

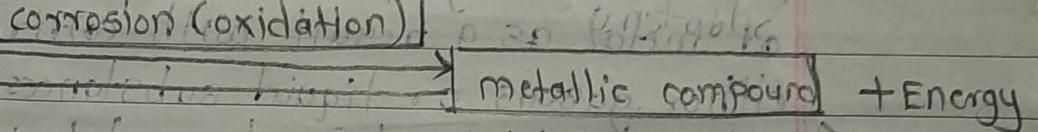
## Corrosion.

Anisomar 20-09-2022

- Corrosion is nothing but the deterioration of a substance due to its reaction with its environment.
  - Deterioration is continuously taking place.
  - Deteriorative mechanisms are different for three types of materials
    - In metals materials loss either by dissolution or by formation of non metallic scale or film.
    - Ceramic materials are relatively resistant to deterioration which usually occurs at elevated temperatures.
    - In polymers degradation occurs due to heat and radiation.
  - Corrosion is general term applied to the deterioration of metal as a result with environment consisting of either gaseous or liquid substances.
  - It may also be defined as deterioration of a metal by chemical or electrochemical reaction with its environment.
  - corrosion is an important factor in chemical process plant
- All metals and alloys are susceptible to corrosion. Gold has excellent resistance to corrosion under atmospheric condition but it gets readily corroded when exposed to mercury at ambient temperature.
- iron gets rusted in the atmosphere but it does not corroded in mercury.
  - Thus several metals and alloy perform effectively in a given environment.
  - further there are several methods to effectively control and minimize corrosion.

## Causes of corrosion

- most of metals exist in nature in combined forms as their oxides, carbonates, sulphides, chlorides.
- The compounds represent their thermodynamically stable state.
- During the extraction of metals, these oxides are reduced to metallic state by supplying considerable amount of energy.
- Hence isolated pure metals are <sup>metal</sup> regarded as excited state than their corresponding oxides. So metals have natural tendency to go back to their combined state (mineral one).



(A state of oxidation is higher & (A state of reduction (higher energy) metallurgy (Reduction) & lower energy)

Example formed at room temperature

Corrosion can be defined as any process of deterioration (or destruction) and consequent loss of solid metallic material through an unwanted chemical or electrochemical attack by its environment starting at its surface

### example

① Rusting of iron: It has taken in air and water. Rusting of iron oxide is formed when exposed to the atmospheric condition.

A layer of reddish scale or power of oxide ( $\text{Fe}_2\text{O}_3$ ) is formed

### ② Corrosion of Cu

Formation of green film of basic carbonate [ $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ] on the surface of copper, when exposed to moist air containing carbon dioxide



## Theories of corrosion

### (a) Nature of corrodent :-

corrosion, classified

usually involves <sup>Dry</sup>

→ occurs reaction with  
gases at high temp

<sup>Wet</sup>

→ ~~occurs~~ occurs in presence of  
water or conducting  
liquid

### (b) Mechanism of corrosion :- involve direct chemical attack or indirect electrochemical attack

### (c) Appearance of corroded metal :-

corrosion may be either uniform or it is localized  
and only small areas are attacked

→ metal is not present in pure state

metal corroded in the form of impurities of metals

- ① Dry corrosion  
② Wet corrosion
- ① Dry or chemical or Atmospheric corrosion

- Dry corrosion occurs mainly by direct attack of atmospheric gases such as oxygen, halogens, hydrogen sulphide, nitrogen, and sulphur dioxide etc. on the surface of metals.
- The metal forms corresponding compounds such as oxides, sulphides, carbonates etc.
- This type of corrosion forms solid layer of corrosion products of different kinds (less than  $300^{\circ}\text{A}$ )
- If the layer formed is very thin it is called 'film' and if it exceeds this value it is called 'scale'.
- The action of some organic or anhydrous inorganic liquids on metals also causes this type of corrosion.

This type of corrosion is divided into following classes.

- i] corrosion due to oxygen - leading to formation of metal oxides
- ii] corrosion due to other gases - leading to formation of other compounds
- iii] corrosion due to other corrosive liquids - such as other molten metals.

### ① corrosion due to oxygen :-

- This type of corrosion occurs due to attack of atmospheric oxygen on metal surface either at low or high temperature. forming metal oxide as
- $$\text{Metal} + \text{oxygen} \longrightarrow \text{Metal oxide}$$

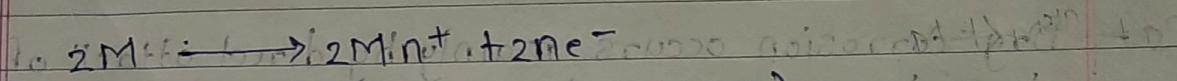
Normally more active metals get corroded faster than less active metal.

e.g. alkali metals and alkaline earth metal (Li, Na, Ca, Mg)

get oxidized at low temp

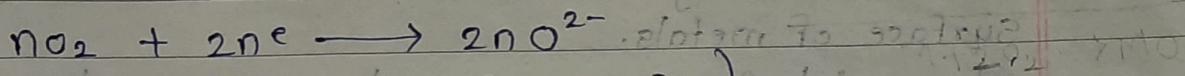
- all metals (except Ag, Au and Pt) are oxidized at high temperature

with no loss in density, no pitting.

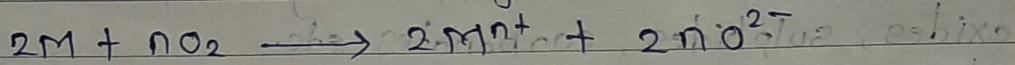


oxidized, exposed metal, loss of electrons

diffusion of oxide ions through scale, oxygen, thickness  $\rightarrow O^{2-}$



so there is oxidation (gain of  $e^-$ ), loss of  $O^{2-}$



metals oxidation react with  
oxide metal oxide

solid halide salt will form an insoluble salt

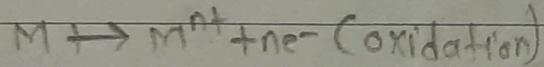
Mechanism: - i) when salt dissolves in water

anions exchange with cations to form salt

Surface of the metal is oxidized to form oxide scale which forms a barrier for further oxidation. oxidation is continuous under following two cases

i] The metal diffuses outward through the scale to the surface

ii] oxygen diffuses inward through the scale to the underlying metal



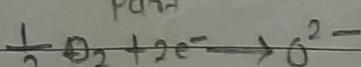
inward diffusion

of oxide ions

through scale

( $O^{2-}$ )

Reaction at exposed  
part



(Reduction)

excess of sub. dissolved

Metal (M)

to expose underlying film

to expose underlying film

to expose underlying film

outward diffusion of metal

ion through scale

( $M^{n+}$ )

oxidation corrosion of metals

- The nature and stability of oxide film depends on temperature, humidity and atmospheric conditions
- The corrosion depends upon the type of the oxide film.
- It can be classified as:
  - i] stable oxide film  porous  non-porous
  - ii] unstable oxide film
  - iii] volatile oxide film

### Pilling - Bedworth rule

According to it, an oxide is protective or non-porous, if the volume of the oxide is at least as great as the volume of the metal form which is formed:

- an oxide is protective or non-porous, if the volume of the oxide is at least as great as the volume of the metal form which is formed;
- on the other hand, if the volume of oxide is less than the volume of the metal, the oxide layer is porous and hence non-protective, because it cannot prevent the access of oxygen to the fresh metal surface below.

#### I] Stable oxide film

If the oxide film is stable, it acts as a protective coating to the metal surface.

- A stable layer of metal oxide is formed which is impermeable, and this protects the metal from the further corrosion.

#### (a) porous oxide layer

- If oxide film formed on metal surface is porous in nature, the rate of further corrosion is not reduced much.
- e.g. alkali metals such as Li, Na, K or alkaline earth metals such as Ca, Mg etc.

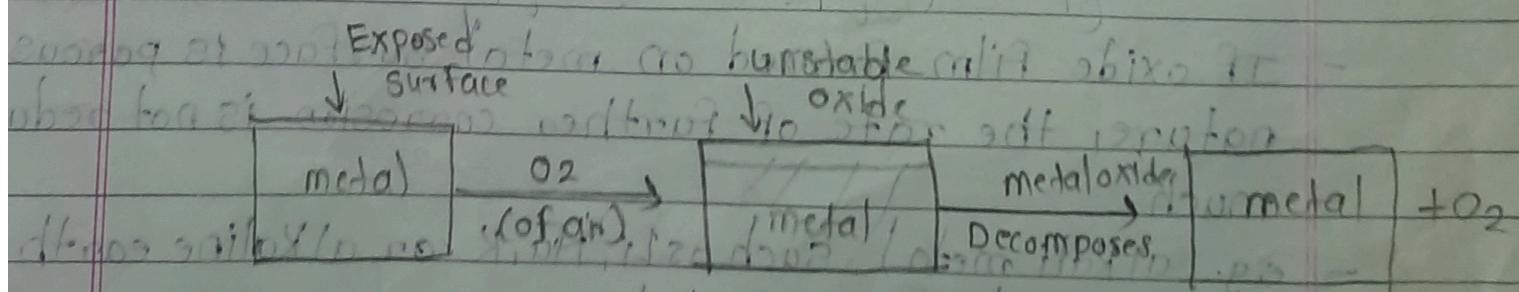
- These metals react with oxygen forming oxide such as  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$  etc.
- where volume of oxide formed is less than the volume of the reacted metal.  $\text{e.g. } \text{Al} + \text{O}_2 \rightarrow \text{Al}_2\text{O}_3$
- Hence porous oxide scale permits free access of oxygen to the underlying metal surface (through cracks and pores) thus corrosion continues non-stop.

### (b) Nonporous oxide film

- If the oxide film formed is non-porous in nature the rate of corrosion reduces considerably and in most of cases corrosion of metal stops.  $\text{e.g. } \text{Al} + \text{O}_2 \rightarrow \text{Al}_2\text{O}_3$
- The metals like Al, Cr, Fe, Pb, Ti etc. form their oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  etc.  $\text{molar ratio} = 1:1$
- where volume of oxide formed is greater than the volume of the reacted metal.  $\text{e.g. } \text{Al} + \text{O}_2 \rightarrow \text{Al}_2\text{O}_3$
- Hence in non-porous oxide film no leaving any access for further attack of oxygen thereby stopping further corrosion.

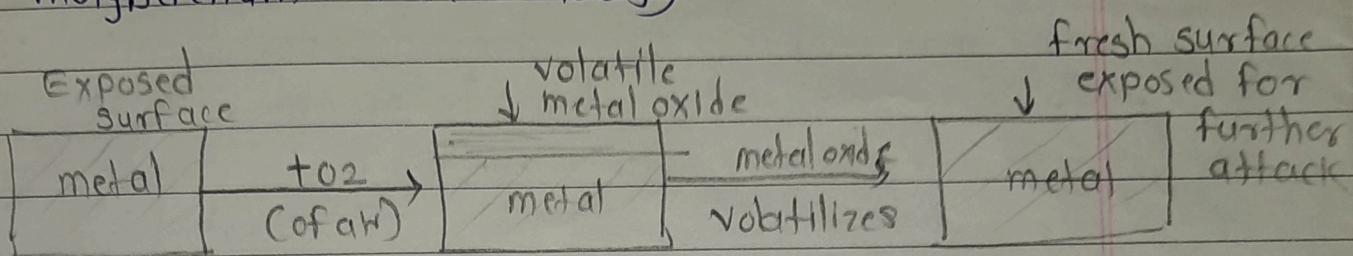
### (c) Unstable oxide film :-

- If the oxide film formed is unstable it decomposes on the metal surface forming back the metal and oxygen.
- $\text{Metal} + \text{O}_2 \rightarrow \text{Metal Oxide} \rightarrow \text{Metal} + \text{O}_2$
- Thus oxidation corrosion does not occur
- e.g. gold, platinum, silver etc.

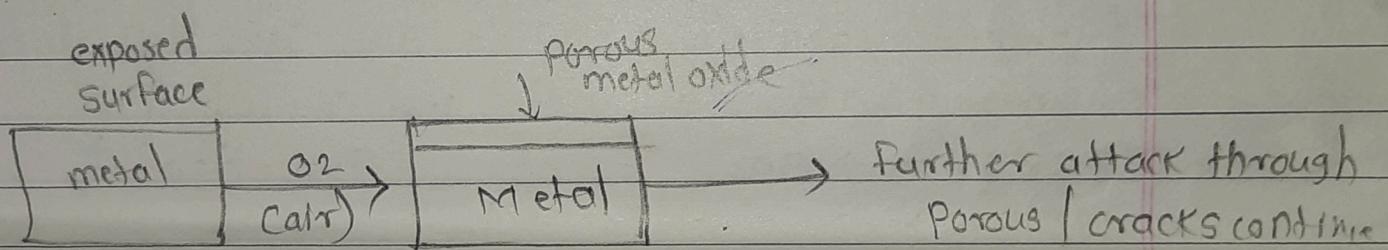


### (3) Volatile oxide film

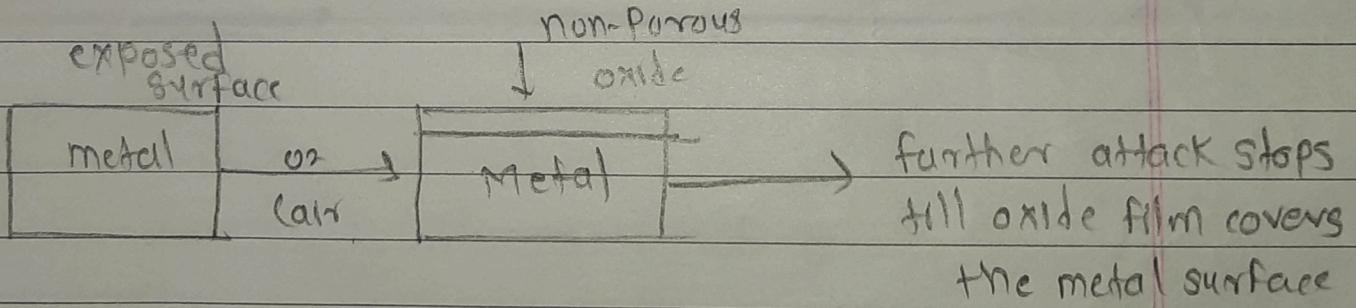
- If the metal oxide film is volatile the oxide is volatilized as soon as it is formed and hence the underlying metal surface is exposed for further attack  
 eg. molybdenum oxide ( $\text{MoO}_3$ ) film is volatile



### Volatile oxide layer:



### Porous oxide layer



### Non-Porous oxide layer

### ii) corrosion due to other gases

- Gases like carbon dioxide, sulphur dioxide, nitrogen oxides, chlorine and fluorine under dry conditions corrode metals.
- The degree of corrosion depends upon chemical affinity of metal
- The degree of attack depends on the formation of protective or non-protective films on the metal surface.
- $\text{Cl}_2$  attacks the metal to form metal chloride generally it forms of porous film  
$$\text{M} + \text{Cl}_2 \rightarrow \text{MCl}_2$$
e.g.  $\text{Mg} + \text{Cl}_2 \rightarrow \text{MgCl}_2$
- Sulphur containing gas like  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{H}_2\text{S}$  formed during combustion attack on metal and corrode them  
$$\text{S} + \text{O}_2 \rightarrow \text{SO}_2$$
      
$$\text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$$
  
$$\text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeS} + \text{H}_2$$
- In petroleum industry,  $\text{H}_2\text{S}$  gas at high temperature react with steel forming  $\text{FeS}$  scale

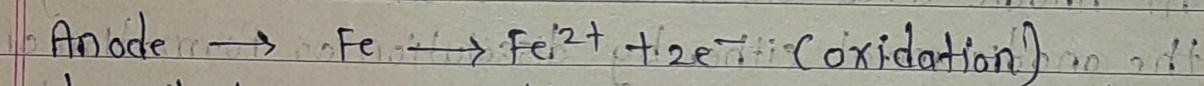
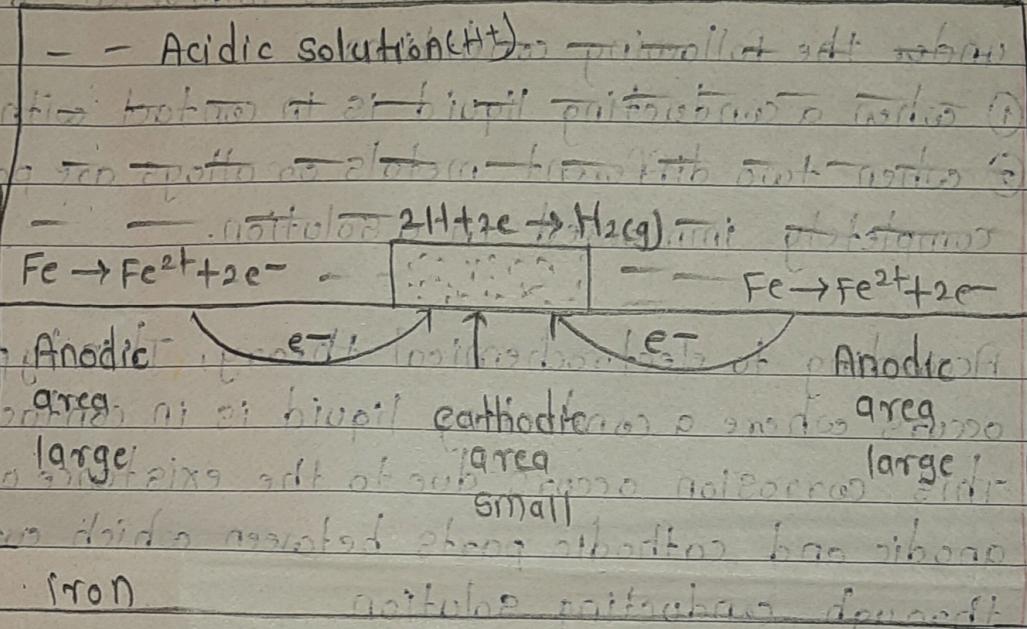
## Wet corrosion or electrochemical corrosion

- when metal surface is in immediate contact of aqueous acidic, alkaline / neutral electrolyte solutions, the short circuited galvanic cells get set all along the surface of the metal
  - wet corrosion also known as immersed corrosion occurs under the following conditions:-
    - ① when a conducting liquid is in contact with the metal
    - ② when two different metals or alloys are partially or completely immersed in a solution.
  - According to electrochemical theory, This type of corrosion occurs where a conducting liquid is in contact with the metal, this corrosion occurs due to the existence of separate anodic and cathodic parts between which current flows through conducting solution
  - At Anodic area oxidation reaction occurs thereby destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.
- ### Mechanism

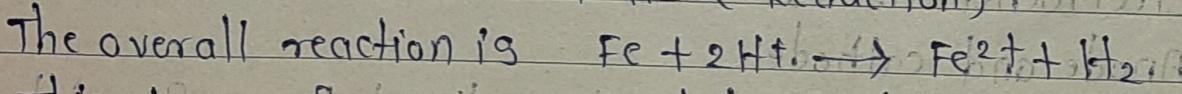
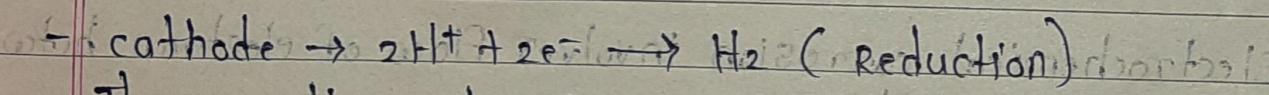
- Electrochemical corrosion involves flow of electron between Anode and cathode
- The anodic reaction involves dissolution of metal liberating free electrons  
$$\text{Metal} \rightarrow \text{Metal}^{+} + \text{e}^{-}$$
- The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen  
$$2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2$$

# ① Hydrogen evolution mechanism

This type of corrosion occurs in acidic medium e.g. considering metal Fe, anodic reaction is dissolution of ions as ferrous ions with liberation of electrons.



The electron released flows through the metal from anode to cathode, where H<sup>+</sup> ion of acidic solution are eliminated as hydrogen gas.

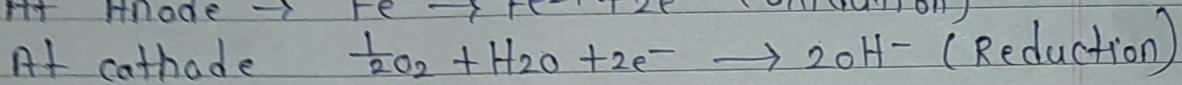
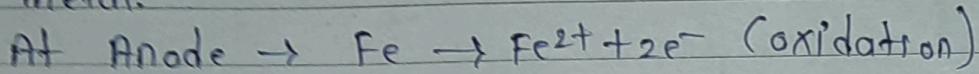


This type of corrosion, metal ion dissolved in solution and hydrogen ions come out of solution in the form of gas

- All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H<sub>2</sub> gas
- The anodes are large areas, whereas cathodes are small areas

## ② Absorption of oxygen :-

- For example, rusting of iron in neutral aqueous solution of electrolyte in presence of atmospheric oxygen
- Usually surface of iron is coated with a thin film of iron oxide.
- If the film develops cracks, anodic areas are created on the surface, while metal parts act as cathode
- It shows that anode are small areas while the rest metallic part form large area. cathodes.
- The electron flow from anode to cathode through iron metal.

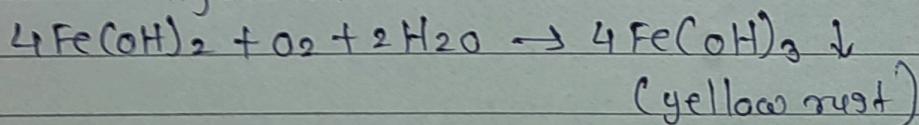


overall

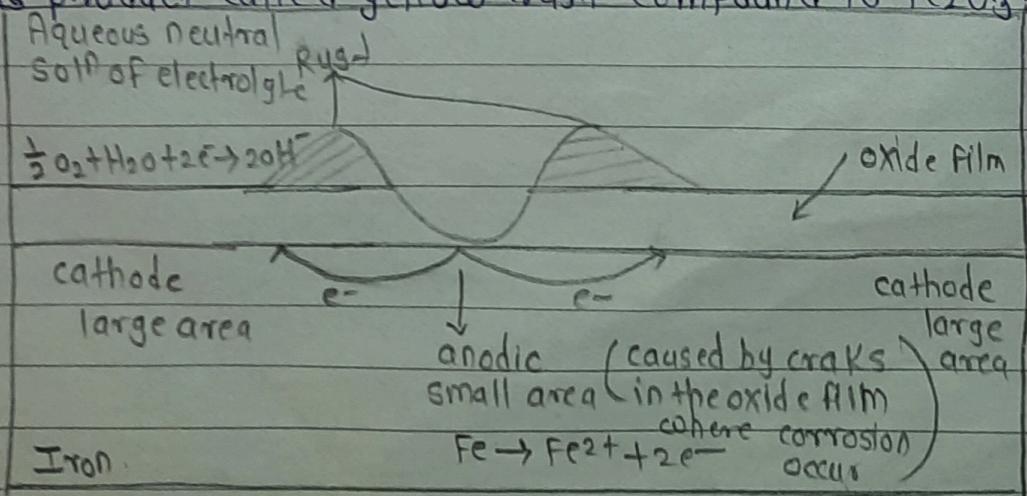
The ferrous ions at anode and hydroxyl ions at the cathode diffuse towards each other i.e.  $\text{Fe}^{2+}$  ions diffuse towards anode and  $\text{OH}^-$  ions diffuse towards cathode and then they combine to form ferrous hydroxide



If oxygen in excess, Ferrous hydroxide is easily oxidized to ferric hydroxide.



This product called yellow rust compound to  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ .



**Ques 1: Types of corrosion**

### ① concentration cell corrosion

- This type of corrosion is due to the electrochemical attack on the metal surface exposed to electrolyte of varying concentration or air/gassing generation.

- This type of corrosion is due to:

i) Difference in concentration of metal ions

ii) Difference in temperature

iii) Difference in the exposure to air/oxygen

- Differential aeration corrosion is the most common and important type of concentration cell corrosion

- When metal is exposed to different air concentrations it has been found to be poorly oxygenated if the metal become anodic and highly oxygenated part become cathodic

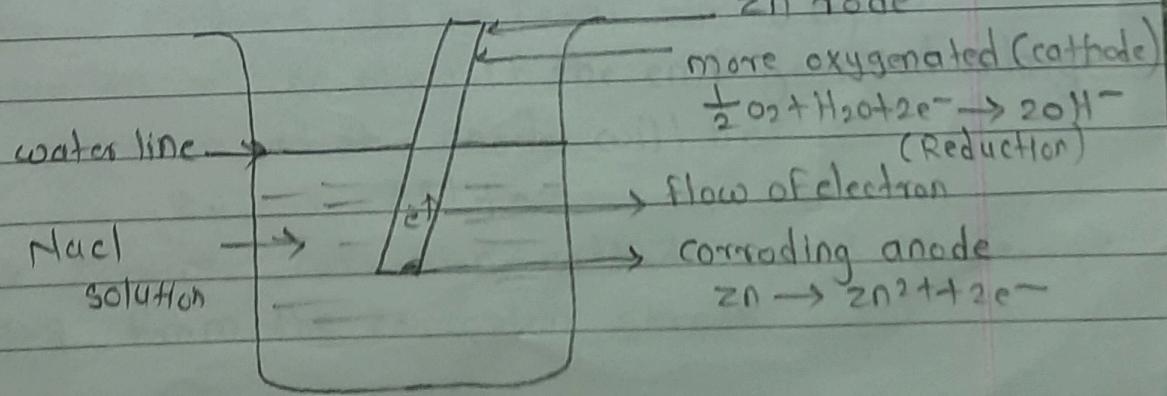
- The potential difference is created which causes the flow of electrons from anode to cathode

- For e.g.

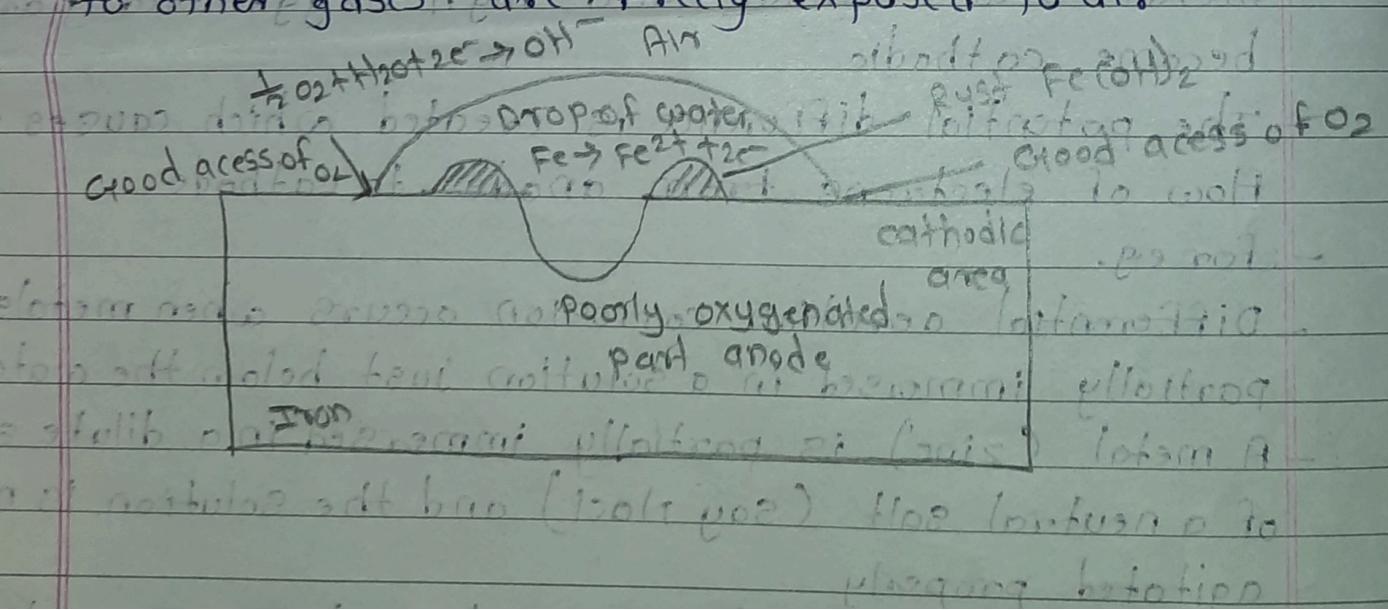
- Differential aeration corrosion occurs when metals are partially immersed in a solution just below the waterline. A metal (zinc) is partially immersed in a dilute solution of a neutral salt (say NaCl) and the solution is not agitated properly

- The parts above and closely adjacent to the waterline are strongly aerated and act as cathode

- The parts immersed to greater depth show a smaller oxygen concentration, i.e. poorly aerated and act as anode

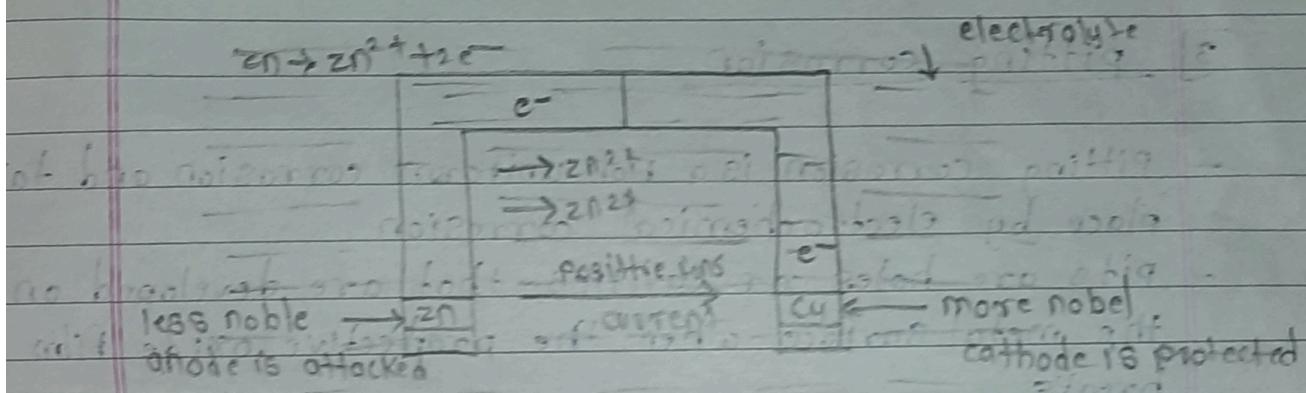


- Hence, difference of potential is developed which causes flow of current between the two differentially aerated areas.
- zinc will dissolve at the anodic areas
- $$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad (\text{Oxidation})$$
- oxygen will take up electrons at the cathodic area to form  $\text{OH}^-$  ions
- $$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- \quad (\text{Reduction})$$
- circuit gets completed by flow of  $\text{OH}^-$  ions through the electrolyte and flow of electrons from anode to cathode through metal
- similarly corrosion of iron by water droplets (or salt soln) can be easily explained. Areas covered by droplets, having no access of oxygen become anodic with respect to other regions which are freely exposed to air.



## ② Galvanic or Bimetallic corrosion

- It is wet type corrosion.
- When two dissimilar metals are in electrical contact with each other and are exposed to an electrolyte, a potential difference is created between two dissimilar metals.
- This potential difference produces electron flow between them. The less noble metal will dissolve and act as an anode while more noble metal will act as cathode. This type of corrosion is called galvanic corrosion.



- Two dissimilar metals, zinc and copper plates are in electrical contact with each other and are immersed into a solution of an electrolyte, and one is basal.
  - The more electropositive metal zinc placed higher in electrochemical series acts as an anode and is attacked and gets dissolved.
  - Copper lower in electrochemical series acts as cathode.
  - Zinc undergoes oxidation releasing electrons and forms Metal ions.
  - Released electrons are taken up by ions causing reduction at the cathode.
  - The emf is generated due to oxidation-reduction reaction causing dissolution of metal at anode causing corrosion.
  - The flow of electrons will be from zinc to copper.
  - The corrosion will be more if the emf generated is large.
- The reaction at the anode will be
- $$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$$
- In the galvanic corrosion cathodic metal is always protected from the corrosion attack.