

ELECTROCHEMISTRY

It is a branch of chemistry which deals with the transformation of chemical energy to electrical energy and vice versa.

Electrochemical Cell: A device which converts chemical energy to electrical energy and vice versa is known as cell.

Electrochemical Cells are of two types : (1) Galvanic cell or Voltaic cell and (2) Electrolytic cells

| Galvanic cell or Voltaic Cell | Electrolytic cell |
|--|--|
| Cell which converts chemical energy to electrical energy. | Cell which converts electrical energy to chemical energy. |
| Redox reaction takes place which is spontaneous and it is responsible for the production of electrical energy. | Redox reaction is non spontaneous and electrical energy is supplied so that the reaction may take place. |
| Electrodes used are of dissimilar material. | Electrodes used may be of similar or different material. |
| Each electrode is dipped in electrolytic solution of its own ions. | Both electrodes are dipped in same electrolytic solution. |
| Salt bridge is used. | Salt bridge is not used. |
| Anode is negative and cathode is positive. | Anode is positive and cathode is negative. |
| Electrons move from anode to cathode in external circuit. | Electrons are supplied by battery and enter through cathode and come out through anode . |
| eg: Daniel cell. | eg : lead acid storage battery. |

ELECTRODE POTENTIAL

“Electrode potential is the measure of the tendency of metallic electrode to lose or gain electrons, when it is in contact with its own salt solution.”

“Standard electrode potential is the potential difference set up between the metal and its own salt solution of 1M concentration at 25 °C at equilibrium.”

Electrode potential is of two types:

1. **Oxidation potential:** It is the measure of tendency of an electrode to lose electrons or to get oxidised is called its oxidation potential.



2. **Reduction potential:** It is the measure of tendency of an electrode to gain an electron or to get reduced is called its reduction potential.



Electrode potential depends on:

1. Nature of metal and its ions
2. Temperature
3. Concentration of ions in the solution

EMF (ELECTROMOTIVE FORCE OR CELL POTENTIAL)

EMF is the potential difference between the two electrodes of the cell when either no or negligible current is allowed to flow in the circuit.

E.M.F = Reduction Potential of cathode – Reduction Potential of anode

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

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{right}} - E^{\circ}_{\text{left}}$$

The cell reaction is feasible only when E_{cell} is positive.

STANDARD HYDROGEN ELECTRODE (SHE) OR NORMAL HYDROGEN ELECTRODE (NHE)

Since half cell in an electrolytic cell can work only when combined with other half cell, so it's impossible to determine the absolute electrode potential of a single electrode. Thus, to determine the electrode potential of a half cell, the electrode is connected to a reference electrode whose potential is fixed to 0.0 V. This reference electrode is known as SHE/NHE.

NERNST EQUATION

We know that, $\Delta G = -nFE$
 $\Delta G^\circ = -nFE^\circ$

Also, $\Delta G = \Delta G^\circ + RT \ln Q$

So, $-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + RT \ln Q$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$$

At standard temperature $T = 298 \text{ K}$, $R = 8.314 \text{ J/K mol}$, $F = 96500 \text{ C}$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log_{10} Q \quad \text{Eq. 1}$$

Q (Reaction Quotient): It is defined at any stage of Reaction at the stage **other than equilibrium**.

For a cell reaction: $aA + bB \rightarrow cC + dD$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

K_{eq} (Equilibrium Constant): It is defined for the reaction **only at the stage of equilibrium**.

For a cell reaction: $aA + bB \rightleftharpoons cC + dD$

$$K_{\text{eq}} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At equilibrium: $Q = K_{\text{eq}}$ and $\Delta G = 0$, Therefore, $E = 0$

Equation 1 will become

$$E^\circ_{\text{cell}} = \frac{0.0592}{n} \log_{10} K_{\text{eq}}$$

For a cell reaction: $aA + bB \rightleftharpoons cC + dD$

$$Q = K_{\text{eq}} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Here, Equation 1 will be written as:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{nF} \log_{10} \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

OR

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log_{10} \frac{\text{Product}}{\text{Reactant}}$$

→ Nernst Equation

$$E_{\text{cell}} = E^\circ_{\text{cell}} + \frac{0.0592}{n} \log_{10} \frac{\text{Reactant}}{\text{Product}}$$

Relation between EMF of cell and ΔH , ΔS and ΔG

From Gibbs-Helmholtz equation, we have:

$$\Delta G = \Delta H + T \left[\frac{\delta(\Delta G)}{\delta T} \right]_P \quad \text{—————} \quad (1)$$

Also, $\Delta G = -nFE$ ————— (2)

From eq. 1 and 2 :

$$-nFE = \Delta H + T \left[\frac{\delta(-nFE)}{\delta T} \right]_P$$

$$-nFE = \Delta H - nFT \left[\frac{\delta E}{\delta T} \right]_P$$

Dividing by nF on both the sides:

$$-E = \frac{\Delta H}{nF} - T \left[\frac{\delta E}{\delta T} \right]_P$$

$$E = -\frac{\Delta H}{nF} + T \left[\frac{\delta E}{\delta T} \right]_P \quad \text{—————} \quad (3)$$

Where, $\left[\frac{\delta E}{\delta T} \right]_P$ is known as Temperature Coefficient.

Equation (3) is used to calculate heat of reaction (ΔH) from measured EMF & temp. coefficient of EMF of reaction.

We know that decrease in free energy of the system is given by: $\Delta G = -nFE$

differentiating ΔG with respect to temperature at constant pressure gives:

$$\left[\frac{\delta(\Delta G)}{\delta T} \right]_P = -nF \left[\frac{\delta E}{\delta T} \right]_P \quad \text{—————} \quad (4)$$

From equation 1 and 4:

$$\Delta G = \Delta H - nFT \left[\frac{\delta E}{\delta T} \right]_P \quad \text{—————} \quad (5)$$

Also, $\Delta G = \Delta H - T\Delta S$ ————— (6)

From eq. 5 and 6:

$$\Delta H - T\Delta S = \Delta H - nFT \left[\frac{\delta E}{\delta T} \right]_P$$

$$\Delta S = nF \left[\frac{\delta E}{\delta T} \right]_P \quad \text{—————} \quad (7)$$

From above equation entropy change of a reaction (ΔS) can be calculated from the temperature coefficient of EMF.

From eq. 2, 6 and 7

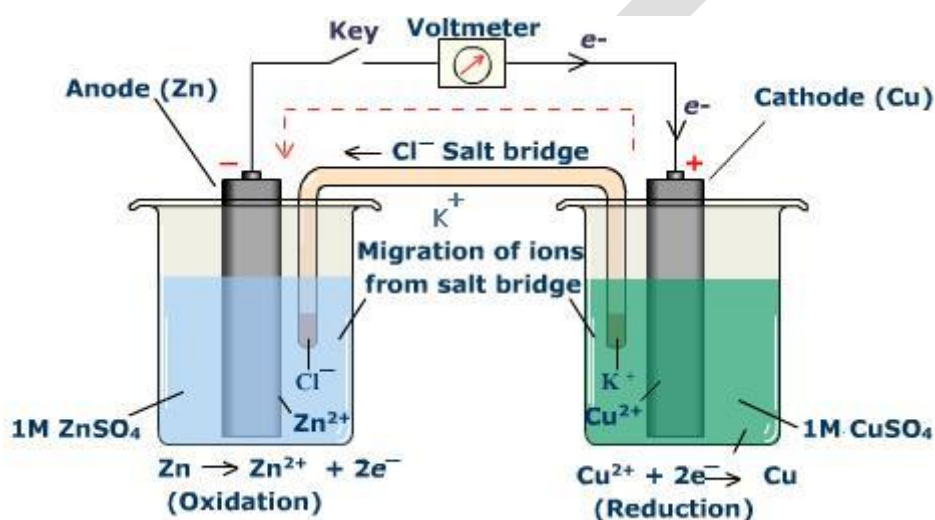
$$-nFE = \Delta H - nFT \left[\frac{\delta E}{\delta T} \right]_P$$

$$\Delta H = nF \left[T \left(\frac{\partial E}{\partial T} \right)_P - E \right]$$

Electrochemical series: The arrangement of elements in order of increasing reduction potential values is called electrochemical series. With the help of this series we can:

- When two metals are in contact we can predict which metal will act as anode and which will act as cathode. (The one with lower reduction potential act as anode and is corroded).
- Feasibility of the reaction: If the EMF of cell is positive, then only the reaction is feasible.
- Replacement tendency of metals: The metal placed higher in series can replace the metal placed below it in electrochemical series.
- Evolution of hydrogen: All the metals placed above hydrogen in series can evolve hydrogen.

GALVANIC CELL or VOLTAIC CELL



At Anode: $\text{Zn} \longrightarrow \text{Zn}^{+2} + 2\text{e}^-$

At Cathode: $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$

Overall reaction: $\text{Zn} + \text{Cu}^{+2} \longrightarrow \text{Zn}^{2+} + \text{Cu}$

Cell Representation: $\text{Zn(s)} \mid \text{ZnSO}_4(\text{sol}) \parallel \text{CuSO}_4(\text{sol}) \mid \text{Cu(s)}$

OR $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$

LEAD ACID STORAGE CELL

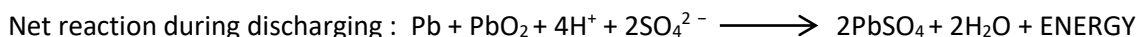
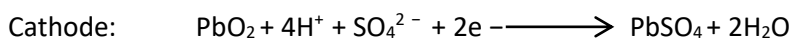
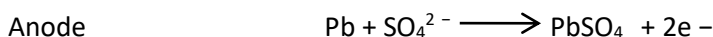
- It is both a voltaic cell and an electrolytic cell.
- It is a secondary storage battery, as it can be recharged.
- It is called lead acid because it contains acid as an electrolyte and plates are made up of lead.

Construction:

- Anode**: Made of lead grid filled with spongy lead.
- Cathode**: Made of a lead grid filled with PbO₂
- Electrolyte**: 28-30% solution of H₂SO₄ (d=1.31 g/cm³ ; 38% by mass) in a hard rubber or plastic container (ebonite case).
- The battery consists of **6 such cells connected in series**: since each cell has an emf of about 2V, the overall **emf of the battery is 12V**.
- The cathode and anode plates are arranged alternatively, separated by thin perforated plastic or fibre glass.

Working:

During Discharging: When the battery supplies current or electrical energy. During recharging, lead acid storage cell operates like galvanic cell or voltaic cell.



H_2SO_4 is used up during discharging so level of acid falls. When the density falls below 1.20g/cm^3 the battery needs recharging.

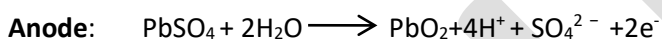
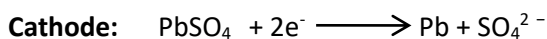
Also precipitate of lead sulphate is formed during discharging which completely covers both anode & cathode. As a result, cell stops working, Then, it needs to be recharged.

During recharging cell operates like an electrolytic cell. Lead sulphate formed is used up during recharging.

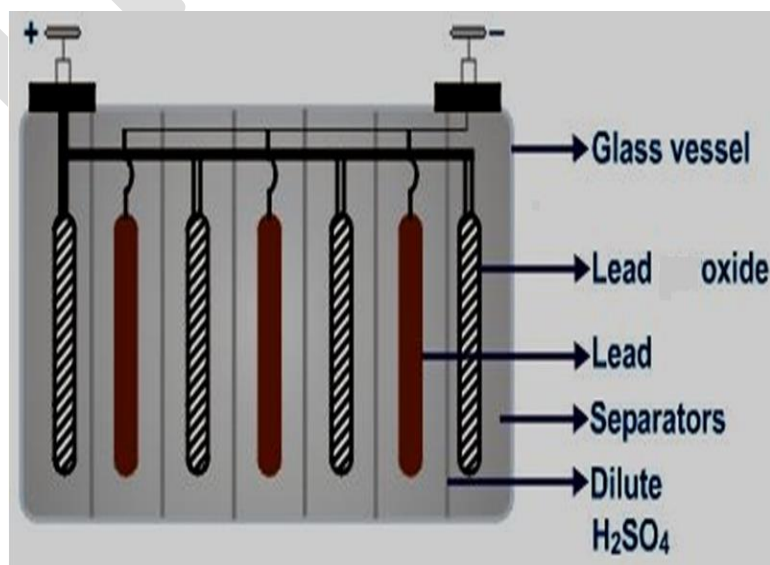
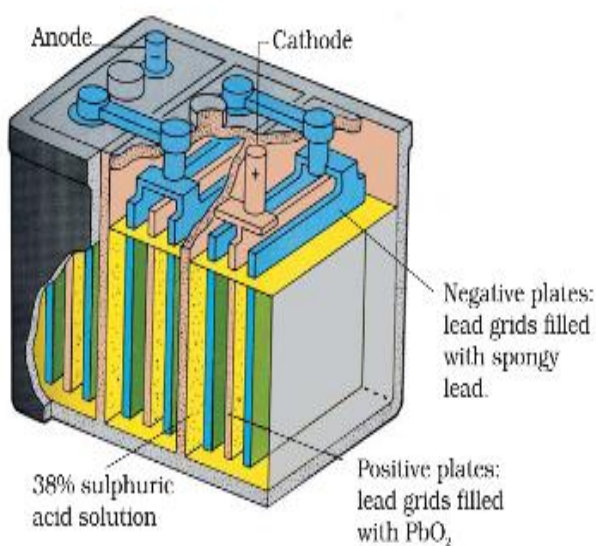
Recharging is done by passing an external emf greater than 2V. Electrode reactions are reverse of those during discharging.

The cell could be recharged because solid lead sulphate is formed during discharging which acts as a reactant in recharging.

During Recharging: During recharging, lead acid storage cell operates like an electrolytic cell.



The net cell reaction during charging and discharging process for a cycle:



CORROSION

Corrosion is a process of gradual destruction or deterioration of metals by chemical or electrochemical attack of environment. Ex: Rusting of iron, tarnishing of silver etc.

Units of Corrosion:

Mils per year (MPY)

Milligram per decimetre square per day (MDD)

1 mil = 1/1000 inch

REASON / CAUSES OF CORROSION

ORES OR METAL COMPOUND

Stable form with lower energy

Extraction of metal (+energy)

Corrosion (- energy)

METAL (PURE)

unstable due to higher energy

FACTORS AFFECTING CORROSION:

Rate and extent of corrosion depends upon :

- 1 Nature of metal
- 2 Nature of environment

NATURE OF METAL :

1. Position of metals in galvanic series:

- a) If two metals are in electrical contact, then the metal placed higher in galvanic series acts as anode and get corroded.
- b) Greater is the difference in the position of the metals in the galvanic series, faster is the rate of corrosion.

2. Relative areas of anode and cathode :

Rate of corrosion \propto Cathodic area/ Anodic area

3. Purity of metal: The impurities present in metal results in setting up small electrochemical cells leading to corrosion.

4. Physical state of metal: Rate of corrosion \propto 1/ grain size of metal

5. Nature of oxide film : If the oxide film formed on metal surface is porous and loosely held , then the corrosion of the metal takes place very rapidly.

6. Solubility of corrosion products : If corrosion products are soluble then metal corrodes rapidly and continuously.

7. Volatility of corrosion products : If the corrosion products formed are volatile, then there is rapid and continuous corrosion.

NATURE OF CORRODING ENVIRONMENT:

1) Temperature: Rate of corrosion \propto Temperature

2) Moisture: Moisture acts as solvent for corrosion. So, Rate of corrosion \propto Moisture

3) pH: Generally acidic medium leads to more corrosion.

4) Nature of corroding medium: Nature of anions, cations and their conducting nature affects the rate of corrosion.

5) Presence of impurities and suspended particles in atmosphere: Corrosive gases, fumes of sulphuric acid and hydrochloric acid, suspended particles like NaCl, charcoal, etc. increases the rate of corrosion.

Corrosion law – Pilling Bedworth rule –The oxide layer acts as a protective or non-porous barrier, if the volume of the oxide is at least as great as the volume of the metal from which it is formed.

On the other hand -if the volume of the oxide layer is less than the volume of metal, the oxide layer is porous and hence non-protective.

$$\text{Specific volume ratio} = \frac{\text{volume of metal oxide}}{\text{volume of metal}}$$

ELECTROCHEMICAL / WET THEORY OF CORROSION

Electrochemical corrosion involves flow of electrons between anode and cathode.

Electrochemical theory of corrosion is explained by two mechanisms:

1. Oxygen absorption mechanism (in neutral and alkaline medium).
2. Hydrogen evolution mechanism (in acidic medium).

For Ex: Rusting of iron.

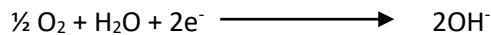
Mechanisms:

OXYGEN ABSORPTION MECHANISM (in basic or neutral medium)

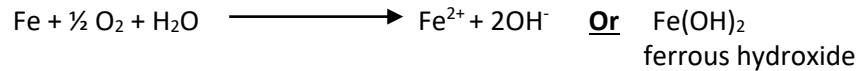
Reaction at ANODE (OXIDATION)



Reaction at CATHODE (REDUCTION)

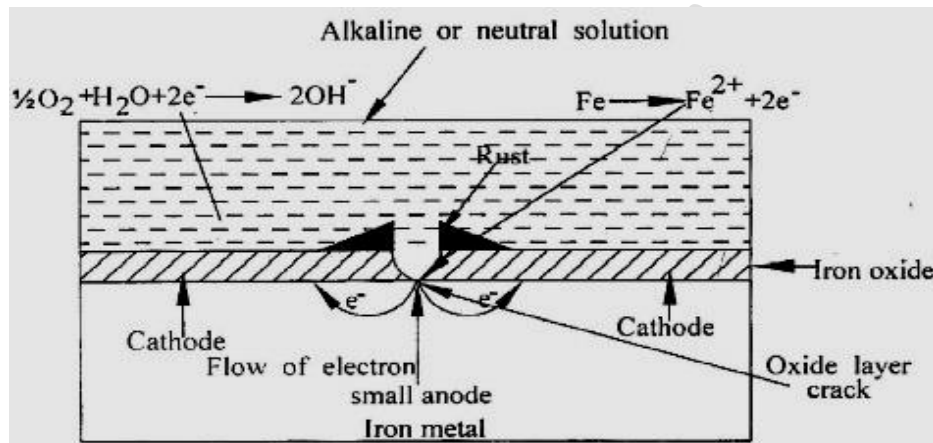


OVERALL REACTION



If enough O_2 is present: Fe(OH)_2 is oxidised to rust: $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (Yellow rust)

In limited supply of oxygen Black Magnetite is formed: $\text{Fe}_2\text{O}_3 \cdot \text{FeO} \cdot 6\text{H}_2\text{O}$ (Black magnetite)

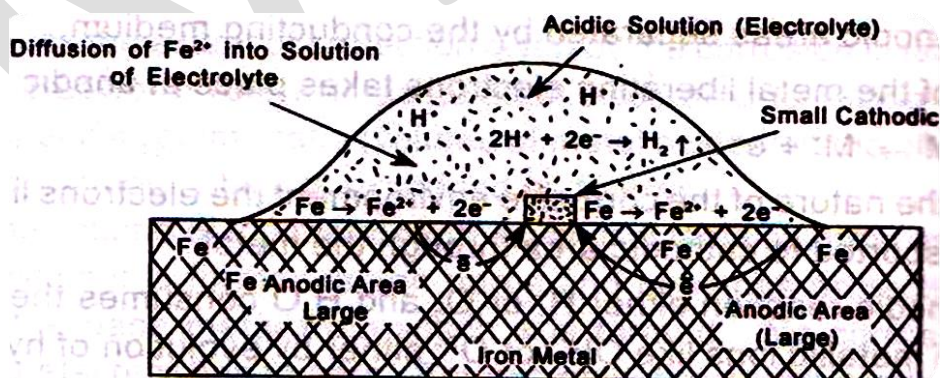
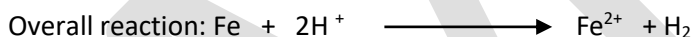
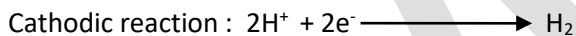
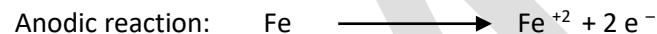


Mechanism of wet corrosion by oxygen absorption mechanism

(Small anodic area and large cathodic area, so higher rate of corrosion)

HYDROGEN EVOLUTION MECHANISM (In acidic medium)

All the metals placed above H_2 in electrochemical series, corrodes in acidic solution by hydrogen evolution mechanism.



Mechanism of wet corrosion by hydrogen evolution mechanism

CHEMICAL CORROSION OR DRY CORROSION

Corrosion that takes place in the absence of electrolyte, due to direct attack of gases on metals is called dry corrosion.

This type of corrosion takes place at elevated temperature and corrosion is uniform over metal surface.

E.g. attack of oxygen on iron.

Mechanism:

At anode (oxidation): $2M \longrightarrow 2M^{n+} + 2ne^{-}$

At cathode (Reduction): $O_2 + 2ne^{-} \longrightarrow nO^{2-}$

Overall Reaction: $2M + O_2 \longrightarrow 2M^{n+} + nO^{2-}$

Oxidation occurs first at the surface of the metal and a scale of metal oxide is formed on the surface of the metal and it tends to act as a barrier for further oxidation.

Nature of the oxide formed: - It plays an important role in further oxidation corrosion process. When the oxide film formed is:

i) Stable layer: - A stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Such a layer will be impervious in nature and hence behaves as protective coating, thereby shielding the metal surface. Consequently further oxidation corrosion is prevented. E.g.: Al, Sn, Pb, Cu, etc. form stable oxide layers on surface thus preventing further oxidation.

ii) Unstable Layer: - The oxide layer formed decomposes back into metal and oxygen Metal oxide metal + oxygen. Consequently oxidation corrosion is not possible in such cases. Eg: Ag, Au and Pt do not undergo oxidation corrosion.

iii) Volatile Layer: The oxide layer formed is volatile in nature and evaporates as soon as it is formed. There by leaving the under lying metal surface exposed for further attack. This causes rapid continuous corrosion, leading to excessive corrosion eg: Mo- molybdenum forms volatile MoO_3 layer.

iv) Porous Layer: Contains pores and cracks. In such a case the atmospheric oxygen has access to the underlying surface of the metal through the pores or cracks of the layer, there by corrosion continues until the entire metal is converted to its oxide. Eg: Iron when attacked by H_2S at high temperature forms porous FeS layer.

PREVENTION OF CORROSION

Corrosion can be prevented by the following methods:

1. PROPER DESIGN

- Avoid sharp bends and sharp corners.
- Avoid contact of dissimilar metals in presence of corroding medium.
- There should be proper drainage.
- When the two dissimilar metals are to be used in contact, anodic area should be large and cathodic area should be small.
- If two dissimilar metals have to be used in contact, their position in electrochemical series should as close as possible.
- If two metals have to be coupled use insulation between them.

2. MODIFICATION OF ENVIRONMENT

- removing moisture by using silica gel.
- Removing oxygen by adding oxygen scavengers like hydrazine
- By adjusting pH using pourbaix diagram.

3. BY USING INHIBITORS: The substances which are added from outside to inhibit the corrosion are known as inhibitors.

There are two types of inhibitors.

a) ANODIC INHIBITORS

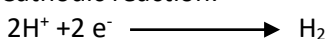
They react with the metallic ions of anode and form insoluble precipitate which is adsorbed on metal surface forming a protective film/barrier. Ex: alkalis, phosphates, chromates, etc.

b) CATHODIC INHIBITORS

They decrease the rate of reaction thereby reducing rate of overall corrosion.

i) IN ACIDIC MEDIUM

Cathodic reaction:

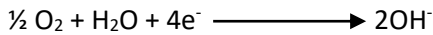


Cathodic inhibitors slow down the diffusion of H^{+} ions through cathode and thus reduces corrosion rate.

Ex – Amines, Mercaptans, ureas, thioureas, etc.

ii) IN NEUTRAL /ALKALINE MEDIUM

Cathodic reaction:



Cathodic inhibitors remove O_2 that is being used at cathode, thereby reducing corrosion.

Ex: O_2 scavengers like Na_2SO_3 , N_2H_4 , etc.

4. CHANGINING THE OPERATING VARIABLES: lowering the temperature, selecting suitable pH.

5. PROTECTIVE COATINGS

(a)**Organic coating:** includes use of paints, varnishes, etc. which acts as organic barrier between metal and environment.

(b)**Inorganic coating:** inorganic surface barriers produced by chemical/ electrochemical reactions at the surface of base metal coatings are used for paints. Ex – phosphates, chromates , etc.

(c)**Metallic coatings:** In metallic coatings one metal is coated over another metal. There are two types of metallic coatings: anodic coating and cathodic coating.

ANODIC COATING or SACRIFICIAL COATING

1. Base metal is coated with a metal which is more reactive.
2. Protects the underlying base metal sacrificially.
3. Known as anodic coating as the reduction potential of coated metal is less than that of base metal.
4. If there are pores, cracks, or breaks in such a coating base metal is not corroded till all the coated metal is consumed.
5. Zn, Cd, Al are generally used as sacrificial coatings.
6. Ex: galvanised iron (coating of Zn on Fe)

CATHODIC COATING or NOBLE COATING

1. Base metal is coated with a metal which is less reactive (more noble) in its comparison.
2. Protects the base metal due to its noble character.
3. Also known as Cathodic coating as reduction potential of coated metal is more than that of base metal.
4. If there are pores, break, etc. corrosion takes place because of small anodic area and large cathodic area.
5. Ni, Ag, Cr, Pb, etc. are used generally for noble coating.
6. Ex: coating of Sn on Fe.

6. Modification of metal

Metal can be modified by annealing, refining and alloying.

7. CATHODIC PROTECTION

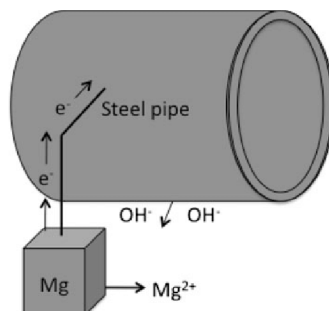
The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection.

There are two types of cathodic protection

- (a) Sacrificial anodic protection.
- (b) Impressed current method.

SACRIFICIAL ANODIC PROTECTION

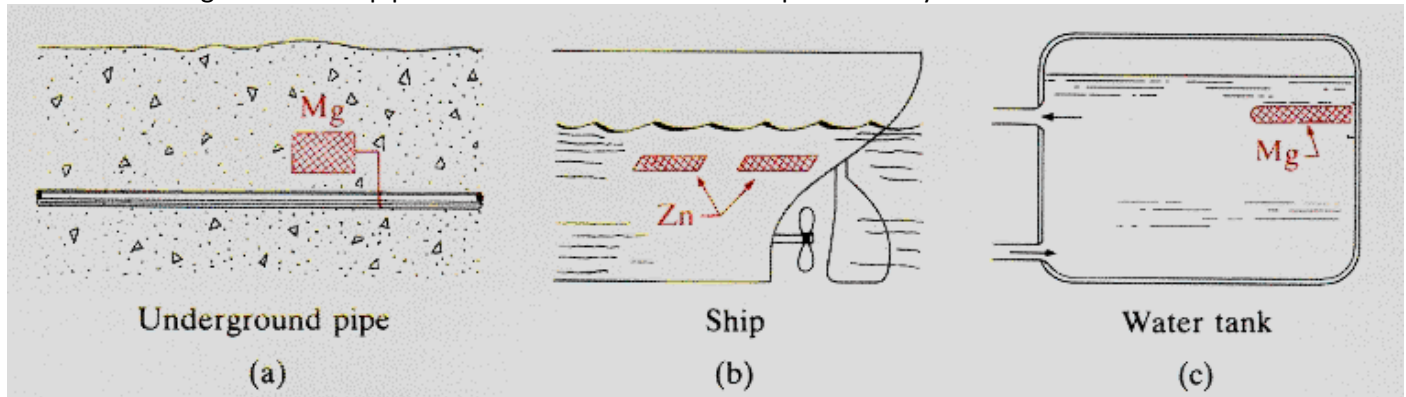
Base metal is connected by a wire to a more reactive metal so that the base metal becomes cathode and more reactive metal becomes anode.



The anodic metal gets corroded slowly, while the base metal (cathodic) is protected. The more active metal is called sacrificial anode and is replaced by a fresh one, when it is completely consumed. Mg, Zn, Al and their alloys are generally used as sacrificial anodes.

Ex: 1. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

2. The underground water pipelines and water tanks are also protected by sacrificial anode method.

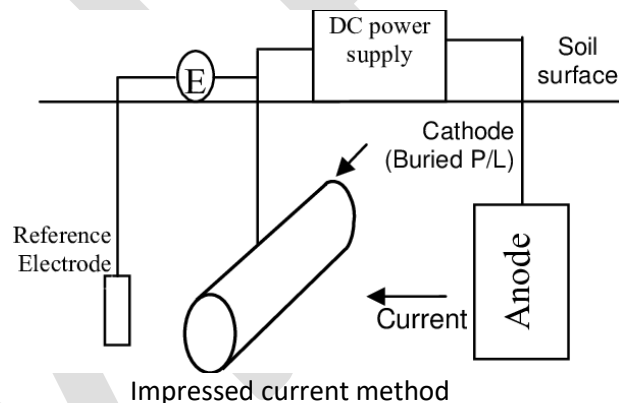


IMPRESSED CURRENT CATHODIC PROTECTION

In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.

The impressed current is slightly higher than the corrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.

The impressed current is taken from a battery or rectified on A.C. line. The impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers etc.



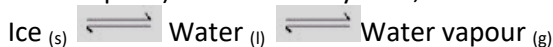
PHASE RULE

Statement Of Phase Rule

For any heterogeneous system in equilibrium, sum of Degree of freedom (F) and the number of phases (P) equals to the number of components plus two.

$$F + P = C + 2$$

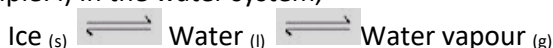
Phase (P) : A phase is defined as “ chemically homogeneous, physically distinct and mechanically separable part of system. Example: i) In the water system,



There are three phases : solid, liquid and gas. So, $P = 3$

Component (C) : Component is defined as “ the smallest number of constituents of a system, by means of which the composition of each phase can be expressed .

Example: i) In the water system,



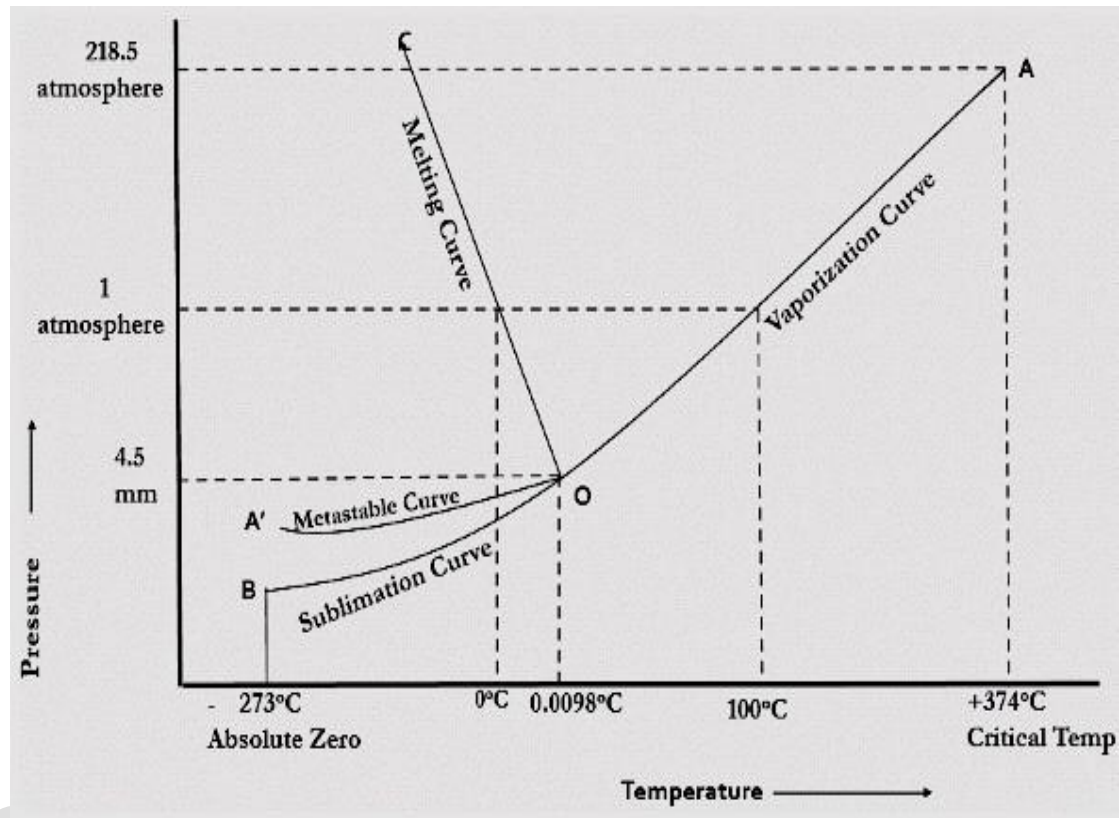
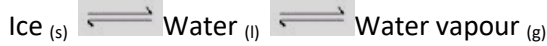
All three phases can be represented by H_2O , so it is a one component system.

Degree of freedom: Degree of freedom is defined as the minimum number of independent variables such as temperature, pressure and concentration, which must be fixed in order to define a system completely.

Ex: For a system consisting of water vapour phase only, we must state the values of both the temperature and pressure in order to define the system completely. So, the degree of freedom is two and the system is bi variant.

Application of phase rule to water system (One Component System)

Since all the phases of water can be represented by H_2O , it is one-component system i.e. $C=1$.



Phase diagram for water system

The phase diagram of water consists of:

1) Areas: There are three areas in diagram.

a) Area AOC (Water- $\text{H}_2\text{O}_{(l)}$)

b) Area COB (Ice- $\text{H}_2\text{O}_{(s)}$)

c) Area BOA (Water Vapour- $\text{H}_2\text{O}_{(g)}$)

2) Curves: 3 stable and 1 metastable curve.

a) Curve AO- Vapourisation Curve.

b) Curve OC- Fusion Curve or Melting curve.

c) Curve OB- Sublimation Curve.

d) Curve OA'- Metastable curve.

3) Equilibrias: There are 4 equilibrias in the diagram.

a) $\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(l)}$ Along the Melting curve.

b) $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(g)}$ Along the Vapourisation curve.

c) $\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(g)}$ Along the sublimation curve.

d)) $\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{H}_2\text{O}_{(l)}$ At triple point 'O'.

4) Points: One point i.e. Triple point 'O'.

| S.No. | Areas/curves/Points | Equilibrias | Phases (P) | $F=C-P+2$ | Remarks |
|-------|---|---|------------|-------------------|--|
| 1. | Areas: Area AOC | Water- $\text{H}_2\text{O}_{(l)}$ | 1 | $F=1-1+2$ $=2$ | System is bivariant. Both T and P can be varied. |
| | Area AOB | Water Vapour- $\text{H}_2\text{O}_{(g)}$ | 1 | $F=1-1+2$ $=2$ | System is bivariant. Both T and P can be varied. |
| | Area COB | Ice- $\text{H}_2\text{O}_{(s)}$ | 1 | $F=1-1+2$ $=2$ | System is bivariant. Both T and P can be varied. |
| 2. | Curves: Curve AO: Vapourisation Curve | $\text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(g)}$ | 2 | $F=1-2+2$ $=1$ | System is univariant. Either T or P can be varied. |
| | Curve OC: Fusion Curve or Melting curve | $\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(l)}$ | 2 | $F=1-2+2$ $=1$ | System is univariant. Either T or P can be varied. |
| | Curve OB: Sublimation Curve | $\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(g)}$ | 2 | $F=1-2+2$ $=1$ | System is univariant. Either T or P can be varied. |
| 3. | Point 'O' | $\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(g)}$ $\rightleftharpoons \text{H}_2\text{O}_{(l)}$ | 3 | $F=1-3+2$ $=0$ | System is invariant. Neither T nor P can be varied. |

Triple point: The point in phase diagram of water at which all the three phases solid, liquid and vapour are at equilibrium. This point at .0098°C and 4.5 mm Hg is called a triple point.

At this point system is invariant (F=0). In other words, there is no degree of freedom at O, i.e., neither pressure nor temperature can be altered, even slightly, without causing the disappearance of one of the phase.

$$F = C - P + 2$$

$$= 1 - 3 + 2 = 0$$

Metastable curve OA': As water does not always freeze at 0°C, so if the vessel containing water and vapour is perfectly clean and free from dust, it is possible to super – cool water several degrees below its freezing point 0°C. The dotted curve OA', a continuation of vaporization curve AO, represents the pressure curve of super cooled water. This curve represents a metastable system. On slight disturbance, the super cooled water at once changes to solid ice. It may be noted that metastable vapour pressure of super cooled water is higher than the vapour pressure of ice.

It's impossible to have a quadruple point in a one component system:

In a quadruple point in a one component system, the value of P (phase) will be 4.

So, substituting the values of C and P in phase rule equation we get:

$$F = C - P + 2$$

$$F = 1 - 4 + 2$$

$F = -1$; which is not possible.