

Types of corrosion

- Dry corrosion (chemical corrosion)
- Wet corrosion (electrochemical corrosion)

❑ Criteria for Electrochemical Corrosion

1. Formation of galvanic cells on the surface of metal generating anodic and cathodic areas.
2. Presence of conducting liquid with the formation of electrochemical cells.
3. At anode of metal surface, oxidation [Corrosion] takes place by liberating electrons.
4. At cathode, reduction [No corrosion] takes place

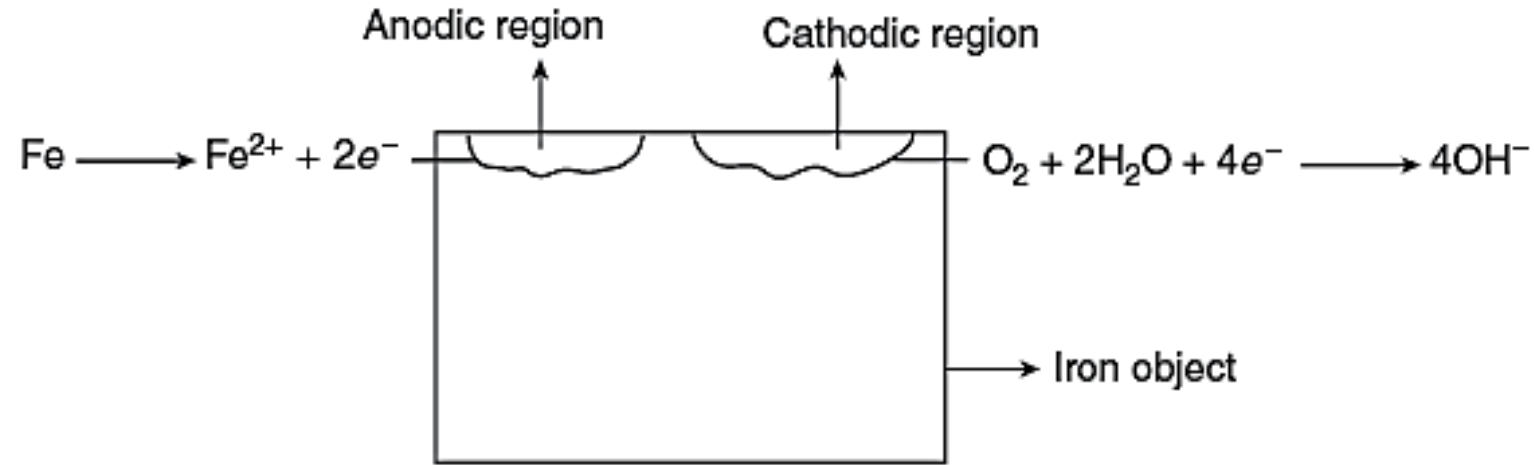
The rate of the electrochemical corrosion will depend on the solubility of the corrosion product.

- If soluble: rate of corrosion will be high
- If insoluble: rate of corrosion will be very low.

- ⇒ In wet corrosion, a **conducting liquid (electrolyte)** is in contact with a metal or two dissimilar metals or alloys are partially dipped in the electrolyte
- ⇒ It occurs when electrons from metal surface are transferred to a suitable electron acceptor or depolarizer. Generally water is present to serve as a medium for the transport of ions
- ⇒ The most common depolarizers are oxygen, acids, the cations of less active metals
- ⇒ As the electrons flow through the metallic object itself, the anodic and cathodic regions can be at widely separated locations
- ⇒ Generally, Anodic regions tend to develop at locations where the metal is stressed
- ⇒ Contact with a different kind of metal, either direct or indirect, can lead to corrosion of the more active one

⇒ based on Nernst theory

➤ According to which all metals have a tendency to pass into solution. If a metal having higher electrode potential comes into contact with another metal having a lower electrode potential, a **galvanic cell** is set up



➤ The metal having the Lower electrode (reduction) potential becomes **Anodic** and goes into solution to a measurable extent. The other becomes **Cathodic** and does not enter solution. The extent of galvanic corrosion depends upon the difference in the electrode potential of the two electrodes and their respective areas.

✓ The greater the difference in the potentials: the greater will be the corrosion.

✓ Smaller the area of anode as compared to cathode: attack will be more

Oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive & the electrons can flow through the metal from the anodic to the cathodic regions. The presence of water is necessary in order to transport ions to and from the metal

- General/Uniform corrosion
- Hydrogen evolution type corrosion
- Oxygen consumption type corrosion
- Galvanic corrosion
- Concentration cell corrosion
- Pitting corrosion
- Stress corrosion

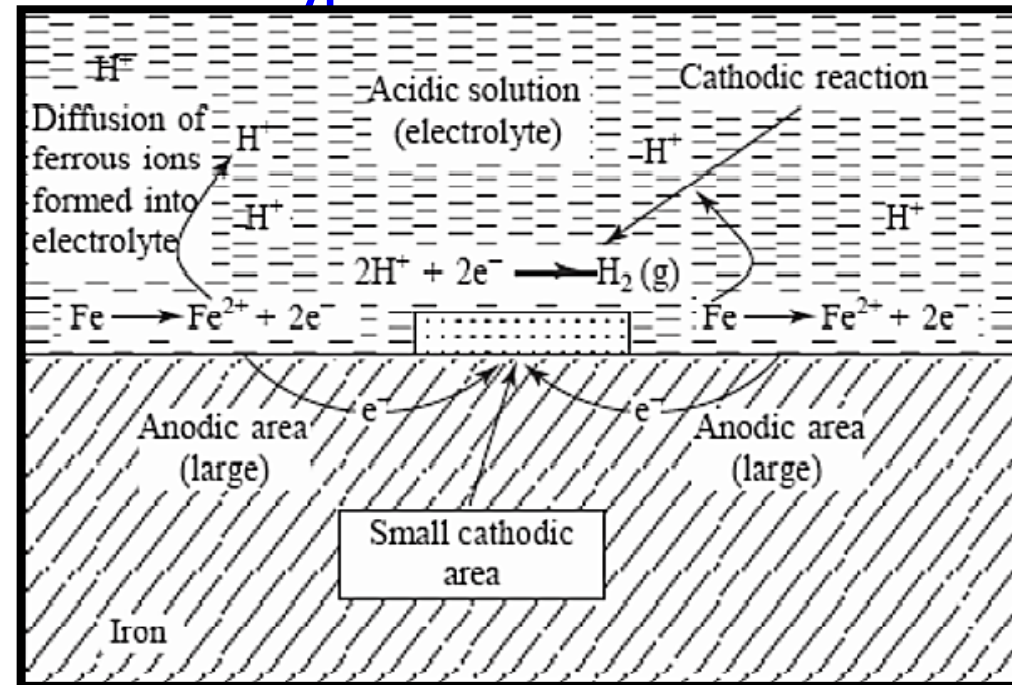
❑ Uniform Electrochemical Corrosion

- The electrochemical reactions (in aqueous or atmospheric media) proceed **uniformly over the entire exposed metal surface**.
- General corrosion represents the greatest destruction of metal. But, general corrosion is less dangerous than the other corrosion forms because the life of equipment or structures can be accurately estimated from simple corrosion tests and sometimes by visual inspection.



❑ Hydrogen evolution type corrosion

- It occurs when metals are in contact with **an acidic sol.**
- **All metals above hydrogen in electrochemical series can show this type of corrosion**



← *Rusting of iron metal in acidic env. takes place in this way*

⇒ Metal ions produced at the **anode dissolves** in the electrolyte while **hydrogen evolves** at the **cathode**.

⇒ Hence, this type of corrosion causes “displacement of H⁺ ions from the **acidic solution** by metal ions”

⇒ **Anodic areas are large & Cathodic areas are small.**

Wet or Electrochemical Corrosion

❑ Oxygen consumption type corrosion

➤ It occurs when metals are in contact with neutral solutions like water with dissolved oxygen (DO)

Rusting of iron is an example of this type of corrosion

The oxide of iron covers the surface of the iron.

The **small scratch** on the surface creates **small anodic area** and rest of the surface acts as cathodic area.

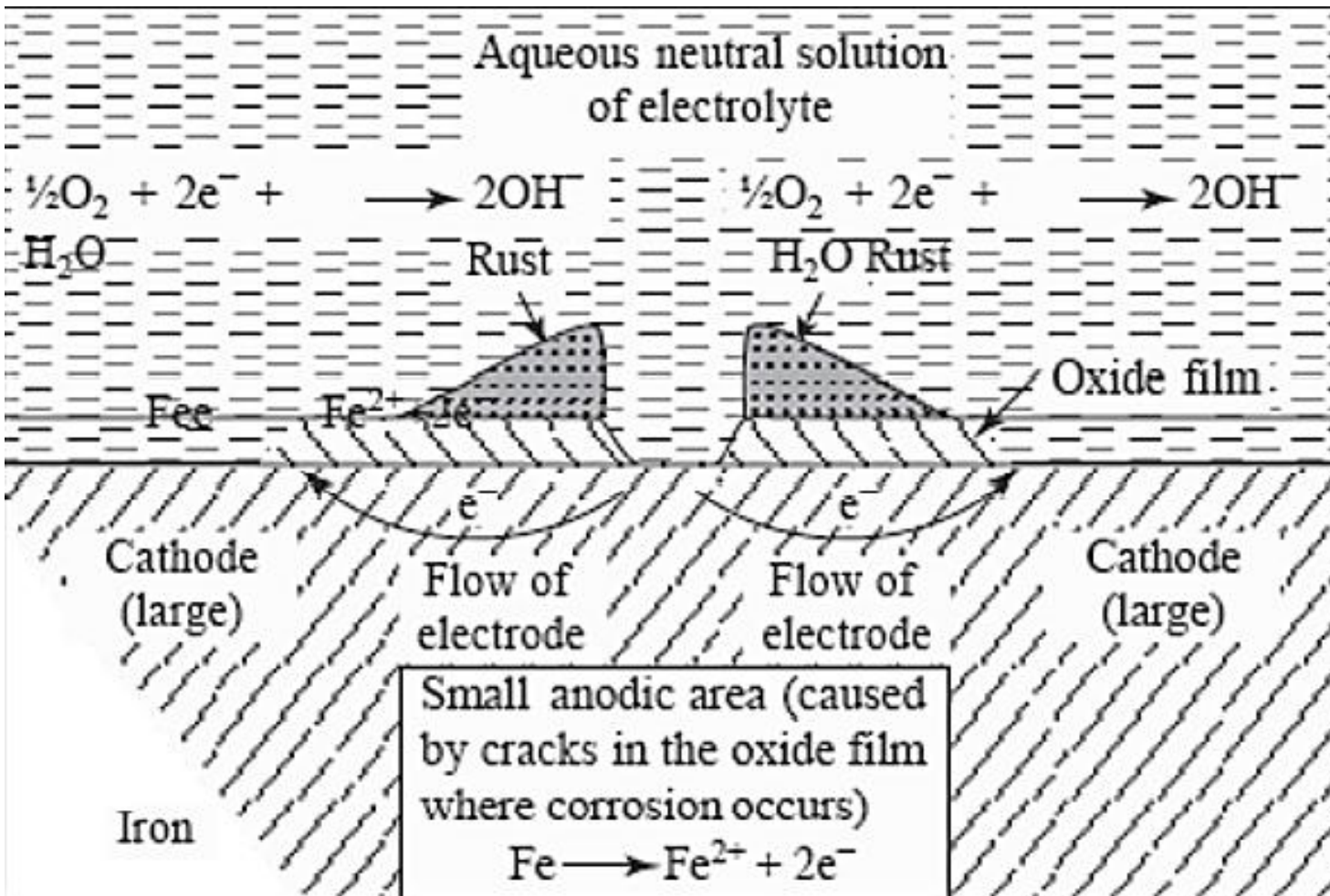
@Anode Oxidation occurs

$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$ (These electrons move from anode to cathode and react with the electrolyte and oxygen giving)

@Cathode Reduction occurs



The Fe^{2+} at the anode and OH^- at the cathode diffuse and react to produce $\text{Fe}(\text{OH})_2$ which gets further oxidized to $\text{Fe}(\text{OH})_3$ (rust).



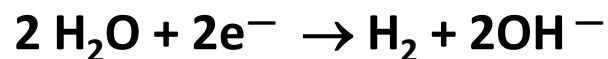
❑ The reactions involved with Fe are as follows:

- **Anodic reaction:** Metal undergoes oxidation (corrosion) with positive release of electrons: $\text{Fe} \rightarrow \text{Fe}^{+2} + 2\text{e}^-$
- **Cathodic reactions:** These reactions are dependent on the constituents of the corrosion medium.

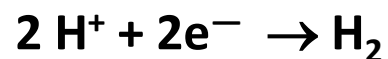
If the solution is aerated and almost neutral, **oxygen is reduced in presence of H_2O to OH^- ions.**



If the solution is de-aerated and almost neutral, **H_2 is liberated along with OH^- ions.**



If the solution is de-aerated and acidic, **H^+ ions are reduced to hydrogen gas.**



❑ Galvanic corrosion or Differential metal corrosion/Bi-Metallic Corrosion

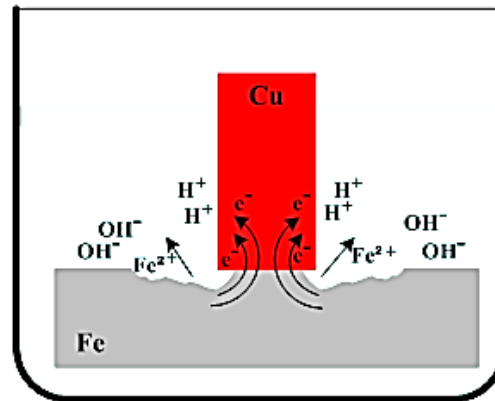
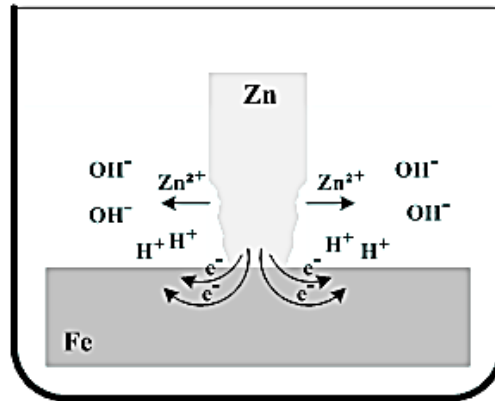
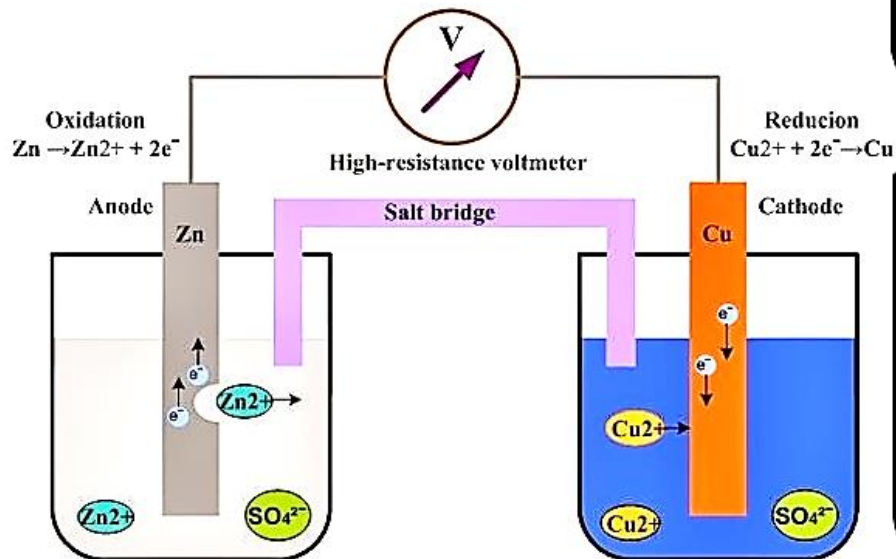
- Galvanic corrosion occurs when two different metals are located together in a corrosive electrolyte
- A **galvanic couple forms between the two metals**, where one metal becomes the anode and the other the cathode
- Metal with **lower reduction potential (anode)** undergoes oxidation and the metal with **higher reduction potential (cathode)** undergoes reduction
- **The anode or sacrificial metal**, corrodes and deteriorates faster than it would alone, while the cathode deteriorates more slowly than it would otherwise
- **Anodic area** always undergoes corrosion and **cathodic area** remains unaffected
- Galvanic corrosion can only occur when **there exists an electric conducting path** connecting the metals, eg., an electrolyte

❑ **Three conditions** must exist for galvanic corrosion to occur:

- Presence of electrochemically dissimilar metals
- The metals must be in electrical contact, &
- The metals must be exposed to an electrolyte

A metal placed low in the electrochemical series is said to be anodic to the one placed above it

Galvanic cell



Electrochemical series

Electrode	Electrode reaction	E^0/V
Au Gold	$\text{Au}^{3+} + 3\text{e}^- \rightleftharpoons \text{Au}$	+1.43
Ag Silver	$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$	+0.80
Cu Copper	$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$	+0.34
H Hydrogen	$\text{H}^+ + \text{e}^- \rightleftharpoons \text{H}$	0
Pb Lead	$\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$	-0.13
Sn Tin	$\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}$	-0.14
Ni Nickel	$\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni}$	-0.25
Cd Cadmium	$\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}$	-0.40
Fe Iron	$\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$	-0.44
Zn Zinc	$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-0.76
Ti Titanium	$\text{Ti}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ti}$	-1.63
Al Aluminium	$\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}$	-1.66
Mg Magnesium	$\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}$	-2.37
Na Sodium	$\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na}$	-2.71
K Potassium	$\text{K}^+ + \text{e}^- \rightleftharpoons \text{K}$	-2.93
Li Lithium	$\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}$	-3.05

Cathodic
(least active)

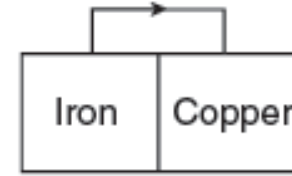
(most active)
Anodic

Electrochemical series

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Cathodic
(least active)

(most active)
Anodic

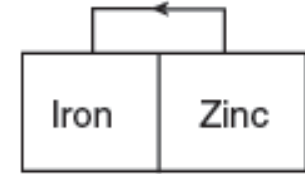


Bimetallic couple of iron and copper.

➤ Fe is anodic to Cu, Ni and Sn

When Zn is dipped in 1N H_2SO_4 , the rate of corrosion is quite slow. But, addition of Cu the rate of corrosion increases significantly.

In Zn-Cu, Zn acts as anode & Cu acts as cathode



Bimetallic couple of iron and zinc.

➤ Fe is **cathodic** to Zn, Mg

Other examples of **Galvanic corrosion**:

1. Buried iron pipeline connected to zinc bar.
2. Steel pipe connected to copper plumbing.
3. Steel propeller shaft in bronze bearing.
4. Zinc coating on mild steel.
5. Lead-tin solder around copper wires.