

# **Chapter-III Electrochemistry**

By: Dr. Manoj Acharya VIT, Bhopal

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Syllabus				
Module No.	Syllabus			
Module – 03 Electrochemistry	Electrochemistry - Corrosion: Introduction to Electrochemical reactions; Redox-reactions; Nernst equation; Problem solving using Nernst equation. Standard Reduction Potentials; Cell potentials and Free Energy, Types and Mechanism of corrosion Galvanic Corrosion; Determination of spontaneity of Corrosion, Relationship between corrosion and entropy, enthalpy and free energy.			
	Corrosion prevention: Cathodic protection – sacrificial anodic and impressed current protection methods; Electrolysis-electroplating-process and typical applications, metal cladding; Coating processes – PVD and CVD and applications.			

# **Text Books / Reference Books**

- 1) O. G. Palanna, Engineering Chemistry, Tata McGraw Hill Education
- 2) Jain P. C. and Monica Jain, Engineering Chemistry, Dhanpat Rai Publishing Company Ltd.
- 3) R. L. Madan, Physical Chemistry, McGraw Hill Education
- 4) Dara S. S., Umare S. S., Engineering Chemistry, S. Chand & Company Ltd.
- 5) Shashi Chawala, Chemistry, Dhanpat Rai & Co. New Delhi

Electrochemistry is a branch of physical chemistry which deals with the interrelationship between electrical energy and chemical energy & vice versa.

#### **Redox Reaction**

Redox reactions are those involving oxidation and reduction of the chemical species.

#### **Oxidation Reaction**

Oxidation reactions may be defined as a process in which an ion or an atom loses one or more electrons. It is also known as **deelectronation**.

Loss of electron results in increase of positive charge.

Loss of electron results in decrease of negative charge.

#### **Reduction Reaction**

Reduction reactions may be defined as a process in which an ion or an atom gain one or more electrons. It is also known as **electronation**.

Gain of electron results in decrease of negative charge.

#### Gain of electron results in increase of negative charge.

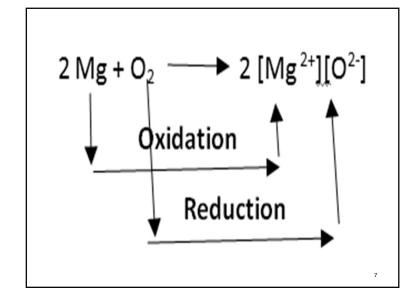
A substance (atom, ion or molecule) which losses electrons to other substance is called a **reducing agent or redundant.** 

Reducing agents are electron donors. After reducing other substance, reducing agent themselves get oxidised.

A substance (atom, ion or molecule) which accepts electrons from other substance is called a **oxidising agent or oxidant.** 

Oxidising agents are electrons acceptors. After oxidising other substance, oxidising agent themselves get reduced.

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# **Types of Redox reactions**

Direct Redox Reaction

Indirect Redox Reaction

#### **Direct Redox Reaction:**

Those reactions in which oxidation & reduction takes place in the same vessel.

For eg. A) Displacement of Cu from  $CuSO_4$  when zinc rod is dipped in it:  $Zn (s) + CuSO_4 (aq) \rightarrow ZnSO_4 (aq) + Cu (s)$ 

B) Reduction of HgCl<sub>2</sub> to Hg<sub>2</sub>Cl<sub>2</sub> by SnCl<sub>2</sub>

#### **Indirect Redox Reaction:**

Those reactions in which oxidation & reduction takes place in different vessel.

For e.g. – Electrochemical cell which is used to convert chemical energy produced in a redox reaction into electrical energy.

#### Electrochemical Cell

Electrochemical cell is a device which is used to convert chemical energy into electrical energy and vice versa.

#### Types of Electrochemical Cell

Galvanic Cell / Voltaic Cell

**Electrolytic Cell** 

#### Galvanic Cell / Voltaic Cell

It converts chemical energy into electrical energy/electrical charges.

Galvanic cell consist of two half cells. In one half of cell oxidation reaction takes place while reduction takes place in another half of cell.

KNO<sub>3</sub>.

Both the electrodes are

connected with the help of a

wire and two solutions are

A salt bridge is a U-shaped

tube containing concentrated

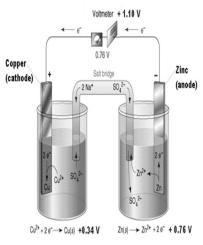
solution of KCl or K<sub>2</sub>SO<sub>4</sub>,

connected by a salt bridge.

Function of salt bridge-

The function of *salt bridge* is to allow the movement of ions from one solution to another, without mixing of the two solutions.

It maintain the electrical neutrality of the solution.



 $Cu^{2+} + Zn(s) \longrightarrow Zn^{2+} + Cu(s)$ 

# Types of Galvanic Cell / Voltaic Cell

Galvanic Cell are of three types-

- a) Primary Cell (Daniel Cell, Dry Cell, Zn-HgO Cell)
- b) Secondary Cell (Ni-Cd Cell, Li-ion Cell, Pb-Acid Battery)
- c) Concentration Cell (Cu Concentration Cell, Zn Concentration Cell)

# a) Primary Cell (Daniel Cell)

Daniel cell consist of two half cells. In one half of cell oxidation reaction takes place while reduction takes place in another half of cell.

A zinc rod is dipped in zinc sulphate solution in a beaker while copper rod is dipped in copper sulphate solution in another beaker.

Electrons flow in the outer circuit in the wire but inner circuit is completed by the flow of ions from one solution to another solution through salt bridge.

Oxidation takes place at zinc electrode known as "Anode", Reduction takes place at copper electrode known as "Cathode".

Electrons are produced at zinc electrode due to Oxidation and it is named as "Negative Pole" the copper electrode act as "Positive Pole".

Electrons flows from "Negative Pole" to "Positive Pole" in the external circuit. Ideally current flows in opposite direction.

The oxidation of Zn to Zn<sup>2+</sup> produces excess of Zn<sup>2+</sup> in the solution similarly reduction of Cu<sup>2+</sup> to Cu results in excess of SO<sub>4</sub><sup>2-</sup> ions in the solution. To maintain the electrical neutrality of the solutions in two beakers, the cations and anions moves through the salt bridge, this completes the inner circuit.

As Copper from  $\text{CuSO}_4$  solution deposits on copper electrode and  $\text{SO}_4^{2\text{-}}$  ions moves to the other side and the concentration of  $\text{CuSO}_4$  decreases as the cell operates, as a result the current falls with the passage of time.

$$\overline{\text{Zn (s)} + \text{Cu}^{2+}(\text{aq})} \longrightarrow \overline{\text{Zn}^{2+}(\text{aq}) + \text{Cu (s)}}$$
 Overall Reaction

# Representation of Galvanic Cell

$$Zn(s); Zn^{2+}(1M) || Cu^{2+}(1M); Cu$$

Oxidation; Anode; LHS | Reduction; Cathode; RHS

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# anode $\longrightarrow$ Zn|ZnSO<sub>4</sub>( $a_{ZN^{2+}}$ = 0.0100)||CuSO<sub>4</sub>( $a_{Cu^{2+}}$ = 0.0100)|Cu $\longleftarrow$ cathode Solution in contact with anode & its concentration due to salt bridge cathode & its concentration

#### **EMF of Electrochemical Cell**

$$\begin{array}{llll} E_{Cell} = & E_{Cathode} & - & E_{Anode} \\ E_{Cell} = & E_{Right} & - & E_{left} \\ E_{Cell} = & E_{Cu2+/Cu} & - & E_{Zn/Zn2+} \end{array}$$

The cell reaction is feasible only when  $\mathbf{E}_{\text{Cell}}$  has positive value.

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# **Nernst Equation**

It tell about the effect of electrolyte concentration on electrode potential. Its of two types-

#### 1) Nernst Equation for Electrode 2) Nernst Equation for Cell

#### **Nernst Equation for Electrode**

$$M^{n+}(aq) + ne^- \longrightarrow M(s)$$

$$E = E^{\circ} - 2.303 \frac{RT}{nF} * \log \frac{a_{product}}{a_{reactact}}$$

Where E = Electrode Potential

 $E^{o}$  = Standard Electrode Potential

F = Faraday of electricity (96500 coulomb)

T = Temperature (298K)

R = Gas Constant (8.314 J/K mole

a = activity

$$E = E^{\circ} - \frac{0.0595}{n} * \log \frac{a_{product}}{a_{reactact}}$$

In dilute solution, activity may be replaced by molar concentration.

$$E = E^{\circ} - \frac{0.0595}{n} * \log \frac{1}{M^{n}}$$

From the above equation

- a) The electrode potential (E) increases as [M<sup>n+</sup>] is increased.
- b) The electrode potential (E) decreases as temperature is increased.

# **Nernst Equation for Cell**

Nernst equation can also be applied to any cell reaction such as

$$aA + bB \longleftrightarrow cC + dD$$

$$E = E^{\circ} - 2.303 \frac{RT}{nF} \log \frac{C^{\circ} Dd}{A^{a} Bb}$$

For dilute solution

$$2M_1(s) + M_2^{n+}(aq) \longleftrightarrow 2M_1^{+}(aq) + M_2(s)$$

E = E° - 0.0595 / n \* log[(
$$M_1^+$$
)<sup>2</sup>/ $M_2^{n+}$ )]  
Activity of solids =  $M_1 = M_2 = 1$ 

Calculation of Equilibrium Constant (K) from Nernst Equation

$$E^{\circ} = 2.303RT / nF * log K$$

$$E^{o} = 0.0595 / n * log K$$

# **Numerical: Annexure -1**

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# b) Secondary Cell (Storage Batteries)

Secondary cells are chargeable and can be used again. The cell reactions are reversible and are called reversible cells.

During discharging the cell act as voltaic cell converting chemical energy into electrical energy.

During charging the cell act as electrolytic cell by converting electrical energy into chemical energy. Hence they are also called as storage batteries.

For example: Li-ion battery, Ni-Cd Cell, Lead-Acid Cell.

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# c) Concentration Cell

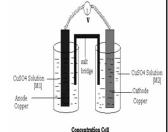
In concentration cell the emf arises due to the change in the concentration of either or electrolyte or the electrodes.

Concentration cell is in contrast to galvanic cell where emf arises from the decrease in free energy ( $\Delta G = -nFE$ ) of the chemical reaction taking place in the cell.

#### Concentration cell are of two types:-

Electrode Concentration Cell

Electrolyte Concentration Cell



#### **Electrode Concentration Cell**

In electrode concentration cell the electrode themselves have different concentration. They are of two type-

- a) Gas Electrode Concentration Cell
- b) Amalgam Electrode Concentration Cell

#### **Gas Electrode Concentration Cell**

Gas electrode concentration cell consist of two hydrogen electrodes maintained at different partial pressure of the hydrogen gas ( $p_1 \& p_2$  respectively) and dipped in the **same solution** of the electrolyte HCl solution.

Anode	Electrolyte	Cathode
$Pt, H_2(g) / P_{H2} = p_1$	HCl solution activity = $a_{H+}$	$/ H_2 (g), Pt$ $P_{H2} = p_2$

$$H_2(p_1) \longrightarrow 2H^+(a_{H^+}) + 2e^-$$

Oxidation Reaction

$$2H^{+}\left(a_{H^{+}}\right) \; + \; 2e^{-} \; \longrightarrow \; H_{2}\left(p_{2}\right)$$

Reduction Reaction

$$H_2(p_1) \longrightarrow H_2(p_2)$$

Overall Reaction

#### **EMF of Gas Electrode Concentration Cell**

$$E = E^{\circ} - 2.303RT / 2F * log[p_2/p_1]$$
  
 $E^{\circ}$  for Hydrogen Electrode = 0 Volt

$$E = -2.303RT / 2F * log[p_2/p_1]$$

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$$E = 2.303RT / 2F * log[p_1/p_2]$$

At 298 K

$$E = 0.0591 / 2 * log[p_1/p_2]$$

#### **EMF of Amalgam Electrode Concentration Cell**

 $E = E^{o} - 2.303RT / nF * log[a_{2}/a_{1}]$ 

 $E^{o} = 0$ ; Standard electrode potential will be same for both the electrode

$$E = -2.303RT / nF * log[a_2 / a_1]$$

or

$$E = 2.303RT / nF * log[a_1 / a_2]$$

At 298 K

$$E = 0.0591 / n * log[a_1/a_2]$$

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#### **Amalgam Electrode Concentration Cell**

Amalgam electrode concentration cell consist of two amalgamated metal rod with different activities are dipped in the same solution of the electrolyte solution.

#### 

 $M (a_1) \longrightarrow M (a_2)$  Overall Reaction

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#### **Electrolyte Concentration Cell**

Electrolyte concentration cell consist of two identical electrodes immersed in two solution of same electrolyte at different concentration.

# Anode Salt Bridge Cathode

$$\label{eq:molar} \textit{M} \, / \, \textit{Mn} + \, \left( \textit{C}_1 \, \textit{molar} \right) \qquad \qquad / / \qquad \quad \textit{M}^{\textit{n+}} \left( \textit{C}_2 \, \textit{molar} \right) / \, \textit{M}$$

$$M \longrightarrow M^{n+} + ne^{-}$$
 Oxidation Reaction

$$M^{n+} \quad + \; ne^{\text{-}} \quad \longrightarrow \qquad \qquad M \qquad \qquad Reduction \; Reaction$$

$$M(C_1) \longrightarrow M(C_2)$$
 Overall Reaction

**EMF of Electrolyte Concentration Cell** 

 $E = 2.303RT / nF * log[C_2 / C_1]$ 

At 298 K

 $E = 0.0591 / n * log[C_2 / C_1]$ 

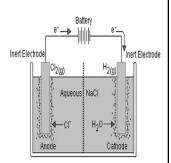
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# **Electrolytic Cell**

It converts electrical energy into chemical energy.

At the electrodes, non-spontaneous redox reaction takes place only when electrical energy is passed.

The electrodes may be same or different metals & both electrodes are inserted in the same electrolytes solution.



Anode is positive electrode and cathode is negative electrode of the cell. **No salt bridge is used.** 

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#### **Electrode Potential**

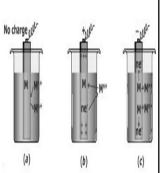
The tendency of metal to get oxidised or reduced when it is placed in a solution of its own salt is called Electrode Potential.

If metal undergoes oxidation then the positive metal ions may pass into the solution.

 $M \longrightarrow M^{n+} + ne^{-}$ 

If metal undergoes reduction then the negative ions may get deposited over the metal.

$$M^{n+}$$
 +  $ne^ \longrightarrow$   $M$ 



Three possibilities when a strip of metal M is placed in a solution containing its ions M°+

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#### **Standard Electrode Potential**

It is the measure of the tendency of a metallic electrode to lose electron or gain electron when it is in contact with a solution of its own salt of 1 Molar concentration at 25°C and 1 bar pressure.

$$E^{\text{o}}_{\mbox{ cell}} = E^{\text{o}}_{\mbox{ cathode}}$$
 -  $E^{\text{o}}_{\mbox{ anode}}$ 

Standard Hydrogen Electrode / Normal Hydrogen Electrode is used as reference electrode for determining Standard Electrode Potential whose electrode potential is "Zero".

# Reduction Potential or Redox Potential or Oxidation/Reduction Potential

Redox potential is the measure of the tendency of chemical species to acquire electrons and thereby get reduced. Its measured in "Volts".

Oxidation potential measures the power of a substance/system to add oxygen or to remove hydrogen or lose electrons.  $$_{\rm 28}$$ 

Reduction potential measures the power of a substance/system to add hydrogen or to remove oxygen or attract electrons.

As the redox potential increases in value and turns positive its ability to oxidise increases. When it decreases in value and turns negative its reducing ability is enhanced.

As corrosion involves redox reaction, redox potential becomes the indicator of the possibility of electrochemical activity likely to lead to corrosion or resistance to corrosion.

# Electrochemical Series (Importance of Reduction Potential)

A series in which the reduction electrode potential of various electrodes have been arranged in the increasing order is called "Electrochemical Series".

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Potential (V)	Reduction Half-Reaction		
2.87	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$		
1.51	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$		
1.36	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(ag)$		
1.33	$Cr_2O_2^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$		
1.23	$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$		
1.06	$Br_2(l) + 2e^- \longrightarrow 2Br^-(aq)$		
0.96	$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + H_2O(l)$		
0.80	$Ag^{+}(nq) + e^{-} \longrightarrow Ag(s)$		
0.77	$Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq)$		
0.68	$O_2(g) + 2H^+(ag) + 2e^- \longrightarrow H_2O_2(ag)$		
0.59	$MnO_2^-(aq) + 2H_2O(l) + 3e^- \longrightarrow MnO_2(s) + 4OH^-(aq)$		
0.54	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$		
0.40	$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$		
0.34	$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$		
0	$2H^+(aq) + 2e^- \longrightarrow H_2(g)$		
- 0.28	$Ni^{2+}(aq) + 2e^{-} \longrightarrow Ni(s)$		
-0.44	$Fe^{2+}(aq) + 2e^{-} \longrightarrow Fe(s)$		
- 0.76	$Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$		
-0.83	$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$		
-1.66	$Al^{3+}(aq) + 3e^{-} \longrightarrow Al(s)$		
- 2.71	$Na^+(aq) + e^- \longrightarrow Na(s)$		
- 3.05	$Li^+(aq) + e^- \longrightarrow Li(s)$		

# **Application of Electrochemical Series**

#### To predict the relative oxidising & reducing power of electrode-

The species above hydrogen are strong reducing agent & their standard reduction potential is negative while the species below hydrogen are strong oxidising agents & have positive value of standard reduction potential.

# To predict whether the metal will react with acid to liberate hydrogen gas-

The species above hydrogen are strong reducing agent & have great tendency for oxidation so they displaces hydrogen from acids.

#### To predict the spontaneity of any redox reaction-

For spontaneity  $\Delta G^{\circ} = -nFE^{\circ}_{cell}$  should be negative therefore  $E^{\circ}_{cell}$  should be positive.

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#### To determine the Equilibrium constant- $E^{\circ} = 2.303RT / nF * log K$

#### **Cell Potential**

The potential difference between the two electrodes of a galvanic cell is called Cell Potential.

$$\boldsymbol{E}_{cell} = \boldsymbol{E}_{cathode}$$
 -  $\boldsymbol{E}_{anode}$ 

# Free Energy / Gibb's Energy

The Gibb's energy (G) of a system is a measure of its capacity to do useful work. It is a part of the total energy of the system that is freely available for conversion into useful work, hence it is called Free Energy.

It is the amount of work that a thermodynamic system can perform. The free energy is the internal energy of the system minus the amount of energy that can not be used to perform work.

$$\Lambda G = \Lambda H - T\Lambda S$$

Gibb's Energy Criteria for Spontaneity					
ΔΗ	ΔS	ΔG	Occurrence of Reaction		
-ive	+ive	-ive	Spontaneous		
-ive	-ive	-ive, $(\Delta H > T\Delta S)$	Spontaneous		
+ive	+ive	-ive, ( <b>TΔS&gt;Δ H</b> )	Spontaneous		
+ive	-ive	+ive	Non-spontaneous		

#### **Standard Gibbs Free Energy**

$$\Delta G^{\circ} = -nFE^{\circ}_{cell}$$

#### **Standard Gibbs Free Energy**

- 1) Helps in predicting the feasibility of reaction.
- 2) If  $E_{cell}^o = Positive$

 $\Delta \mathbf{G}^{\circ}$  = Negative- Reaction will be spontaneous

 $E_{cell}^{o}$  = Negative

 $\Delta \mathbf{G}^{\circ}$  = Positive - Reaction will be non-spontaneous

#### Corrosion

- ➤ Corrosion is a damage caused to a metal by chemical, electrochemical or even biological reactions with its environment.
- ➤ Corrosion is the process of conversion of metal into their oxides by reaction with moisture and other gases present in the atmosphere.
- > Corrosion is reverse metallurgical extraction process.

### **Factors Influencing Corrosion**

- ➤ Reactivity of Metal: More active metals have high oxidation potential and are readily corroded.
- ➤ Presence of Air & Moisture: Air & Moisture accelerate the corrosion. Presence of gases like SO<sub>2</sub> & CO<sub>2</sub> in air enhances the process of corrosion.
- > Presence of Electrolyte: Electrolyte increases the rate of corrosion.
- > Presence of strains: Corrosion takes place rapidly at bends, joints, scratches and cuts in the metal.
- > Presence of Impurities: Presences of impurities enhances the chance of corrosion.

# **Types of Corrosion**

- ➤ Dry Corrosion
- ➤ Wet Corrosion

# **Dry Corrosion:**

➤When metal gets corrode due to the direct attack of oxygen or corrosive gases like SO<sub>2</sub> & Cl<sub>2</sub> or chemical action on metals through chemical reactions.

#### > Dry Corrosion may be due to

Oxidation Corrosion Corrosion by gases Liquid metal corrosion

#### > Oxidation Corrosion:

When corrosion takes place by direct action of oxygen on metal, it is called oxidation corrosion. Oxidation corrosion takes place in the absence of moisture.

For e.g.- At low temperature Alkali and Alkaline earth metals oxidizes quickly while metals like Fe, Al oxidizes at high temperature.

$$Mg + O_2 \longrightarrow MgO$$
  
 $Al + O_2 \longrightarrow Al_2O_3$ 

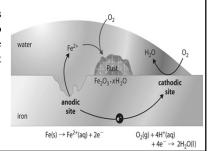
#### > Corrosion by gases:

In the absence of atmospheric moisture few gases like SO<sub>2</sub> & Cl<sub>2</sub> attack the metal which leads to corrosion.

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# **Electrochemical Theory of Corrosion**

- ➤ When a metal (or dissimilar metals) is exposed to an acidic environment then anodic and cathodic areas are developed on the metal surface.
- > A potential difference is created between anodic and cathodic areas due to oxidation and reduction reaction.
- ➤ The flow of electrons takes place from anodic to cathodic area and hence corrosion takes place at "Anodic Area".



# ➤ Liquid Metal Corrosion:

In the type of corrosion when molten liquid is continuously passes on to the solid metal surface or alloy.

#### **Electrochemical or Wet Corrosion**

➤ When corrosion takes place by the transfer of electrons from anodic part to cathodic part of metal through conductive solution, it is called electrochemical corrosion.

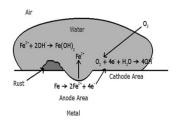
For e.g.- Galvanic Corrosion, Pitting Corrosion, Stress Corrosion, Intergranular Corrosion, Fatigue Corrosion.

> The flow of electrons from anode to cathode takes place by the following process-

- 1) Liberation of Hydrogen / Evolution of Hydrogen
- 2) Absorption of Oxygen

# **Evolution of Hydrogen**

- ➤ The process of dissolution of Iron as Fe<sup>2+</sup> takes place at anodic area of metal.
- ➤ The liberated electron flows from anodic area to cathodic area of metal & give rise to corrosion current.

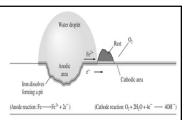


➤ The liberated electron reduces H<sup>+</sup> ion at cathodic area and liberation of hydrogen gas takes place at cathodic area.

# Absorption of Oxygen

ightharpoonup The process of dissolution of Iron as Fe<sup>2+</sup> takes place at anodic area of metal.





> The liberated electron flows from anodic area to cathodic area of metal where its available for reduction & results in the formation of non metallic ions.

$$\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 4OH^-$$

 $\triangleright$  Ferrous Hydroxide is formed due to the diffusion of Fe<sup>2+</sup> & OH<sup>-</sup>.

$$2Fe^{2+} + 4OH \longrightarrow 2Fe(OH)_2$$

> If Oxygen is present in sufficient quantity then Ferrous Hydroxide is oxidized to rust.

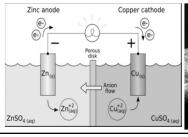
$$4 \text{ Fe} + 3 \text{ O}_2 + 6 \text{ H}_2\text{O} \longrightarrow 2 \text{ Fe}_2\text{O}_3.2 \text{ H}_2\text{O}$$
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# Galvanic Corrosion or Bimetallic Corrosion or Electrochemical Corrosion

When two dissimilar metals or alloys are electrically connected and exposed to electrolyte, *the metal at higher in electrochemical series undergoes corrosion*.

Metals which undergo corrosion when kept in contact in electrically active medium are known as Galvanic Couple.

E.g.- Cu-Zn, Fe-Zn, Fe-Cu, Al-Cu, Fe-Sn, Zn-SS, Zn-Al, Zn-Ag.





#### **Mechanism of Corrosion**

Metal corrosion is chemical or electrochemical surface reactions which results in the change of metal to its oxidized state.

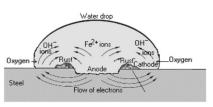
$$4Fe(OH)_2 + 2H_2O + O_2 \longrightarrow 4Fe(OH)_3$$
Ferric Hydroxide

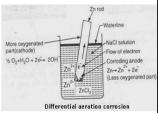
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# Concentration Cell Corrosion, Crevice Corrosion, Gasket Corrosion, Deposit Corrosion, Differential aeration corrosion-

Concentration Cell Corrosion is due to electrochemical attack on the metal surface exposed to electrolyte of varying concentrations. **Metal in contact with lower concentration act as anode and undergoes corrosion.** 

Concentration Cell Corrosion is observed in Chemical plants, storage tanks and marine structures like ships.

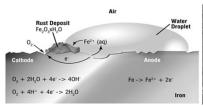


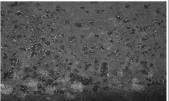


# **Pitting Corrosion**

The localized accelerated attack of a corrosive environment due to the heterogeneity in the metal surface in the formation of pin holes and cavities in the metal is called Pitting Corrosion.

Consider a drop of water on the metal surface. The metal surface which is covered by water droplet has low oxygen concentration and act as anode and suffers corrosion. The uncovered metal surface due to high oxygen concentration act as cathode.





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Formation of small anodic and cathodic area set up potential difference at localized spots to pit, this produces corrosion current. Thus metal under water drop undergoes accelerated corrosion.

Pitting of metal occurs when there is break in the protective layer. It is non uniform corrosion.

Fe 
$$\longrightarrow$$
 Fe<sup>2+</sup> + 2e<sup>-</sup>

$$\frac{1}{2}$$
 O<sub>2</sub> + H<sub>2</sub>O + 2e<sup>-</sup>  $\longrightarrow$  OH<sup>-</sup>

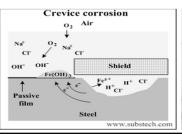
$$Fe^{2+} + 2 OH^{-} \longrightarrow Fe(OH)_{2}$$

$$4 \; Fe \; + \; 3 \; O_2 + \; 6 \; H_2O \; \longrightarrow \; \; 2 \; Fe_2O_3.2 \; H_2O$$

# Crevice Corrosion

Crevice (narrow opening) corrosion is a localized attack on metal adjacent to the crevice between two joining surfaces. The corrosion is confined to localised area of metal. This type of corrosion takes place due to the establishment of concentrated oxygen cell.

Crevice area has lack of oxygen and behaves as anode while the exposed part act as cathode. Crevice corrosion is accelerated attack at the junctions of two metals exposed to corrosive environment.





#### **Corrosion Protection**

The corrosion can be mitigated by any one of the following methods-

- 1) Proper selection & designing of metal equipment, fabrication
- 2) Protective Coating

Metal Coating

Inorganic Coating

Organic Coating

- 3) Cathodic and Anodic Protection
- 4) Corrosion Inhibitors

#### **Cathodic Protection**

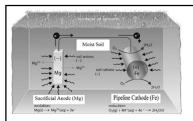
Cathodic protection (CP) is a technique used to control the corrosion of a metal surface by making it the cathode of an electrochemical cell. Metal to be protected from corrosion is connected with a metal which easily corrode "sacrificial metal" to act as the anode. The sacrificial metal then corrode than the protected metal.

Cathodic Protection (CP) is a technology used to protect buried or immersed metals from corrosion. It is defined as the reduction or elimination of the corrosion process by either making the corroding metal a cathode via an impressed direct current (DC) or by connecting it to a sacrificial or galvanic anode.

For structures such as long pipelines where passive galvanic protection is not adequate, an external DC electrical power source is used to provide sufficient current.

#### Sacrificial Anodic Protection

Sacrificial Anodes are highly active metals that are used to prevent a less active metal surface from corroding. Sacrificial Anodes are created from a metal alloy with a **more negative electrochemical potential than the other metal** it will be used to protect. The sacrificial anode will be consumed in place of the metal it is protecting, that is why it is referred to as a "sacrificial" anode. For e.g. Mg, Zn & Al.



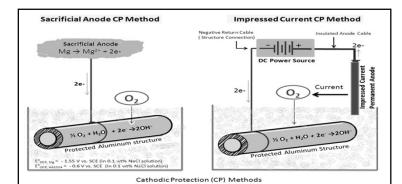


# **Impressed Current Protection**

For large structures galvanic anodes can not economically deliver enough current to provide complete protection. In this method the an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode.

The negative terminal of DC is connected to the corroding metal. The anode is kept in the black fill (Coal+NaCl) to increase the electrical contact with surrounding soil.

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This type of cathodic protection is applied in gysers, water

coolers, water tanks, buried oil & water pile lines, transmission towers.

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# **Electrolysis-Electroplating Process**

Electrolysis is a process, which uses a direct electrical current to break chemical compounds while Electroplating is a process that uses electrical current to reduce dissolved metal cations so that they form a coherent metal coating on an electrode.

Electroplating is the process in which a noble metal is usually deposited on the surface of a metal to prevent rusting. In the process the metal to be electroplated is made cathode and a soluble salt of the sacrifice metal is taken as electrolyte. By applying current, the sacrifice metal deposited on the surface of the metal in the form of layers and thus prevent rusting.

**Electroplating** is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit and the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. 52

# **Use of Electrolysis-Electroplating Process**

Electroplating is done in industries on machines so that they do not react with the raw material & to have anti corrosive coating on the metal.

Electrolysis is extensively used in the extraction of metal from its ores

Various substances are manufactured commercially by using Electrolysis, like Chlorine by the electrolysis of Common salt, Hydrogen by the electrolysis of water, Heavy water (Deutrium oxide) for the use in nuclear reactors.

Metals are purified or refined using electrolytic process.

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# **Coating Process**

A **coating** is a covering that is applied to the surface of an object, usually referred to as the **substrate**. The purpose of applying the coating may be decorative, functional, or both.

Coating process may be classified as under

- 1) Physical Vapour Deposition (PVD)
- 2) Chemical Vapour Deposition (CVD)

# **Physical Vapour Deposition**

PVD Coating - refers to a variety of thin film deposition techniques where solid metal is vaporized in a high vacuum environment and deposited on electrically conductive materials as a pure metal or alloy coating.

Physical Vapour Deposition Coatings are also highly resistant to tarnishing and corrosion enabling them to be used for a wide range of decorative finishes with colours that do not fade.

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A wide variety of types of PVD coatings are available, including Zirconium Nitride (ZrN), Zirconium Carbon Nitride (ZrCN), Titanium Nitride (TiN), Titanium Carbon Nitride (TiCN), Chromium Nitride (CrN), Chromium Carbon Nitride (CrCN), and Chromium Nitride (CrN).

# **Chemical Vapour Deposition**

Chemical Vapour Deposition (CVD) is an atmosphere controlled process conducted at elevated temperatures (~1925° F) in a CVD reactor. During this process, thin-film coatings are formed as the result of reactions between various gaseous phases and the heated surface of substrates within the CVD reactor. As different gases are transported through the reactor, distinct coating layers are formed on the tooling substrate (base for coating process).

The final product of these reactions is a hard, wear-resistant coating that exhibits a chemical and metallurgical bond to the substrate.