



# **CLASSIFICATION OF CORROSION CHAPTER 2**

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## Classification of corrosion :

Corrosion has been classified in many different ways . One method divides corrosion in to **low - temperature and high – temperature corrosion** . Another separates corrosion in to **direct combination ( or oxidation ) and electro – chemical corrosion** . The preferred classification here is ( 1 ) **Wet corrosion** and ( 2 ) **Dry corrosion** .

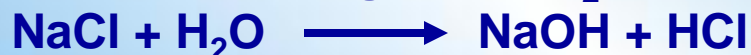
► **Wet corrosion** :- Occurs when a liquid is present . This is usually involves aqueous solution or electrolytes and accounts for the greatest amount of corrosion by far .

**Wet Corrosion** : chemical reaction of a metal with the atmosphere in presence

water like



Salts like NaCl , MgCl , CaCl<sub>2</sub> , ..... etc



corrosion by  $\text{H}_2\text{O} + \text{O}_2$  at room temp. is about 1/20 th to that of  $\text{H}_2\text{O} + \text{chlorides}$

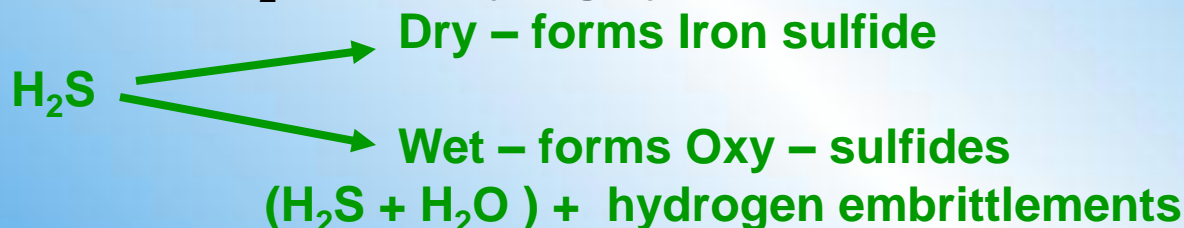


- **Dray Corrosion** : Occurs in absence of a liquid phase or a above the dew point of the environment . Vapors and gases are usually the corrodents . Dry corrosion is most often associated with high temperatures . like Oxidation of metals



**Dry chlorine** is practically non-corrosive to ordinary steel , but moist chlorine dissolved in water , is extremely corrosive and attacks most of common metals and alloys. The reverse is true for Titanium – dry chlorine gas is more corrosive than wet chlorine .

Sulfides  $\text{H}_2\text{S}$  it is very highly corrosive substance.



**$\text{SO}_2$**  : has no corrosion effect but in presence of moisture and oxygen at forms sulfides.

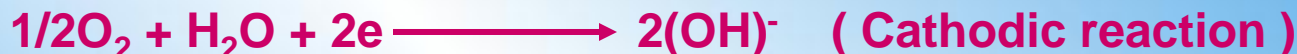


## Electro – Chemical Process :

There are two reactions taking place at the same time,

a) Anodic reaction ( Oxidation ).

b) Cathodic reaction ( Reduction ).

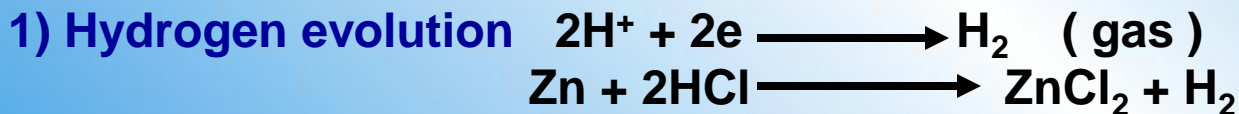


Anodic and Cathodic reaction have to take place at the same rate otherwise the rate of corrosion would become slow .

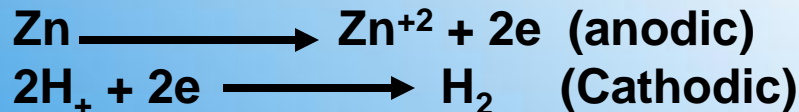
Normally the Cathodic reaction is the rate controlling process .There are various types of Cathodic reactions possible under different conditions :



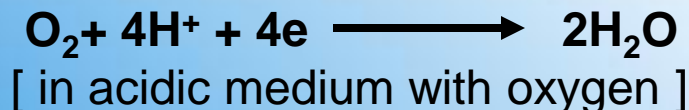
### Cathodic reactions:



Or



### 2) Oxygen reduction





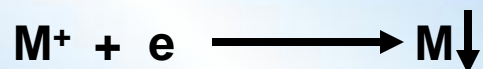
### 3) Oxygen reduction $O_2 + H_2O + 4 e \longrightarrow 4(OH)$

[ in neutral or basic medium ] This is the most kind reaction happens

### 4) Metal Ion reactions



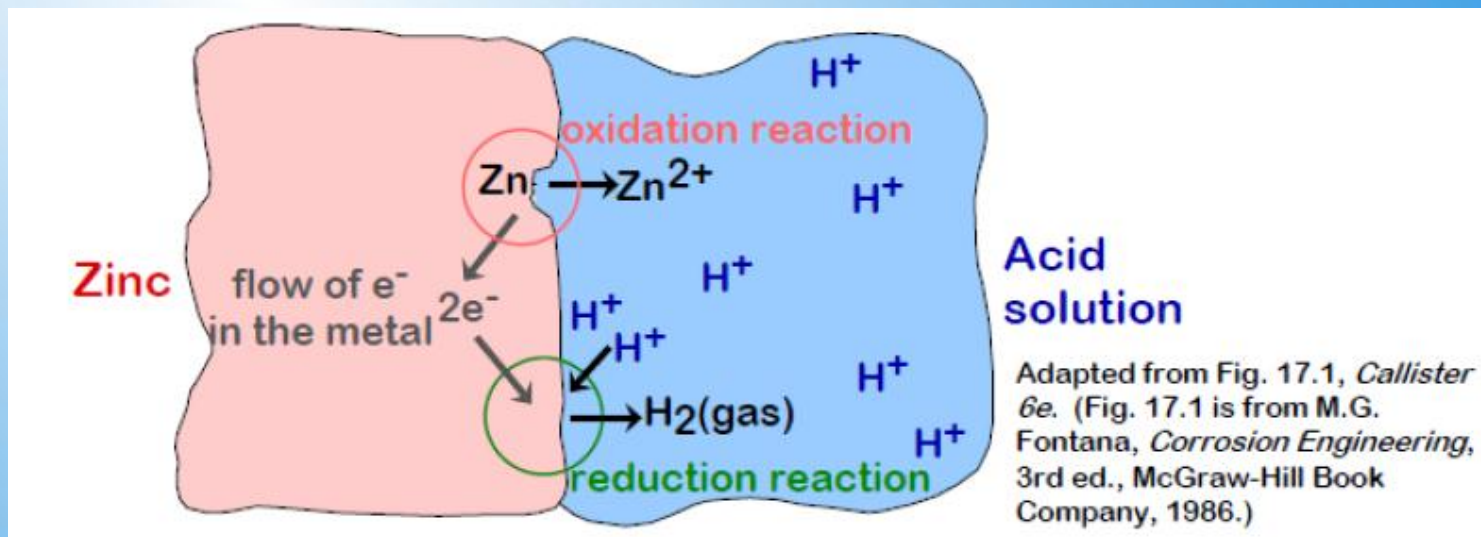
### 5) Metal deposition



An overall electrochemical reaction must consist of at least one **oxidation and one reduction reaction**, and will be the sum of them; often the individual oxidation and reduction reactions are termed **half-reactions**. There can be **no net electrical charge accumulation** from the electrons and ions; that is, the **total rate of oxidation must equal the total rate of reduction**, or **all electrons generated through oxidation must be consumed by reduction**.



## Example 1: Zinc metal immersed in an acid solution containing H<sup>+</sup>



- zinc will experience oxidation or corrosion according to,



- H<sup>+</sup> ions are reduced according to,



- The total electrochemical reaction





**Example 2:** Oxidation or rusting of iron in water, which contains dissolved oxygen, This process occurs in two steps:

➤ Fe is oxidized to Fe<sup>2+</sup> [as Fe(OH)<sub>2</sub>]



➤ Fe<sup>2+</sup> to Fe<sup>3+</sup> [as Fe(OH)<sub>3</sub>]



## Rate of corrosion :-



The most common methods used are

1 – Weight loss in mg or gram.

2 - % weight change.

Poor – sample shape and exposure Time influence results.

3 – Milligram / sq. decimeter / day . ( mdd ).

4 – Grams / sq. decimeter / day .

5 - Grams / sq. centimeter / hour

6 - Grams / sq. meter / hour .

7 - Grams / sq. inch / hour .

8 - Moles / sq. centimeter / hour .

Good – but expressions do not give penetration rates .

9 - Inch / year .

10 - Inch / month .

11 – mm / year most common method .

Better – expressions give penetration rates.

12 – Mils per Year (MPY) . mil = 1/ 1000 .

Best – expresses penetration Without decimals or large numbers.

$$\text{MPY} = \frac{534 W}{DAT}$$

Where

W = weight loss in mg .

D = density of metal in g / cm<sup>3</sup> .

A = area of specimen I sq in .

T = exposure time , hr.



# Polarization :-

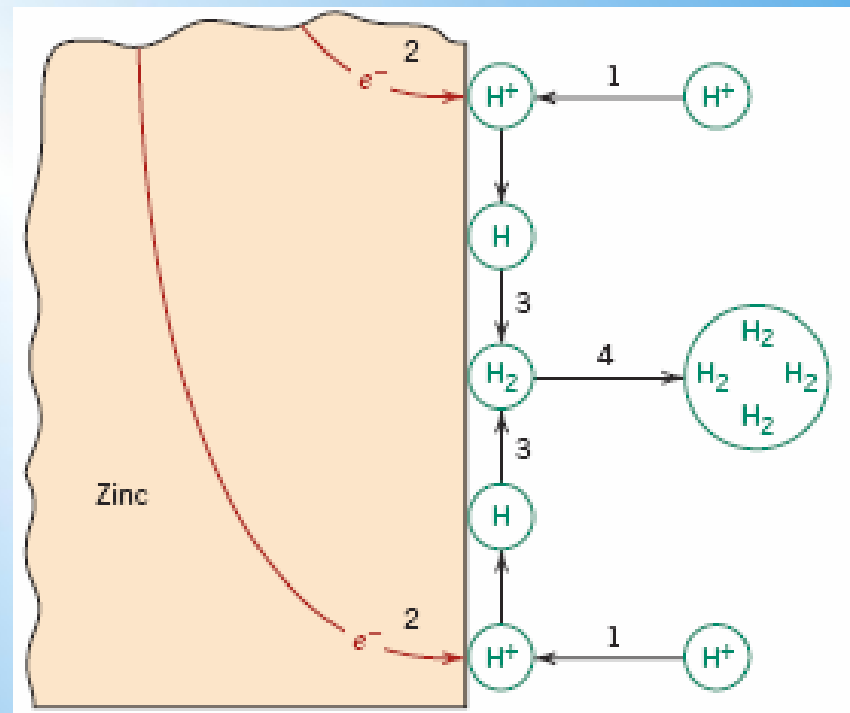
The rate of an **electro-chemical reaction** is limited by various physical and chemical factors. Hence an electro-chemical reaction is said to be polarized or retarded by these environmental factors.

Polarization can be divided in to two different types :

**1 )Activation Polarization :** It is controlled by the **reaction sequence** at metal – electrolyte interface. This is like the hydrogen evolution reaction on zinc during corrosion in acid solution .

- Step 1: adsorb or attracted  $H^+$  to the surface .
- Step 2: electron transfer to  $H^+$  .
- Step 3: reduce the  $H^+$  to  $H_2$  .
- Step 4: hydrogen molecules combine to form a bubble of hydrogen gas .

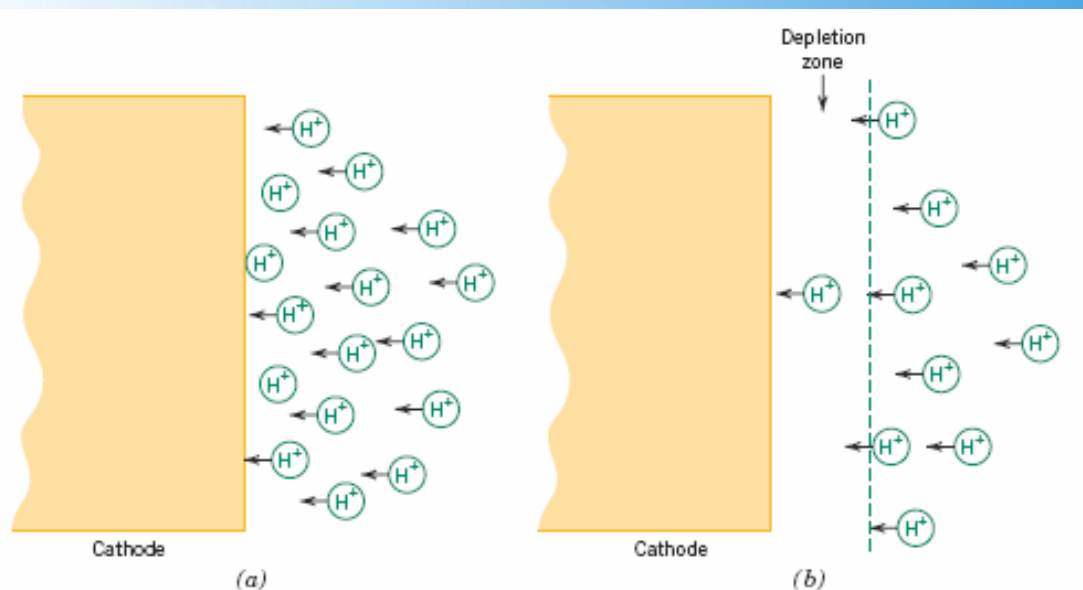
The speed of reduction of hydrogen ions will be controlled by the slowest of these steps.





**2 ) Concentration Polarization :** It is controlled by the **diffusion in the electrolyte** . For the case of **hydrogen evolution** , the number of  $H^+$  in the solution is quite small, and the reduction rate is controlled by the diffusion of hydrogen ions to the metal surface . Reduction rate controlled by **bulk solution** rather than at the **metal surface**.

**Activation polarization** usually is controlling factor during corrosion in media containing a high concentration of active aspects .( concentrated acids ). **Concentration polarization** generally predominates in the dilute acids , aerated salt solutions .



**Figure 17.8** For hydrogen reduction, schematic representations of the  $H^+$  distribution in the vicinity of the cathode for (a) low reaction rates and/or high concentrations, and (b) high reaction rates and/or low concentrations wherein a depletion zone is formed that gives rise to concentration polarization. (Adapted from M. G. Fontana, *Corrosion Engineering*, 3rd

# Passivity :-

The phenomenon is rather difficult to define because of its complex nature and specific conditions under which it occurs.

Passivity refers to the loss chemical reactivity experienced by certain metals and alloys under particular environmental conditions.

Fe ,Ni , Si , Cr , Ti , Al , and their alloys can be passive in certain conditions.

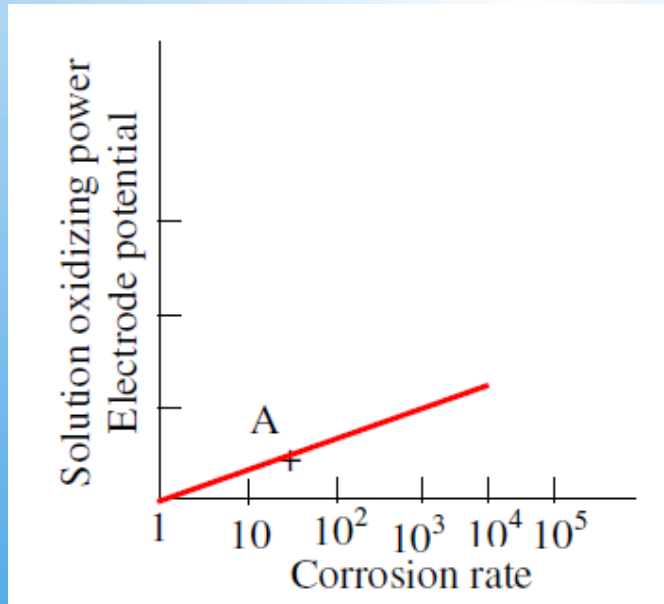


Fig. (1) Corrosion rate of the a metal as a Function of solution oxidizing power ( electrode potential ) active metal (non-passive)

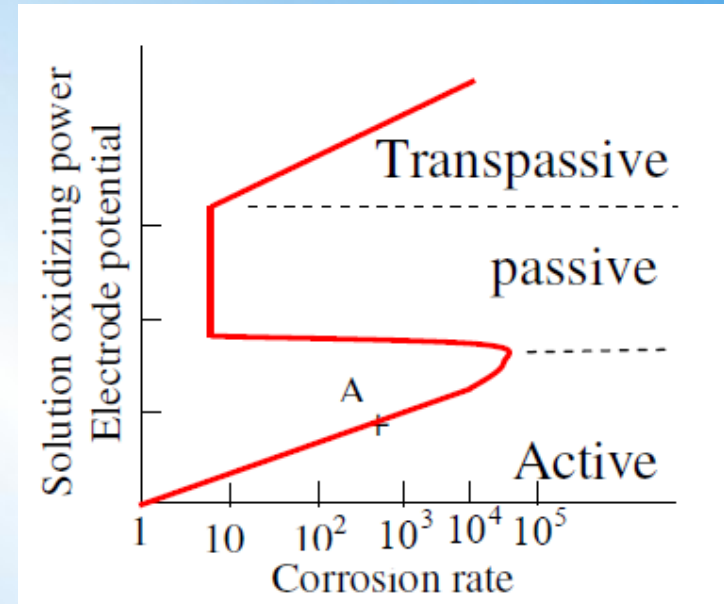


Fig. (2) Corrosion characteristics of an active-passive metal as function of solution oxidizing power



Fig.(1) refer to active metal in air-free acid solution it is corrode and corrosion rate increase by adding oxygen or ferric ions.

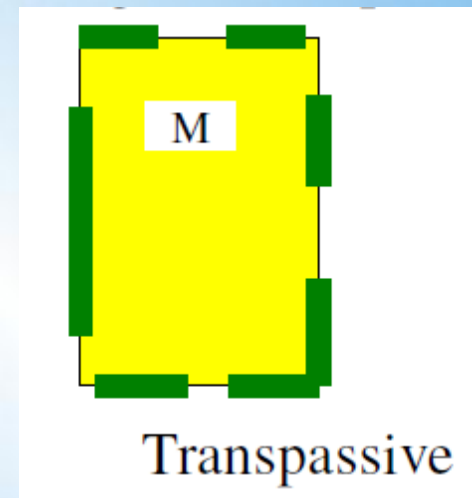
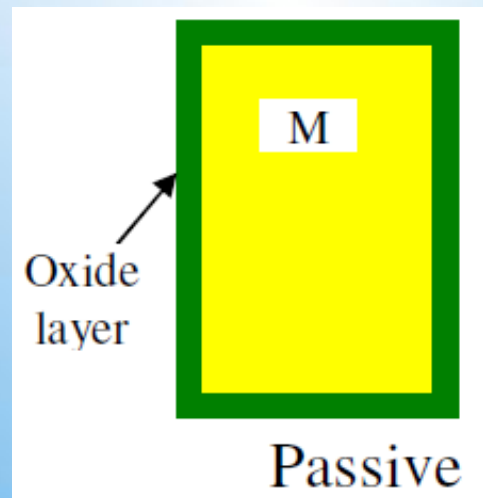
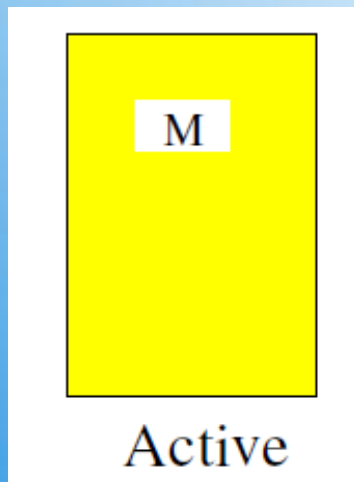
Fig.(2) illustrates the typical behavior of a metal of which demonstrates passive effects .

There are three regions, **Active** , **Passive** & **Transpassive**.

**Active region** : the behavior of a normal metal.

**Passive region**: If more oxidizing agent is added the corrosion rate suddenly decrease, this mean that this region begin.

**Transpassive region**: with further increase in oxidizing agents the corrosion rate again increase with increasing oxidizer power.



# Factors effecting on corrosion rates :



1) **Environments effects:** It is desirable to change process variables.

( i ) **Effect of Oxygen and Oxidizers :** The effect of oxidizers on corrosion Rate can be represented by the graph Shown here .

## Examples

### Region 1

Corrosion rate Oxidizer

Monel alloy in HCl + O<sub>2</sub> ( Ni + Cu alloys )

Cu in H<sub>2</sub>SO<sub>4</sub> + O<sub>2</sub>

Fe in H<sub>2</sub>O + O<sub>2</sub>

### Regions 1 – 2

18Cr-8Ni in H<sub>2</sub>SO<sub>4</sub> + Fe<sup>+3</sup>

Ti in HCl + Cu<sup>+2</sup>

### Region 2

18Cr-8Ni in HNO<sub>3</sub>

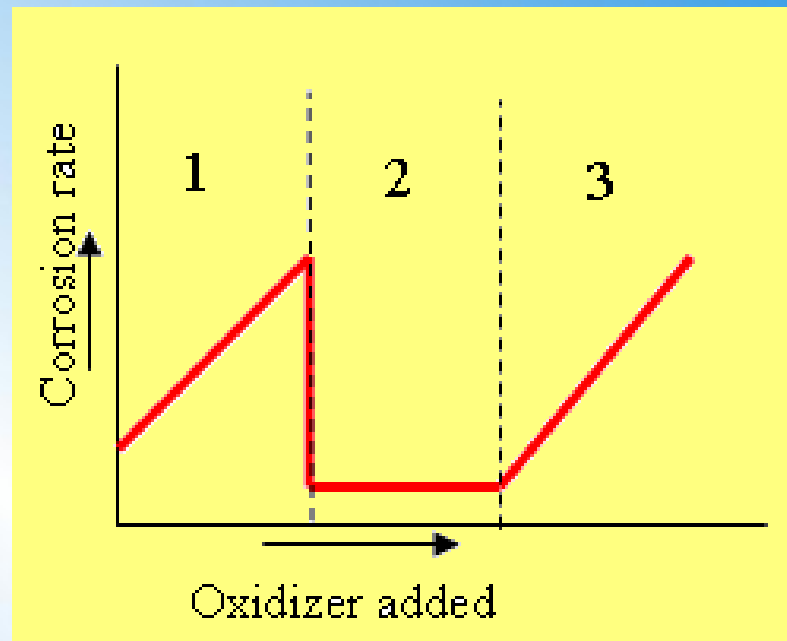
Hastelloy C in FeCl<sub>3</sub> ( Ni alloy with alloying elements )

### Region 2 – 3

18Cr-8Ni in HNO<sub>3</sub> + Cr<sub>2</sub>O<sub>3</sub>

### Region 1 – 2 – 3

18Cr-8Ni in concentrated H<sub>2</sub>SO<sub>4</sub> + HNO<sub>3</sub> mixtures at elevated temperatures.





## (ii) Effects of Velocity : Mean the velocity of medium .

The effects of velocity on corrosion rate are, like the effect of oxidizer additions, complex and depend on the characteristics of the metal and the environment to which it is exposed. If rate of corrosion is controlled by **Activation polarization** then there is no effect of velocity. If the process is diffusion controlled ( **concentration polarization** ). Then the corrosion rate increase with increasing velocity.

### Examples

#### Curve A

Corrosion rate velocity

**1:** Fe in  $H_2O + O_2$

Cu in  $H_2O + O_2$

**1 - 2 :** 18Cr-8Ni in  $H_2SO_4 + Fe^{+3}$

Ti in  $HCl + Cu^{+2}$

#### Curve B :

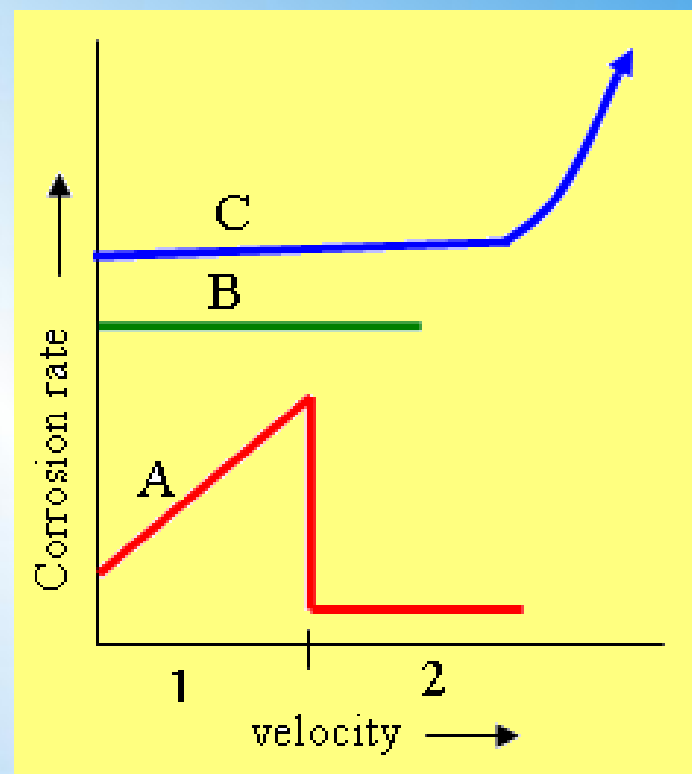
Fe in dilute  $HCl$

18Cr-8Ni in  $H_2SO_4$

#### Curve C :

Pb in dilute  $H_2SO_4$

Fe in concentrated  $H_2SO_4$





**(iii) Effect of Temperature:** Temp. increases the rate of almost all chemical reactions. By increasing Temp. the conductivity of the metal and the medium increases and also the diffusion rate in the medium increase. Therefore the corrosion rate also increases .

### Examples

#### Curve A :

18Cr-8Ni in  $\text{H}_2\text{SO}_4$

Ni in HCl

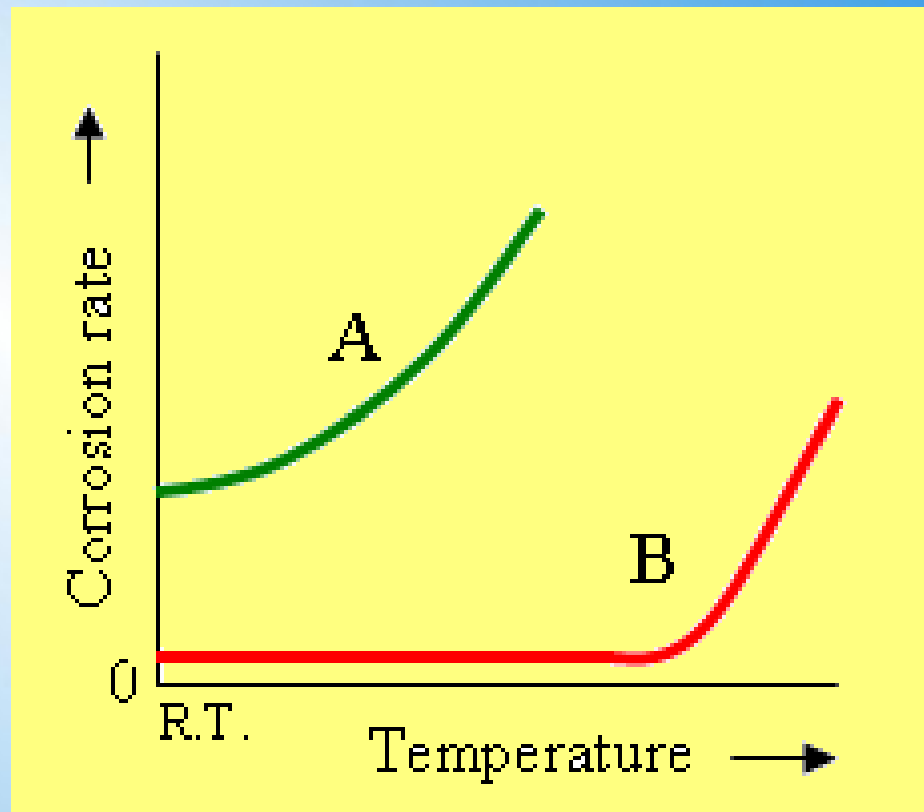
Fe in HF

#### Curve B :

18Cr-8Ni in  $\text{HNO}_3$

Monel in HF

Ni in NaOH





**(iv) Effects of Corrosion Concentration :** ( concentration of corrosive medium ). Many materials which exhibit passivity effects are only negligible affected by wide changes in corrosive concentration ( curve A ). The reduction in rate after a Maximum is due to the difficulty in ionization with the increase in concentration of corrosive medium ( curve B ).

### Examples

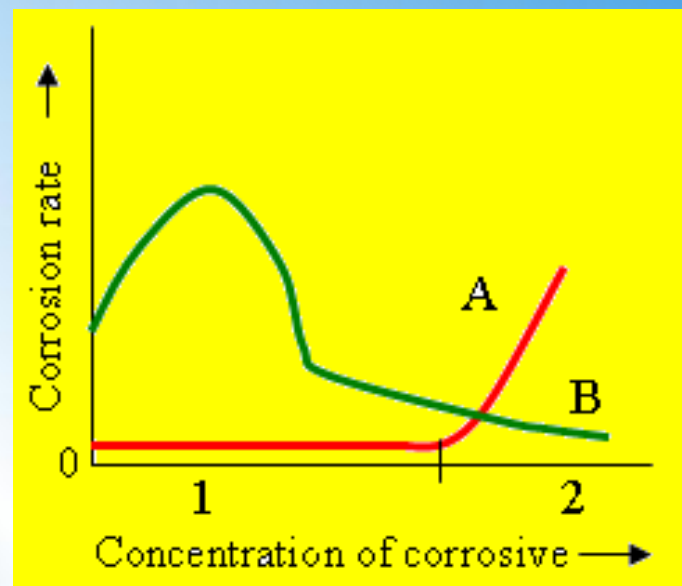
#### Curve A :

**1 :** Ni in NaOH  
18Cr-8Ni in HNO<sub>3</sub>  
Hastelloy B in HCl  
Ta in HCl

**1 – 2 :** Monel in HCl  
Pb in H<sub>2</sub>SO<sub>4</sub>

#### Curve B :

Al in acetic acid and HNO<sub>3</sub>  
18Cr-8Ni in H<sub>2</sub>SO<sub>4</sub> , & Fe in H<sub>2</sub>SO<sub>4</sub>



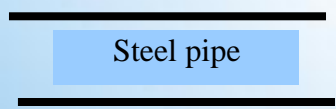




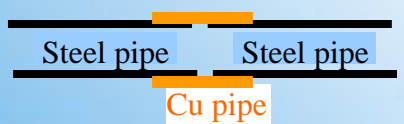
**(V) Effects of Galvanic Coupling :** By this we mean , when two dissimilar metals are in contact each other . Under this condition the corrosion rate of one metals stops and the corrosion rate of the other metal becomes faster . This depends on the Electro-Potential of the two metals.



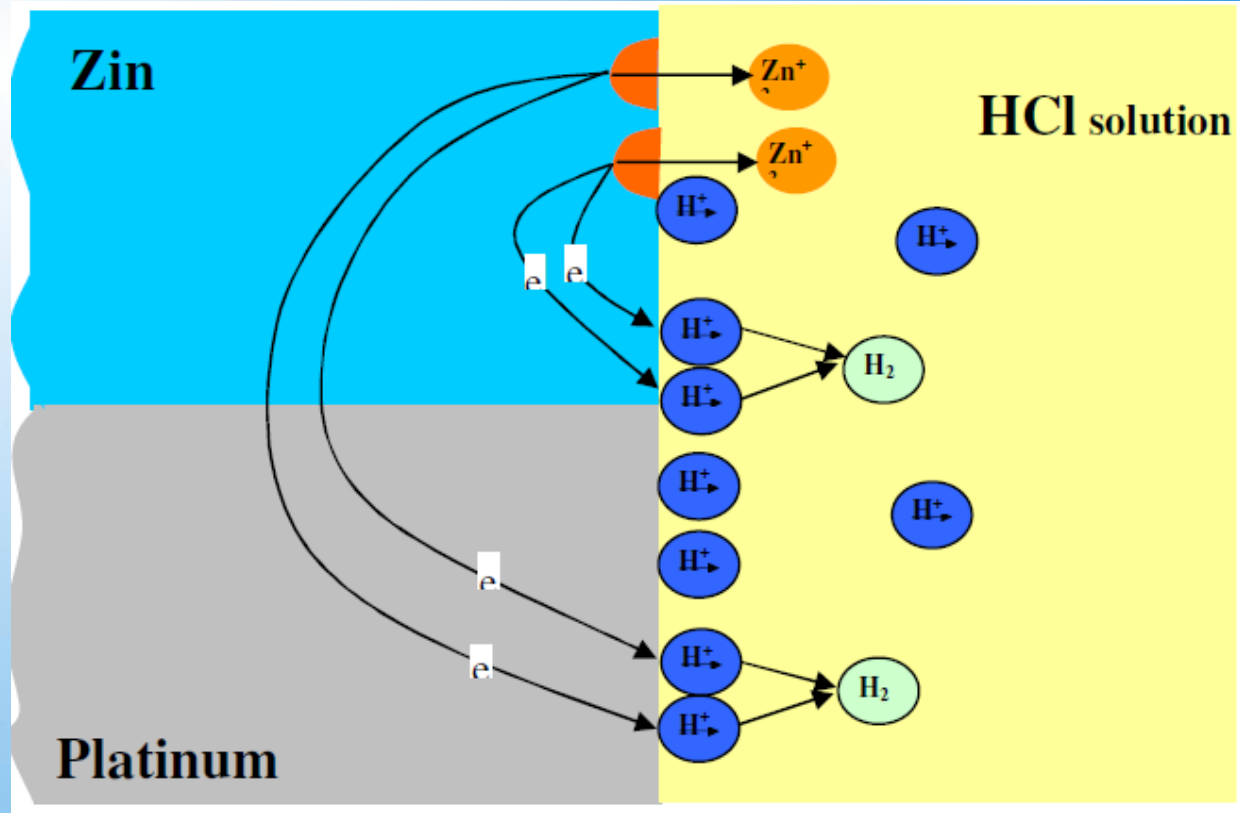
Case 1



Case 2



corrosion rate of iron will be faster





## 2 ) Metallurgical Aspects:

Polycrystalline Would corrode much faster than single crystal. And is due to the presence of grain – Boundaries in Polycrystalline grain boundaries are the regions of high Energy their for their Chemical reactivity is higher than the rest of materials.

1- Effect of Grain boundary.

2- Metal purity.

2-Effect of various phases in the alloys presence of phases alloys have the same effect as Galvanic – coupling in .

3- Different metals.

4- Residual stresses.

5- The strain hardening deformation.

