



1.The standard reduction electrode potential of copper is 0.34 V and the concentration of Cu²⁺ ion is 0.015 M. If the electrode is connected with SHE, find its (i) reduction electrode potential (ii) free energy change of electrode reaction.

2.The EMF of the cell Cd | Cd²⁺ (0.01 M) ||Cu²⁺ (0.5 M)|Cu is 0.79V. Determine the standard electrode potential of Cd electrode, if the standard electrode potential of copper is 0.34 V.

3.Consider an electrochemical cell Mg | Mg²⁺ ||Cd²⁺ |Cd, calculate the voltage of the cell at 25 °C, when [Cd²⁺] = 7x 10⁻¹¹ M and [Mg²⁺] = 1 M. Standard electrode potential of the cell = 1.97 V

4.The E⁰ values of Li/Li⁺, Zn/Zn²⁺, Cu/Cu²⁺, and Ag/Ag⁺ are -3.0 V, -0.77 V, 0.33 V, 0.80 V Respectively. Which Combination of the electrodes will you use to construct a cell of highest emf if the ionic concentrations are 0.1 M, 1M, 10 M and 0.01 M, in the same order. Justify your answer.

5.Consider a concentration cell Cd | Cd²⁺ (0.001 M) ||Ag⁺ (0.01 M)|Ag. Find the EMF of the cell.

6.Calculate the equilibrium constant between silver nitrate and metallic zinc. The standard electrode potential of the cell is 1.56 V. **Ans: 6.192x10⁵²**

1.The standard reduction electrode potential of copper is 0.34 V and the concentration of Cu²⁺ ion is 0.015 M. If the electrode is connected with SHE, find its (i) reduction electrode potential (ii) free energy change of electrode reaction. **Ans: (i) 0.286V, (ii) -55 KJ**

2.The EMF of the cell Cd | Cd²⁺ (0.01 M) ||Cu²⁺ (0.5 M)|Cu is 0.79V. Determine the standard electrode potential of Cd electrode, if the standard electrode potential of copper is 0.34 V. **Ans: -0.4 V**

3.Consider an electrochemical cell Mg | Mg²⁺ ||Cd²⁺ |Cd, calculate the voltage of the cell at 25 °C, when [Cd²⁺] = 7x 10⁻¹¹ M and [Mg²⁺] = 1 M. Standard electrode potential of the cell = 1.97 V **ANS: 1.67 V.**

4.The E⁰ values of Li/Li⁺, Zn/Zn²⁺, Cu/Cu²⁺, and Ag/Ag⁺ are -3.0 V, -0.77 V, 0.33 V, 0.80 V Respectively. Which Combination of the electrodes will you use to construct a cell of highest emf if the cells are at 25 °C and concentrations of the electrolytes are in 1 M.

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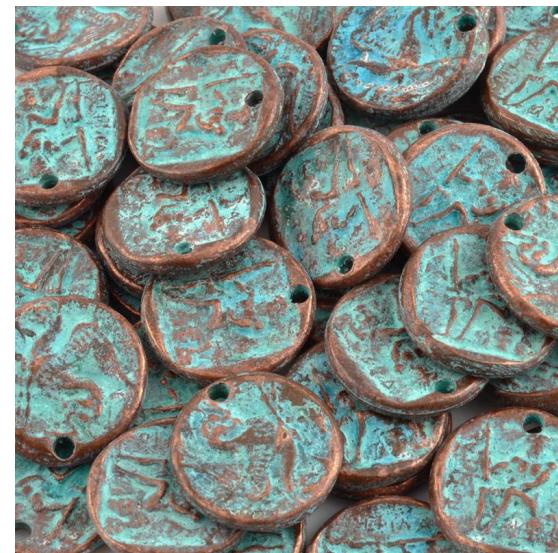
6.Consider a concentration cell Cd | Cd²⁺ (0.001 M) ||Ag⁺ (0.01 M)|Ag. Find the EMF of the cell. **ANS: 0.0591**

7.Calculate the equilibrium constant between silver nitrate and metallic zinc. The standard electrode potential of the cell is 1.56 V. **Ans: 6.192x10⁵²**

Corrosion



Patina

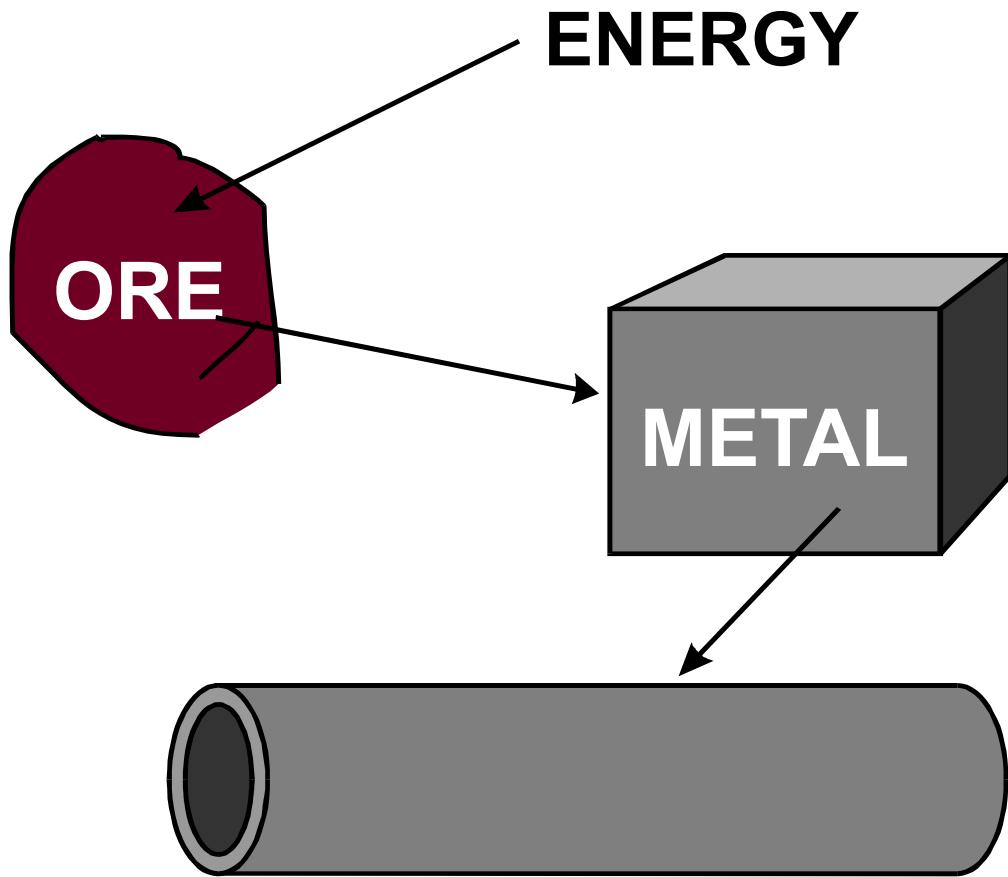
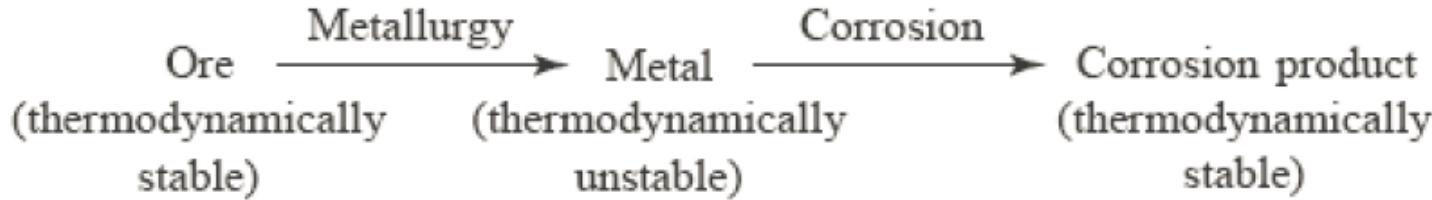


Corrosion

- Corrosion is the **deterioration or destruction** and consequent loss of a solid metallic material due to chemical, electrochemical and other reactions of the **exposed material surface** with the **surrounding environment**.
- Corrosion represents a return of metals to their more natural state as minerals (oxides).
- Deterioration of metals through **oxidation**- usually but not always- to their oxides.
- For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a *patina*.

Corrosion

Why are metals not found in their free state?

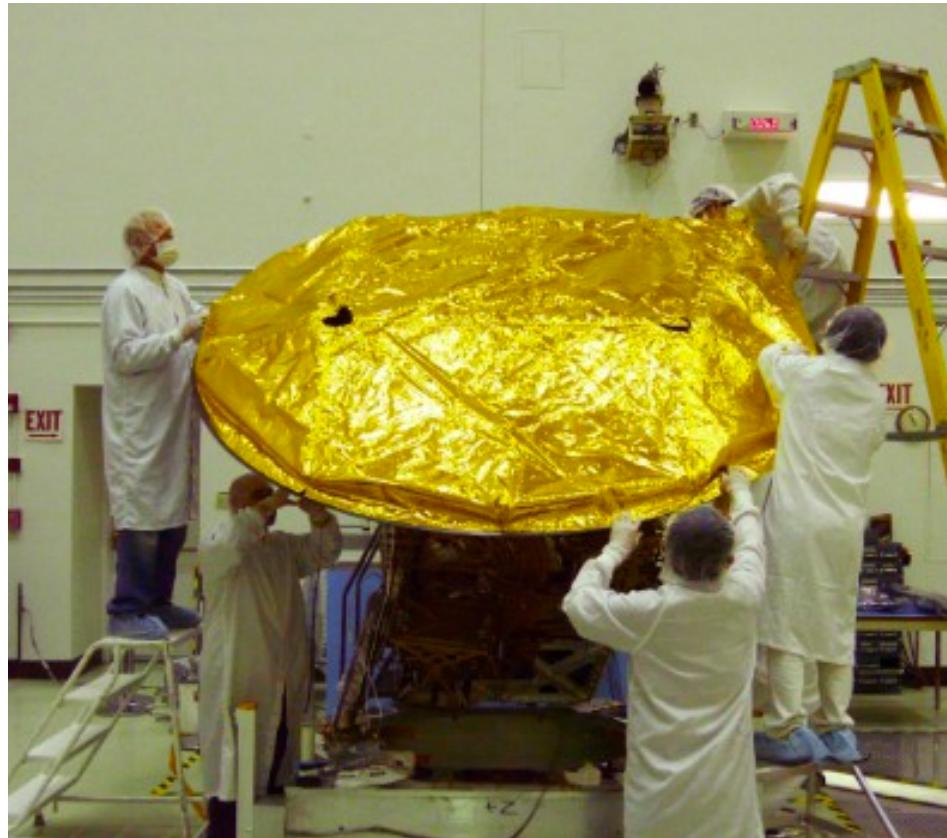


Element	Element Ore	Formula
Aluminium	•Bauxite •Cryolite •Corundum	• $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ • Na_3AlF_6 • Al_2O_3
Zinc	•Zinc blende •Calamine •Zincite	• ZnS • ZnCO_3 • ZnO
Iron	•Haematite •Magnetite •Iron Pyrites •Spathic Iron Ore	• FeO_3 • Fe_3O_4 • FeS_2 • FeCO_3
Copper	•Malachite •Chalcopyrite •Copper Glance	• $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ • CuFeS_2 • Cu_2S
Tin	•Tin Pyrites •Cassiterite	• $\text{Cu}_2\text{FeSnS}_4$ • SnO_2
Silver	Silver Glance	• Ag_2S

Why do metals undergo corrosion?

	Reduction Half-Reaction	E° (V)	
Stronger oxidizing agent	$\text{F}_2(g) + 2 \text{e}^- \rightarrow 2 \text{F}^-(aq)$	2.87	Weaker reducing agent
	$\text{H}_2\text{O}_2(aq) + 2 \text{H}^+(aq) + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(l)$	1.78	
	$\text{MnO}_4^-(aq) + 8 \text{H}^+(aq) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(aq) + 4 \text{H}_2\text{O}(l)$	1.51	
	$\text{Cl}_2(g) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(aq)$	1.36	
	$\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^+(aq) + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O}(l)$	1.33	
	$\text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(l)$	1.23	
	$\text{Br}_2(aq) + 2 \text{e}^- \rightarrow 2 \text{Br}^-(aq)$	1.09	
	$\text{Ag}^+(aq) + \text{e}^- \rightarrow \text{Ag}(s)$	0.80	
	$\text{Fe}^{3+}(aq) + \text{e}^- \rightarrow \text{Fe}^{2+}(aq)$	0.77	
	$\text{O}_2(g) + 2 \text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2(aq)$	0.70	
	$\text{I}_2(s) + 2 \text{e}^- \rightarrow 2 \text{I}^-(aq)$	0.54	
	$\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 \text{e}^- \rightarrow 4 \text{OH}^-(aq)$	0.40	
	$\text{Cu}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Cu}(s)$	0.34	
	$\text{Sn}^{4+}(aq) + 2 \text{e}^- \rightarrow \text{Sn}^{2+}(aq)$	0.15	
	$2 \text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{H}_2(g)$	0	
Weaker oxidizing agent	$\text{Pb}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Pb}(s)$	-0.13	Stronger reducing agent
	$\text{Ni}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Ni}(s)$	-0.26	
	$\text{Cd}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Cd}(s)$	-0.40	
	$\text{Fe}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Fe}(s)$	-0.45	
	$\text{Zn}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Zn}(s)$	-0.76	
	$2 \text{H}_2\text{O}(l) + 2 \text{e}^- \rightarrow \text{H}_2(g) + 2 \text{OH}^-(aq)$	-0.83	
	$\text{Al}^{3+}(aq) + 3 \text{e}^- \rightarrow \text{Al}(s)$	-1.66	
	$\text{Mg}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Mg}(s)$	-2.37	
	$\text{Na}^+(aq) + \text{e}^- \rightarrow \text{Na}(s)$	-2.71	
	$\text{Li}^+(aq) + \text{e}^- \rightarrow \text{Li}(s)$	-3.04	

Why most metals undergo corrosion but not Au, Ag and Pt.

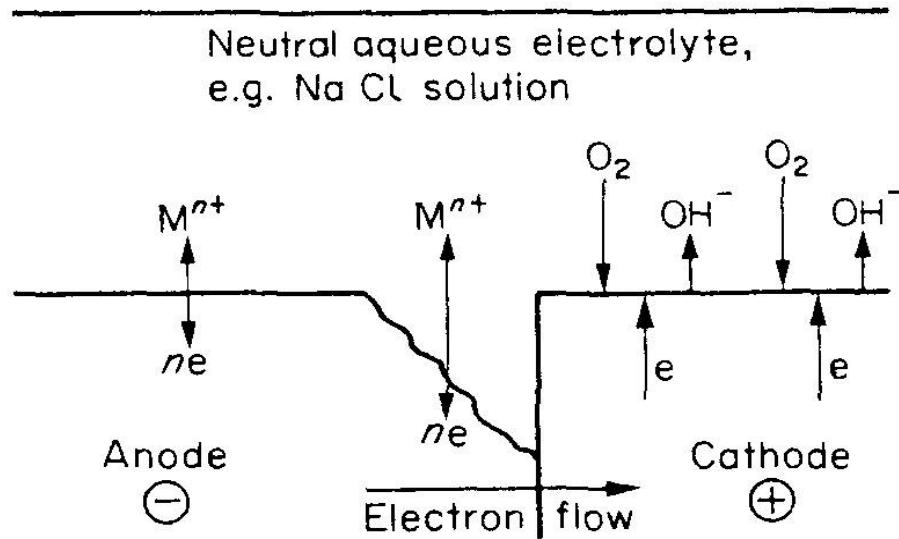


Consequences of Corrosion

- ✓ Due to formation of corrosion product over the machinery, the **efficiency of the machine gets lost.**
- ✓ The **products are contaminated** due to corrosion.
- ✓ The corroded equipment must be replaced frequently.
- ✓ **Plant failure** due to corrosion.
- ✓ Corrosion **releases toxic products**, health hazard, etc.

Basics of Corrosion

Corrosion is essentially the oxidation of metal

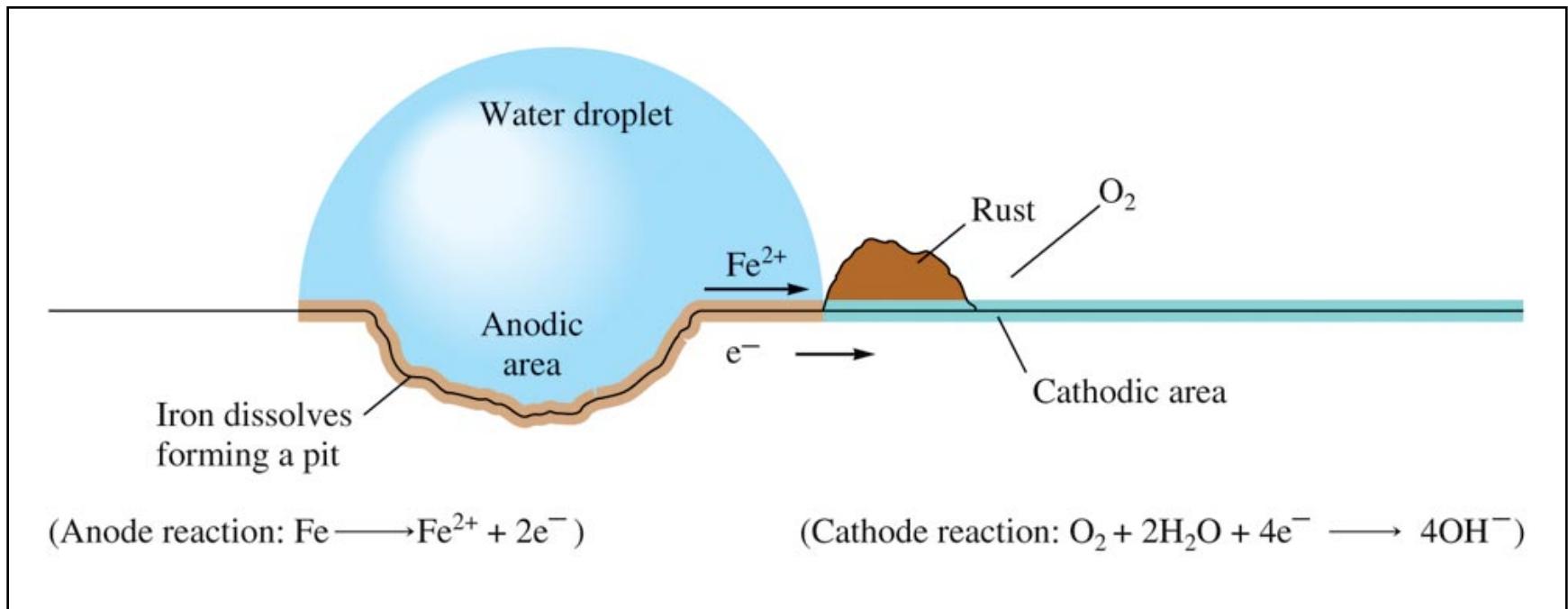


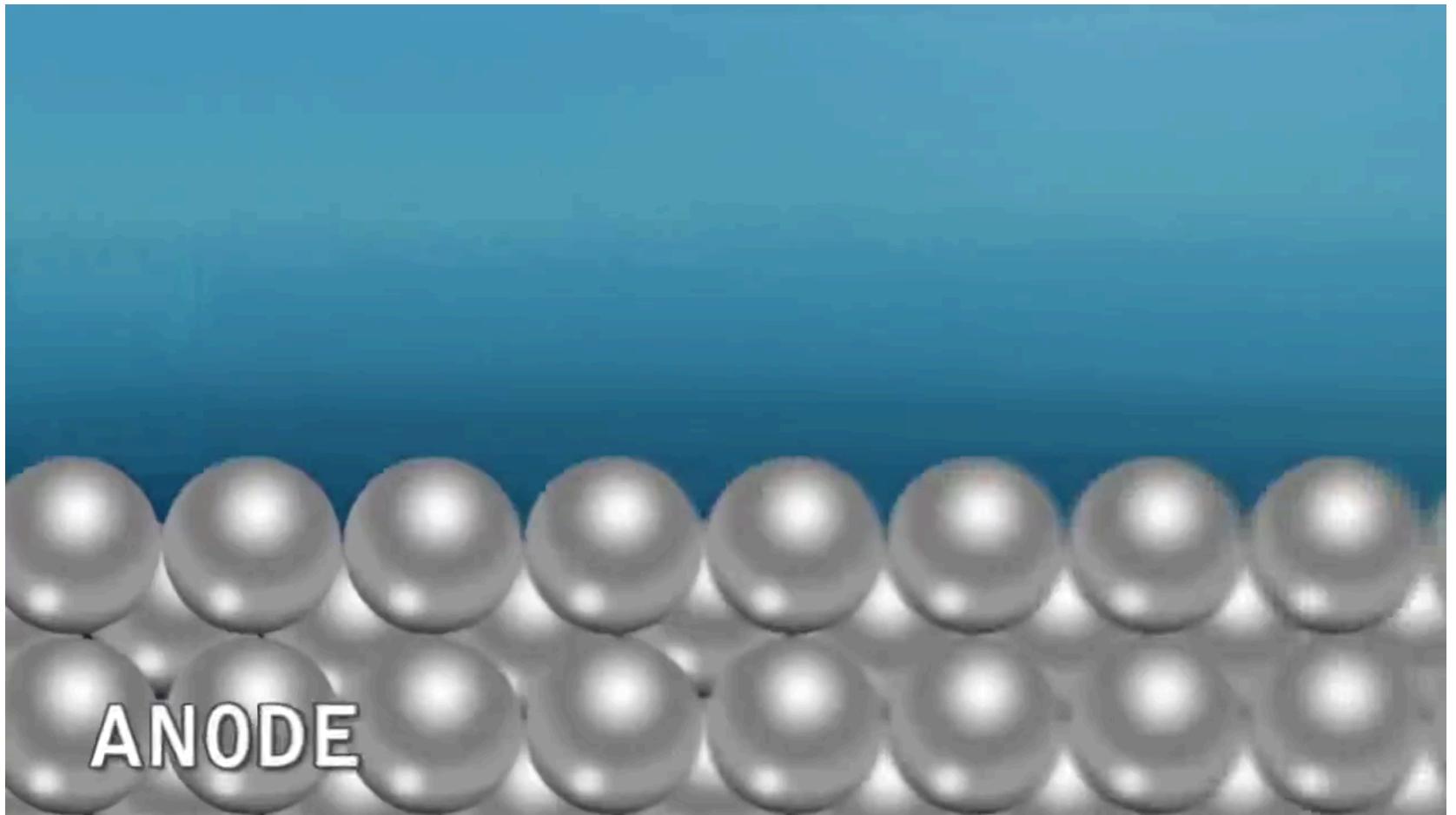
Need:

1. An Anode (where oxidation is taking place)
2. A Cathode (where reduction is taking place)
3. Conductive electrolyte
4. Electrical contact between the Anode and Cathode

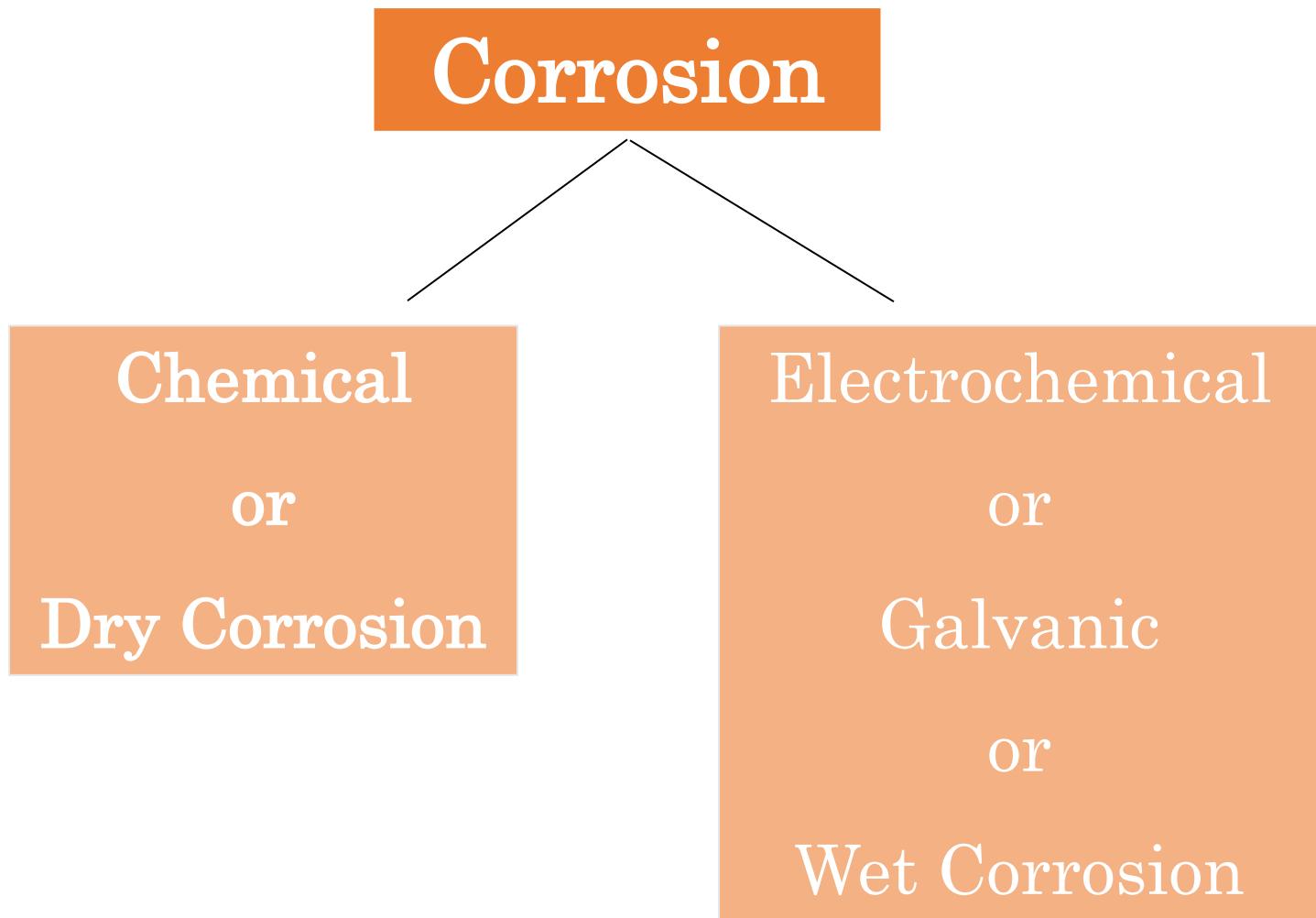
Basics of Corrosion

Corrosion is essentially the oxidation of metal





Different Theories of Corrosion



Activity

H_2O



NaCl
 H_2O



oil
boiled H_2O



CaCl_2



Dry or Chemical corrosion

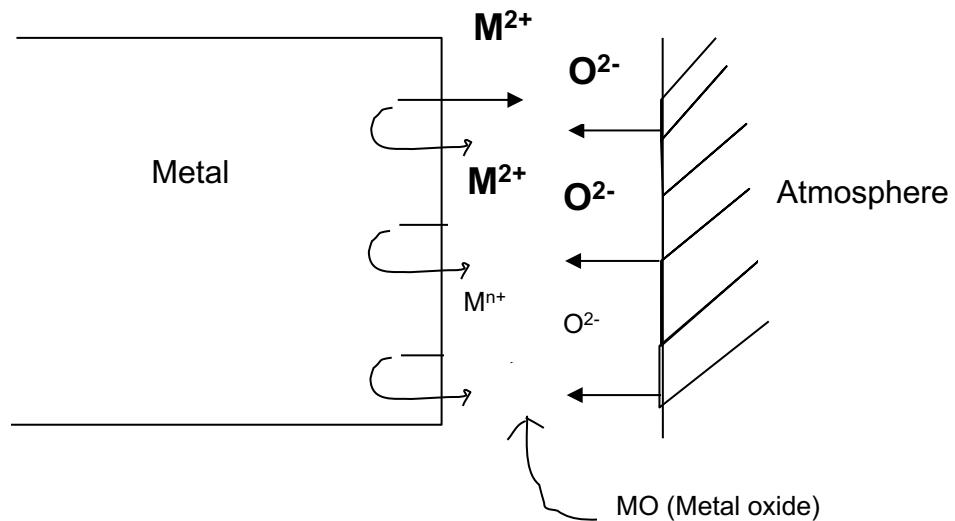
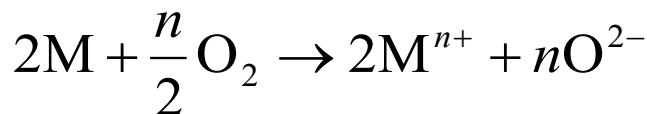
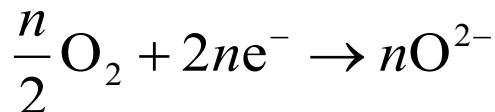
Dry corrosion is due to the attack of metal surfaces by the **atmospheric gases** such as oxygen, hydrogen sulphide, sulphur dioxide, nitrogen, inorganic liquids etc.

There are three (sub-classification) main types of dry corrosion;

1. Oxidation corrosion (or) corrosion by oxygen
2. Corrosion by other gases
3. Liquid – Metal corrosion.

Oxidation Corrosion

- Oxidation corrosion is brought about by the direct attack of oxygen at low or high temperatures on metal surface **in the absence of moisture**.
- Alkali metals like (Li, Na, K, etc) and alkaline-earth metals (Mg, Ca, Sr, etc) are rapidly oxidized at low temperature.
- At high temperature, almost all metals (expect Ag, Au and Pt) are oxidized.



Oxidation Corrosion

The nature of oxide film formed on the metal surface plays an important role in oxidation corrosion.

- **Stable oxide layer:** a protective coating and no further corrosion can occur.
Example: Al, Sn, Pb etc.
- **Unstable oxide layer:** mainly produced on the surface of noble metals, which decomposes back to the metal and oxygen.
Example: Pt, Ag, etc.
- **Volatile oxide layer:** The oxide layer volatilizes as soon as it is formed, leaving the metal surface for further corrosion.
Example: Molybdenum oxide.
- **Porous oxide layer:** Metal oxides having pores and cracks allow penetration of oxygen to the underlying metal, resulting in the complete conversion of metal into its oxide.
Example: Rust

The ratio of the volume of the oxide formed to the volume of the metal consumed is called “**Pilling-Bedworth ratio**”.

$$R_{PB} = \frac{V_{Oxide}}{V_{Metal}} = \frac{M_{oxide} \times \rho_{metal}}{M_{metal} \times \rho_{oxide}}$$

1. If $R_{PB} < 1$, the oxide layer is porous and non-protective.

e.g. Oxides of alkali and alkaline earth metals

2. If $R_{PB} > 1$, the oxide layer is Protective or non-porous.

e.g. Oxides of heavy metals such as Sb, V, W, etc

3. If $R_{PB} = 1$, there will be protective oxide film formation.

e.g. Oxides of Al, Pb, Ni, Cr etc

Corrosion by Other Gases

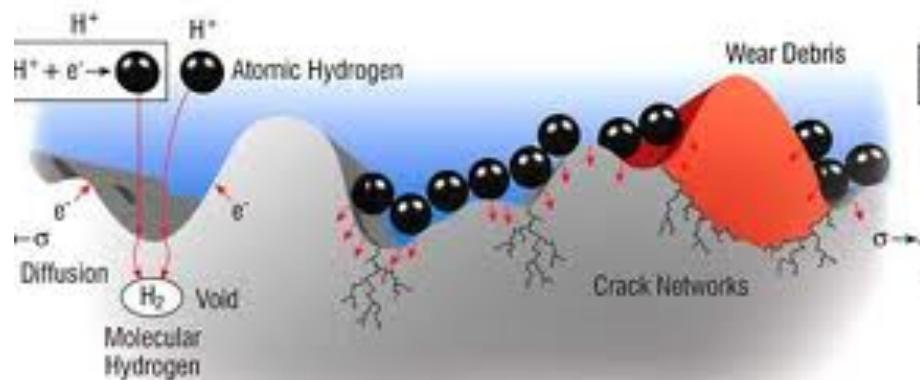
- Corrosion by other gases such as Cl_2 , SO_2 , H_2S , CO_2 , F_2 or NO_x
- The extent of corrosion depends upon the chemical affinity between metal and the gas.
- In dry atmosphere, these gases react with metal and form corrosion products which may be protective or non-protective.
- Protective: Intensity or extent of attack decreases after layer formed.
Dry Cl_2 reacts with Ag and forms AgCl
- Non-protective: Continuous Attack
 SnCl_4 is volatile

Corrosion by H₂

H₂ embrittlement (ordinary temperature)



Formation of cracks and blisters on metal surface due to high pressure of H₂ gas



Hydrogen Blistering
Concentration of hydrogen in void increases, pressure also increases cracking.

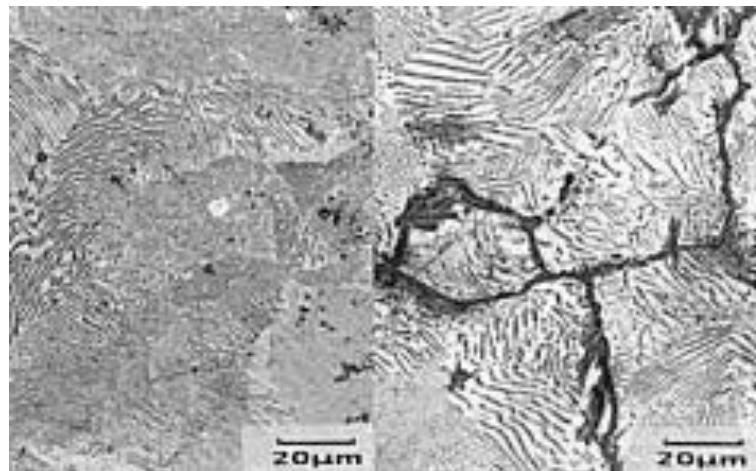
Hydrogen Embrittlement
After penetration, atomic hydrogen reacts to form brittle compounds and increases cracking.



Decarburization (high temp)



The process of decrease in carbon content in steel is termed as decarburization of steel



Liquid- Metal Corrosion

This is due to the chemical action of flowing liquid metal at high temperature on the surface of another metal.

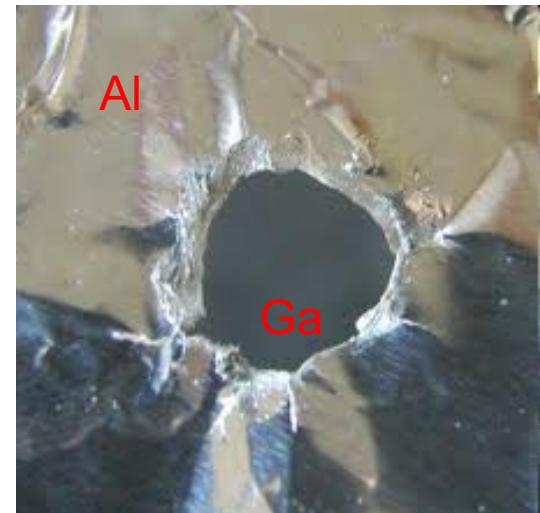
The corrosion reaction involves

- Dissolution of a solid metal by a liquid metal
- Liquid metal may penetrate in to the solid metal.



Solid metal base

Liquid metal



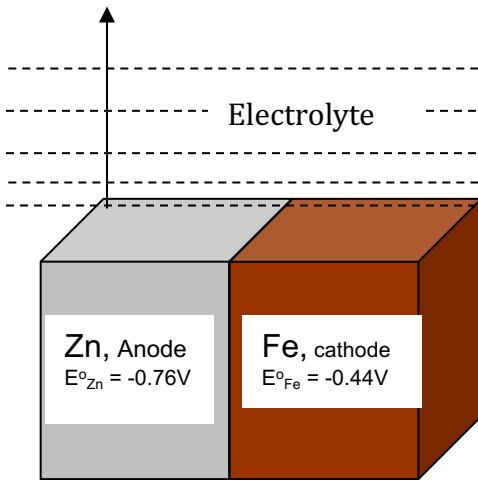
Gallium is corrosive
to Aluminium

Wet or Electrochemical Corrosion

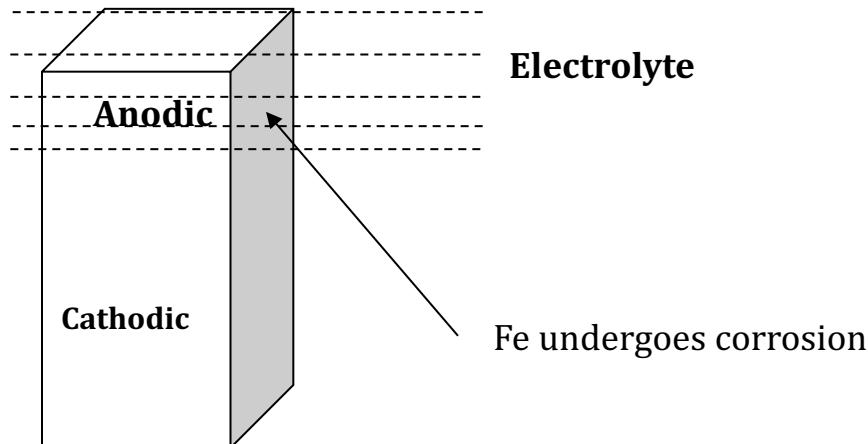
Wet corrosion occurs under the following conditions,

- When **two dissimilar metals** are in contact with each other in the presence of an **aqueous solution or moisture**.
- When conducting liquid is in contact with metal.

Zn undergoes corrosion



Electrolyte



Wet or Electrochemical Corrosion

When one part of the metal acts as anode and the other as cathode and corrosion occurs and the following electrochemical reactions occur.

At anode: oxidation or dissolution of metal takes place at this electrode releasing electrons



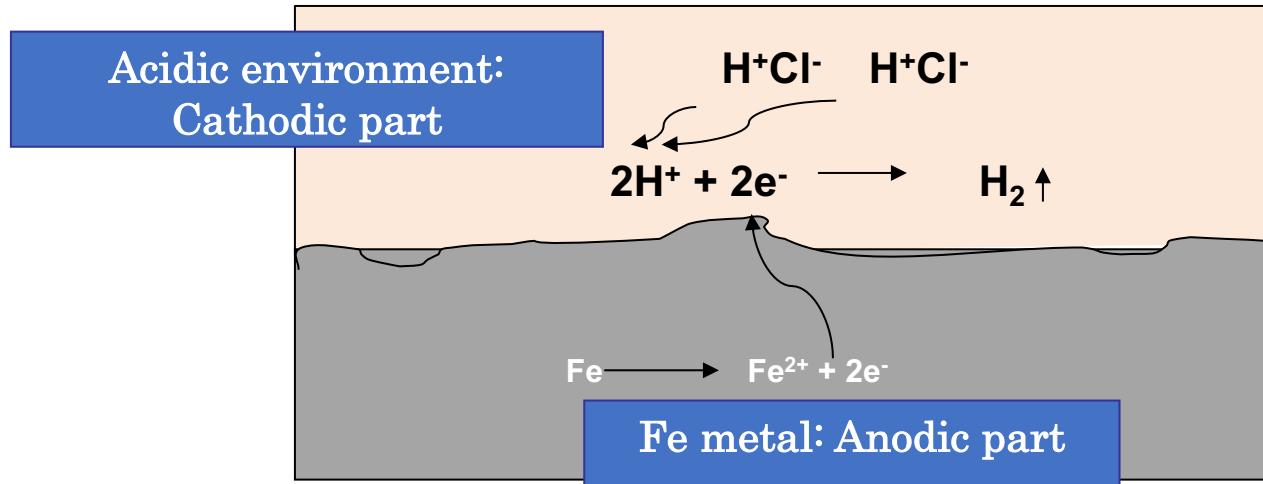
At cathode: Reduction takes place using the electrons released at the anode.

Depends on the nature of the corrosive environment.

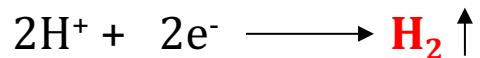
- Hydrogen evolution type corrosion (**Acidic solutions**)
- Hydroxide ion formation corrosion (**Neutral/alkaline medium**)

H₂ evolution corrosion

If the corrosive environment is acidic in nature, hydrogen gas is evolved

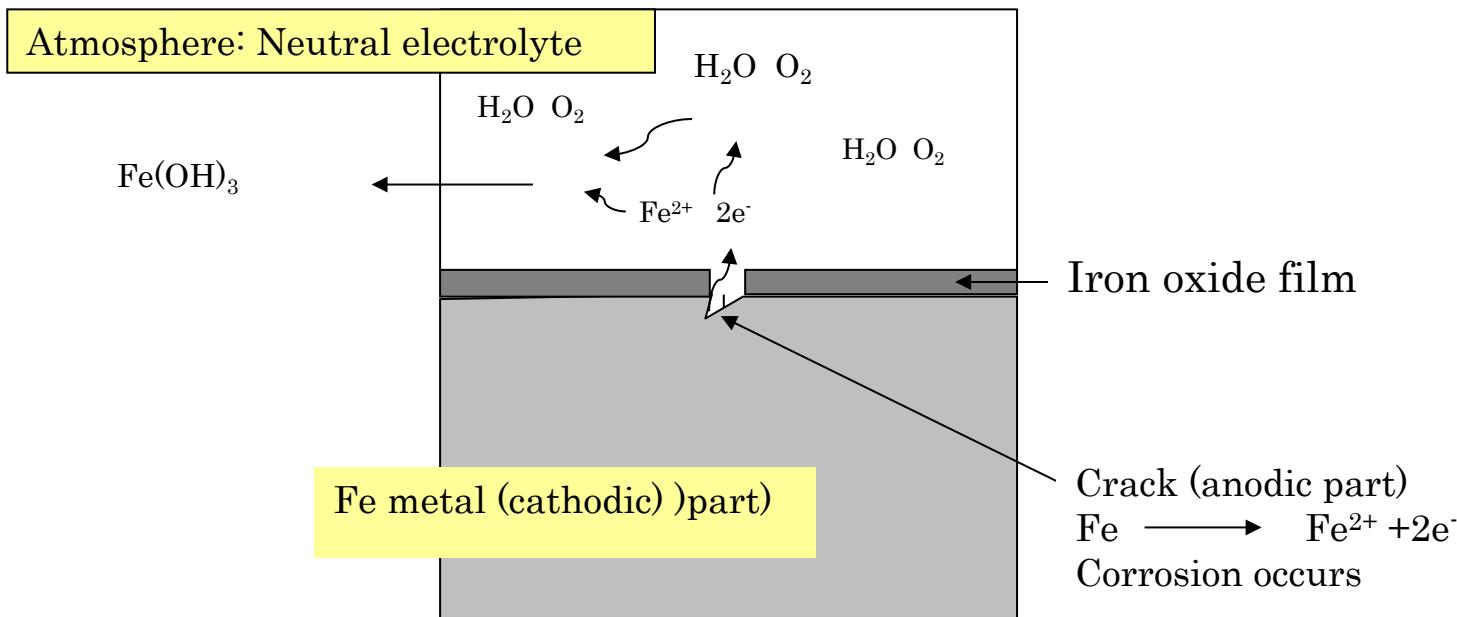
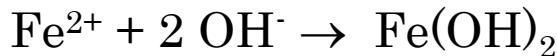
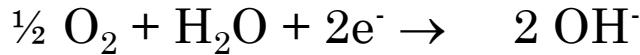


As per the following reaction occurring at the cathode



Formation of OH⁻ Type Corrosion

- **Anode:** Fe undergoes dissolution to Fe²⁺ with the liberation of electrons.
- **Cathode:** Liberated electrons follow from anode to cathode, where dissolved O₂ is consumed to form OH⁻ ions.



Examples for Wet corrosion – Types/Forms

Electrochemical Corrosion

Localized

- Pitting
- Stress Corrosion
- Waterline Corrosion
- Concentration Corrosion
- Inter-granular Corrosion
- Fatigue Corrosion

Differential Metallic or
Bimetallic

Galvanic

More negative electrode
potential act as an anode

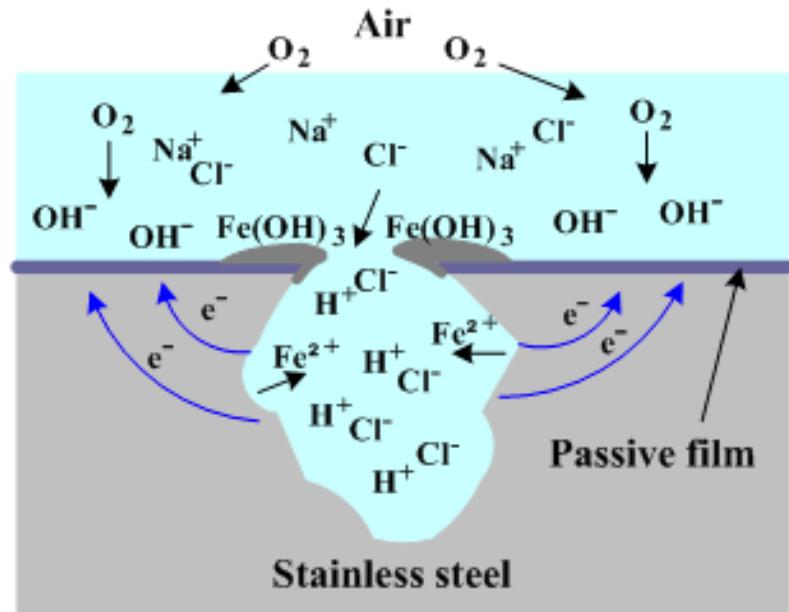
Inter-granular corrosion

- Metals and alloys have micro-structures that are made up of grains, and these grains have boundaries. Intergranular corrosion is an attack along or near the boundaries of several grains while the rest of the grain remains unaffected. This type of attack is caused by local differences in composition.
- When it is severe it causes loss of strength and ductility.



Pitting corrosion

- Pitting occurs when there is a break in the protective oxide layer and imperfections on the underlying metal.
- Caused by localized mechanical damage, chemical damage to a metal's oxide film, or poor application of protective coating.
- "Pits" or "holes" range from deep cavities of small diameter to shallow depressions.

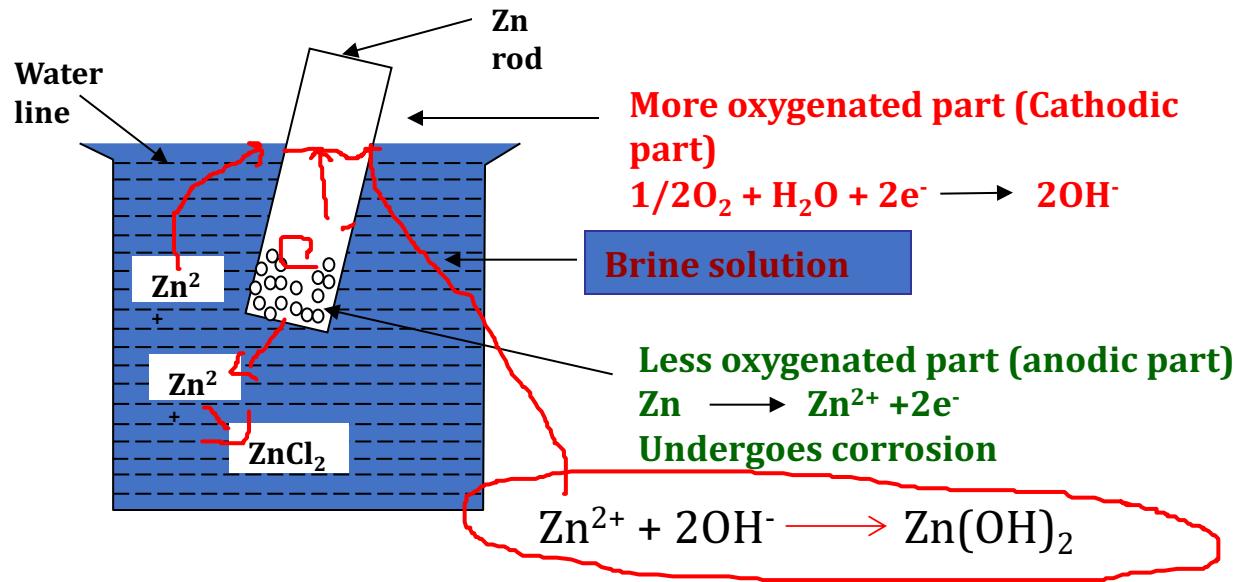


Waterline corrosion

- Occurs when a metal is exposed to varying concentration of oxygen or any electrolyte on the surface of the base metal.

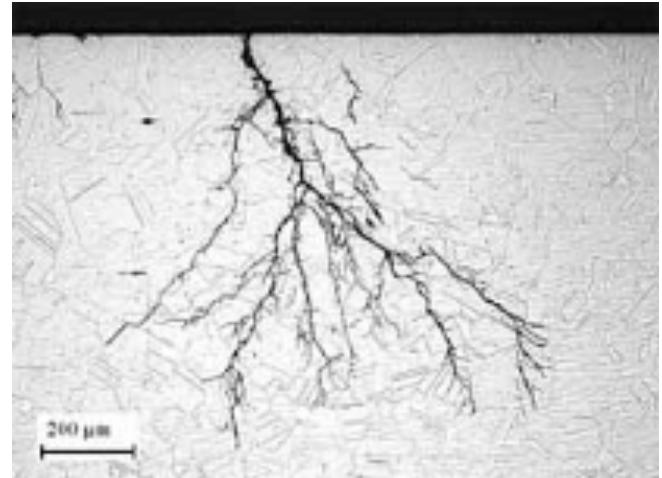
Example

- Metals partially immersed in water (or) conducting solution (called water line corrosion).
- If a metal is partially immersed in a conducting solution the metal part above the solution is more aerated and hence become cathodic.
- On the other hand, the metal part inside the solution is less aerated and thus, become anodic and suffers corrosion.



Stress Corrosion

- Metal develops internal stress during manufacturing process.
- Area under stress is high energy---- tend to oxidize--- ANODE
- Stress free area---- Cathode



Fretting Corrosion

- Fretting corrosion occurs when metals slide over each other and cause mechanical damage to one or both.
- During relative movement of metals, two process may occur, (i) frictional heat is generated, which oxidize the metal to form oxide films. (ii) removal of the protective films resulting in exposure of fresh surface to corrosion attack.
- This can be avoided by using harder materials, minimizing friction by lubrication or by proper designing of the equipment.

Corrosion Fatigue

- Corrosion fatigue is the ability of metal surface to withstand repeated cycle of corrosion. The metal surface is stressed and simultaneously attacked by the corrosive media.
- Pits indicating corrosion are formed initially, which further develops in to cracks.
- The protective surface oxide film reduces corrosion. Under cycling or repeated stress conditions, rupture of protective oxide films takes place at a higher rate than at which new protective films can be formed. So the rate of corrosion is enhanced.

Oxygen concentration Corrosion

- It is due to the presence of oxygen electrolytic cell.
- i.e. diff in the amount of oxygen in solution at one point exists when compared to another.
- Corrosion is accelerated when the O_2 is least, for example, under gasket, stuffing boxes etc.

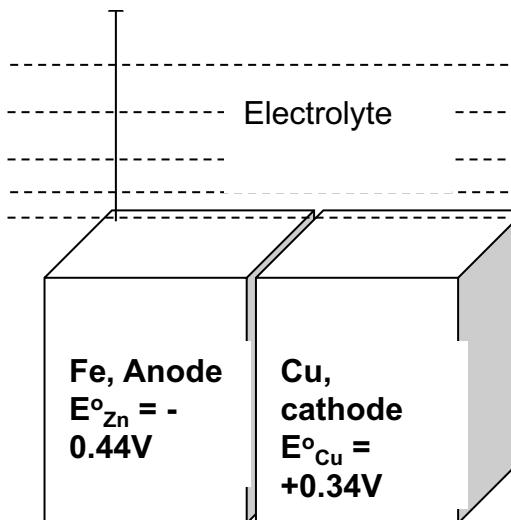
GALVANIC CORROSION

- When two different metals are in contact with each other in the presence of an aqueous solution (or) moisture, galvanic corrosion occurs.
- The more active metal (with more negative electrode potential) acts as anode and the less active metal (with less negative potential) acts as cathode.

e.g. Steel screw in a brass marine hardware corrodes.

- This is due to galvanic corrosion. Iron (higher position in electrochemical series) as anode, is attacked and corroded, while Copper (lower in electrochemical series) acts as cathodic and is not attacked.

Fe undergoes corrosion



Bolt and nuts made of the same metal is preferred, Why?

It is preferred in practice, because galvanic corrosion is avoided due to homogeneous metals (no anodic and cathodic part).



Rusting of a screw
in an door knob

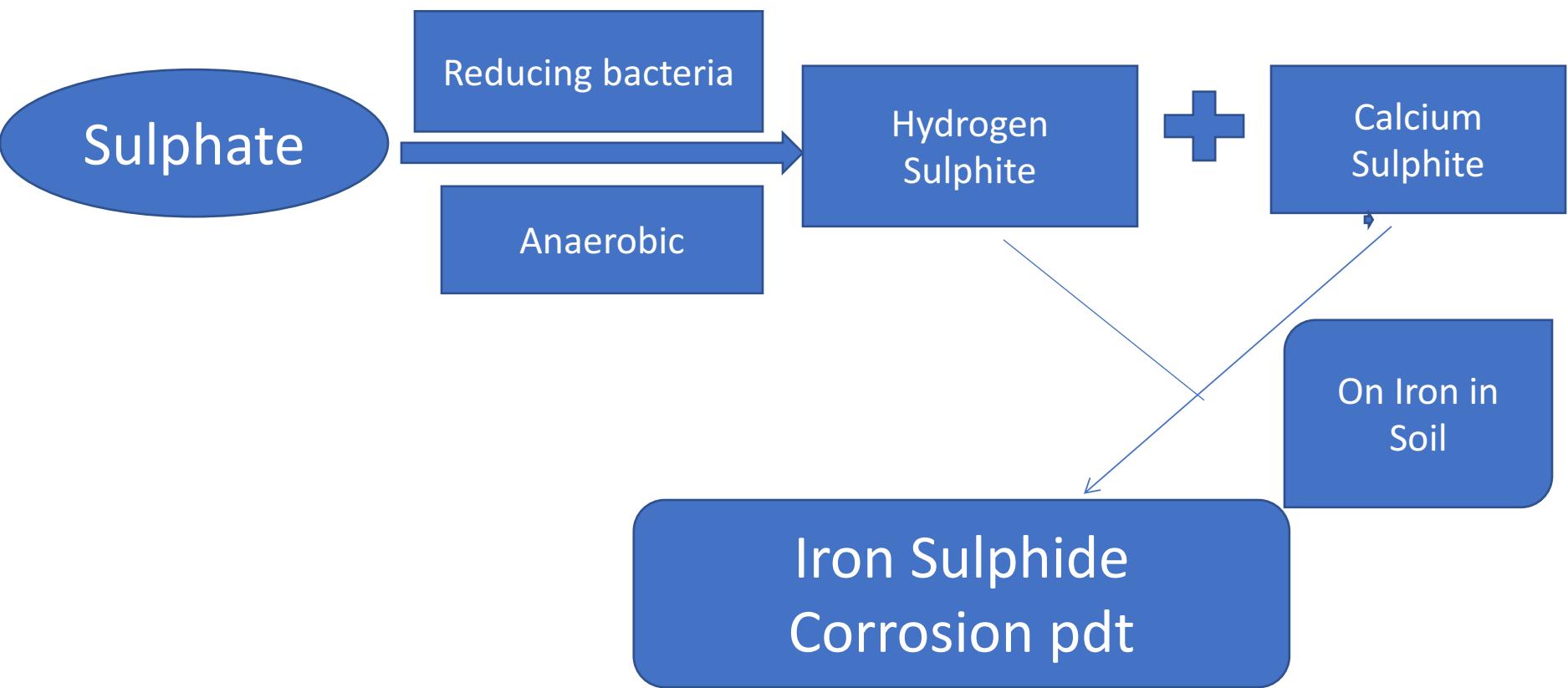


Chemical vs Electrochemical corrosion

Chemical Corrosion	Electrochemical Corrosion
It occurs only in dry condition	It occurs in the presence of moisture or electrolyte
It is due to the direct chemical attack of the metal by the environment	It is due to the set up of a large number of cathodic and anodic areas
Even a homogeneous metal surface gets corroded	Heterogeneous surface or bimetallic contact is required for corrosion
Corrosion products accumulate in the same place, where corrosion occurs.	Corrosion occurs at the anode, while products formed elsewhere
Chemical corrosion is self-controlled	It is continuous process
It follows adsorption mechanism Eg. Formation of mild scale on iron surface	It follows electrochemical reaction Eg. Rusting of iron in moist atmosphere

Biological Corrosion

- The role of biological corrosion may be explained by sulphate reducing bacteria in slightly acidic or alkaline soils.



Galvanic Series

TABLE 1 SIMPLIFIED GALVANIC SERIES

Magnesium	Active (Anode)
Zinc	
Aluminum	
Cadmium	
Steel or Iron	
Cast Iron	
Led	
Nickel	
Brass	
Copper	
Bronze	
Stainless Steel (304)	
Monel Metal	
Stainless Steel (316)	
Silver	
Graphite	
Titanium	
Gold	Noble (Cathode)