

Corrosion

- Corrosion is termed as the chemical or electrochemical reaction between a material and its environment that leads to deterioration of the material and/or its properties
- It is a process through which metals in manufactured states return to their natural oxidation states
- This process is a reduction-oxidation reaction in which the metal is being oxidized by its surroundings, often the oxygen in air
- The reaction is both spontaneous and electrochemically favoured.
- Corrosion is essentially the creation of voltaic, or galvanic, cells where the metal in question acts as an anode and generally deteriorates or loses functional stability.

Effects of corrosion

- Loss of efficiency
- Contamination of product
- Damage of metallic equipments
- Inability to use metallic materials
- Loss of valuable materials such as blockage of pipes, mechanical damage of underground water pipes
- Accidents due to mechanical loss of metallic bridges, cars, aircrafts
- Causes pollution due to escaping products from corrosion
- Depletion of natural resource



- Some of the major harmful effects of corrosion can be summarized as follows:
 - Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown.
 - Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).
 - Loss of time in availability of profile-making industrial equipment.
 - Reduced value of goods due to deterioration of appearance.
 - Contamination of fluids in vessels and pipes
 - Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings
 - Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products

Common metals and Alloys

■ Iron:

- Main corrosion product is rust or iron oxides
- The most familiar form of rust is the reddish coating that forms flakes on iron and steel (Fe_2O_3)
- Rust also comes in other colors, including yellow, brown, orange, and even green! The different colors reflect various chemical compositions of rust.

■ Steel:

- These contain Fe, C, Cr, Ni, Mo, etc
- Main corrosion product is rust or iron oxides, those similar to iron
- Along with iron, other alloying metals (Ni, Cr, Mo) also get corroded due the formation of corresponding oxides



■ Copper:

- Main corrosion products are $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$, patinas as Cu_2O ; posnjakite ($\text{Cu}_4\text{SO}(\text{OH})_6\text{H}_2\text{O}$), brochantite ($\text{Cu}_4\text{SO}_4(\text{OH})_6\text{H}_2\text{O}$), and antlerite ($\text{Cu}_3\text{SO}_4(\text{OH})_4$)s

■ Brass and Bronze:

- Brass contains Cu, Zn
- Bronze contains mainly Cu, Sn
- Main corrosion products are similar to copper corrosion products



Reasons of corrosion

- In nature, most metals (except Au, Pt, etc) prefer existing as thermodynamically more stable compounds, such as, their oxides, carbonates, chlorides, silicates, etc.
- But, during the extraction process at high temperature, the metallic compounds are reduced to their pure metallic state which is, thermodynamically unstable state.
- Hence, the extracted/reduced pure metal will always have a strong tendency to convert itself into the more stable metallic compound oxidized state through corrosion.
- The Gibbs free energy changes of forming oxide and sulphides are negative, so oxidation reaction is usually spontaneous



Types of corrosion

- Corrosion is classified on the basis of nature of the corrodent, mechanism of corrosion, and appearance of the corroded metal

- Dry corrosion (chemical corrosion):

Classified depending on the corroding agent:

- (i) Corrosion by oxidation,
- (ii) Corrosion by gases other than oxygen
- (iii) Corrosion by liquid metals.

- Wet corrosion (electrochemical corrosion):

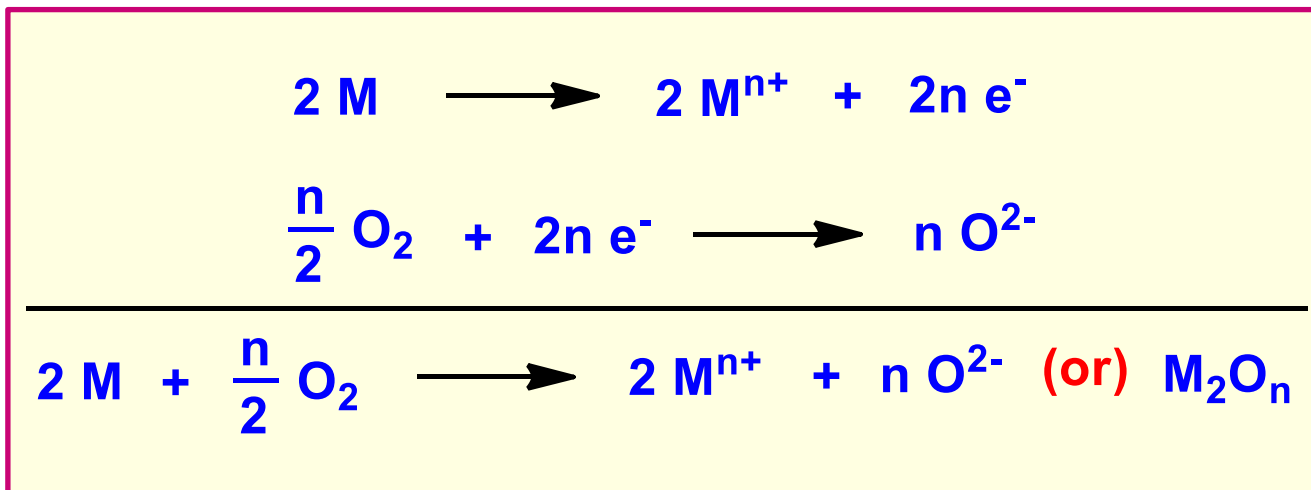
- (i) Evolution of hydrogen-type corrosion,
- (ii) Absorption of oxygen-type corrosion,
- (iii) Galvanic or bimetallic corrosion,
- (iv) Concentration cell corrosion (or water line corrosion).

Dry Corrosion

- This corrosion occurs due to the direct chemical attack of atmospheric gases such as O_2 , halogens, H_2S , SO_2 , N_2 or anhydrous inorganic liquids on the metal surface.
- Dry corrosion occurs when there is no moisture or water to aid corrosion
- This process is very sensitive to temperature
- Under hot conditions, dry corrosion occurs at a much faster rate as compared to normal conditions
- Corrosion is due to adsorption, and the corrosion products accumulate in the same spot where corrosion occurs
- Main types of this corrosion are
 - Corrosion by oxygen (or) oxidation corrosion.
 - Corrosion by other gases like H_2S , SO_2 , N_2 , CO_2 , F_2 etc.
 - Liquid metal corrosion (or) Erosion Corrosion

Oxidation Corrosion

- **Direct action of oxygen** in the absence of moisture at low (or) high temperatures leads to oxidation corrosion
- At high temperatures all metals are attacked by oxygen and are oxidized – except noble metals like Ag, Au, and Pt
- At ambient temperature generally all the metals are slightly attacked.
- **Alkali metals and alkaline earth metals get oxidized readily**
- The reactions in the oxidation corrosion are



Oxidation of metals

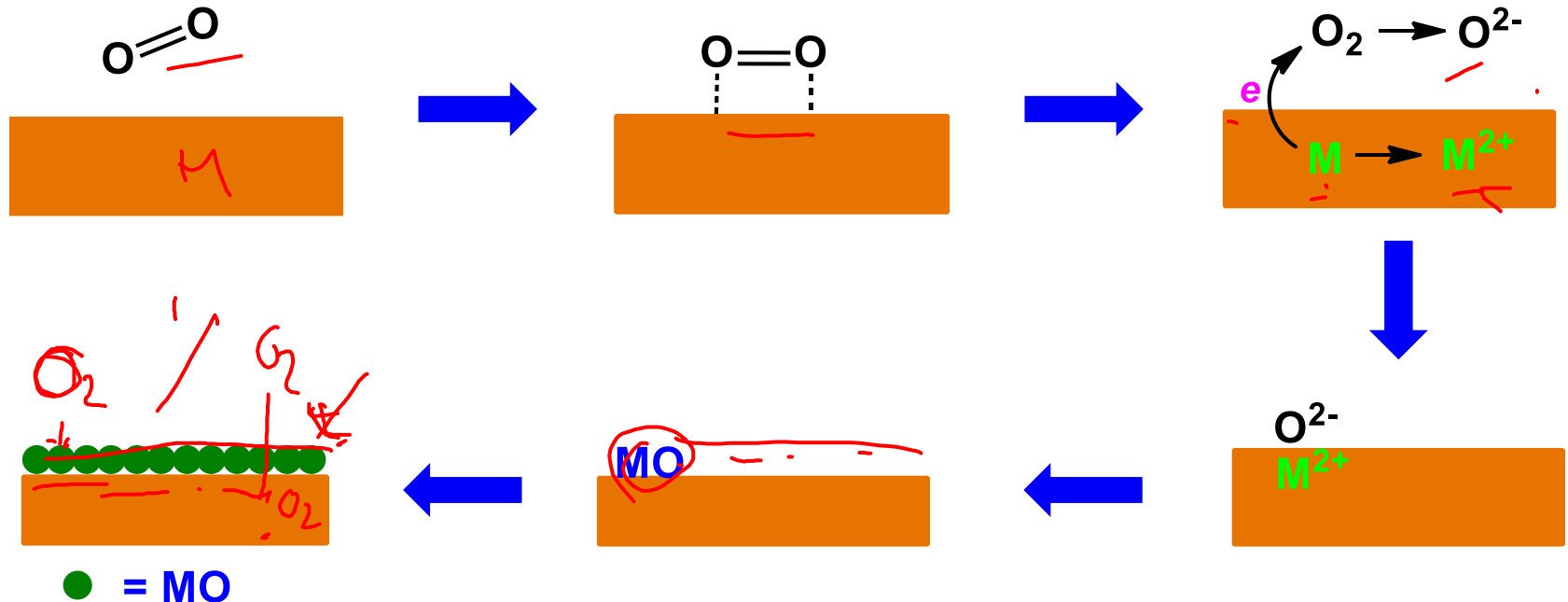
Standard Reduction Potentials in Aqueous Solutions at 25 °C

Oxidizing Agent		Reducing Agent	Reduction Potential (V)
F ₂	+ 2e ⁻ →	2F ⁻	2.87
H ₂ O ₂	+ 2H ⁺ + 2e ⁻ →	2H ₂ O	1.78
MnO ₄ ⁻	+ 8H ⁺ + 5e ⁻ →	Mn ²⁺ + 4H ₂ O	1.51
Au ³⁺	+ 3e ⁻ →	Au	1.50
Cl ₂	+ 2e ⁻ →	2Cl ⁻	1.36
O ₂	+ 4H ⁺ + 4e ⁻ →	2H ₂ O	1.23
Cr ₂ O ₇ ²⁻	+ 14H ⁺ + 6e ⁻ →	2Cr ³⁺ + 7H ₂ O	1.23
Br ₂	+ 2e ⁻ →	2Br ⁻	1.07
NO ₃ ⁻	+ 4H ⁺ + 3e ⁻ →	NO + 2H ₂ O	0.96
Ag ⁺	+ e ⁻ →	Ag	0.80
I ₂	+ 2e ⁻ →	2I ⁻	0.54
Cu ⁺	+ e ⁻ →	Cu	0.52
O ₂	+ 2H ₂ O + 4e ⁻ →	4OH ⁻	0.40
Cu ²⁺	+ 2e ⁻ →	Cu	0.34
2H ₃ O ⁺	+ 2e ⁻ →	H ₂ + 2H ₂ O	0.00
Pb ²⁺	+ 2e ⁻ →	Pb	-0.13
Sn ²⁺	+ 2e ⁻ →	Sn	-0.14
Ni ²⁺	+ 2e ⁻ →	Ni	-0.26
Fe ²⁺	+ 2e ⁻ →	Fe	-0.45
Cr ³⁺	+ 3e ⁻ →	Cr	-0.74
Zn ²⁺	+ 2e ⁻ →	Zn	-0.76
2H ₂ O	+ 2e ⁻ →	H ₂ + 2OH ⁻	-0.83
Mn ²⁺	+ 2e ⁻ →	Mn	-1.19
Al ³⁺	+ 3e ⁻ →	Al	-1.66
Mg ²⁺	+ 2e ⁻ →	Mg	-2.37
Na ⁺	+ e ⁻ →	Na	-2.71
Ca ²⁺	+ 2e ⁻ →	Ca	-2.87
Ba ²⁺	+ 2e ⁻ →	Ba	-2.91
K ⁺	+ e ⁻ →	K	-2.93
Li ⁺	+ e ⁻ →	Li	-3.04

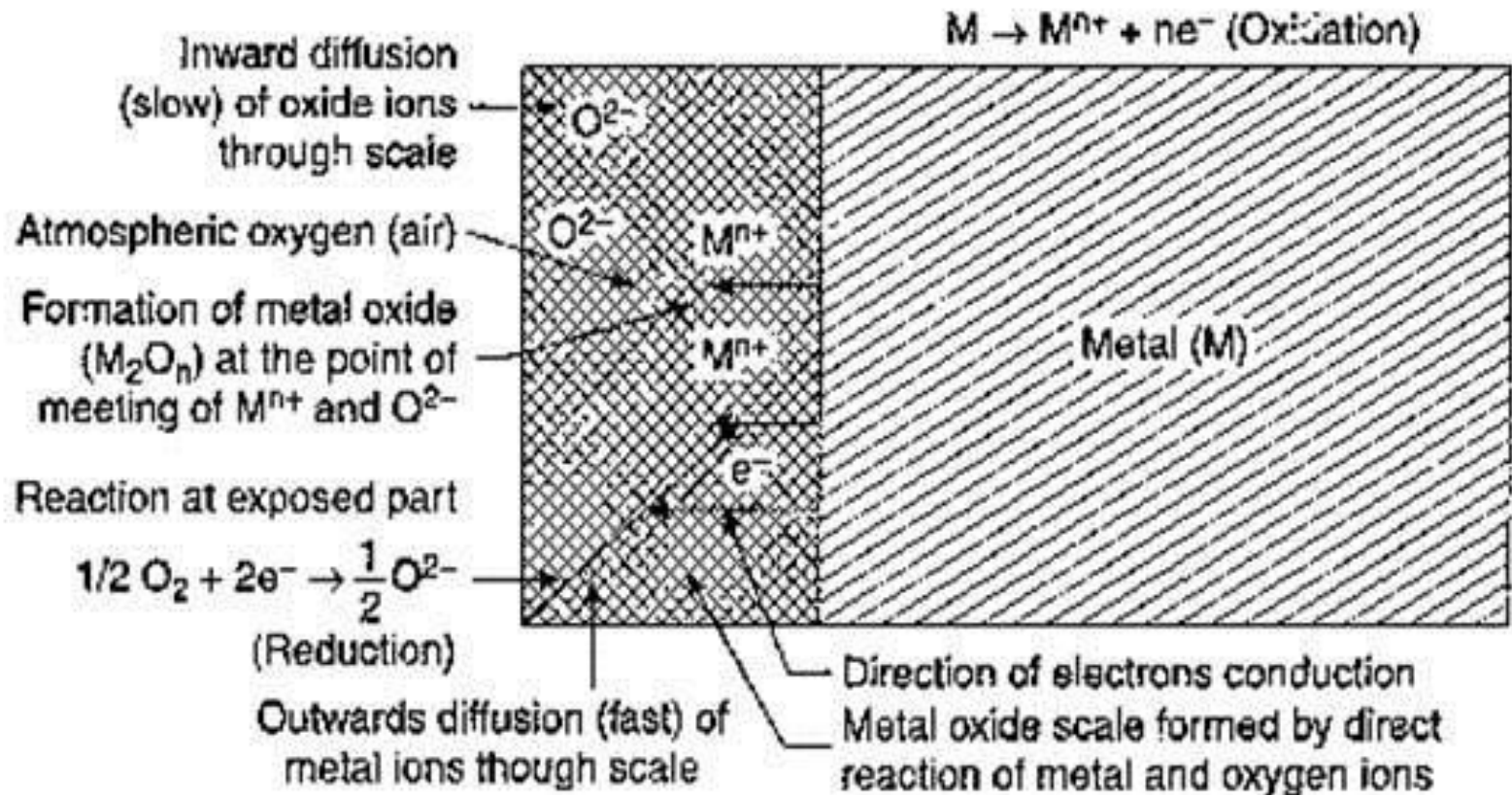


Mechanism of oxidation corrosion

- Oxidation takes place first at the surface of the metal
- Adsorption of oxygen on to the metal surface
- Loss of electron from the metal and gain of electron by oxygen
- Dissociation of oxygen
- Formation of oxide layer onto the metal surface



- For oxidation, either the **metal must diffuse outwards** through the oxide layer to the surface or the **oxygen must diffuse inwards** through the oxide layer to the underlying metal.
- Both transfers occur, but the **outward diffusion of the metal is generally much more rapid than the inward diffusion of oxygen**.
- This diffusion is driven by the size of **metal and oxide ion**



Types of oxide layers

- Nature of the oxide formed plays an important part in oxidation corrosion process
 - As the oxide layer grows the rate of electron transfer decreases
 - The corrosion stops and the metal is made passive

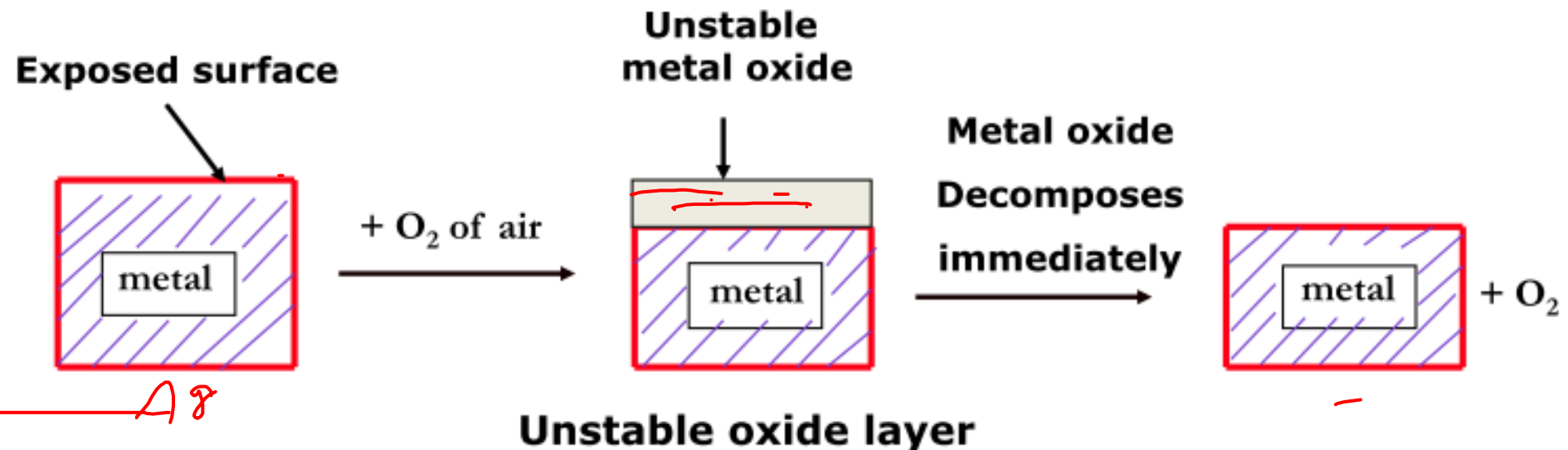
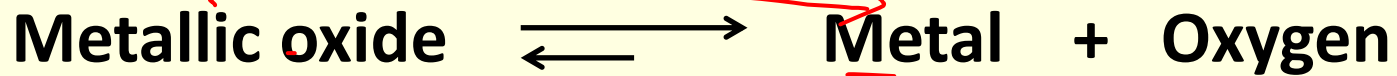
✗ Stable oxide layer (or stable protective oxide layer)

- It is a fine grain of oxide layer which is non-porous and adheres strongly to the metal
- Oxides of Al, Pb, Cu, Ni and Cr which form stable, non-porous and tightly adhering impervious metal-oxide films (<300 Å or 30 nm thick) to the pure metallic surface.
- Such layers prevents oxygen from diffusing through the metal and further attack is stopped.
- Further oxidation corrosion is stopped



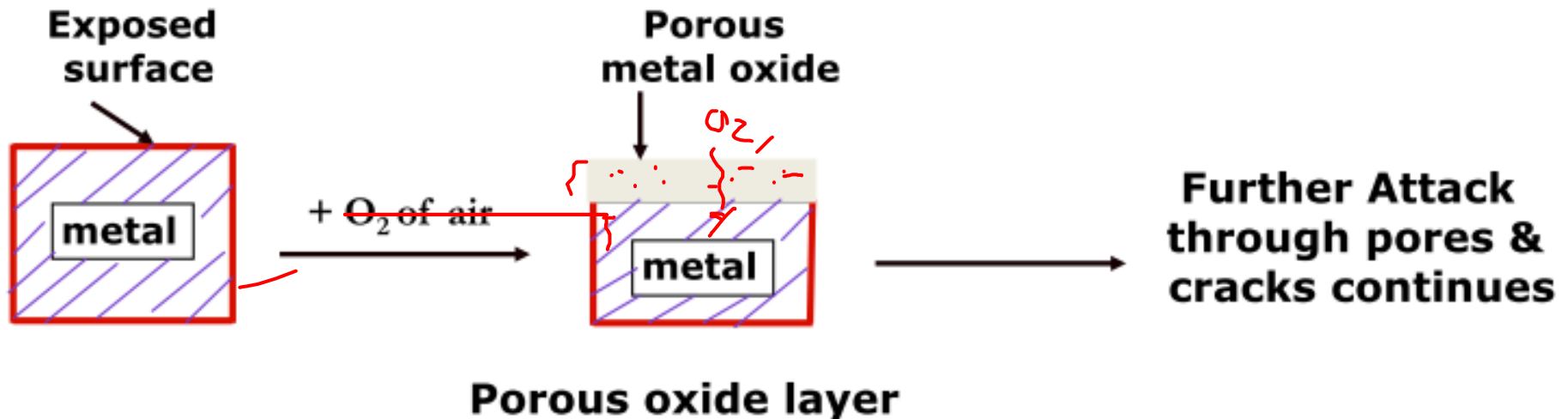
■ Unstable oxide layer

- Oxide layers produced on noble metal surfaces (Pt, Ag, etc) **immediately decompose** back into the metal and oxygen, thereby preventing oxidation corrosion



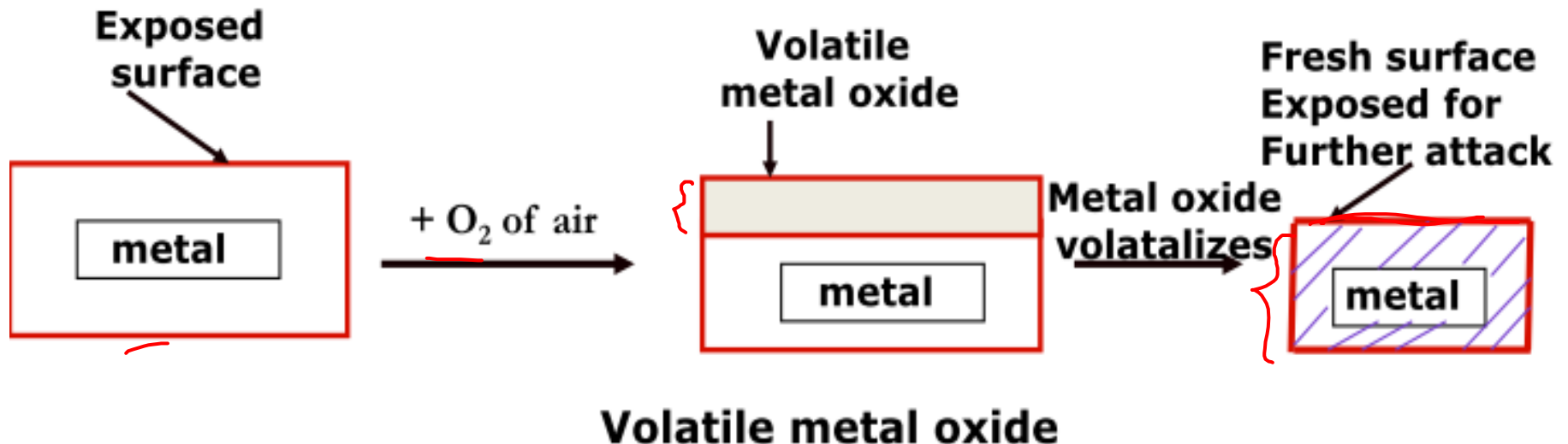
■ Porous oxide layer:

- These oxide layers have minute pores and are not impervious layers.
- Oxygen will diffuse through these pores and cracks promoting further corrosion.
- Fe is a good example of this type of corrosion
- Iron when attacked by H₂S at high temperature forms porous FeS layer



■ Volatile oxide layer:

- These are oxide layers which volatilize (evaporate) as soon as they are formed and hence further corrosion is facilitated.
- The underlying metal surface is exposed for further corrosion. After some time the metal itself will disappear.
- Molybdenum (Mo) is an example of volatile oxide layer corrosion. MoO_3 is volatile (MoO_2 is non-volatile.).



Pilling-Bedworth rule (P-B ratio):

- The protective or non-protective nature of the oxide film is determined by Pilling-Bedworth rule
- The ratio of the volume of the oxide formed to the volume of the metal consumed is called as Pilling-Bedworth ratio or P-B ratio

$$R_{PB} = \frac{V_{\text{oxide}}}{n V_{\text{metal}}} = \frac{M_{\text{oxide}} \cdot \rho_{\text{oxide}}}{n \cdot M_{\text{metal}} \cdot \rho_{\text{metal}}}$$

$$\frac{V_{Fe_2O_3}}{2 \times V_{Fe}}$$

$$R_{PB} < 1$$

R_{PB} = Pilling-Bedworth ratio,

M = atomic or molecular mass,

n = number of atoms of metal per one molecule of the oxide

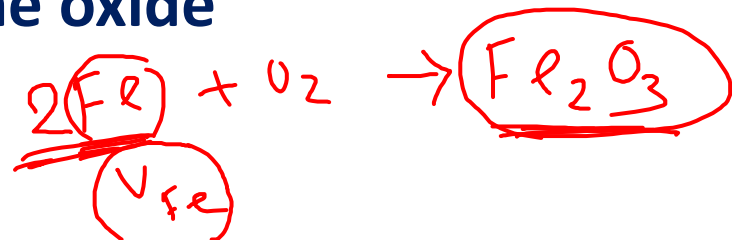
ρ = density, and

V = volume.

$$R_{PB} \sim 1-2$$

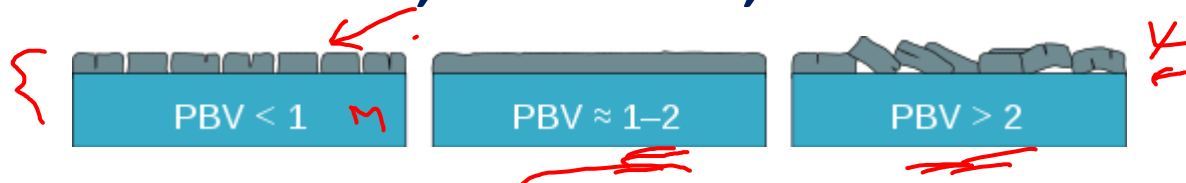
$$R_{PB} > 2$$

$$R_{PB} = \frac{V_{Fe_2O_3}}{2 V_{Fe}}$$



Cases

- On the basis of the P-B ratio, it can be judged if the metal is likely to passivate in dry air by creation of a protective oxide layer
- PB ratio < 1: the oxide coating is broken, no protective effect. (example: magnesium)
 - Alkali and alkaline earth metals: PB < 1 → tensile stresses in oxide film → brittle oxide cracks
- PB ratio > 2: the oxide coating chips off, no protective effect (example: iron)
- PB ratio between 1 and 2: the oxide coating is passivating (examples: aluminum, titanium, chromium containing steels).



Rules


- If the volume of the oxide layer is greater than the volume of the metal, the oxide layer is protective and non-porous
 - Aluminium forms Aluminium oxide whose volume is greater than the volume of the metal (Al). Hence these do not undergo corrosion rapidly
 - R_{pB} of W is 3.6, Cr = 2.0, Ni = 1.6. Hence, the rate of corrosion is very less in tungsten
- If the volume of the oxide layer formed is less than the volume of the metal, the oxide layer is non protective and porous
 - Alkali and alkaline earth metals like Li, Na, K, Mg forms oxides of volume less than volume of metals. Hence these undergo corrosion more rapidly

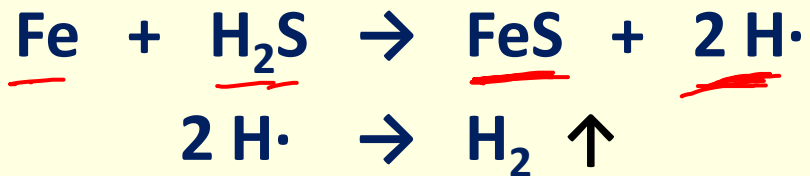
Corrosion by other gases


- In dry atmosphere CO_2 , Cl_2 , SO_2 , F_2 , NO_x etc. are gases which can attack the metal and corrode
- Extent of corrosion depends on the affinity of the metal to the gas.
- These gases chemically react with the metal forming either porous or non-porous layers of films
- Protective or non-porous layer prevents from further attack.
- Non-protective or porous layer expose the underlying fresh metal surface for further attack.
- H_2S gas attacks steel and make them brittle

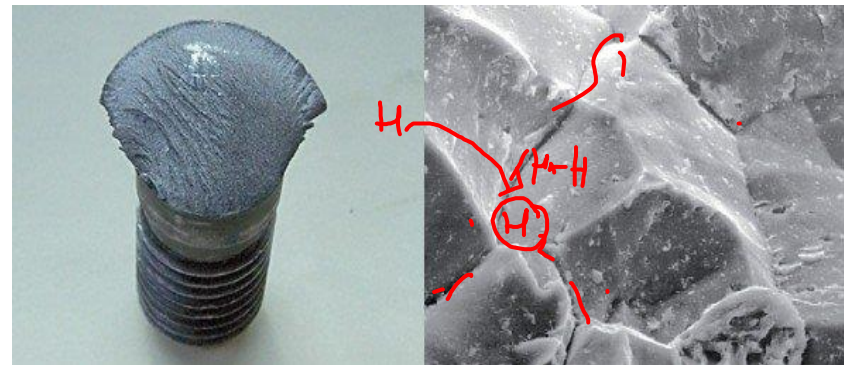


Hydrogen embrittlement

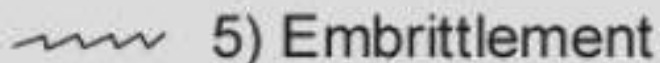
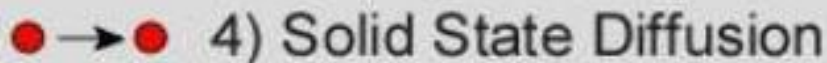
- Hydrogen Embrittlement is a process whereby metals **become brittle and fracture** as a result of the introduction and **diffusion of hydrogen** into the material
- When metals are in contact with H_2S , at ordinary temperature causes **evolution of atomic hydrogen** 
- This **atomic hydrogen diffuses readily into the metal and collects in the voids, where it recombines to form molecular hydrogen**



- Collection of these hydrogen gases in the voids develops very **high pressure, which causes cracks and blisters** on metal leading to hydrogen embrittlement. 



(a) Absorption from $H_2(g)$



Bulk Gas Phase
 H_2

Crack Atmosphere

(1)

Pressure Drop

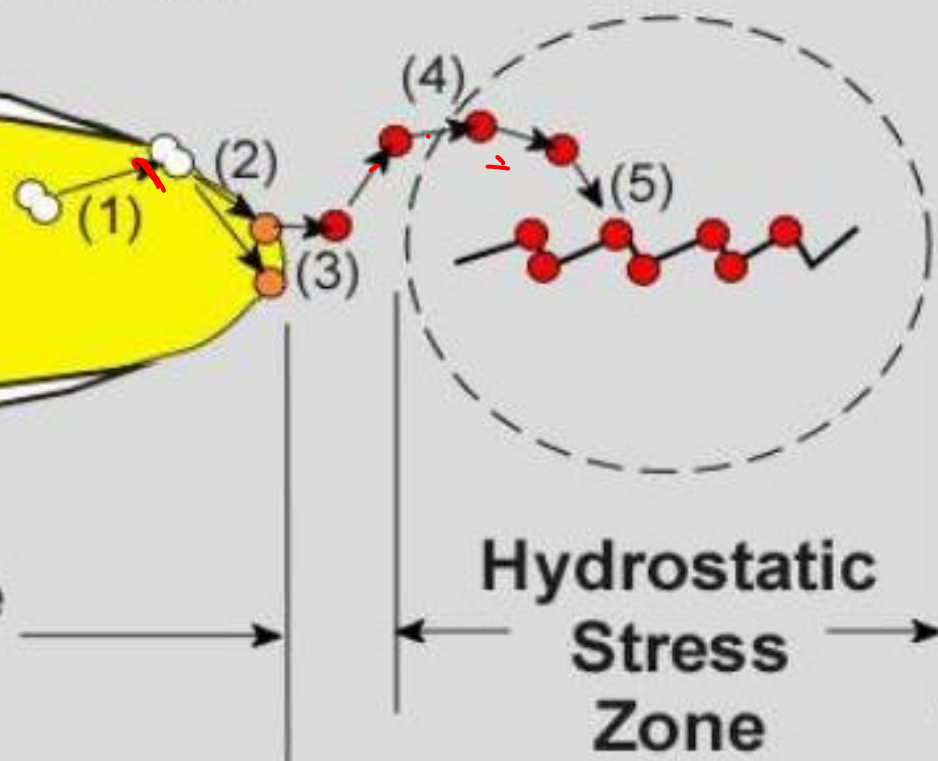
(2)

(3)

(4)

(5)

Hydrostatic Stress Zone

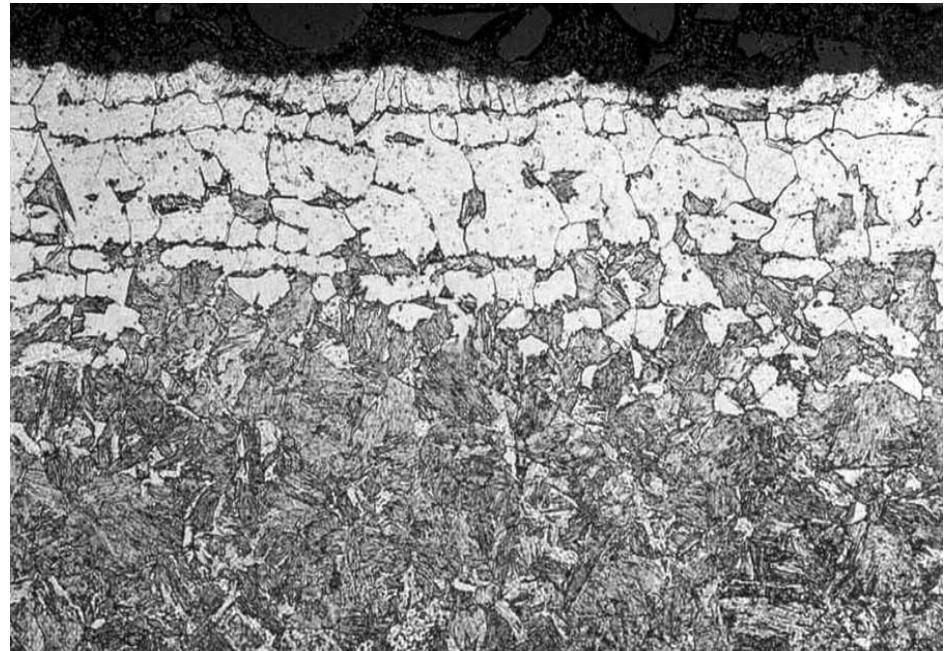


Decarburization

- At higher temperature, atomic hydrogen is formed by the thermal dissociation of molecular hydrogen

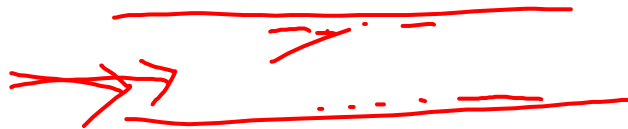


- When steel is exposed to this environment, the atomic hydrogen readily combines with carbon of steel and produces methane gas.
- Thus the formation of methane gas reduces the strength of steel and this process is known as decarburization.



Liquid - Metal corrosion or Erosion- corrosion

- This type of corrosion is experienced in pipe lines used in oil and refineries.
- In metallic pipelines, the fast flow of corrosive liquid or aggressive fluid completely removes the underlying layer of metal in the pipeline due to mechanical abrasion



Corrosion by liquid metal or Liquid metal embrittlement

- Liquid metal (Hg, Zn, Sn, Pb, Cd etc.) flowing at high temperature over the solid metal or alloy can result in
 - Dissolution of the solid metal by the liquid metal (Gold can be corroded by mercury) or
 - Internal penetration of the liquid metal into the solid metal.
- Molten metal atoms penetrate the grain boundaries and fracture the metal.
- Such corrosion is found in devices used in nuclear power plants. It causes brittle failure of metal structure

Wet or Electrochemical Corrosion

- In this type of 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. Water must be present to serve as a medium for the transport of ions
- The most common depolarizers are oxygen, acids, and the cations of less active metals
- Because the electrons flow through the metallic object itself, the anodic and cathodic regions can be at widely separated locations.
- 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

Criteria for Electrochemical Corrosion

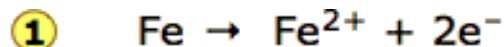
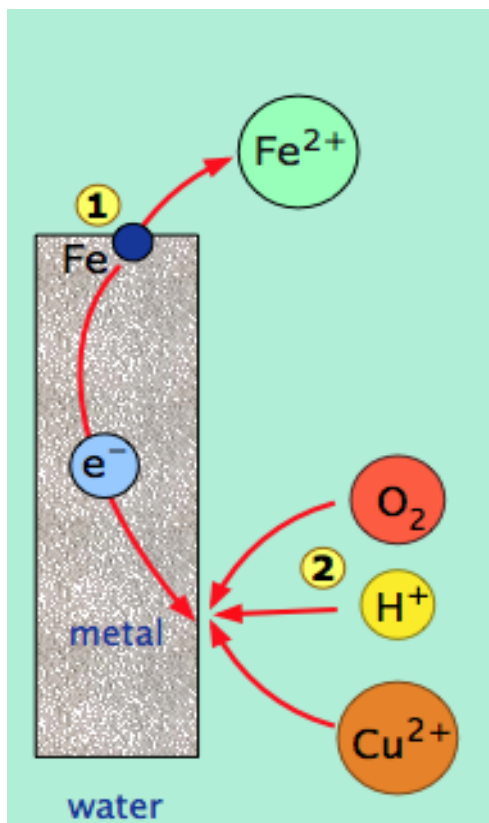
1. Formation of galvanic cells on the surface of metal generating anodic and cathodic areas.
 2. Presence of conducting liquid with the formation of electrochemical cells.
 3. At anode of metal surface, oxidation [Corrosion] takes place by liberating electrons.
 4. At cathode, reduction [No corrosion] takes place
- The rate of the electrochemical corrosion will depend on:
 - If the corrosion product is soluble in the medium, rate of corrosion will be high.
 - If the corrosion product is insoluble in the medium, rate of corrosion will be very low.

Mechanism of Wet Corrosion is 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 higher electrode 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 of the cathode and anode, the greater will be the corrosion.
 - Also the smaller the area of the anode as compared to the cathode, the more will be the attack.

Corrosion Cells and Reactions

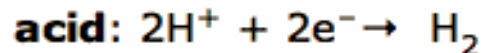
- Oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions
- The presence of water is necessary in order to transport ions to and from the metal



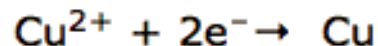
Fe atom at metal surface dissolves into moisture film, leaving negative charge in metal.

- ② Corrosion continues as a *depolarizer* removes electrons from metal.
Common depolarizers are:

oxygen:



cation of more-noble metal:



Types of electrochemical corrosion

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

Uniform or General corrosion

- The electrochemical reactions (in aqueous or atmospheric media) proceed uniformly over the entire exposed metal surface over a large area
- General corrosion represents the greatest destruction of metal
- 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 base metals are in contact with an acidic solution
- Rusting of iron metal in acidic environment takes place in the following way

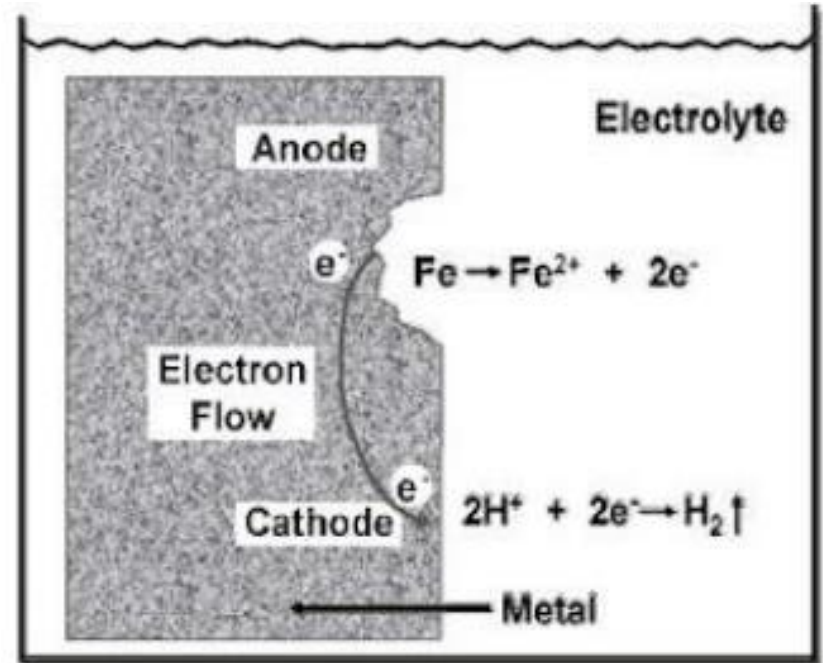
- Anode: Oxidation occurs



- Cathode: Reduction occurs



- The overall reaction is:



- Metal ions produced at the anode dissolves in the electrolyte while hydrogen evolves at the cathode.
- Hence, this type of corrosion causes “displacement of hydrogen ions from the acidic solution by metal ions”
- In this case anodic areas are large and cathodic areas are small.

- **Why O_2 is not present in the acidic environment in this case? Why water and O_2 is not included in the cathodic reaction?**
 - Due to high acid concentration, O_2 if present, will react with H^+ to form H_2O as a by-product and get consumed. Hence, in acidic environment, dissolved oxygen (DO) is not present in the water finally and not included in the equation as a major reactant.
 - Also, for the same reason, no protective oxide layer is formed over the metal surface (different from the oxygen adsorption corrosion)

Oxygen consumption type corrosion

- It occurs when base metals are in contact with neutral solutions like water with dissolved oxygen (DO)
- Rusting of iron is an example of this type of corrosion

- Anode: Oxidation occurs



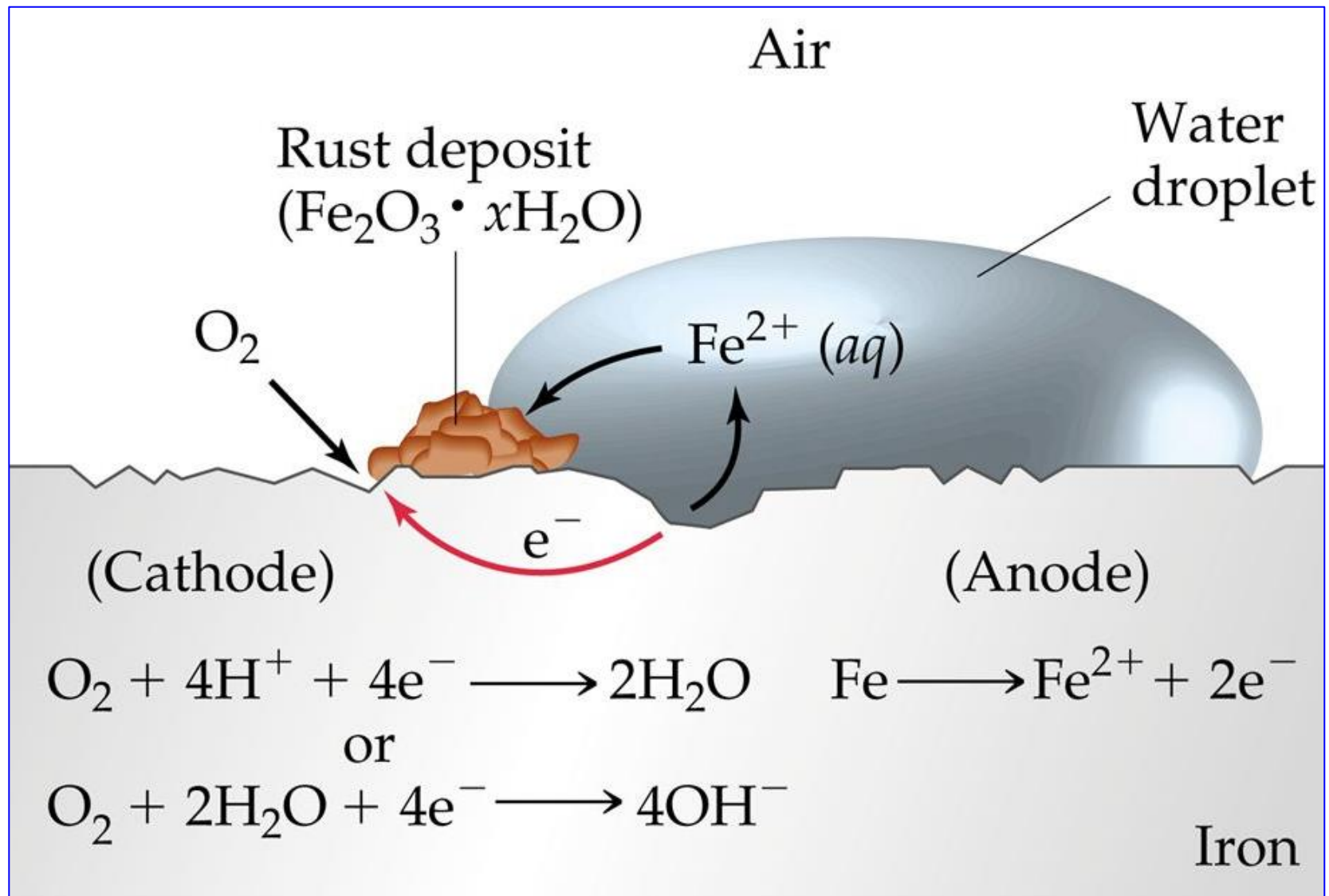
These electrons move from anode to cathode and react with the electrolyte and oxygen giving

- 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):





If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite Fe_3O_4

- In acidic solution, the cathodic reaction leads to water formation



- In basic or neutral solution reduction leads to hydroxyl ion



- In deaerated and acidic solution H^+ ions reduced to hydrogen gas
- Rust is a non-sticking compound i.e., it does not stick to the surface. It peels off exposing fresh iron surface for further rusting.
- Small Fe^{2+} diffuses more rapidly than large OH^- ions. So, corrosion occurs at anode, but rust is deposited at or near the cathode

- Smaller the area of anode compared to cathode will lead to faster corrosion of anode.
 - The corrosion current at anode and at cathode are same. But for small anodic area the current density will be large at anode and larger cathodic area will demand more electron which will be fulfilled by fast reaction at anode (oxidation), i.e. rapid corrosion.

Difference between chemical (dry) corrosion and electrochemical (wet) corrosion

Chemical (dry) corrosion	Electrochemical (wet) corrosion
Chemical corrosion occurs in the dry state.	Electrochemical corrosion occurs the presence of moisture or electrolyte.
Corrosion products accumulate at the same spot where corrosion occurs.	It involves the setting up of a huge number of tiny galvanic cells.
It involves the direct chemical attack of the metal by the environment.	It follows mechanism electrochemical reactions.
It follows absorption mechanism.	It occurs only on heterogeneous metal surface.
It occurs on both homogeneous and heterogeneous surfaces.	Corrosion occurs at the anode but products gather at the cathode.
Uniform corrosion takes place.	Pitting is more frequent especially when the anode area is small.
It is slow process	It is fast process

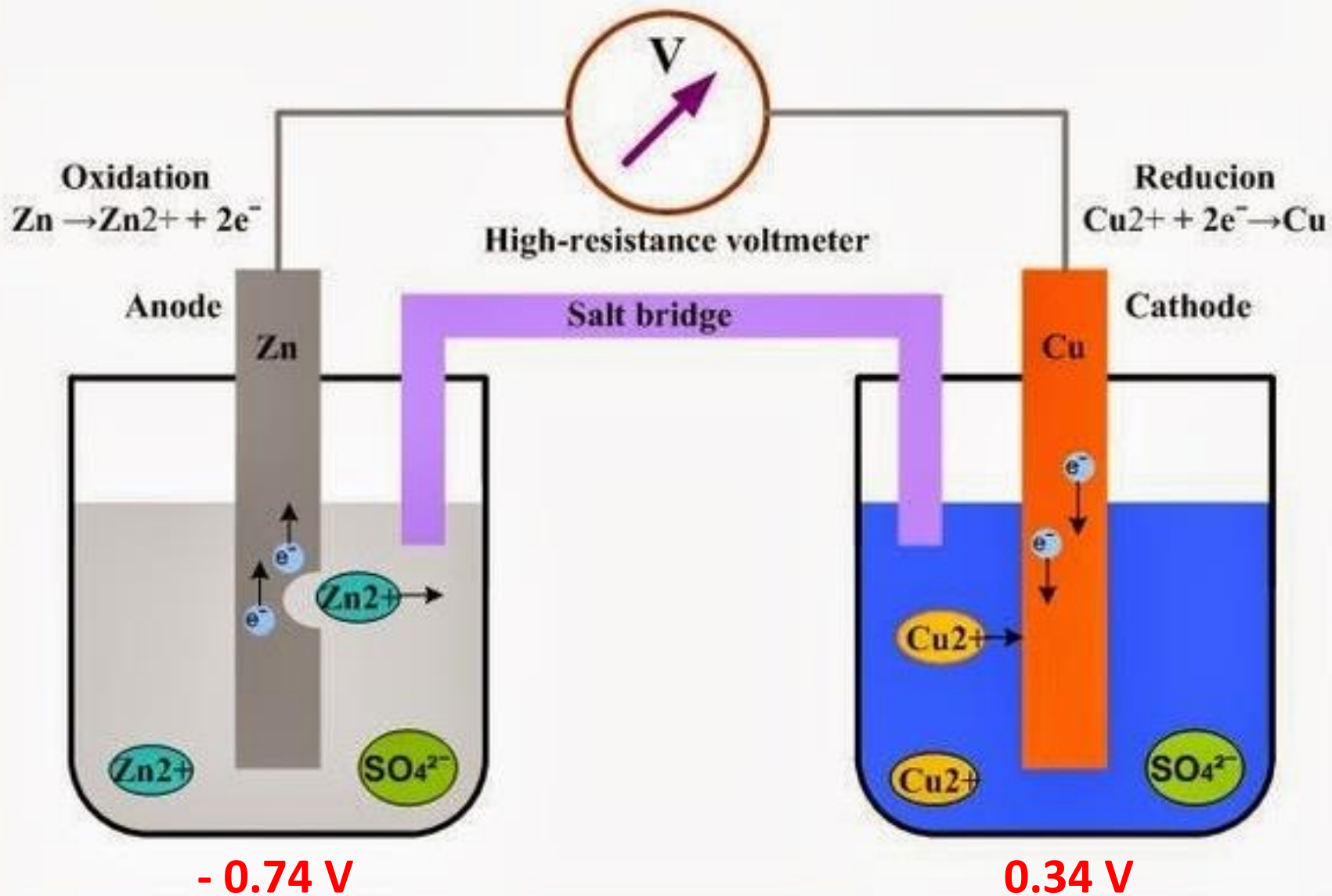
Differential metal corrosion or Galvanic corrosion or Bi-Metallic Corrosion

- Galvanic corrosion, or dissimilar metal 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

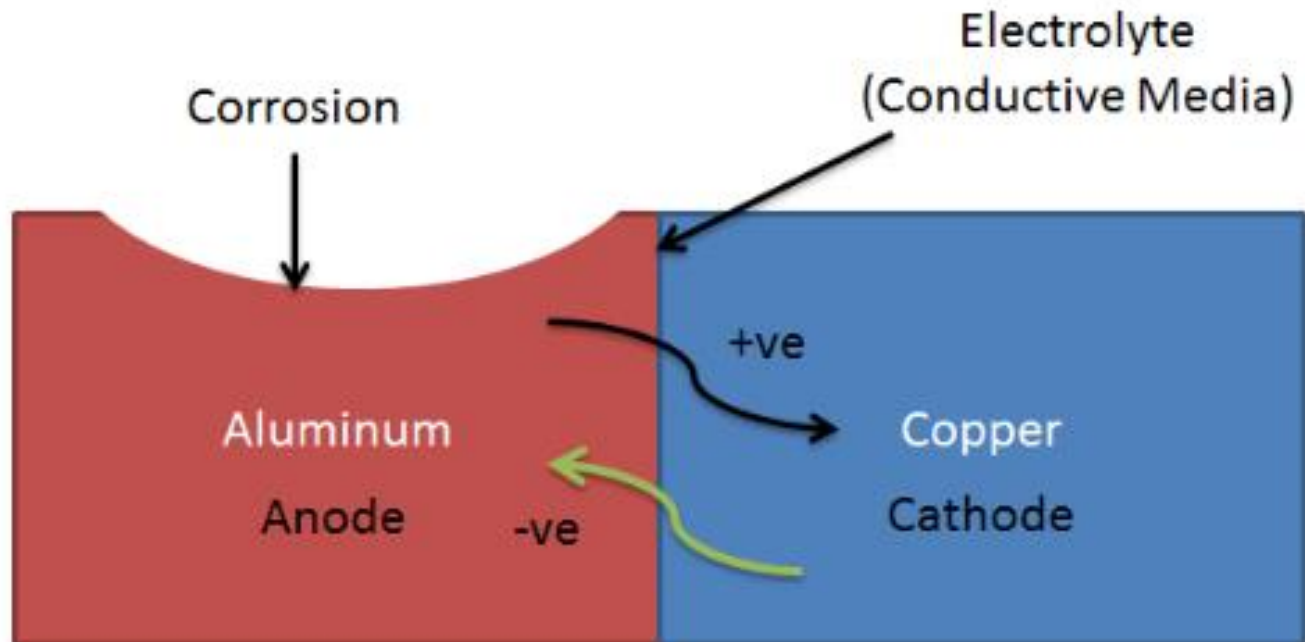
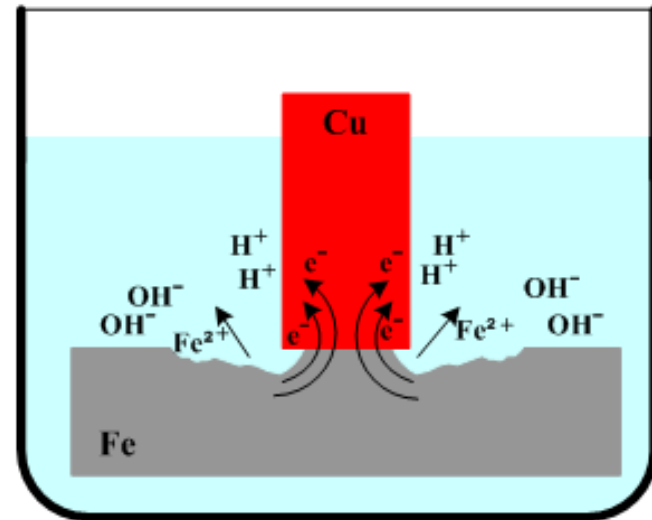
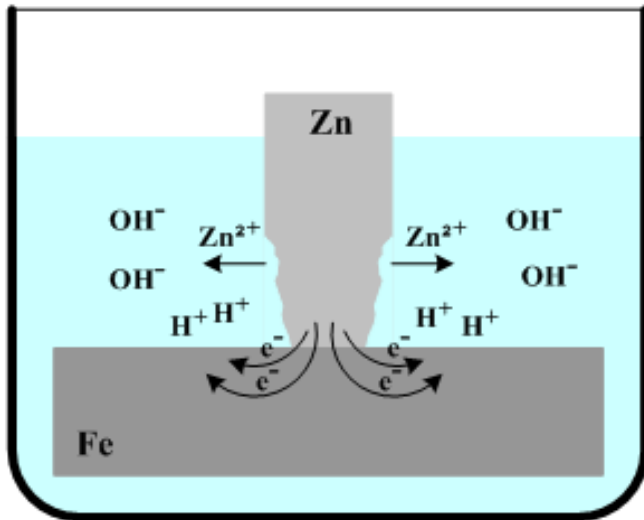


- **Three conditions must exist for galvanic corrosion to occur:**
 - **Electrochemically dissimilar metals must be present**
 - **The metals must be in electrical contact, and**
 - **The metals must be exposed to an electrolyte**

Galvanic cell



Galvanic corrosion



Corrosion Susceptibility of metals

Anodic

Most
susceptible to
corrosive
attack (less
noble)

Least
susceptible
To corrosive
attack
(More noble)

Cathodic



Magnesium and its alloys
Zinc and its alloys
Aluminum and its alloys
Cadmium
Mild Steel
Cast Iron
Stainless steel 13% Cr, type 410 (active)
Lead-tin solder, 50/50
Stainless steel, 18/18 type 304 (active)
Stainless steel, 18/18/3 Mo, type 316 (active)
Lead
Tin
Brasses
Aluminum bronzes
Copper
Copper-nickel alloys
Monel
Titanium and its alloys
Stainless steel, 18/18 type 304 (passive)
Stainless steel, 18/18/3 Mo, type 316 (passive)
Silver
Gold
Platinum

GALVANIC SCALE

FIG 1

