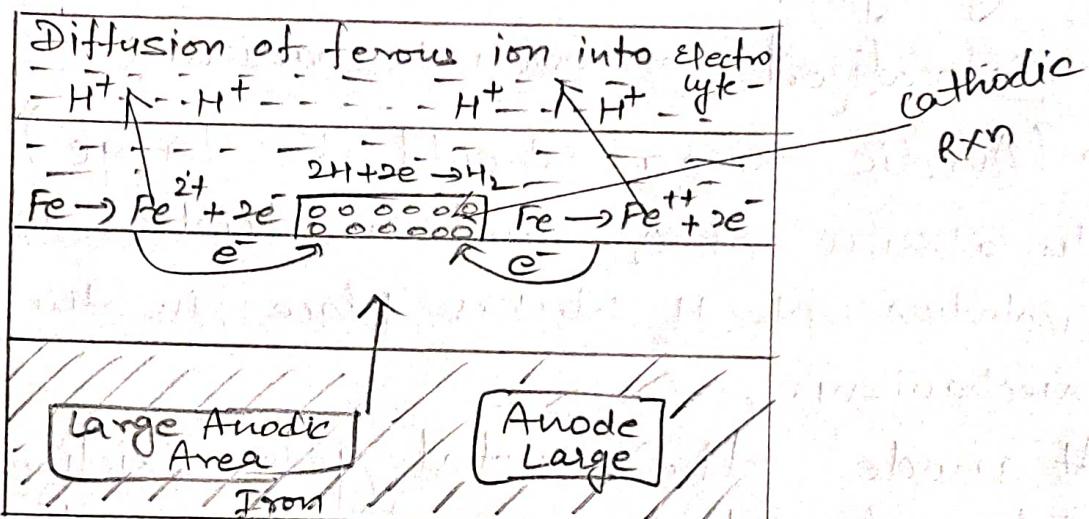
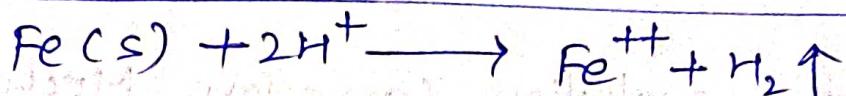
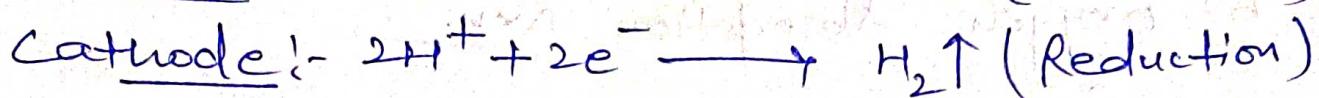
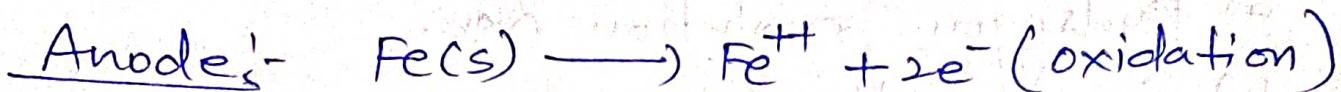
- At anode the metal gets oxidized and the e^- 's released passes to the electrolyte
- The Hydrogen ion (H^+) of the acidic take these e^- release from the anode and H_2 gas is formed.



- In Alkaline or neutral medium and in absence of O_2 the cathodic rxn will take place as follows:-



The whole mechanism can be explained by taking an example of rusting of iron in acidic medium and in absence of O_2



mechanism of H_2 evolution

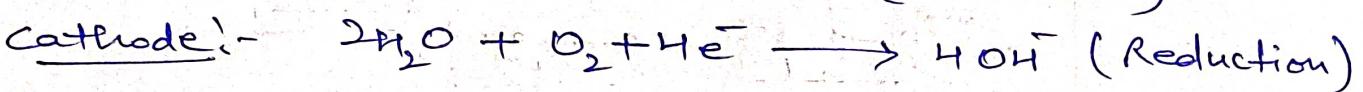
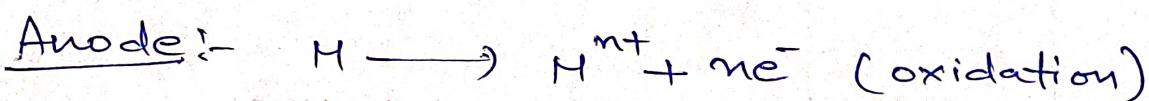
Mechanism

② Oxygen Absorption Corrosion Mechanism :-

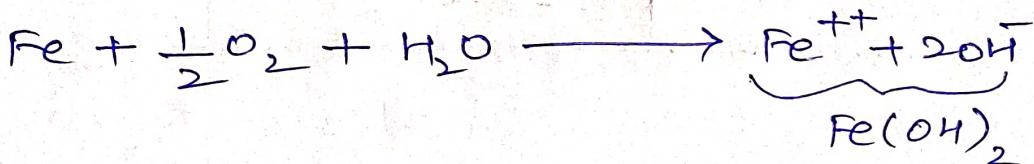
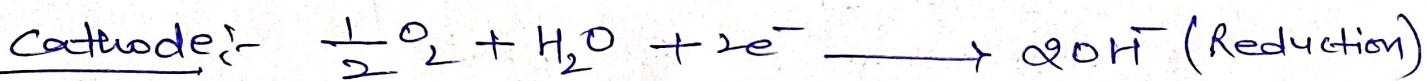
(Anodic Area Small)

This type of corrosion mechanism takes place in presence of atmospheric oxygen and aq. medium. In Neutral or alkaline med.

- Containing O_2 following Rxns will take place
- At anode the metal gets oxidized and the e^- released into the sol^m. These e^- are being taken by the O_2 present at the cathode which reduces to form OH^- ions.

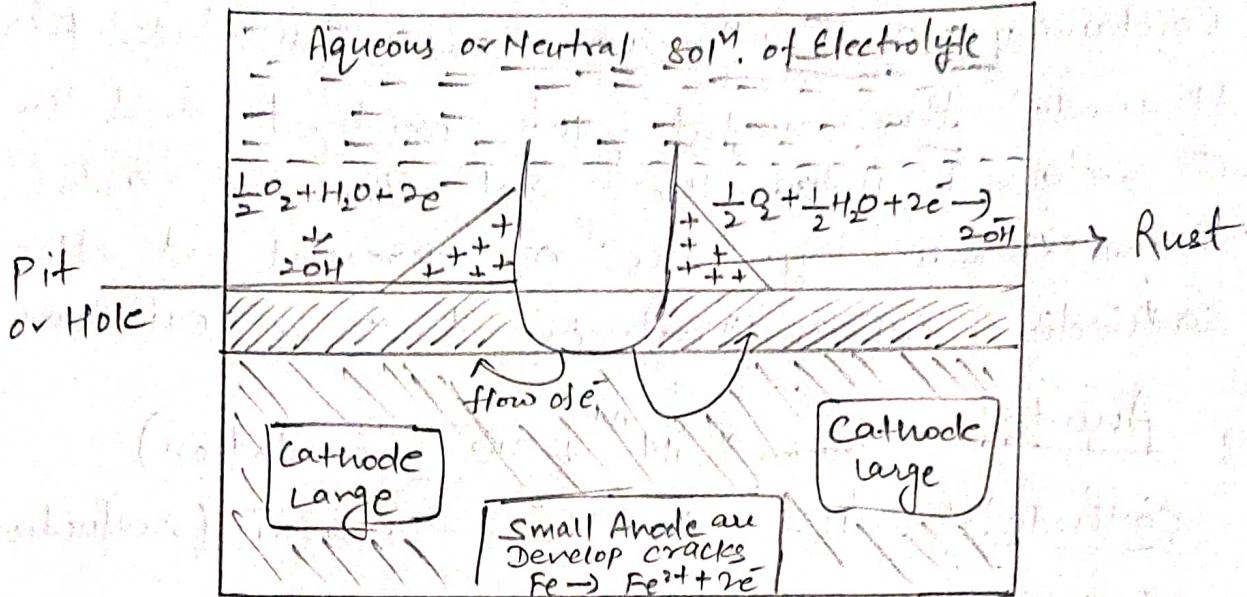
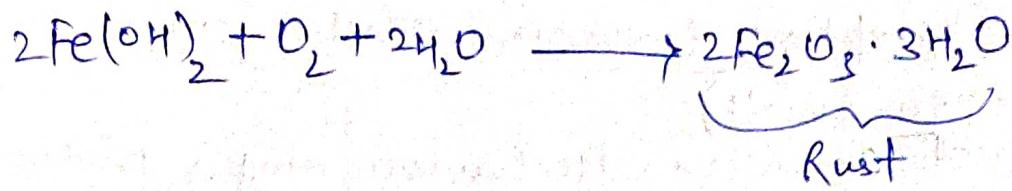


The complete mechanism can be explain by taking an example of Rusting of iron in Neutral aq. sol^m and in presence of O_2 .



The Fe^{2+} ion produced at the Anode and OH^- ion formed at the cathode combines together to form $Fe(OH)_2$

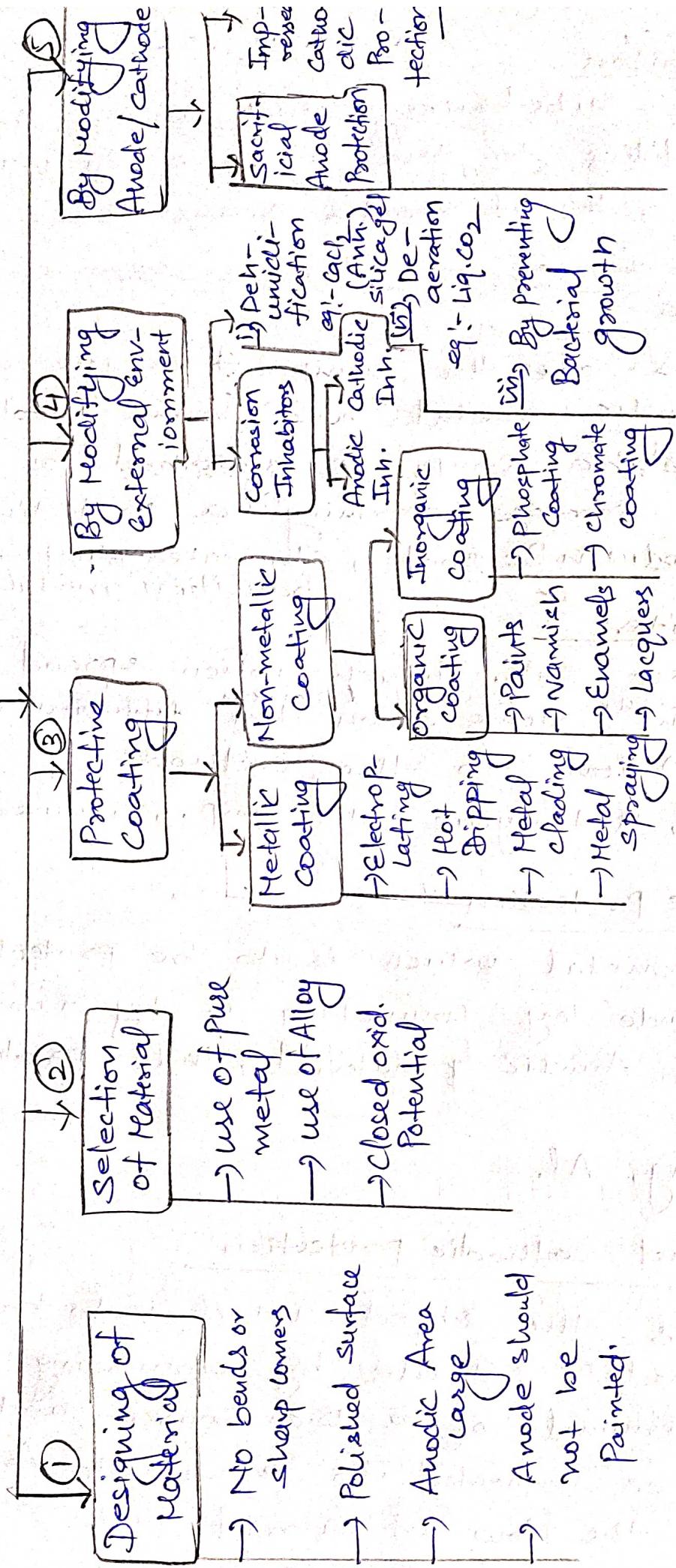
The further oxidation of ferrous hydroxide $[Fe(OH)_2]$ in presence of O_2 will oxidised to form the rust



Mechanism of O_2 Absorption.

J. Syng Methods of corrosion control or prevention of corrosion

corrosion control methods



Corrosion Inhibitors

These are the substances which when added in small quantities to the corrosive environment decreases the rate of ~~reaction~~ corrosion.

Anodic Inhibitors

Anodic Inhibitors are the compound which react with an anodic metal and forms insoluble comp. This insoluble comp. is absorbed on the Anode metal surface forming a protective barrier e.g:- Sodium Benzoate, Chromates phosphates of transition metals.

Cathodic Inhibitors

These are those sub. which when spread in the environment slows down the diffusion of hydrated (H^+) ion to the cathode
e.g:- Amines, Heterocyclic (N_2) comp., Thiourea etc.

Sacrificial Anode Protection

In this the metal which is to be protected is made cathode by connecting it by a wire which act as Anodic of material, thus protecting the cathode.

e.g:- Zinc, Mg, Al.

Impressed current cathodic protection

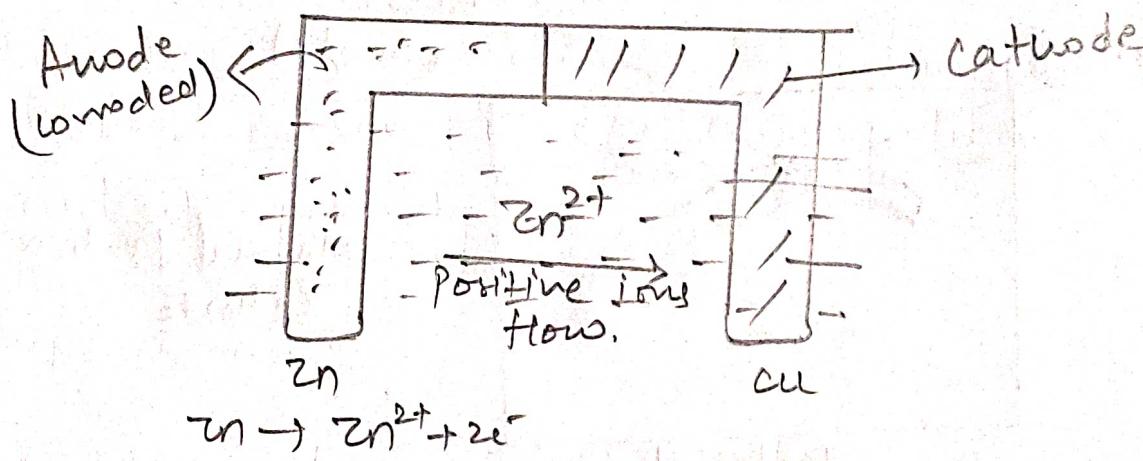
In this process the object which is to be protected is made cathode by connecting it to the -ve terminal of a D.C. source and the +ve terminal is connected to a insoluble Anode thus reversing the flow of current

Corrosion

1) Galvanic Corrosion :-

When Galvanic corrosion is caused when 2 dissimilar metals are electrically connected to each other and exposed to an electrolyte.

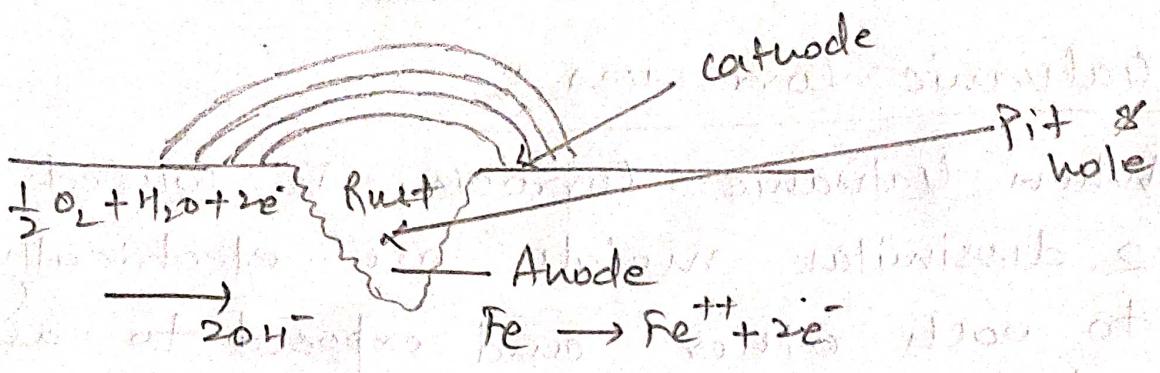
For e.g.: If Zinc and copper are in contact with each other in presence of an electrolyte then Zinc placed higher in Galvanic Series will act as anode and gets corroded, while copper acting as a cathode will be protected.



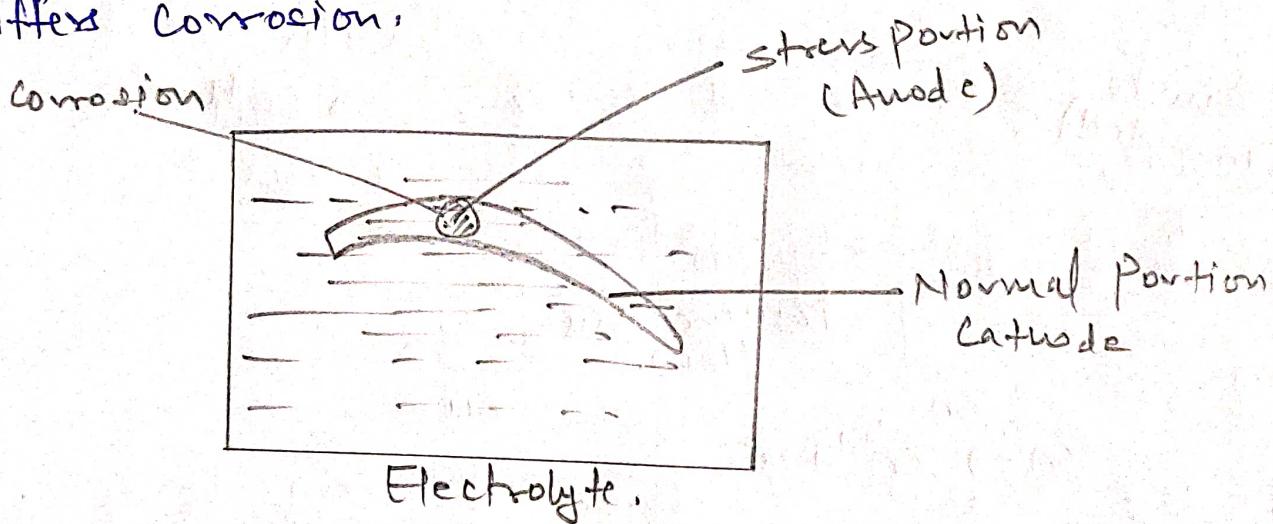
2) Pitting Corrosion :-

Pitting corrosion is another form of localised corrosion and results in the formation of pits and holes in the metal. It usually takes place due to cracking of protective oxide film.

And anode is formed where the film is broken and the unbroken film will act as cathode.

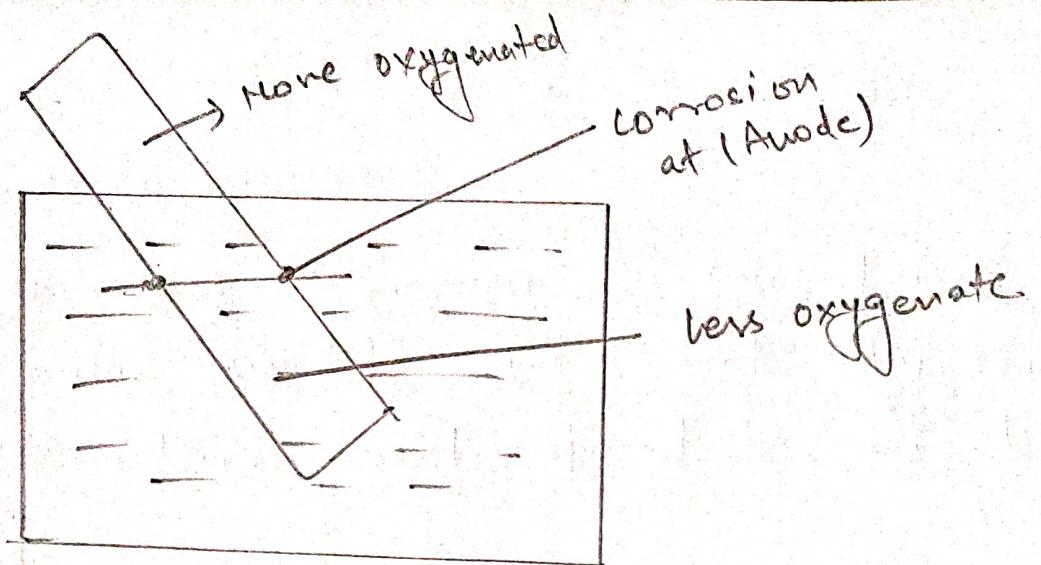


Stress Corrosion! - This type of corrosion takes place due to a combined effect mechanical stress and corrosive environment. The part of metal under stress will act as anode and the normal part will act as cathode and the anodic area suffers corrosion.



Water line or Differential Aeration corrosion

This type of corrosion occurs due to differential aeration areas of metal. The area which is well aerated will act as anode and the area which is less aerated will act as cathode.



Electrolyte