Course Title: Chemistry-ll

Course Code: Sc-203

Semester: 2nd semester

Chapter Title: Metallic Corrosion

Class duration: 4 hr

Definitions

Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. In simple terminology, corrosion processes involve reaction of metals with environmental species.

Types of Corrosion

There are mainly two types of corrosion. These are:

(1)**Dry Corrosion:**

The chemical reaction between metal and gas or liquid in the absence of electrolytes is known as the dry corrosion. An electrolyte is a substance that dissociates into ions in solution or when fused, thereby becoming electrically conducting.

(2) Wet Corrosion:

If the electrolyte causing corrosion is an aqueous solution of acid, salt or alkali, it is known as the wet corrosion.

Theories of Corrosion

1. **Chemical Action Theory or Direct Corrosion:**

The direct corrosion is the simplest corrosion produced by means of a chemical attack and it includes oxidation in which the oxygen of the atmosphere combines with all or a part of the surface of material. The chemical reactions involved are as follows:

$$Fe + O + 2CO_2 + H_2O \rightarrow Fe(HCO_3)_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(i)}$$

$$2Fe(HCO_3)_2 + O \rightarrow 2Fe(OH)CO_3 + 2CO_2 + H_2O \ldots\ldots \text{(ii)}$$

$$Fe(OH)CO_3 + H_2O \rightarrow Fe(OH)_3 + CO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(iii)}$$

The combined action of oxygen, carbon dioxide and moisture on iron results into soluble ferrous bicarbonate $Fe(HCO_3)_2$ as shown by reaction (i).This ferrous bicarbonate is then oxidized to basic ferric carbonate $2Fe(OH)CO_3$ as shown by reaction (ii).

2. **Electro-Chemical Corrosion:**

According to this theory, the corrosion takes place due to chemical reaction in combination with electrolysis. It takes place at or near room temperature when the metal comes into contact with moisture or with aqueous solutions of salts, acids or bases. In electro-chemical corrosion, the cathodic and anodic regions of the metal surface are involved. The metal surface from which current leaves the electrolyte and returns to the metal is called the cathode. The cathodic area does not corrode and it remains unchanged by the corrosion attack.

Factors affecting corrosion rate

Different factors affecting the corrosion rate are as follows:

1. Diffusion: The corrosion rates of metals are affected by the diffusion of reactants to and from the metal surface. Freshly exposed bare steel surfaces will corrode at a greater rate than those covered with a compact layer of rust. The corrosion rate is also heavily controlled by the diffusion of oxygen through the water to the steel surface. In areas where oxygen diffusion is prevalent, corrosion appears to occur at faster rates.
2. Temperature: Metals corrode at faster rates at higher temperatures than at lower temperatures.
3. Conductivity: For corrosion to occur there must be a conductive medium between the two parts of the corrosion reaction. Corrosion will not occur in distilled water and the rate of corrosion will increase as the conductivity increases due to the presence of more ions in the solution. The corrosion rate of steel reaches a maximum close to the normal ionic content of sea water.
4. pH: pH of a solution also affect the corrosion depending upon the nature of the metals.

Rusting of Iron

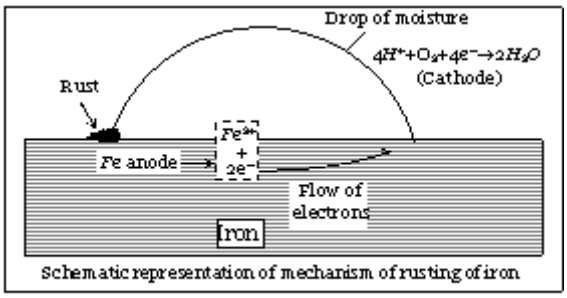
Rusting of iron refers to the formation of rust, a mixture of iron oxides, on the surface of iron objects or structures. This rust is formed from a redox reaction between oxygen and iron in an environment containing water

The overall rusting involves the following steps:

(i) Oxidation occurs at the anodes of each electrochemical cell. Therefore, at each anode neutral iron atoms are oxidised to ferrous ions.

At anode: $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$.

Thus, the metal atoms in the lattice pass into the solution as ions, leaving electrons on the metal itself. These electrons move towards the cathode region through the metal.



Schematic representation of mechanism of rusting of iron

Fig. 12.7

(ii) At the cathodes of each cell, the electrons are taken up by hydrogen ions (reduction takes place). The H^+ ions are obtained either from water or from acidic substances (e.g. CO_2) in water

$$H_2O \longrightarrow H^+ + OH^-$$

or $$CO_2 + H_2O \longrightarrow H^+ + HCO_3^-$$

At cathode:

$$H^+ + e^- \longrightarrow H$$

The hydrogen atoms on the iron surface reduce dissolved oxygen.

$$4H + O_2 \longrightarrow 2H_2O$$

Therefore, the overall reaction at cathode of different electrochemical cells may be written as,

$$4H^+ + O_2 + 4e^- \longrightarrow 2H_2O$$

(iii) The overall redox reaction may be written by multiplying reaction at anode by 2 and adding reaction at cathode to equalise number of electrons lost and gained i.e.

Oxidation half reaction: $Fe(s) \rightarrow Fe^{3+}(aq) + 2e^{-}] \times 2 \quad (E = -0.44V)$

Reduction half reaction: $4H^{+} + O_2 + 4e^{-} \rightarrow 2H_2O \quad (E = 1.23V)$

Overall cell reaction: $2Fe(s) + 4H^{+} + O_2 \rightarrow 2Fe^{3+}(aq) + 2H_2O$

Methods of corrosion control

The following methods are used to protect metals against corrosion:

I. Surface coating: The structure is coated with a layer of other metal which may be more noble than the structure or less noble than it, e.g. steel structures can be coated with copper which is more noble than steel or zinc which is less noble.

II. Inhibitors: Corrosion inhibitors are substances that are added in small amount (e.g 0.1%) to the corrosive medium stop or slow down electrochemical corrosion reactions on a metal surface.

III. Proper equipment design: The equipments should be designed in such a way that less surface of it is exposed for corrosion.

IV. Electrical protection: Electric protection is a method to reduce corrosion by minimizing the difference in potential between anode and cathode. This is achieved by applying a current to the structure to be protected from some outside source.