2 Electrochemical Aspect of corrosion

Corrosion is a result of two or more electrochemical reactions carried out on two electrode immersed in electrolyte producing what is called a (Galvanic Cell).

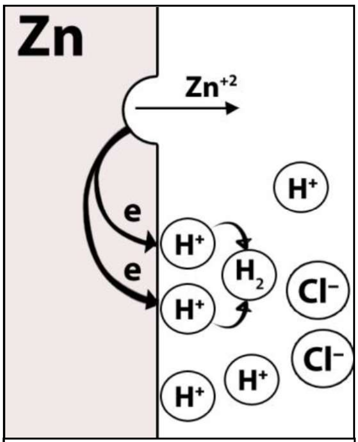
- The electrode at which chemical oxidation occurs is called (Anode).
- The electrode at which chemical reduction occurs is called (Cathode).
- The electrochemical nature of corrosion can be shown by the attack of zinc (Zn) by Hydrochloric acid (HCl).

$Zn + 2\ HCl \rightarrow ZnCl_2 + H_2$ …….. (1)

This equation can written in a simple form

$Zn + 2\ H^+ \rightarrow Zn^{+2} + H_2\uparrow$ …….. (2)

Hydrogen gas is evolved and zinc dissolved forming a solution of zinc chloride (ZnCl).



Electrochemical reaction occurring during corrosion of zink in air free hydrochloric

- Zinc is oxidized to zinc ions and hydrogen ions are reduced to hydrogen. Equation(2) is divided into two reactions the oxidation of zinc and the reduction of hydrogen ions :

$Zn \rightarrow Zn^{+2} + 2e$ :: Oxidation, Anodic reaction ::

$2\ H^+ + 2e \rightarrow H_2$ :: Reduction, Cathodic reaction ::

- An Oxidation or Anodic reaction → increase in valance or a production of electron.
- Reduction or Cathodic reaction → decrease in valance charge or the consumption of electrons.

:: NOTES ::
During metallic corrosion the rate of oxidation equals the rate of reduction in terms of electron production and consumption.

- Iron (Fe) and aluminum, like zinc (Zn) are also rapidly corroded by hydrochloric acid (HCl). The reaction are :

$Fe + 2\ HCl \rightarrow FeCl_2 + H_2\uparrow$ …..(5)

$2\ Al + 6\ HCl \rightarrow 2\ AlCl_3 + 3\ H_2\uparrow$ …..(6)

$Zn \rightarrow Zn^{+2} + 2e$ ….. (3)

$Fe \rightarrow Fe^{+2} + 2e$ ….. (7)

$Al \rightarrow Al^{+3} + 3e$ ….. (8)

The general equation of these reactions is $M \rightarrow M^{+n} + ne$ (Oxidation reaction)

$2\ H^+ + 2e \rightarrow H_2\uparrow$ (Reduction reaction)

- **Example (2) :**

  Iron (Fe) is immersed in water (H_2O) write the anodic and cathodic reactions ?

:: Solution ::

The anodic reaction is:

$Fe \rightarrow Fe^{+2} + 2e$

Since the medium is exposed to the atmosphere, it contains dissolved oxygen, water and sea water are nearly neutral and thus the cathodic reaction is:

$O_2 + 2\,H_2O + 4e \rightarrow 4\,OH^-$

$2Fe + 2\,H_2O + O_2 \rightarrow 2\,Fe^{+2} + 4\,OH^- \rightarrow 2\,Fe(OH)_2\downarrow$

$Fe(OH)_2$ precipitates from solution and is unstable and is oxidized to ferric salt ($Fe(OH)_3$) as the following reaction :

$2\,Fe(OH)_2 + H_2O + {}^1/_2\,O_2 \rightarrow 2\,Fe(OH)_3\downarrow$

:: Important – save it ::

The most common cathodic reactions are:

1- Acid free oxygen solutions : Hydrogen evolution :

   $2\,H^+ + 2e \rightarrow 2\,H_2$

2- Acid solutions contains dissolved oxygen : Oxygen reduction :

   $O_2 + 4\,H^+ + 4e \rightarrow 2\,H_2O$

3- Neutral or basic solutions (water, sea water) : Oxygen reduction :

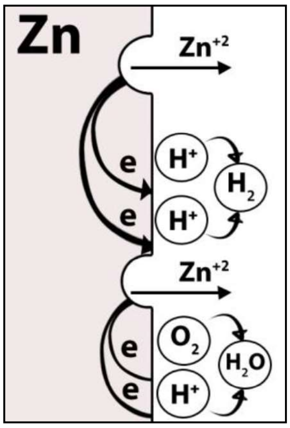
   $O_2 + 2\,H_2O + 4e \rightarrow 4\,OH^-$

4- Metal ion reduction

   $M^{+3} + e \rightarrow M^{+2}$ i.e. ($Fe^{+3} + e \rightarrow Fe^{+2}$)

All of the above reactions are similar – they consume electrons.
In general corrosion of metals usually occurs at the anode.

- Acid solution containing dissolved oxygen will be more corrosive than air-free acid because there are two cathodic reactions.
- The same effect is observed if any oxidizer is present in acid solution.



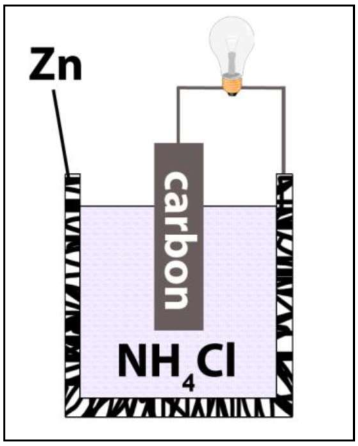
For example:

Metal corrode much more rapidly in commercial (HCl) due to the additional cathodic reaction as a result of the presence of impurities (Ferric Chloride)

$Fe^{+3} + e^- \rightarrow Fe^{+2}$

Similarly, iron will not corrode in air-free water because of no possible cathodic reaction.

The Dry – Cell :: Analog & Faraday's law :: :



Corrosion process in aqueous media is similar to that taking place in a dry cell made up of a center carbon electrode and zinc cup electrode separated by (NH_4Cl)

$Zn \rightarrow Zn^{+2} + 2\ e^-$

> The amount of zinc that corrode is directly proportional to the flow of electricity through the cell according to the Faraday's Law

Mass of reacting metal = KIt
Where :
I : Current in amperes (A).
t : Time is second.
K: Constant called electrochemical equivalent, For (Zn) $K=3.39 * 10^{-4}\ {}^{gm}/_{coulomb}$

In general a combination of two electrode immersed in an electrolyte called (Galvanic Cell).