Introduction :

- Corrosion is a process of gradual deterioration or eating away of a metal from its surface due to the unwanted chemical or electrochemical reaction of metal with its environment.
- For example, formation of a layer of reddish scale or hydrated ferric oxide (Fe_3O_4) on the surface of iron, also known as "rusting of iron".
- Another example is formation of green film of basic carbonate $[CuCO_3 + Cu(OH)_2]$ on the surface of copper, when exposed to moist air containing carbon dioxide.

Cause of corrosion :

- Metals exist in nature in the form of carbonates, sulphides and sulphates.
- These chemically combined states of metal "known as ore" has a low energy and is thus thermodynamically stable state of metal. A considerable amount of energy is required during metallurgy. The extracted metal has higher energy and thus it is thermodynamically unstable state. Metals do this interacting chemically or electro-chemically with its environment to form compound at the surface and thus metal undergo corrosion.



Corroded metal is thermodynamically more stable than pure metal but due to corrosion useful properties of a metal such a malleability, ductility and electrical conductivity are lost.

Effects of corrosion :

Effects of corrosion are given below:

- (i) Loss of useful properties of metal and thus loss of efficiency.
- (ii) Decrease in production rate, because efficiency is less and replacement of corroded equipment or machinery is time consuming.
- (iii) Increase in maintenance and production cost.
- (iv) Contamination of product.

Theories of Corrosion :

Different theories of corrosion are:

- (1) Acid theory
- (2) Direct chemical attack or dry corrosion theory
- (3) Electrochemical or wet corrosion theory.

(1) Acid Theory :

This theory is particularly applicable to rusting of iron in the atmosphere.

According to this theory, rusting of iron is due to the continued action of oxygen, carbon dioxide and moisture, converting the metal into a soluble ferrous bicarbonate which is further oxidised to the basic ferric carbonate and finally converted to hydrated ferric oxide. Chemical reactions are:

 $Fe + O + 2 CO_2 + H_2O \longrightarrow Fe (HCO_3)_2$ $2 Fe (HCO_3)_2 + H_2O + O \longrightarrow 2 Fe (OH) CO_3 + 2CO_2 + 2H_2O$ $2 Fe (OH) CO_3 + 2H_2O \longrightarrow 2 Fe (OH)_3 + 2CO_2$

This theory is supported by the following facts:

- (i) Rust analysis shows the presence of ferrous. and ferric carbonates alongwith hydrated ferric oxide.
- (ii) Retardation of rusting in presence of added lime or NaOH to the water in which iron is immersed.

Electrochemical or Wet corrosion theory :

It takes place under moist or wet conditions through the formation of short circuited galvanic cells. Electrochernical or wet corrosion is more common than dry corrosion. Electrochemical corrosion involves:

- (i) Separate 'anodic' and 'cathodic' areas between which current through the conducting medium.
- (ii) Occurrance of oxidation (corrosion) at anodic areas which generates metallic ions,
- (iii) Non-metallic ions like OH- or O²⁻ are formed at cathodic areas, and
- (iv) Diffusion of metallic and non-metallic ions towards each other through conducting medium and formation of corrosion product somewhere between anodic and cathodic areas.

For example:

- Rusting of iron in neutral aqueous solution of electrolyte in the presence of oxygen or in acidic environment with evolution of hydrogen.
- Fe²⁺ ion originates at anode and OH- ions originate from cathode. Smaller Fe²⁺ ions diffuse more rapidly than the larger OH- ions, so corrosion occurs at the anode, but corrosion product rust deposited near cathode.

The electrons released at anode are conducted to the cathode and are responsible for various cathodic reactions like

(i) Hydrogen evolution: In absence of O_2

(a) In acidic medium: $2H^+ + 2e^ H_2$ (b) In neutral or alkaline medium:

 $2H_2O + 2e^ H_2 + 2OH^{-tim}$