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## Corrosion

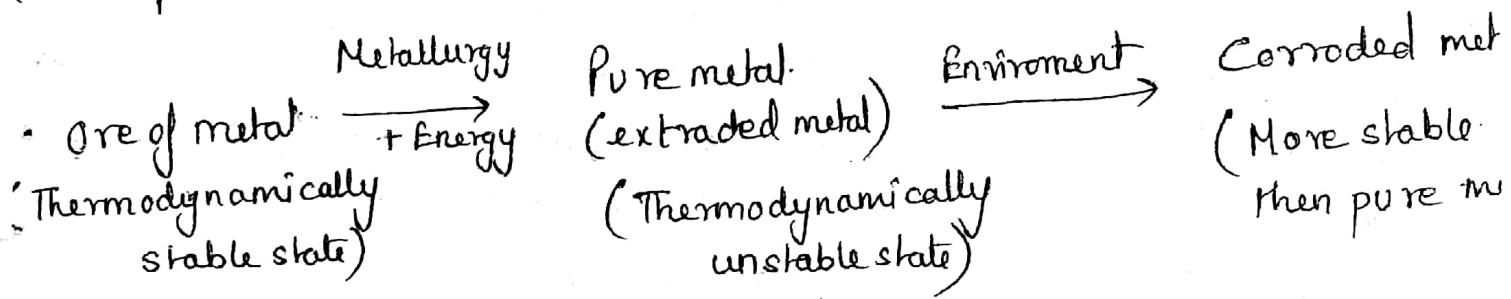
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Definition

"Degradation or deterioration of metal by chemical (or electrochemical) reaction with its environment." { degradation or deterioration means decrease in useful properties of material like malleability, ductility }

### Cause of corrosion / Reason of corrosion

Metal exist in nature in form of oxides, sulphides, sulphates and carbonates, these chemically combined state of metal is called as 'ore' and it has low energy and is thermodynamically stable state for metal. During metallurgy (metal extraction) consider energy is required & the extracted metal (from ore) has high energy and is thermodynamically unstable. Thus Unstable Metal again try to go to stable state, and metal do it by interacting chemically electrochemically with their environment to form surface compound. and thus metal undergo corrosion



\* Corroded metal is more stable than pure metal but due to corrosion useful properties of metal like malleability, ductility are lost.

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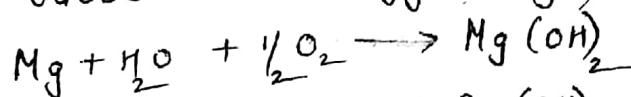
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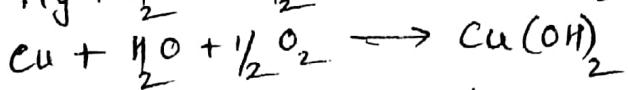
## (2) Thermodynamics of Corrosion:-

- A) Corrosion reaction is spontaneous & feasible if  $\Delta G^\circ < 0$   
 B) Corrosion reaction is non-spontaneous & not feasible  
     if  $\Delta G^\circ > 0$

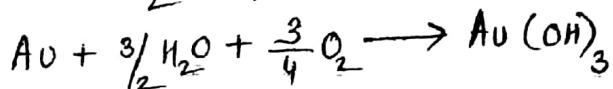
( $\Delta G^\circ = \text{Gibbs free energy change}$ )



$$\Delta G^\circ = -142,600 \text{ cal.}$$



$$\Delta G^\circ = -28,600 \text{ cal.}$$



$$\Delta G^\circ = +15,700 \text{ cal.}$$

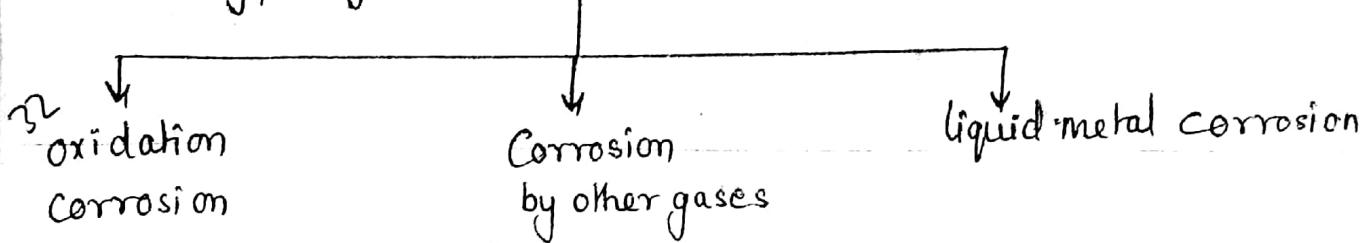
\* Mg has high tendency to corrode than Cu, Au have no tendency to corrode.

### Theories of Corrosion

#### A) CHEMICAL OR DRY CORROSION

This type of corrosion takes place by direct chemical contact, this type of corrosion takes place when metal surface comes in direct contact with atmospheric gases such as oxygen, halogens, hydrogen sulphide etc. or due to anhydrous inorganic liquids. The product formed after corrosion can be insoluble, soluble or liquid product.

##### Types of chemical or dry corrosion



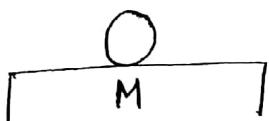
#### (1) Oxidation Corrosion :-

Due to direct action of oxygen on metals, oxidation coros

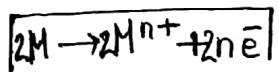
Takes place at low or high temperature. Oxides of metals (3) are formed due to the corrosion by oxygen. Oxidation. Corrosion take place in absence of moisture.

Mechanism of (Dry corrosion or) Oxidation corrosion (Wagner theory)

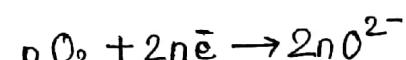
→ Oxygen get adsorbed on surface of metal by physical adsorption, which is changed to chemisorption due to rise in temperature



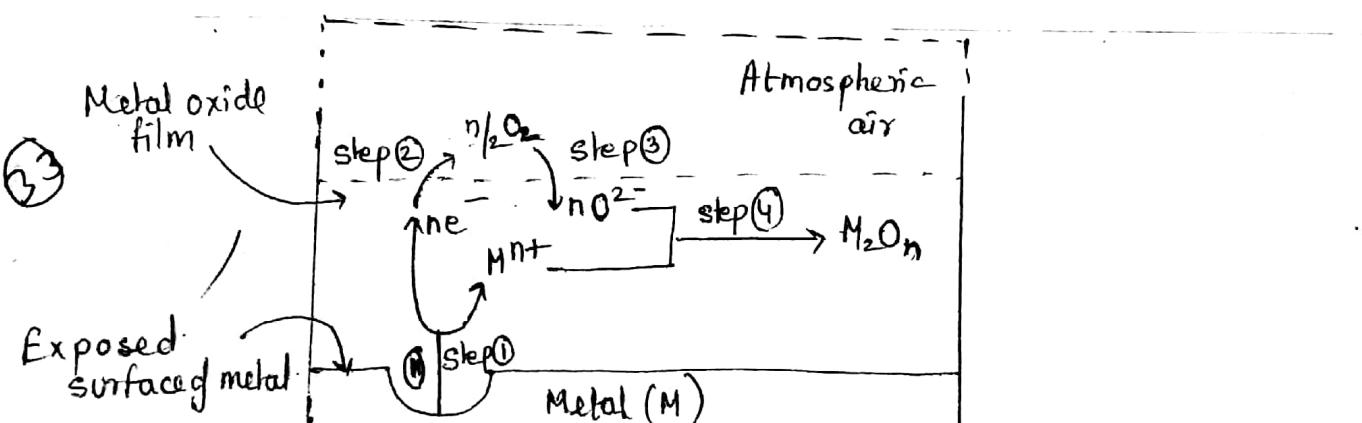
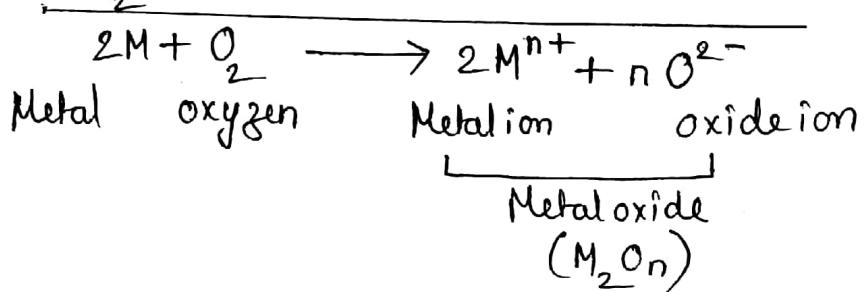
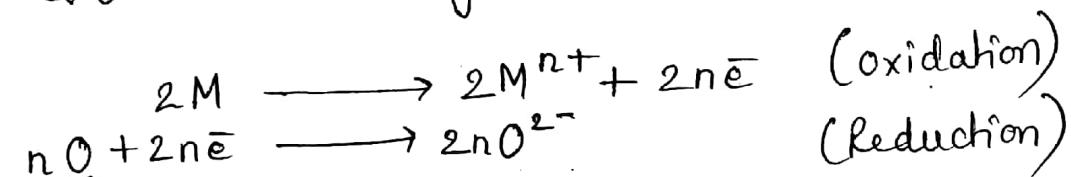
→ When temperature increases metal get oxidized to metal ions (i.e. metal loses electron)



→ The electrons from metals are taken up by oxygen, due to which it gets reduced (converted) to oxide ion



→  $M^{n+}$  &  $O^{2-}$  combine to form metal oxide. ( $M_2O_n$ )



The layer of metal oxide form barrier between the metal and the atmospheric oxygen and does not allow further oxidation or corrosion of metal. As the metal cation is much smaller in size, so the outward diffusion of metal ion is very rapid, so corrosion continues due to rapid diffusion of highly mobile cations (metal ions) (6)

Nature of oxide film:-

If the thickness of oxide layer is less than  $300\text{ \AA}$  then such

layer is called as film

If thickness of oxide layer exceeds  $300\text{ \AA}$  then such layer

is called as scale

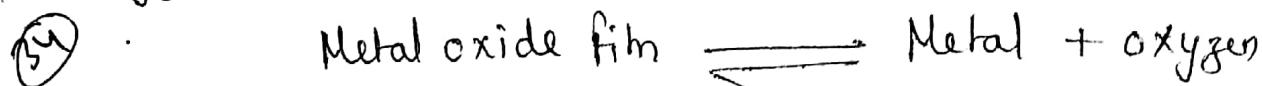
FILM CAN BE DIVIDED INTO

- Stable film
- Unstable film
- Volatile film
- Porous film.

1) STABLE FILM :- Stable film is fine grained in structure and it tightly adheres (stick) to metal surface, and thus the stable film can be impervious (no penetration) in nature and prevent penetration of oxygen into the metal.

Stable film form protective coating on the metal and prevent further corrosion. Oxide films on Al, Cr, Cu etc are stable film, so these metals are employed for alloy formation with other reactive metal to protect them from corrosion.

2) UNSTABLE FILM :- The oxide film which is formed on surface of metal when decomposes back into metal and oxygen then film is called unstable film.



Unstable film is formed by oxides of Ag, Au & Pt, so these metal do not undergo

3) VOLATILE FILM :— (B) when the metal oxide film volatizes (5)  
from surface of metal as soon as it is formed. Then such film is called volatile film. Due to the volatile film underlying (below) metal get exposed to oxygen and thus rapid and continuous corrosion takes place.

Example →  $\text{MoO}_3$  (molybdenum oxide film) is volatile so it undergoes excessive corrosion

4) POROUS FILM :— When the metal oxide film formed is porous or have cracks then such film is called porous film. Due to porous nature oxygen diffusion takes place causing corrosion.

Example → Metal oxide film of alkali and alkaline earth metals fall under this category.

### Pilling Bedworth Rule:

Oxide layer can be protective or non protective, it depends upon the ratio of volume of metal oxide to the volume of metal consumed. It is known as Pilling Bedworth ratio.

$$\text{Pilling Bedworth ratio} = \frac{\text{Volume of metal oxide formed}}{\text{Volume of the metal consumed}}$$

If volume of metal oxide film is less than the volume of the respective metal from which it is formed, then ratio is less than unity, then oxide film is non protective in nature

< 1

If volume of metal oxide film formed is equal or greater than the respective metal from which it is formed, then ratio is more than unity, then metal oxide film is protective in nature

> 1

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## B) ELECTROCHEMICAL OR WET CORROSION

This type of corrosion occurs at a solid-liquid interface when the metals are in contact with the moist air or any liquid medium. It is also known as immersed corrosion.

The electrochemical corrosion occurs due to existence of separate anodic and cathodic area having conducting medium like water, acids for conduction of electrons, ions.

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Oxidation take place in anode area and reduction take place in cathode area, the electron flow from anode to cathode when they are at different potentials.

Example:- Corrosion of iron articles, known as Rusting, and corrosion product is called rust

Corrosion takes place as follows:

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### Anodic Reaction / Reaction at anode

Ixidation reaction takes place at anode, here metal atom loses their electrons to the environment and pass into the solution as metallic ions ( $M^{n+}$ )



Thus metal get destroyed by dissolving or changing into metallic ions. Thus corrosion takes place at anodic area (at anode) of metal.

### Cathodic Reaction / Reaction at Cathode

The electrons which are released from anode are consumed in reactions at cathode.

In the basis of corrosive environment, the reactions at cathode result in evolution of hydrogen or absorption of Oxygen.

Reaction in Cathode in the absence of oxygen.

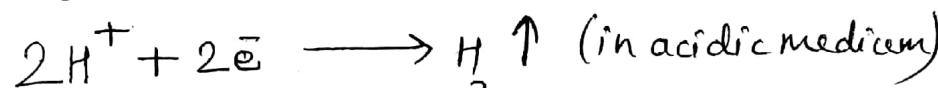
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A) In acidic environment

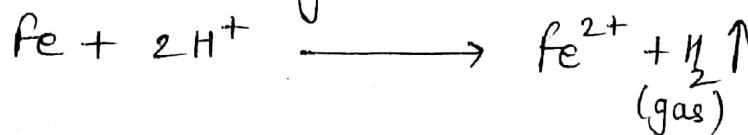
In the absence of oxygen and in the acidic environment hydrogen is evolved (produced) at cathode.

The electrons

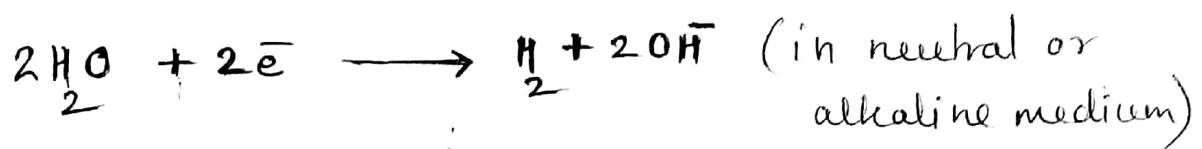
leased from the anode is taken up by the  $H^+$  ions of acidic solution, and they are released or eliminated as hydrogen gas



Overall reaction of Anode & Cathode

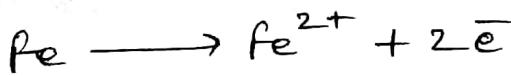


(B) In alkaline or neutral solution  
 In absence of oxygen and in the alkaline or neutral environment, the electron released from anode are taken up by  $\text{H}_2\text{O}$

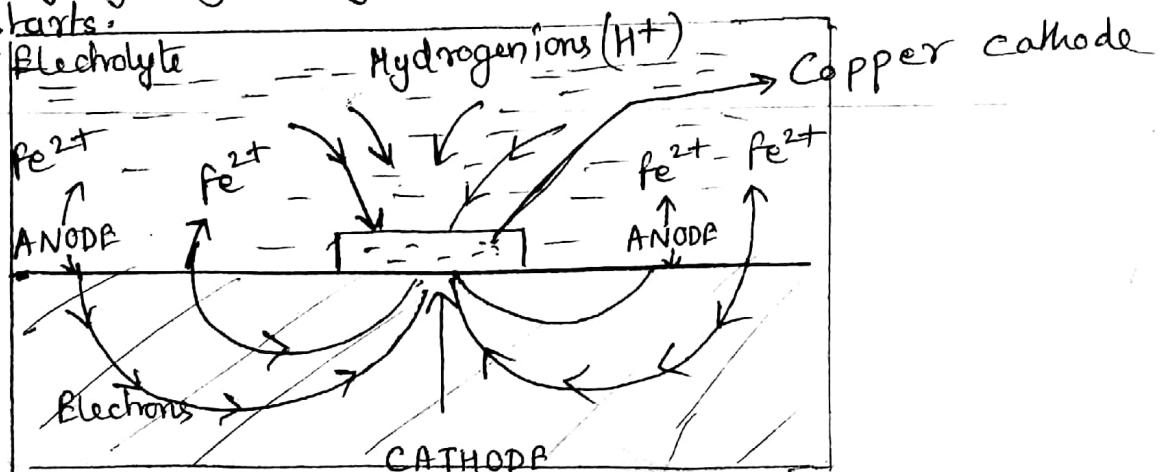


The electrons which are released at anode, flow through metal surface (electronic conductor) to cathode.

Consider that an iron vessel contain an acid solution on its surface, and a piece of copper is lying on it. The contact between the iron vessel and copper piece in the presence of electrolyte forms a corrosion cell. Copper piece act as cathode, and iron becomes anode. The anode i.e. iron surface is corroded because iron ion pass into the solution



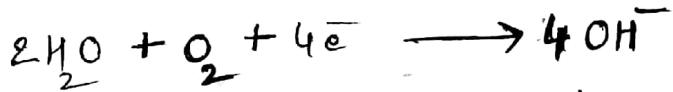
The free electrons concentrate on cathode (copper) by flowing through metal, hydrogen ion which are present in the acid get concentrated on cathode & take up the electrons & evolve as hydrogen gas which concentrate on cathode surface & form insulating layer slowing down or stopping electrochemical action. This is called cathodic polarization, if hydrogen layer broke or swept away then corrosion starts.



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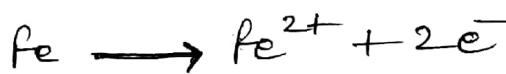
Reaction in Cathode in the presence of oxygen

In presence of atmospheric oxygen and in neutral/aqueous solution or weakly alkaline solution following reaction takes place

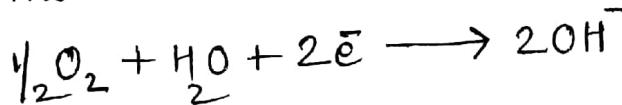


The overall reaction can be explained as

Anode reaction:-



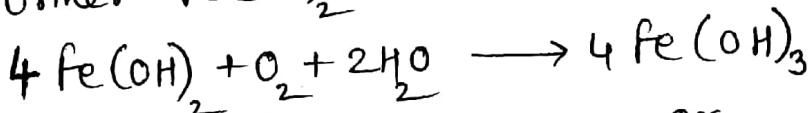
Cathode reaction:-



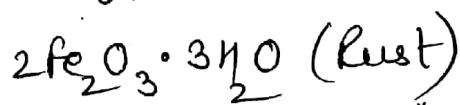
The  $\text{Fe}^{2+}$  ion produced at anode travel to cathode region through moisture and react with  $\text{OH}^-$  ions produced at cathode



further  $\text{Fe}(\text{OH})_2$  oxidizes as



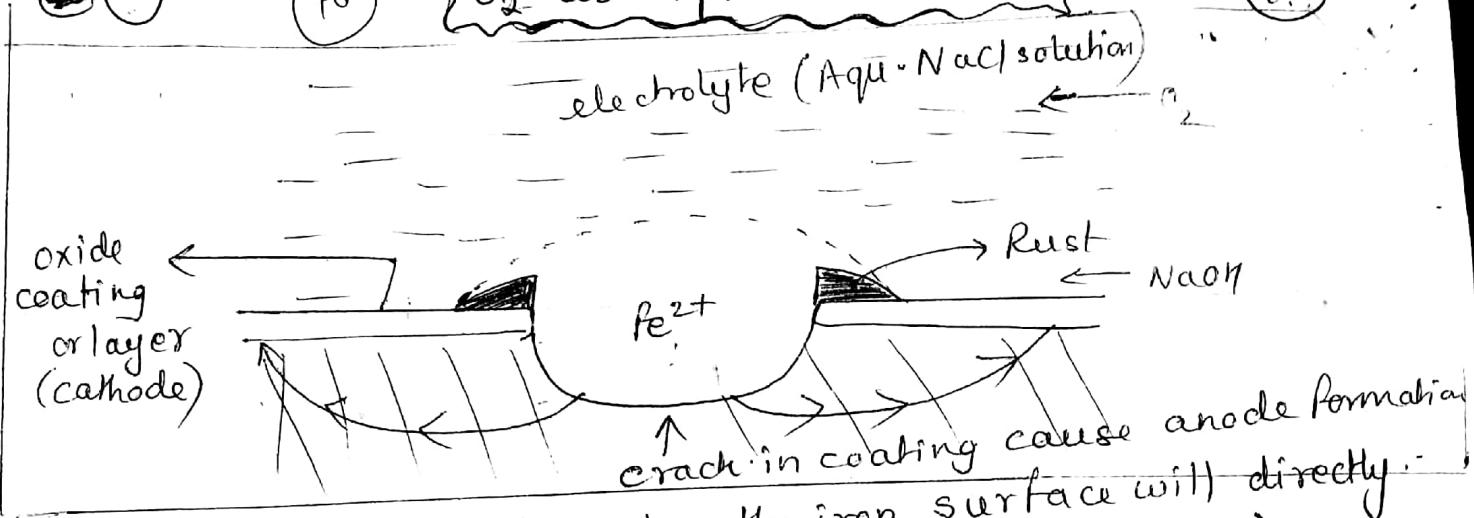
or



Corrosion occurs at anode, but the rust is formed near cathode, because smaller  $\text{Fe}^{2+}$  ions produced at anode diffuse rapidly towards cathode as compared to diffusion of layer  $\text{OH}^-$  ions towards the anode.

O<sub>2</sub> absorption Mechanism Consider a situation than an iron vessel contain salt solution containing dissolved gases. The surface of vessel contains an oxide film coating of metal. This oxide film develop a crack.

## O<sub>2</sub> absorption Mechanism



Due to the presence of crack, the iron surface will directly come into contact with the electrolyte (salt solution). This a surface of crack will act as anode and the surface of oxide coating will act as cathode. The area of anode is very small and cathode area is very large, under such conditions, the whole current will be concentrated at very small area. This result in very strong attack on the iron surface which is exposed by crack. This type of attack, where anode area is very small & cathode area is large is called localized attack.

further corrosion occur

as mentioned above

## Types of corrosion

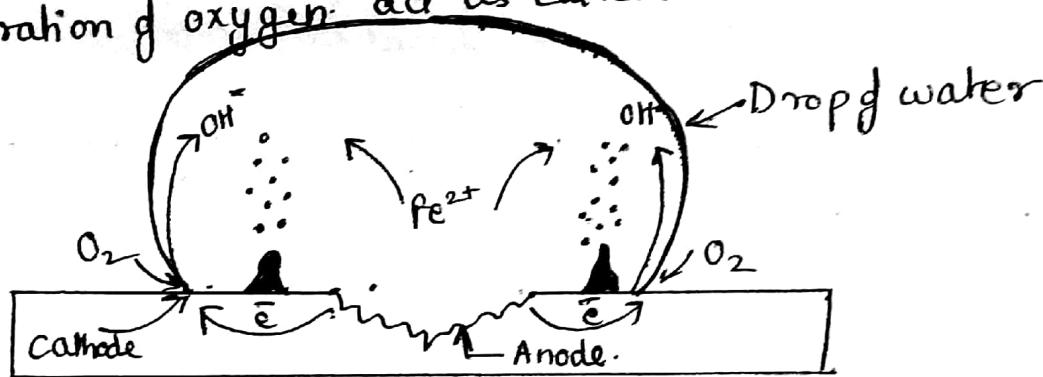
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### A) Corrosion by Oxygen

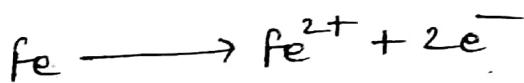
#### (e) i) PITTING CORROSION

The localised accelerated attack of a corrosive environment, due to the heterogeneity in the metal surface, resulting in the formation of pin holes, pits and cavities in the metal is called pitting corrosion.

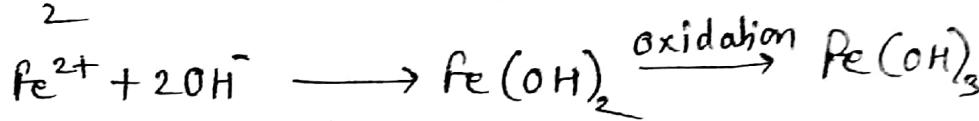
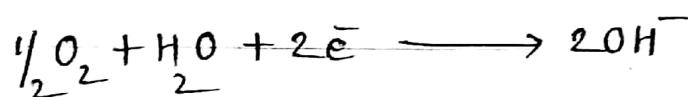
Consider a drop of water which is resting on the surface of metal. The metal surface, which is covered by the drop, has low oxygen concentration and so it acts as anode and suffer corrosion. The uncoated metal surface, due to high concentration of oxygen act as cathode.



action at anode



reaction at cathode



Due to the formation of small anodic area and large cathodic area, potential difference is set up at localised spots to pit. Thus metal under water drop undergo accelerated

corrosion while when it is <sup>12</sup> submerged in water corrosion is <sup>12</sup> less. Pitting corrosion is a non-uniform corrosion which result from localized accelerated attack of corrosive environment on localized area resulting in the formation of pits, cavities & pin-holes in metal.

When once a small pit is formed.

The rate of corrosion will be increased.

### Causes or reasons of Pitting corrosion:-

- a) Chemical attack
- b) Turbulent flow of a solution over metal surface
- c) Non uniform stresses causing straining of metal
- d) Non uniform rough surfaces.
- e) Scratches or cut edges.

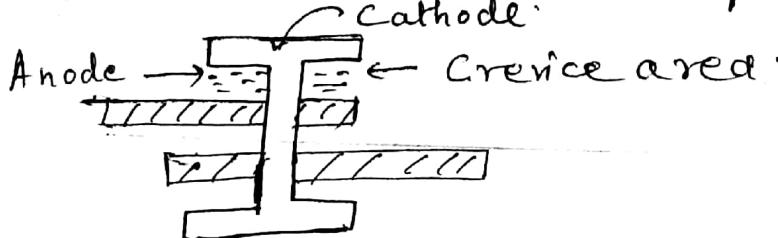
### Prevention of Pitting corrosion:-

- a) Using pure metals devoid of or free of any impurities
- b) Proper polishing of metal surfaces
- c) Properly designing metal structures.

## 2) Crevice Corrosion

Consider a crevice between different metallic objects

Example → nut, bolt & rivets in contact with liquid.



Crevice area <sup>is</sup> has lack (less) of oxygen, and so it becomes anode region, The exposed area become cathode, corrosion take place at anode.

Hence,

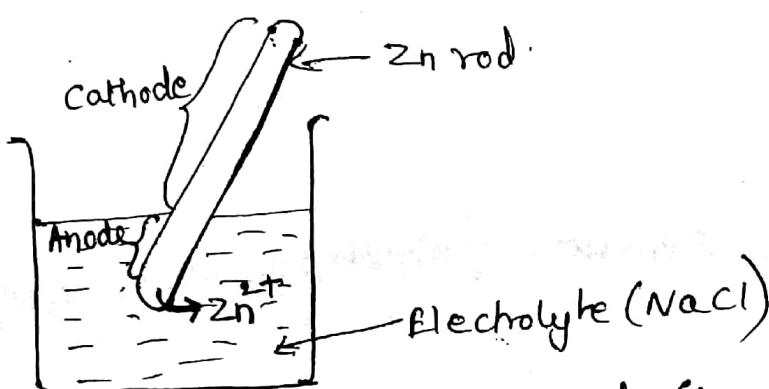
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"Cerice corrosion is thus, accelerated attack at the junction of 2 metals exposed to a corrosive environment"

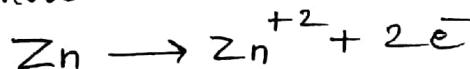
3) Concentration Cell Corrosion or differential Aeration Corrosion:

This type of corrosion occurs due to the electrochemical attack on the metal surface and when a metal surface is partially immersed (dipped) in an electrolyte and partially exposed to air



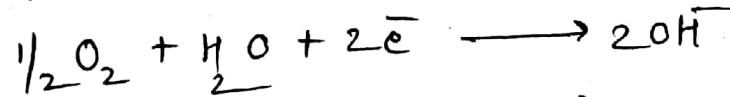
The metallic part which is poorly oxygenated (have less oxygen) become the anode part and, here oxidation take place.

Reaction at Anode:-



The metallic part which is well oxygenated (have good oxygen) become the cathode part, here reduction takes place.

Reaction at Cathode:-

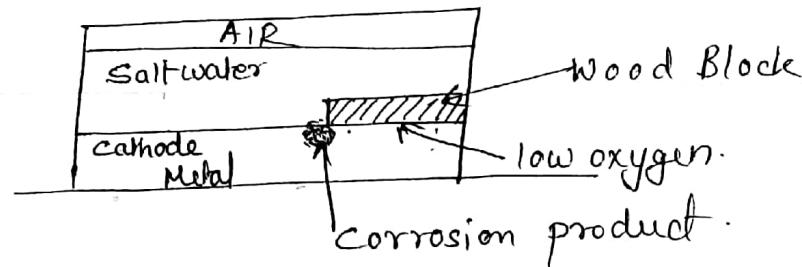


$Zn^{+2}$  &  $OH^-$  ions interact to give  $Zn(OH)_2$ , so corrosion occurs at anode.

Concentration cell corrosion occurs due to following:-

- ① Due to accumulation of dirt, sand, scale or other contamination on metal, such part

2) By partially covering metals with blocks of wood or piece of glass, due to covering, the covered part become less oxygenated, thus corrosion occurs.



3) Due to Wire fence kind of structures; the point at which wire cross is less accessible to air than rest of the fence. So point of wire crossing act as anode and undergo corrosion.

4) Water-line Corrosion :-

"The differential aeration corrosion of metals in metallic tanks partly filled with water, just below the water line is called water line corrosion"

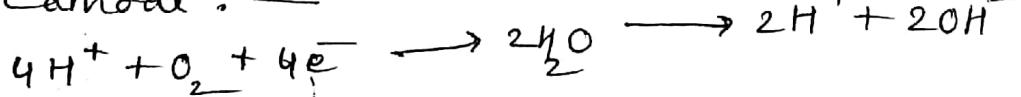
When the metallic tank is partially filled with water then the concentration of oxygen above the water surface is greater than that in the under the surface when water is stagnant. Thus oxygen concentration cell is generated.

In oxygen concentration cell, metal just above the water level is cathodic and metal below the water level is anodic (anode part)

Reaction at Anode :-



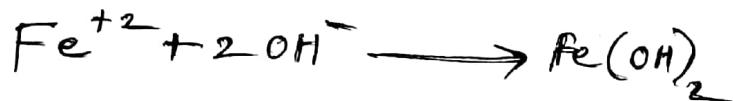
Reaction at Cathode :-



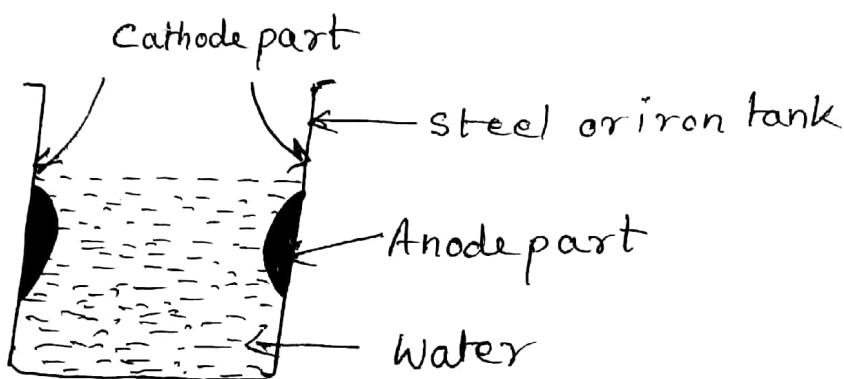
Net reaction

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(15)



Corrosion occur at anode part, and cathode part is completely unaffected by corrosion. When water is relatively free from acidity, then little corrosion take place.



### 5) Underground or Soil Corrosion

In soil, due to moisture, bacteria, micro organism and electrolyte corrosion occurs, and it is further promoted or enhanced by differential aeration.

Example:- Buried pipeline and cable passing from one type of soil to another suffer corrosion due to differential aeration, lead

Lead pipelines passing through clay and then through sand suffer from corrosion, as clay is less aerated than sand, so corrosion of lead pipeline take place in clay. In water logged soil microbial corrosion take place.

### B) Corrosion of metals by acids:-

#### Amphoteric Corrosion

Aluminium is amphoteric in nature, it means ~~it is~~ corrosion can occur in it in both alkaline & acidic environments, aluminium is active from thermodynamic point of view.

In the

oxygen containing environment (air, water), aluminium is rapidly covered with the oxide layer, oxide layer is non reactive and it prevent corrosion. If the oxide film get damaged by scratches, then new oxide film is immediately formed on the surface of aluminium. Thus aluminium gives excellent corrosion protection factor which affect stability of Aluminium oxide layer:-

- a) Oxide layer is not stable in acidic ( $\text{pH} < 4$ ) or alkaline ( $\text{pH} > 9$ ) environments.
- b) Aggressive ions (chlorides, fluorides) may attack the oxide layer locally.
- c) Certain elements (Ca, Tl, In, Sn & Pb) may incorporate in the oxide layer and destabilise it

Pitting Corrosion occurs in Aluminium & its alloys:-

Pitting corrosion is a highly localized type of corrosion in the presence of aggressive chloride ions.

The area inside the pit act as anode, and other phase in alloys of aluminium act as cathode.

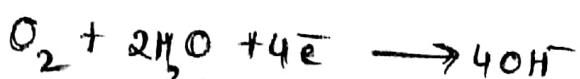
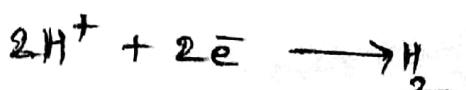
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### Anodic Reaction:



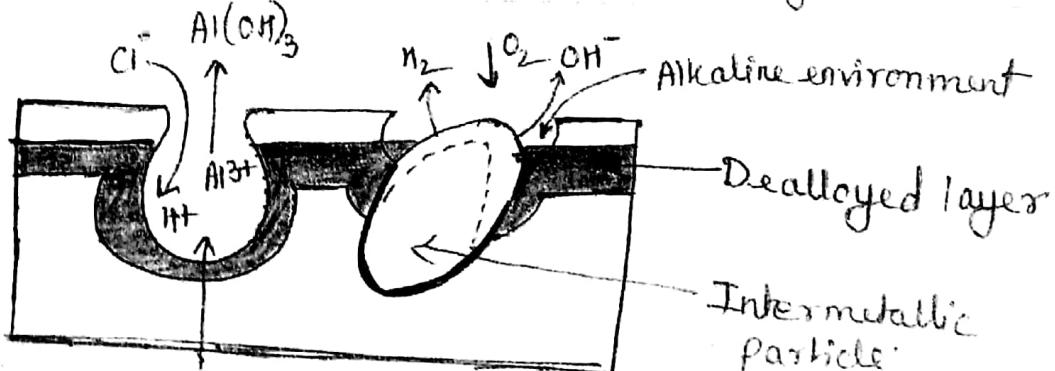
To balance the positive charge, chloride ion migrate into the pit, resulting in HCl formation inside the pit, and it thus results in accelerated pit propagation.

### Cathodic Reaction:



Hydrogen evolution & oxygen reduction occurs at intermetallic cathodes, the reduction reaction will cause local alkalisation around cathodic particles.

Aluminium oxide is not stable in alkaline environment and gets dissolved (alkaline pits). The active aluminium component of the particles also dissolve selectively, thus enriching the surface with iron & increasing its cathodic activity.

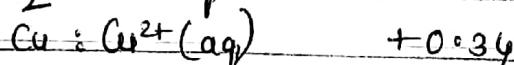
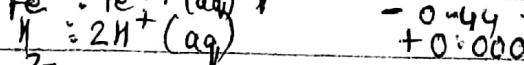
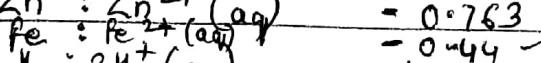
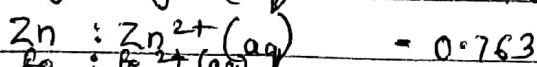
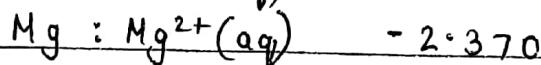
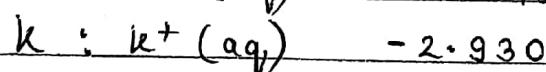
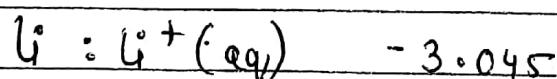


## Electrode Potential :-

It means the electron donating or losing capacity.

When the elements are arranged in decreasing order of their standard electrode potentials, then an electrochemical series

(F.C.S) is obtained. Elements which occupy higher positions in electrochemical series are said to be highly electro-positive and those elements which are placed in lower positions are said to be highly electro-negative. Metal high in the series have high ability to loose electron and are easily oxidised, whereas metal at lower positions loose their electron with difficulty and are not corroded easily.



increasing  
↑ tendency for  
oxidation

↓  
Increasing tendency  
for reduction

c)

## (15) ~~No~~ Corrosion by Metal to Metal Contact (19)

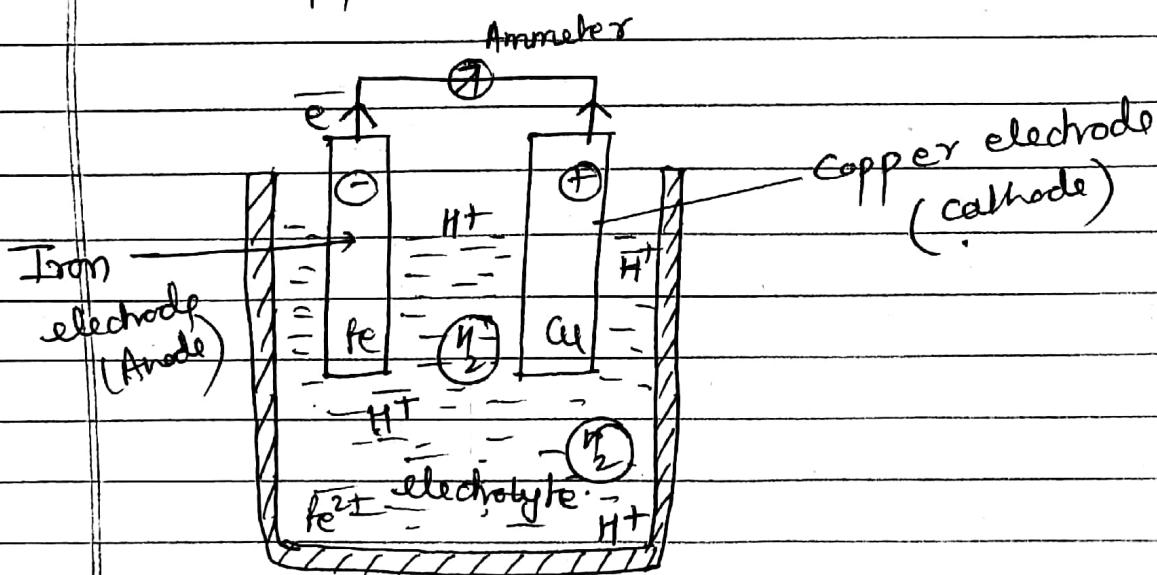
Types of Corrosion / Bimetallic / Galvanic corrosion

### (1) Galvanic Corrosion :— (Galvanic Cell)

When electrical contact is made between two metal placed in electrolyte solution, then the metal with lower value of electrode potential (t) oxidise while other metal with higher value of electrode potential get reduced (Er).

The oxidised metal get corroded and such a corrosion is called Galvanic corrosion.

### Iron Copper Galvanic corrosion



A galvanic cell consisting of iron & copper electrodes.

Anode

The metal (iron) which is higher up in the electrochemical series with more negative electrode Potential will form anode

Fe, act as anode.

- The reaction which take place at anode are:



These electrons at iron anode, flow to copper electrode through external wire.

- The copper electrode will have extra electrons.

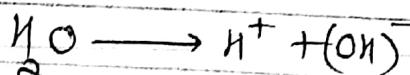
Thus (Fe) Iron metal ~~will~~  
potential is oxidised to its ions and so corrosion occurs at anode.

- The  $\text{Fe}^{2+}$  ions formed are further oxidised to  $\text{Fe}^{3+}$  ion by oxygen present in water electrolyte.

### Cathode

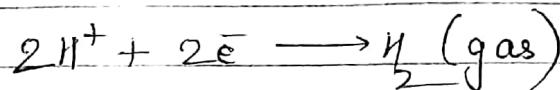
No corrosion occurs at the cathode (copper)

Hydrogen ions ( $\text{H}^+$ ) are produced due to the dissociation of water.



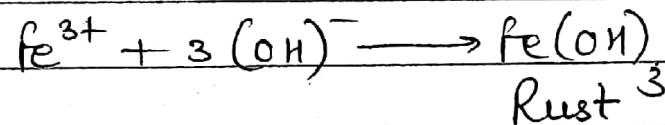
These hydrogen ions ( $\text{H}^+$ ) take up the extra electrons which are available at cathode, and hydrogen gas is formed.

21



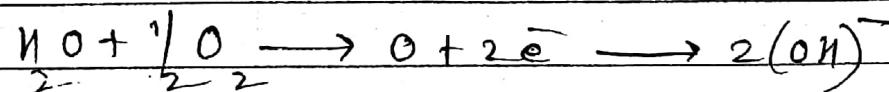
The concentration of  $H^+$  ions increases if water is acidified, and thus rate of reaction increase by acidified water (electrolyte)

Now only  $OH^-$  ions are present at cathode. (becuz  $H^+$  ions form  $H_2$  gas), any  $Fe^{3+}$  ions present, move towards the cathode and react with  $OH^-$  ion.



This ferric oxide is hard rust, which is formed on cathode or it falls at bottom of container.

The oxygen dissolved in water, give rise to another reaction at cathode.

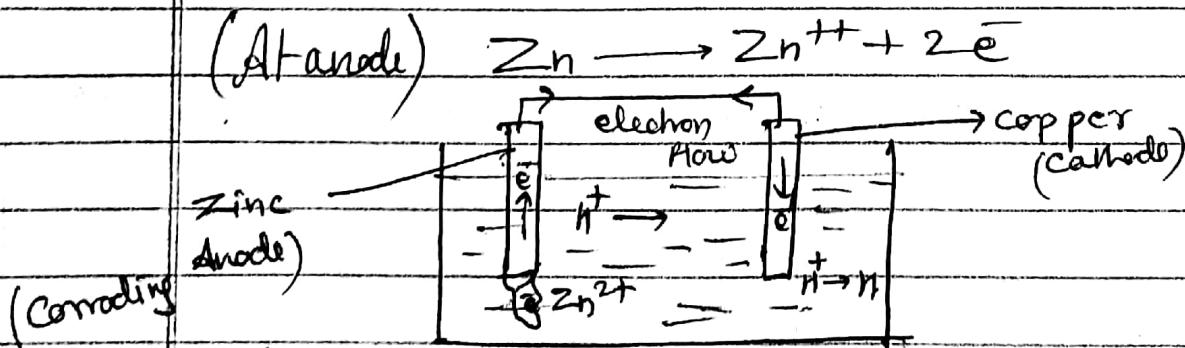


due to oxygen formation of  $OH^-$  ion increases, so more electrons flow toward cathode from anode, increasing corrosion rate.

## Zinc Copper galvanic cell.

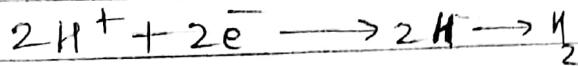
If a strip of pure zinc is kept in a beaker containing dilute acid, then we see that no hydrogen is liberated. The Zinc ion formed pass into solution and form a film of positively charged ions around metal, this film prevent the hydrogen ion from acid to come in contact with zinc surface, and receive electrons from it.

But when we keep a strip of pure copper, which is less active metal into the acid solution & connect these two strips of Zinc & copper by copper wire, then Zinc forms zinc ions, by losing 2 electrons. Thus Zinc get corroded & it forms anode.



The electrons from Zinc flows through wire to copper strip, where copper strip ~~provides~~ supply necessary electrons to combine with hydrogen ions ( $H^+$ ) to form hydrogen atom & molecules.

At cathode



In a Galvanic cell, rate of corrosion increases due to following

- 1) If there is large difference in electrode potential between 2 electrodes
- 2) By making the electrolyte more acidified.
- 3) By increasing concentration of oxygen, preferably near cathode.

Galvanic corrosion can be minimised by.

- a) By avoiding galvanic couple
- b) By providing an insulating material between the 2 metals.

One can use the thermodynamics to evaluate the corrosion tendency, provided the chemical make-up of the local environment at the surface of the metal is known. However, thermodynamic principles do not provide any information regarding the rate of corrosion and are thus, useless for lifetime prediction of metals.

### 7.5 Kinetics of Corrosion

The nature of the metal and the corroding environment, the concentration of corroding medium, temperature, pH, purity of the metal, porosity and volatility of corrosion products etc. are various factors, which affect the rate of corrosion.

### 7.6 Mechanism of Corrosion

Corrosion starts by the flow of electricity between certain areas of a metal surface through a solution (*i.e.*, environment) capable of conducting an electric current. This electrochemical action causes destructive alteration or eating away of a metal at areas, which are called anodes. The electrons leave the metal and enters the environment, to which it is exposed. Hence, *it is the anode that corrodes*.

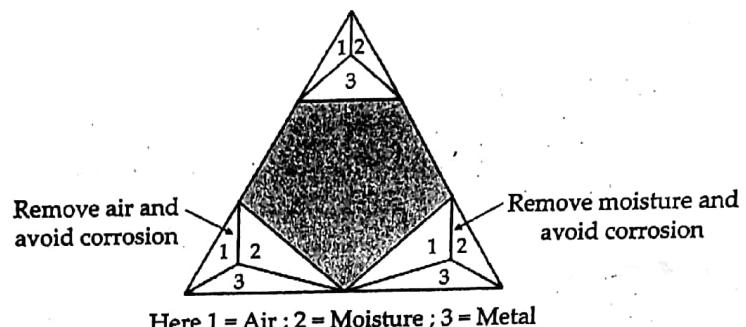


Figure 9 Corrosion triangle.

### 7.7 Consequences of Corrosion

The consequences of corrosion are large and the effects of these on the safe, reliable and efficient operation of structures or equipment are often more serious than the simple loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small. Some of the major harmful effects of corrosion are :

- (i) Blockage of pipes by solid corrosion products, and mechanical damage to valves, pumps, etc.
- (ii) Loss of technically important surface properties of a metallic component. These include heat transfer or surface reflectivity across a surface, electrical conductivity of contacts, ease of fluid flow over a pipe surface, frictional and bearing properties etc.
- (iii) Perforation of pipes and vessels allowing escape of their contents and possible harm to the surroundings. *For example*, if the condenser tubes are perforated then corrosive sea water may enter the boilers of a power station, while a leaky domestic radiator can cause huge damage to carpets and decorations.
- (iv) Reduced value of goods due to deterioration of appearance.
- (v) Injuries to people or even loss of life arising from structured breakdown or failure of cars, aircraft, bridges etc.
- (vi) Contamination of fluids in vessels and pipes. *For example*, beer goes cloudy when small quantities of heavy metals are released by corrosion.

- (vii) Added complexity and expense of equipment, which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.
- (viii) Decrease in production rate because efficiency is less and replacement of corroded equipment is time-consuming.
- (ix) Increase in maintenance and production cost.
- (x) Metal prosthetic devices are used in the body but corrosion continues to create problems. Examples include :
  - (a) Failures through broken connections in pacemakers.
  - (b) Inflammation caused by corrosion products in the tissue around implants.
  - (c) Fracture of weight-bearing prosthetic devices like metallic hip joint (whose use was essential to alleviate some of the problems of arthritic hips).
- (xi) Corrosion can also lead to serious deterioration of the artistically and culturally significant gilded bronze statues, precious artifacts inside the museums or outside.

## 7.8 Corrosion Losses

India loses one tonne of steel every 15 seconds on account of corrosion.

India has been losing around ₹2 lakh crore every year owing to corrosion in various sectors, including infrastructure, utility services, production, manufacturing, defence and nuclear sectors.

## 7.9 Corrosion Prevention and Control

Around half of India's corrosion losses (around Rs. 1 lakh crore) could be saved by awareness of following facts :

- (i) The provision to control corrosion should be done at the very design state of the plants installation.
- (ii) It should be followed by proper selection of material technology, continuous monitoring and timely evaluation.
- (iii) The use of inferior, low cost anti-corrosive measures should be avoided because in the long run they prove to be more expensive.
- (iv) The use of suitable, predictive, preventive and corrective measures should be adopted.

# 8

## TYPES AND MECHANISM OF CORROSION

### 8.1 Chemical or Dry Corrosion

When metal surface is in immediate proximity to atmospheric gases or anhydrous liquid, a direct chemical interaction between the two leads to *chemical or dry corrosion*.

It is of following *three* types :

❖ Oxidation corrosion      ❖ Liquid metal corrosion      ❖ Corrosion by other gases

#### 8.1.1 Oxidation Corrosion (Corrosion by Oxygen)

*"When corrosion takes place by direct action of oxygen on metal, it is called oxidation corrosion."*