

# Module 3

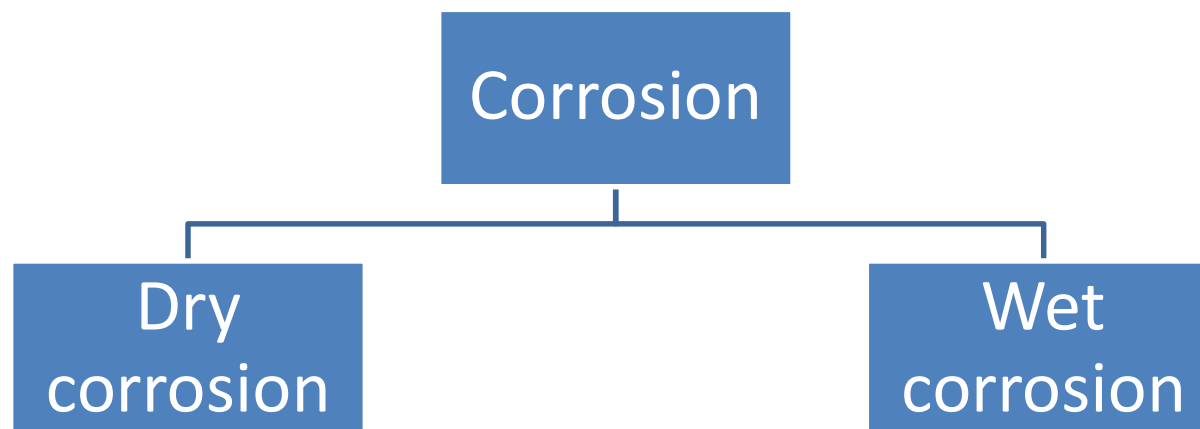
Corrosion Types and mechanism – dry and wet corrosion;  
Forms of corrosion –

- Differential aeration
- Pitting
- Galvanic
- stress corrosion cracking

- Corrosion is the unwanted reaction or destruction of a metal component by the environment, by chemical or electrochemical attack starting on the surface of a metal
- It's the reverse of the process of extraction of metal from their oxides
- E.g rusting of iron causes the reddish scale and powder of  $\text{Fe}_3\text{O}_4$
- The green film of basic carbonate on the surface of copper
- Corrosion causes huge damages to machinery, equipments and metal products

### Why do metals corrode?

Thermodynamically, pure metals are less stable than their compounds found in ores, which are less energetic (more stable) than their metal counterparts.



# Dry or chemical corrosion

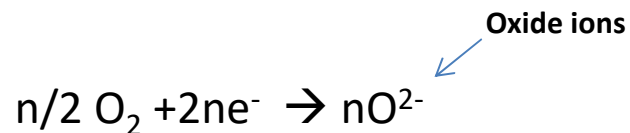
The direct chemical action of environmental/ atmospheric gases like oxygen, halogen, H<sub>2</sub>S, SO<sub>2</sub> or anhydrous inorganic liquids with metal surface

## a) Oxidation corrosion

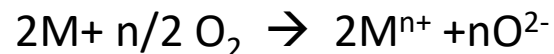
- This happens by the direct action of oxygen at low or high temperatures on metals, usually in the absence of moisture
- Alkali and alkaline earth metals are oxidised at low temperatures



loss of electrons (oxidation)



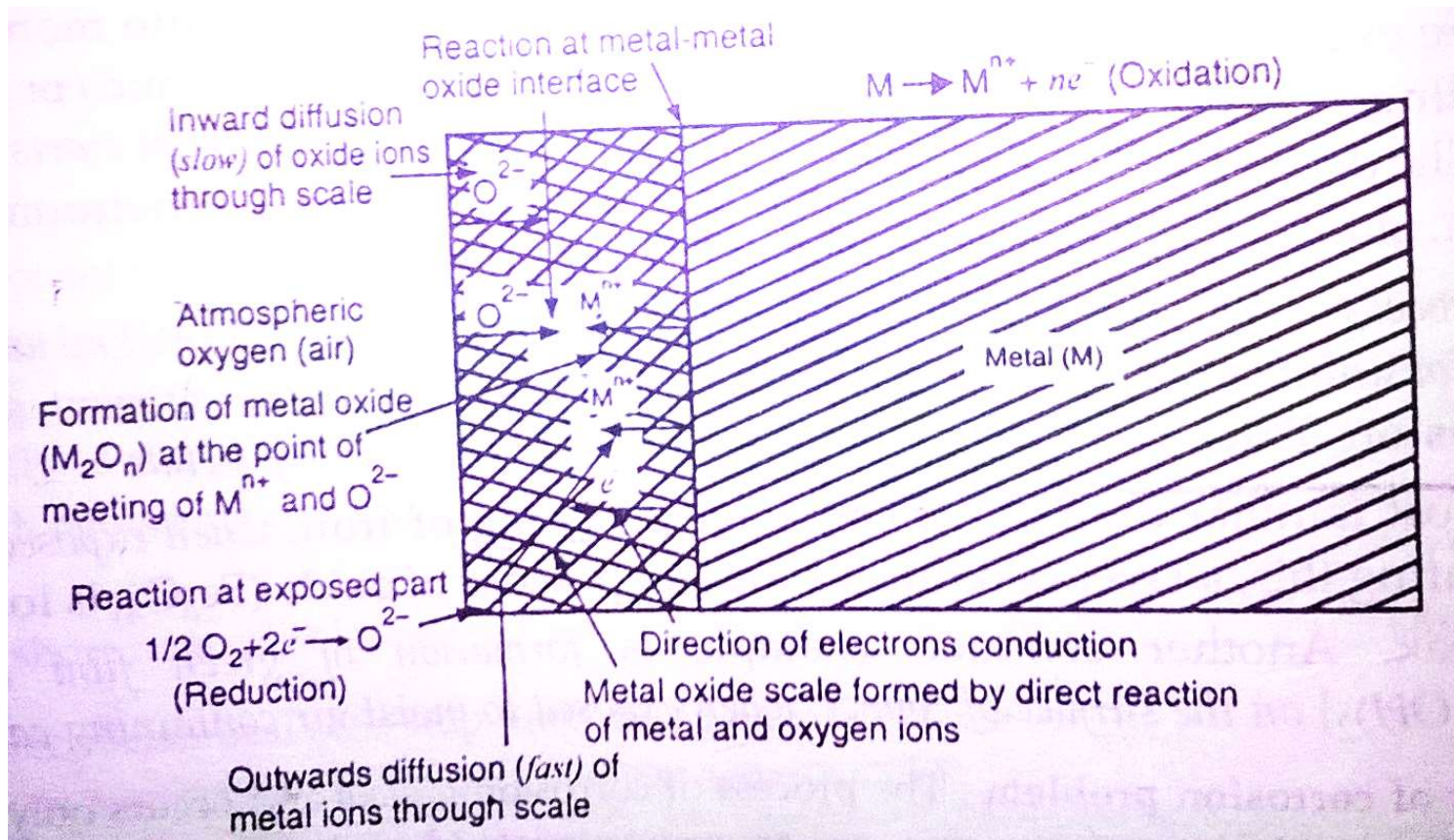
gain of electrons (reduction)



net reaction

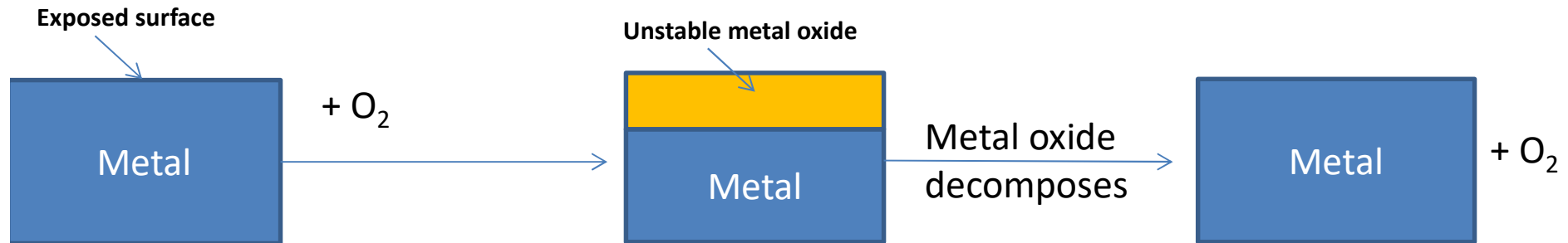
# Mechanism of oxidation corrosion

- At surface oxidation forms a metal oxide layer that tends to restrict further oxidation
- When layer < 30nm, its called a **film**; when layer > 30nm its called a **scale**
- For oxidation to continue, metal must diffuse outwards or oxygen must diffuse inward
- Outward diffusion of metal is more rapid due to smaller size of metal atoms than oxygen.

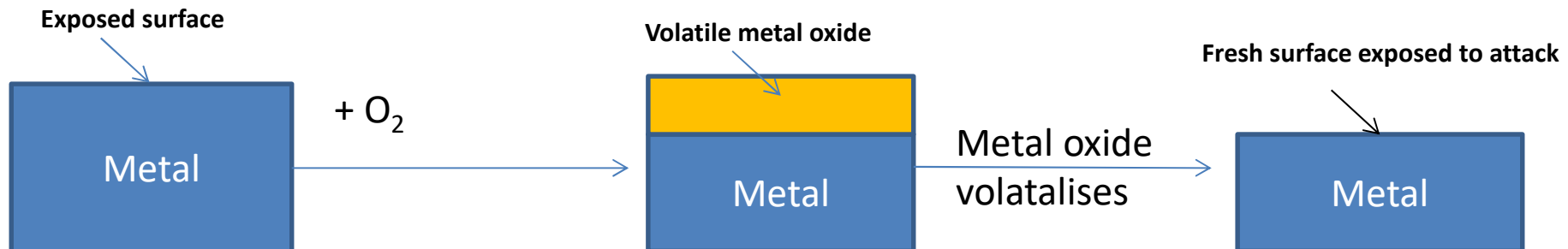


## Nature of oxide layer

- 1. Stable layer** - it is fine-grained and adheres very strongly to the parent metal surface
  - This layer can be **impervious** which cuts off penetration of oxygen inwards, thus shielding the metal surface
  - Oxides of Al, Sn, Pb, Cu are stable and impervious and form protective layers
- 2. Unstable layer**- the oxide layer decomposes back to metal and oxygen
  - As a consequence, no oxidation corrosion occurs. E.g Ag, Au and Pt

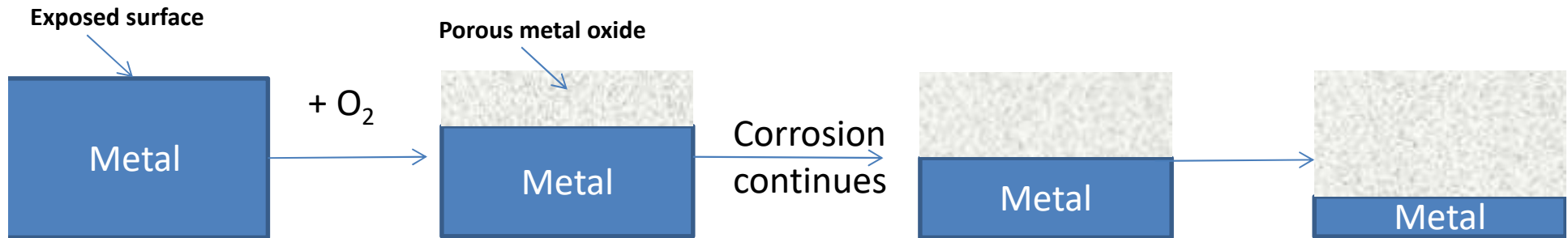


- 3. Volatile layer** – oxide layer formed volatilises, making underlying metal exposed for further attack, causing continuous rapid corrosion. E.g. Molybdenum



#### 4. Porous layer – oxide layer formed is porous and has cracks.

- Oxygen diffuses through the cracks and corrosion is unobstructed, till the entire metal is completely converted to the oxide



#### Pilling- Bedworth rule

- If the volume of the oxide formed is less than the volume of metal, the layer will be porous and will be non-protective
- Alkali and alkaline earth metals form oxides of lower volume than the metal volume
- Al forms oxides of higher volume and hence the layer is protective

## **b) Corrosion by gases like $\text{SO}_2$ , $\text{CO}_2$ , $\text{Cl}_2$ , $\text{H}_2\text{S}$ , $\text{F}_2$**

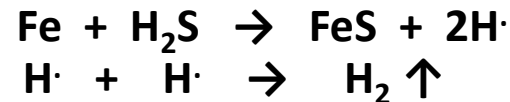
- Extent of corrosion depends on the affinity of metal towards the particular gas
- Degree of attack depends on whether a protective or non-protective layer is formed
- Dry  $\text{Cl}_2$  attacks Ag to form a protective, non porous AgCl layer
- Dry  $\text{Cl}_2$  attacks Sn to form a volatile  $\text{SnCl}_4$  layer, causing the destruction of the metal
- In petroleum industry,  $\text{H}_2\text{S}$  at high temperatures attack steel forming FeS scales, which affect normal operations

## **c) Liquid metal corrosion**

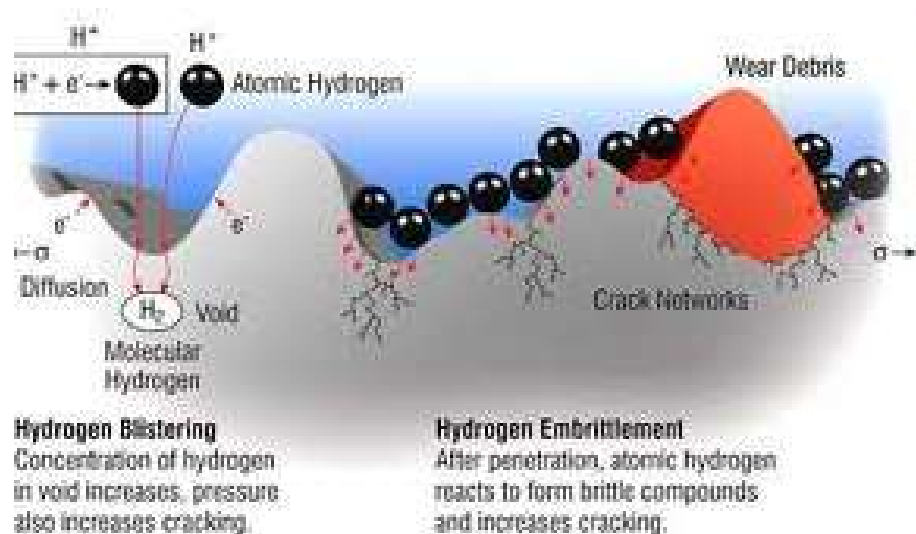
- When molten liquid metal passes over solid metal or alloy surface, it can
  - i. Dissolve the metal surface or
  - ii. Penetrate into the solid metal surface and weaken it
- Occurs in equipment used in nuclear power generation

- **HYDROGEN EMBRITTLEMENT** - Contact of metal with  $H_2S$  results in the generation of atomic hydrogen

E.g



- Corrosion caused by the exposure of metal to hydrogen environment.
- **Hydrogen in atomic state diffuses** into the metal matrix by permeating into the grains and collects in the voids present in the metal. The hydrogen atoms combine to form  $H_2$  gas.
- **A very high pressure is developed, which results in cracks and blisters on metal.** This process is called hydrogen embrittlement.

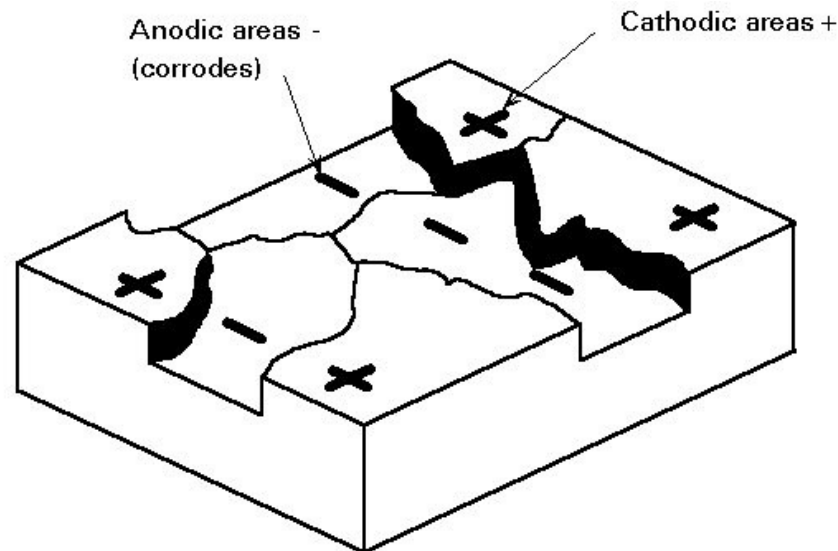




# Wet or electrochemical corrosion

## Wet corrosion happens when

1. A conducting liquid is in contact with a metal or
  2. Two dissimilar metals are in contact with a solution
- Corrosion happens due to the existence of anodic and cathodic regions on the surface of the metal, between which a current flows through the conducting solution
  - Anodes and cathodes may arise from differences in the constituent phases of the metal itself, from variations in surface deposits or coatings on the metal, or from variations in the electrolyte.
  - The metal may be immersed in an electrolyte or the electrolyte may be present only as a thin condensed or adsorbed film on the metal surface.



Pure water has poor electrical conductivity and the corrosion rate will be much lower than an acid solution of high conductivity

- At anode the metal gets oxidised and is dissolved or converted to combined forms such as oxides. In wet corrosion , corrosion always happens at the anode
- At cathode, usually dissolved constituents gain electron and form anions ( $O^{2-}$ ,  $OH^-$  etc)
- The metal ions at anode and the anions at cathode diffuse towards each other and form the corrosion product somewhere in between
- In summary, wet corrosion involves
  1. Formation of anodic and cathodic regions in contact with each other
  2. Presence of a conducting medium
  3. Corrosion at the anodic region alone
  4. Formation of corrosion product in between the anodic and cathodic region

# Mechanism of Wet corrosion

- At anode, metal dissolves as the metal ion by losing electrons during oxidation



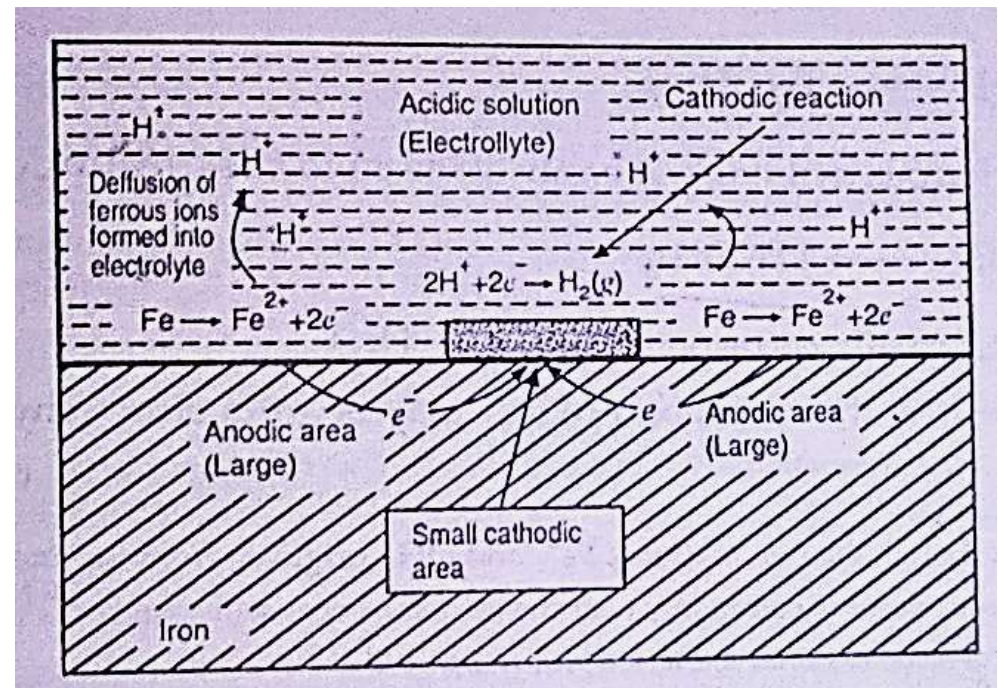
- The cathodic reduction can either lead to a) hydrogen evolution or b) absorption of oxygen

## Corrosion with H<sub>2</sub> evolution

- This occurs in acidic environments
- The electrons released by the oxidation (corrosion) process flows to the cathode, where they combine with the H<sup>+</sup> ions to evolve H<sub>2</sub> gas

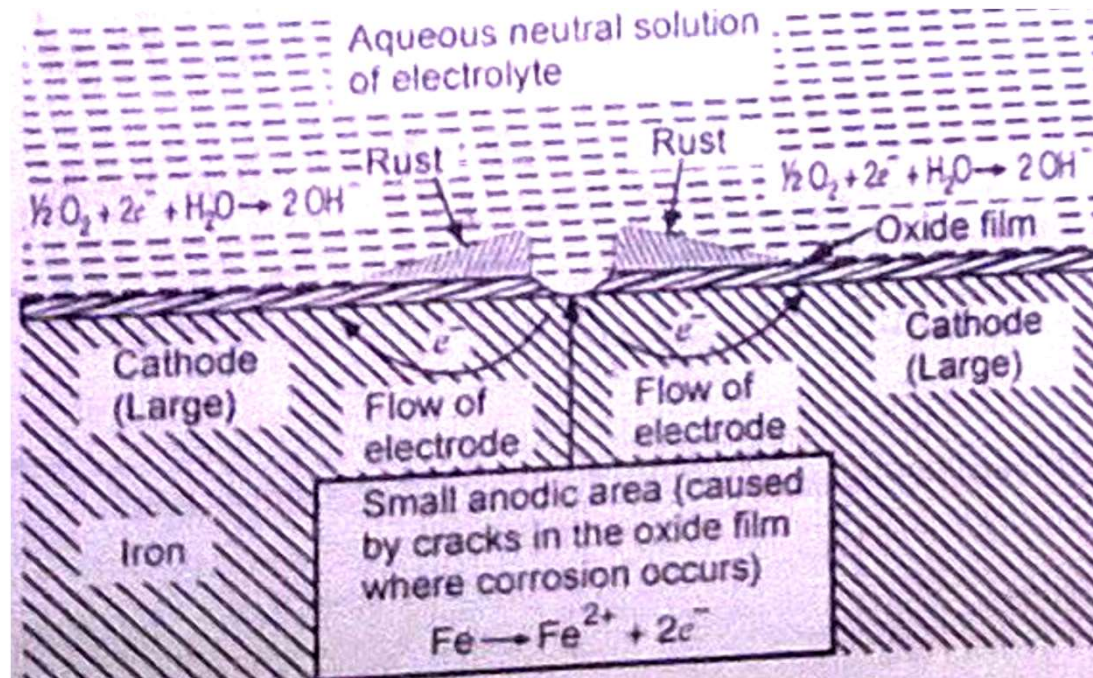


- Overall reaction is



## Corrosion with absorption of oxygen (in neutral medium)

- Rusting of iron in aqueous electrolyte solution (NaCl) in presence of oxygen
- Surface is usually coated with a thin film of iron oxide, which can develop cracks
- Anodic areas are created on the surface during such cracking

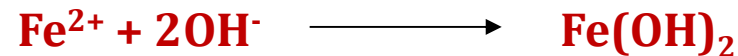


- the anodic areas are small and the cathodic areas are large
- At anode iron oxidises to  $\text{Fe}^{2+}$  with liberation of electrons  

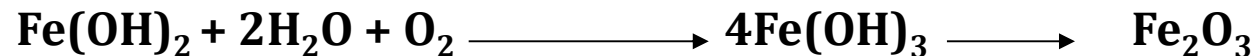
$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$$
- The electrons flow to the cathodic area, where they interact with dissolved oxygen



- $\text{Fe}^{2+}$ , formed earlier, diffuses to the surface and form ferrous hydroxide



- If enough oxygen is present, ferrous hydroxide is oxidised to ferric hydroxide, which is called yellow rust, which actually is  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$



- If enough oxygen is not present, ferrous hydroxide is oxidised to black anhydrous magnetite  $\text{Fe}_3\text{O}_4$

- Though  $\text{Fe}^{2+}$  and  $\text{OH}^-$  are formed at anode and cathode respectively, rust is usually formed near the cathode, because of the faster diffusion of the smaller  $\text{Fe}^{2+}$  ions
- Increase in oxygen content has two effects:
  1. Forces the cathodic reaction to the right, producing more  $\text{OH}^-$  ions
  2. Removes more electrons and so accelerates the corrosion at the anode.
- Thus oxygen presence greatly accelerates the rusting process

## The Electrochemical series

Metal	Potential in volts	
$\text{Li}^+ + 1\text{e}^- = \text{Li}$	<b>-3.05</b>	Anodic
$\text{K}^+ + 1\text{e}^- = \text{K}$	<b>-2.93</b>	
$\text{Ca}^{2+} + 2\text{e}^- = \text{Ca}$	<b>-2.90</b>	
$\text{Na}^+ + 1\text{e}^- = \text{Na}$	<b>-2.71</b>	
$\text{Mg}^{2+} + 2\text{e}^- = \text{Mg}$	<b>-2.37</b>	
$\text{Al}^{3+} + 3\text{e}^- = \text{Al}$	<b>-1.66</b>	
$\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}$	<b>-0.76</b>	
$\text{Cr}^{3+} + 3\text{e}^- = \text{Cr}$	<b>-0.74</b>	
$\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}$	<b>-0.44</b>	
$\text{Ni}^{2+} + 2\text{e}^- = \text{Ni}$	<b>-0.23</b>	
$\text{Sn}^{2+} + 2\text{e}^- = \text{Sn}$	<b>-0.14</b>	Cathodic
$\text{Pb}^{2+} + 2\text{e}^- = \text{Pb}$	<b>-0.13</b>	
$\text{H}^+ + 1\text{e}^- = 1/2\text{H}_2$	<b>0.00</b>	
$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$	<b>+0.34</b>	
$\text{Ag}^+ + 1\text{e}^- = \text{Ag}$	<b>+0.80</b>	
$\text{Pt}^{4+} + 4\text{e}^- = \text{Pt}$	<b>+0.86</b>	
$\text{Au}^+ + 1\text{e}^- = \text{Au}$	<b>+1.69</b>	
$1/2 \text{F}_2 + 1\text{e}^- = \text{F}^-$	<b>+2.87</b>	

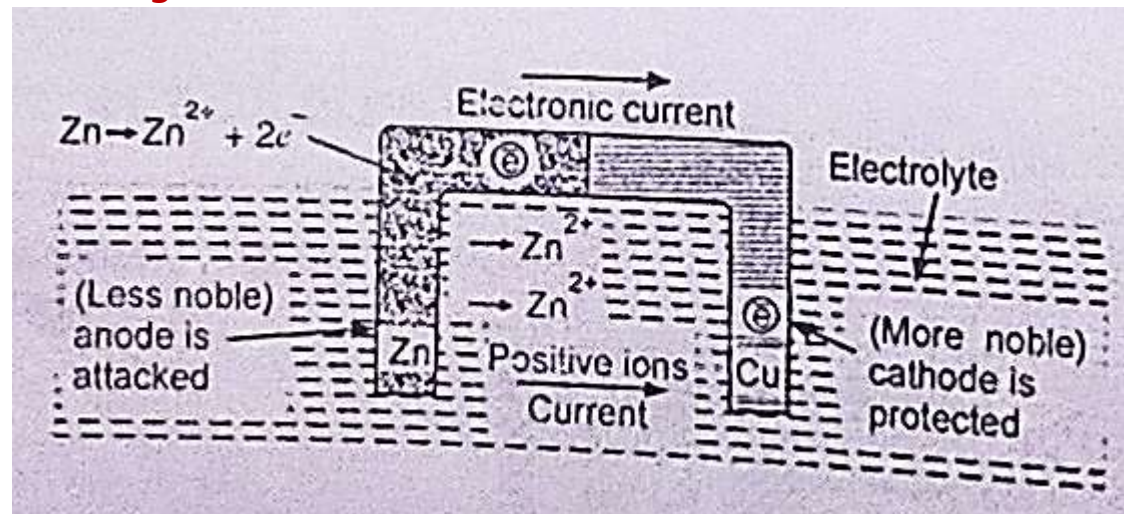
Standard Electrode (  $E^\circ = 0.00\text{V}$  at std condition )



# Types of corrosion

## 1) Galvanic or bimetallic corrosion

- When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in the electrochemical series will undergo corrosion
- E.g Zinc and copper metals
- Zinc forms the anode and is corroded and gets dissolved
- In acidic solution,  $H_2$  is evolved and in neutral or slightly alkaline solutions, oxygen absorption takes place
- **Examples**
  - *Steel screws in brass material*
  - *Lead-antimony solder around copper wire*
  - *Steel propeller shaft in bronze bearing*
  - *Steel pipe connected to copper plumbing*





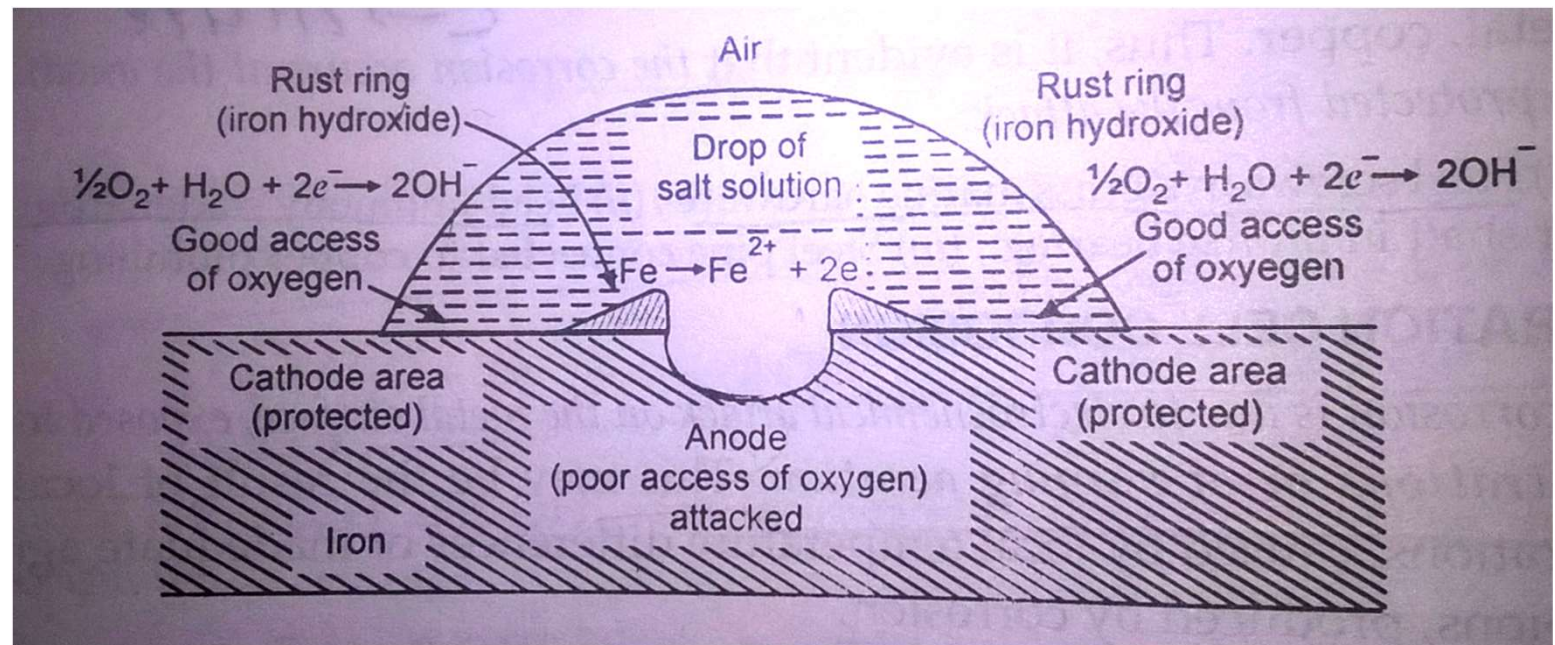
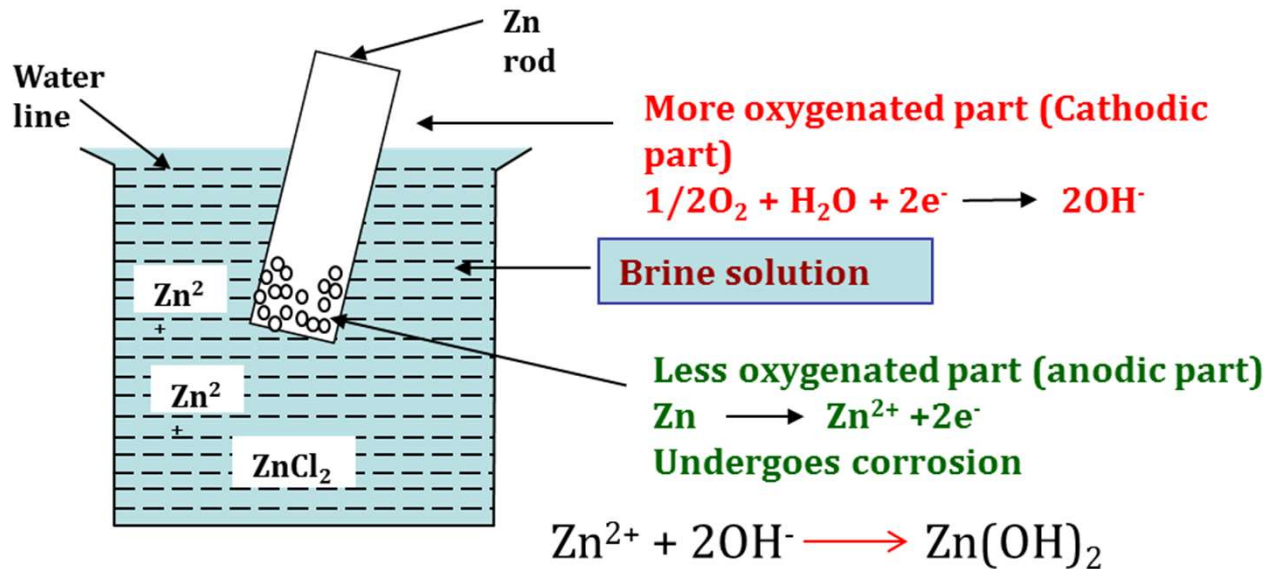
# Concentration cell corrosion

- Concentration cell corrosion happens when metal is exposed to electrolyte of varying concentration or aeration
- It may be due to local differences in metal-ion concentration caused by temperature difference or inadequate agitation or due to slow diffusion of metal ions

## 2) Differential aeration corrosion

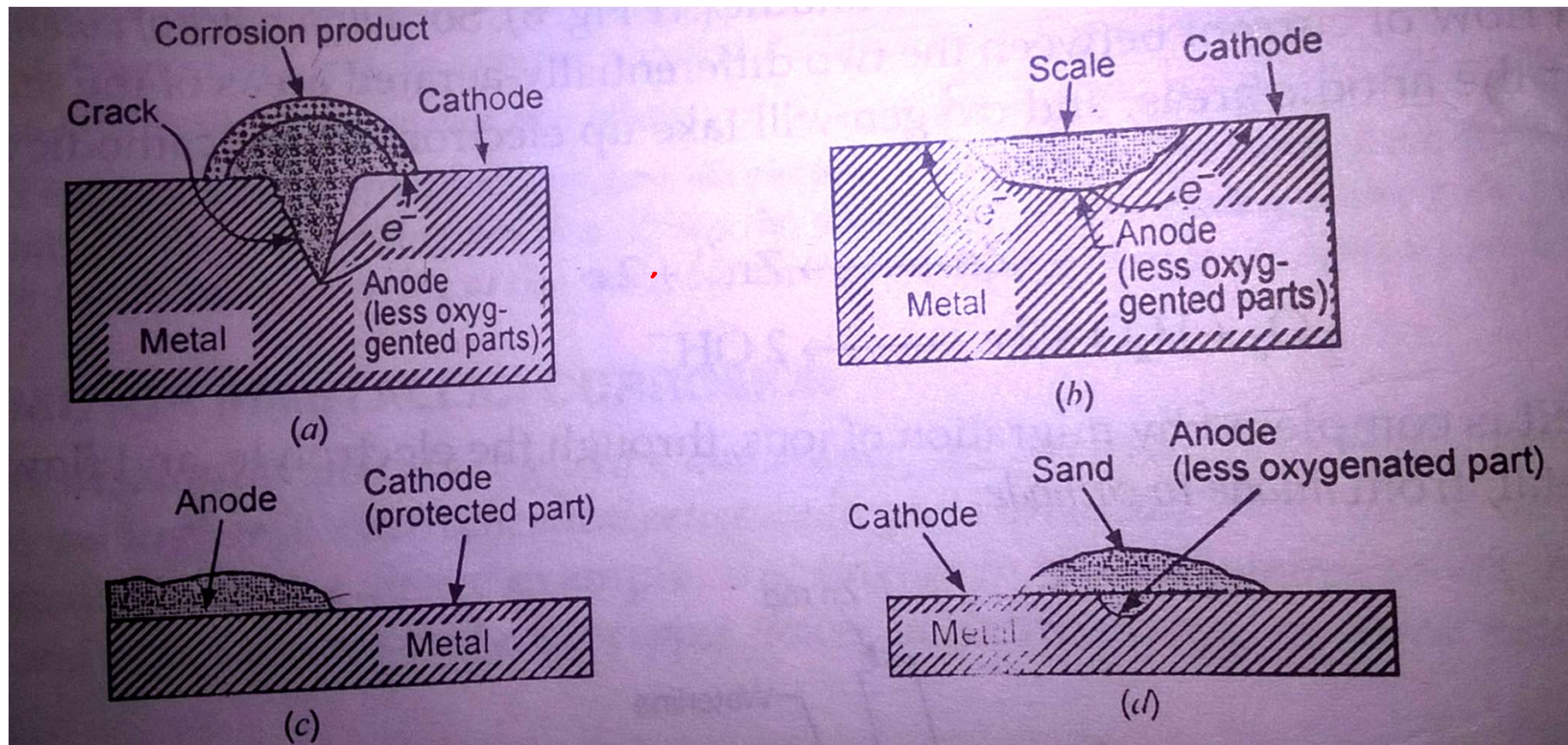
- The most common type of concentration cell
- Happens when one part of metal is exposed to a different air concentration from the other part
- This causes a potential difference between differentially aerated areas
- Poorly oxygenated parts are anodic and *vice versa*
- Metals partially immersed in 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.

- Similarly, iron corrodes under drops of water (salt solution)
- Thus oxygen concentration cell happens where there is less oxygen concentration



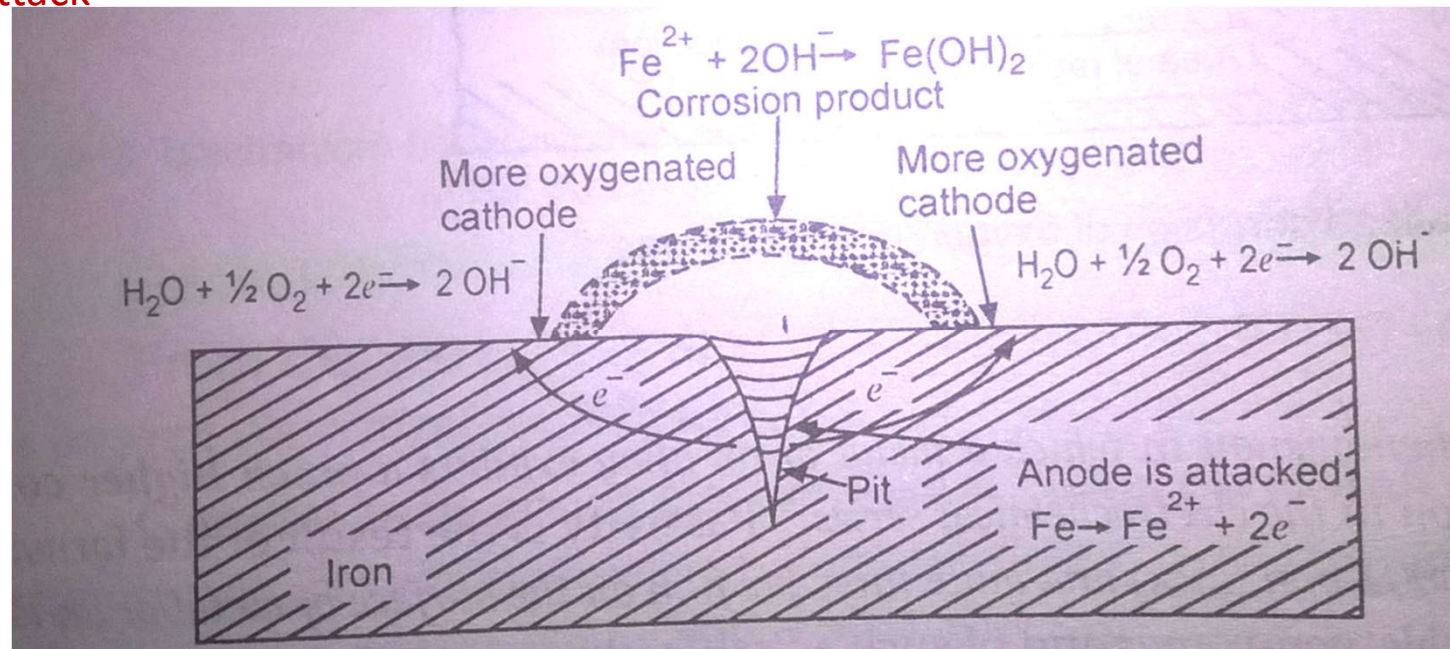


- Corrosion is accelerated in apparently inaccessible places, because the oxygen deficient areas serve as anodes. Hence cracks and crevices act as focal points of corrosion
- Accumulation of dirt, sand, scale or other contaminations accelerate the corrosion leading to localised corrosion due to short supply of oxygen
- Metals exposed to aqueous media corrode under blocks of wood or pieces of glass.
- Accumulated corrosion product further accelerates the process by reducing oxygen supply

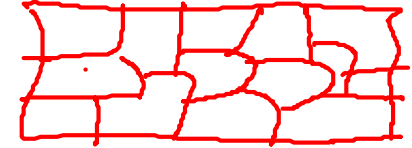


### 3) Pitting corrosion

- A localised accelerated attack resulting in formation of cavities around which the metal is relatively unattached
- It results in formation of pinholes, pits and cavities in the metal, giving rise to small anodic and large cathodic areas
- Breakdown of the protective film may be due to
  1. Surface roughness or non-uniform finish
  2. Scratches or cut edges
  3. Local straining of metal
  4. Alternating stresses
  5. Sliding under load
  6. Chemical attack

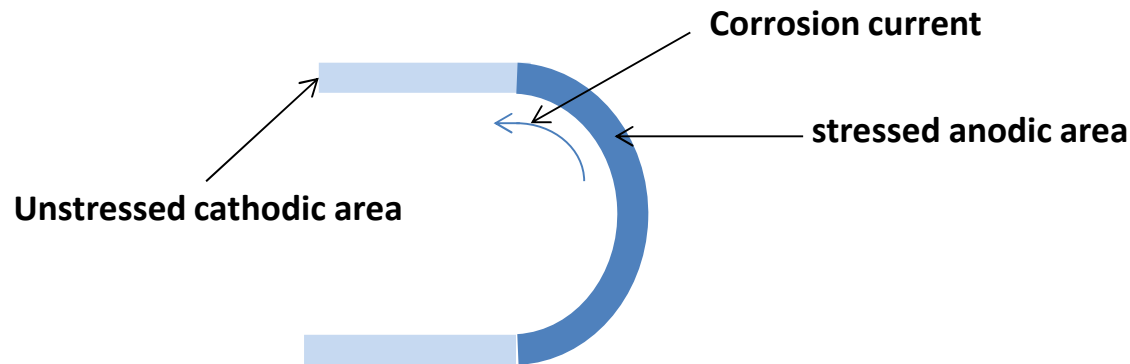


## 4) Stress corrosion cracking (SCC)



- Stress corrosion cracking (SCC) is a progressive fracturing that occurs in metals as a result of the combined influence of tensile stress and a corrosive environment.
- Tensile stress may be due to any mechanical operation like cold working, welding, bending, pressing, riveting, hammering
- Highly localised corrosion takes place, under specific corrosive environment
- E.g KOH/NaOH solution attacks stressed mild steel
  - Stressed portion of brass corrodes in ammonia environment

### Stress corrosion in a bent metal strip



- Stressed portion of metal acts as anodic area wrt unstressed portion and undergoes corrosion



# Types of Stress corrosion

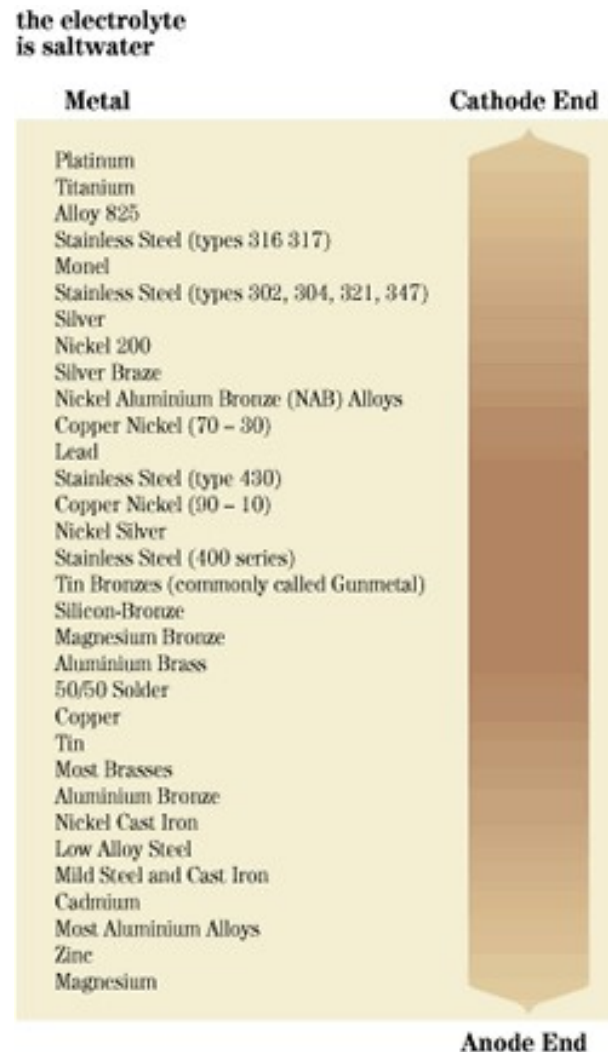
- **Season cracking**- a term applied to corrosion of copper alloys, mainly brasses.
- Pure copper is immune, but presence of small amounts of alloying elements (P, As, Sb, Zn, Al, Si) result in sensitivity towards stress
- E.g. alpha brass undergoes intergranular cracking in an environment containing traces of ammonia
- The attack occurs along the grain boundaries which become more anodic



- **Caustic embrittlement**- occurs in mild steel exposed to alkaline solution at high temperatures and stress
- Usually associated with steam boilers and heat transfer equipments
- Highly alkaline water attacks the stressed portion of iron through NaOH formation
- Concentration cell forms around the crevices, formed by the leaching of Fe by NaOH, rivets and joints and further stress corrosion propagates

# Galvanic series

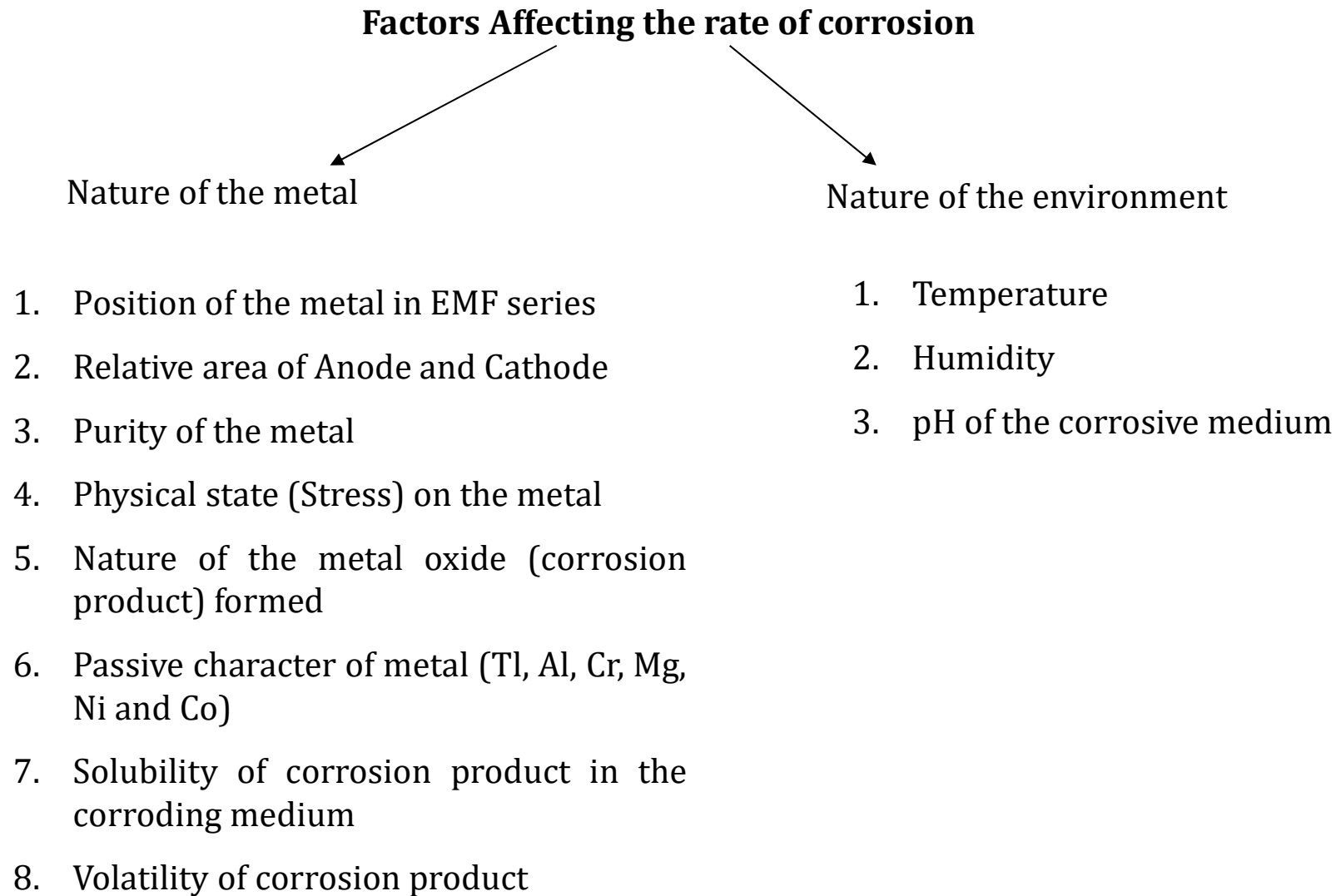
- Though electrochemical series is a good tool to predict the corrosion of metals, there are exceptions
- E.g though Ti is above Ag, it is less reactive than Ag towards corrosion
- In Zn-Al couple, Zn is corroded despite being lower than Al in the series
- Both these are the result of formation of protective oxide layer



- Factors that enhance corrosion and choice of parameters to mitigate corrosion.



Refer to your textbook and study in detail all the effects of the following factors:

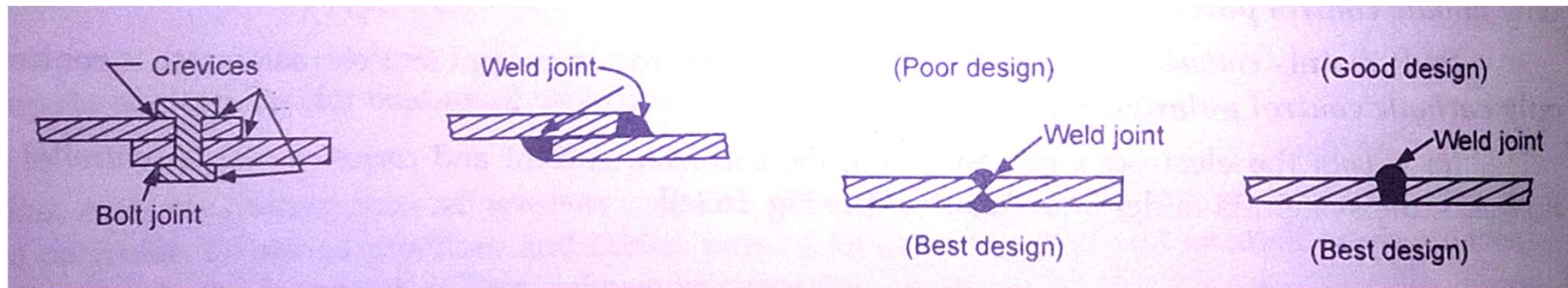


# Parameters for mitigating corrosion

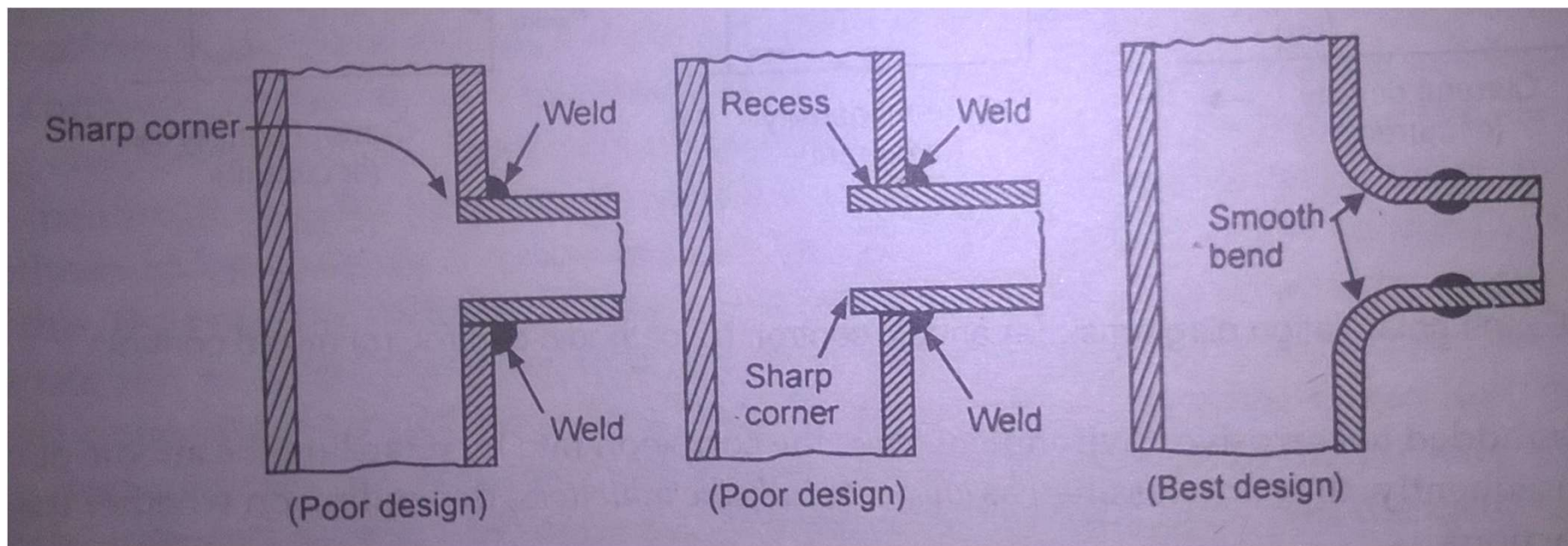
## 1) Proper design

- The design of material should be in such a way that even if corrosion occurs, it occurs uniformly and not in an intense and localised fashion
- Avoiding contact of dissimilar metals in presence of a corroding solution - If not, corrosion will be localised on the more active metal and the less active metal stays protected
- When two dissimilar metals have to be in contact, the anodic metal should have a large surface area than the cathodic metal (as small as possible)
- When two dissimilar metals have to be in contact, they should be as close together as possible in the electrochemical series
- When direct joining of two dissimilar metals is unavoidable, an insulating fitting maybe applied in between to avoid direct contact between the two metals
- The anodic metal should not be painted or coated, when in contact with a dissimilar cathodic metal. Any break in coating will lead to rapid localised corrosion
- In homogeneities in metal as well as corrosive environment must be prevented.
  - A proper design should eliminate presence of crevices (even in same metal) because crevices permit concentration differences
  - Bolts and rivets are undesirable for this reason. Instead a butt-weld is preferred

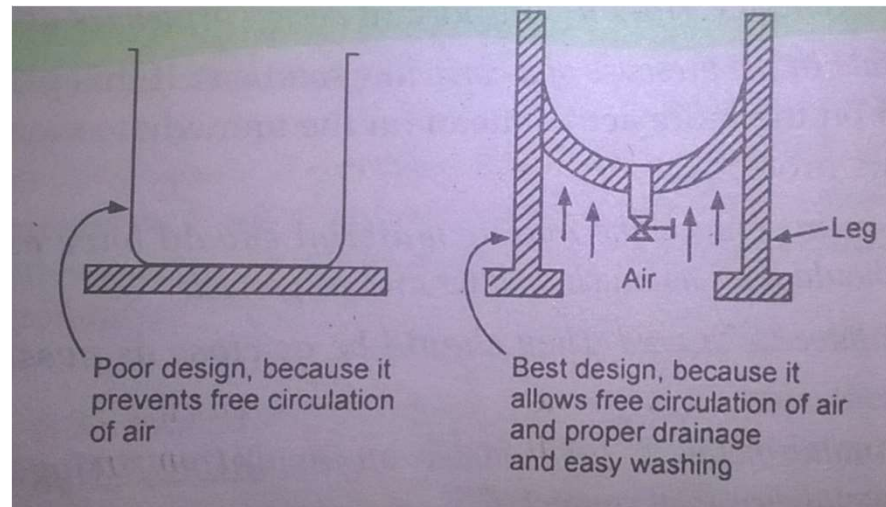
- When its not possible to avoid crevices, coating with paint or with an impervious material can deny access to the corrosive medium at these joints (crevices)



- Sharp corners and recesses should be avoided, as two or more metal parts are joined together, as they favour formation of stagnant areas and accumulation of solids.
  - Also they create problems in cleaning and flushing operations



- If possible, the equipment should be fitted with legs to allow free circulation of air and prevent stagnant pools or damp areas



- Proper design should prevent subjecting some areas to stress (cold worked part). A galvanic couple could be set up if a non-stressed area of the metal are in contact

## 2) Using pure metal

- Impurities cause heterogeneity, which decreases corrosion resistance
- Metals such as Al & Mg , gain an impervious oxide coating during the purification process, making the metal passive towards corrosion
- Corrosion resistance of purified metals depends on the environment to which they are exposed. E.g purified Al will get corroded, if kept in alkaline medium
- In many cases pure metals are avoided due to
  - High costs of purifying
  - Inadequate mechanical properties like softness and low strength
- Purification of metals is of use only under conditions in which corrosion occurs by a purely electrochemical mechanism and not by direct chemical attack

## 3) Using alloys

- Noble & precious metals (Au, Pt) are corrosion resistant
- Many metals are made corrosion resistant by alloying them with other metals, maintaining perfect homogeneity
- E.g Cr is best suited for iron or steel because their film is self healing
- Steel containing upto 13% Cr are used in cutlery and surgical instruments
- Ferrite stainless steel (13 – 25% of Cr) is used in turbines and heat resistant parts

#### 4) Modification of the environment

- Corrosive nature of environment can be reduced by
  - Removal of the harmful constituents or by
  - Addition of substances that will neutralise the corrosive constituents
- **Deaeration**- by adjustment of temperature and mechanical agitation, dissolved oxygen is expelled and thus prevents the formation of oxygen concentration cell type corrosion
  - The method also removes CO<sub>2</sub>
- **Deactivation** – addition of chemicals that rapidly combine with O<sub>2</sub>. e.g Sodium Sulphite or hydrazine



- **Dehumidification** – reduces moisture content to minimum levels so that corrosion maybe prevented. Alumina or silica gels are used in closed areas to adsorb moisture
- **Alkaline neutralisation** – acid character of environment (due to presence of H<sub>2</sub>S, HCl, CO<sub>2</sub>, SO<sub>2</sub> etc) is neutralised by alkaline neutralisers such as NH<sub>3</sub>, NaOH, lime, naphthenic soaps
  - Neutralisers are introduced in liquid or in vapour form to the corroding parts
  - Controlling corrosion in refinery equipments