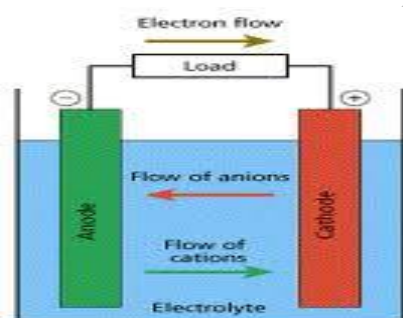


UNIT-II

ELECTROCHEMISTRY & CORROSION

- **Electrode:** Medium through which an electric current enters or leaves the electrolyte is called an electrode.
- Electrode may be a rod or a plate.
- Electrode connected to a negative terminal is cathode. It allows the current to enter the electrolyte.
- Electrode connected to a positive terminal is anode. It allows the current to leave the battery.
- Outside the electrode current flows from anode to cathode, inside the electrolyte it flows from cathode to anode.
- **Electrolysis:** The process of decomposition of the electrolyte on passing electric current through its aqueous solution or in its molten state is called Electrolysis.
- The apparatus used for the purpose of electrolysis is called as cell.
- **cell:** A cell may be defined as a single arrangement consisting of two electrodes, electrolyte and capable of producing electricity due of chemical reaction & vice versa



Terminology for Redox Reactions:

- **OXIDATION**—loss of electron(s) by a species; increase in oxidation number; increase in oxygen.
- **REDUCTION**—gain of electron(s); decrease in oxidation number; decrease in oxygen; increase in hydrogen.
- **OXIDIZING AGENT:** electron acceptor; species is reduced.

- **REDUCING AGENT:** electron donor; species is oxidized.

ELECTROCHEMICAL CELL:

A cell may be defined as a single arrangement consisting of two electrodes, electrolyte and capable of producing electricity due of chemical reaction and vice versa.

Electro chemical cells are of 2 types, viz:

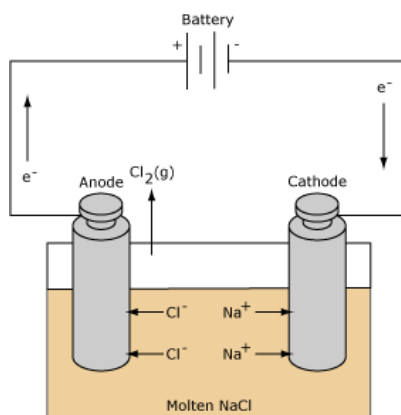
1. Galvanic (or) Voltaic cell
2. Electrolytic cell

Galvanic (or) Voltaic cell:

- The redox reaction in a galvanic cell is a spontaneous reaction.
- These cells use the energy released from spontaneous chemical energy to generate electricity. For this reason, galvanic cells are commonly used as batteries.
- Galvanic cell reactions supply energy which is used to perform work. The energy is harnessed by situating the oxidation and reduction reactions in separate containers, joined by an apparatus that allows electrons to flow.
- A common galvanic cell is the Daniel cell.

Electrolytic Cells

- The redox reaction in an electrolytic cell is nonspontaneous.
- Electrical energy is required to induce the electrolysis reaction.
- An example of an electrolytic cell is shown below, in which molten NaCl is electrolyzed to form liquid sodium and chlorine gas.
- The sodium ions migrate toward the cathode, where they are reduced to sodium metal.
- Similarly, chloride ions migrate to the anode and are oxidized to form chlorine gas.
- This type of cell is used to produce sodium and chlorine.
- The chlorine gas can be collected surrounding the cell. The sodium metal is less dense than the molten salt and is removed as it floats to the top of the reaction container.



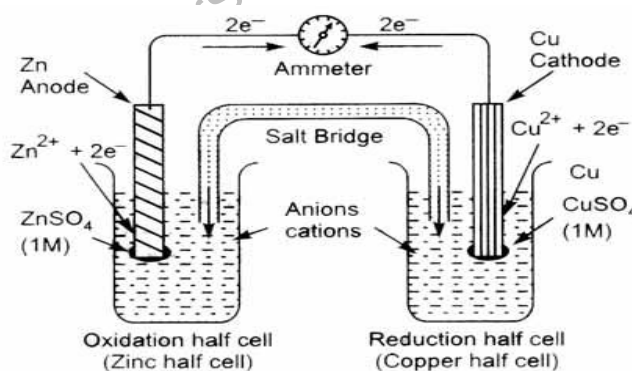
Electrolytic Cell

Galvanic cell:

- It is a device which converts chemical energy into electrical energy.
- When a system consists of two electrodes dipped into an electrolyte solution and electrodes connected by some metallic conductor outside the electrolyte, this produces an electric current in external circuit called a galvanic cell.
- In galvanic cell cathode has higher potential than anode.

Eg: Daniel cell

- Daniel cell is a Zinc-Copper cell that can be represented as $\text{Zn}/\text{ZnSO}_4//\text{CuSO}_4/\text{Cu}$
- Zinc rod is dipped in Zinc Sulphate solution, Cu rod is dipped in Copper Sulphate solution



Daniell cell

- And the 2 electrodes are connected through salt bridge, Ammeter or Volt meter.
- When these connections are made current flows in external circuit.

Observation:

- The direction of deflection of ammeter indicates flow of electrons is from Zn rod to Cu rod Zn rod starts dissolving in solution to form Zn^{+2} in solutions.
- Therefore weight of Zn rod decrease. Here Zn is releasing electrons therefore Oxidation half cell reaction.

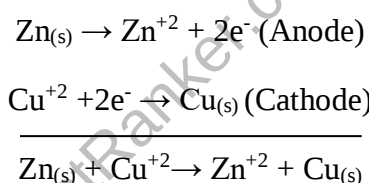
At Anode: $\text{Zn}_{(s)} \rightarrow \text{Zn}^{+2} + 2e^-$ (OHR (Oxidation Half cell Reaction))

- Zn rod pushes the electrons into the external circuit, indicates that it is acting as a negative pole. Therefore in electrochemical cell anode is negatively charged electrode.
- The electrons released by Zn flow in external circuit and reaches Cu rod.
- Cu^{+2} ions present in solution gains electrons and reduce to Cu rod. Therefore weight of Cu rod increases.
- Cu is taking electrons hence reduction takes place.

At Cathode: $\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu}_{(s)}$ (RHR (Reduction Half cell Reaction))

- Cu rod takes the electrons from external circuit indicates that it is acting as +ve pole.
- Therefore in electrochemical cell cathode is positively charged electrode.

Total cell reaction = OHR+ RHR



- Due to reaction, potential difference between 2 electrodes of Cu, Zn is produced in the form of current in the external circuit.
- It is also known as EMF or the cell potential.

Function of salt bridge:

- ✓ It provides diffusion of ions in internal circuit.
- ✓ That is cations diffuse from anode to cathode & anions diffuses from cathode to anode through the salt bridge.
- ✓ As a result, accumulation of charge at the electrodes in the external circuit to continue the cell reactions.
- ✓ Salt bridge is made up of KCl (or) NH_4OH (or) Agar Agar.

Reduction Potential:

- ❖ In an electrochemical cell, the electrode having highest reduction potential undergoes reduction. That is it acts as cathode.
- ❖ The electrode having lowest reduction potential undergoes oxidation. That is it acts as anode.
- ❖ $Zn < Fe < H_2 < Cu < Ag$.
- ❖ If a cell is constructed by Fe & Cu electrodes Fe is anode & Cu is Cathode because Cu has more reduction potential.
- ❖ For any electrode it's reduction potential = -ve oxidation potential.
- ❖ R.P = -ve O.P
- ❖ E.g.: R.P of Cu = 0.43 Volts $\Rightarrow E_{Cu^{+2}/Cu} = 0.34$ V, O.P of Cu = -0.34 $\Rightarrow E_{Cu^{+2}/Cu} = -0.34$ V.

Electrochemical series:

- The arrangement of elements in the order of their standard electrode potential is referred to as electrochemical series.
- Generally electrode potential is expressed as reduction potential.
- Increasing order of standard reduction potential at 25°C electrochemical series is Standard electrode potential.

Electrochemical series of few elements is as follows:

Standard Reduction Potentials

Reduction Half-Reaction	E° (V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	1.50
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O$	1.33
$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O(l)$	1.23
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	-0.23
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.37
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.04

Ox. agent strength increases

Red. agent strength increases

Electrode Potential or Single Electrode Potential: (E)

- When a metal rod is dipped in its ion solution, potential difference arises between electrode and the electrolytic solution in which it is dipped.
- This potential difference is called electrode potential.
- The potential of the electrode depends on
 - i. Nature of electrode
 - ii. Conc. Of electrolyte solution
 - iii. Temperature.
- It is not possible to determine the potential of an electrode directly. But, potential difference between electrodes can be determined.
- Therefore to determine the potential of electrode standard hydrogen electrode is taken as a reference electrode, and its electrode potential is taken as zero Volts.
- EMF of an electrochemical cell can be calculated by electrode potential of anode and cathode.

$$E_{\text{Cell}} = \text{Reduction Potential of Cathode} - \text{Reduction Potential of Anode.}$$

- $E_{\text{Cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$
- $E_{\text{Cell}} = E_{\text{Right}} - E_{\text{Left}}$

- E.g.: Galvanic cell.
- $\text{Zn}_{(s)}/\text{Zn}_{(aq)}^{+2} // \text{Cu}_{(aq)}^{+2}/\text{Cu}_{(s)}$
- $E_{\text{Cell}} = E_{\text{Cu}^{+2}/\text{Cu}} - E_{\text{Zn}/\text{Zn}^{+2}}$
- Consider Zn –Cu cell reaction $\text{Zn}_{(s)} + \text{Cu}^{+2} \rightarrow \text{Zn}^{+2} + \text{Cu}_{(s)}$
- O.H.R - $\text{Zn}_{(s)} \rightarrow \text{Zn}^{+2} + 2e^-$ (Anode), $E_{\text{Zn}/\text{Zn}^{+2}} = -0.76$
- R.H.R - $\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu}_{(s)}$ (Cathode), $E_{\text{Cu}^{+2}/\text{Cu}} = 0.34$
- $E_{\text{Cell}} = 0.34 - (-0.76) = 1 \text{ Volt}$.

Types of electrodes:

- Nernst equation is applicable to the half cell reactions. Few half cell reactions & corresponding Nernst expressions for some important electrodes is discussed below.

Redox electrode:

- Platinum rod dipped in a mixture of 2 different oxidation states of a metal (or) two redox states of any compound is called a redox electrode. A very good example of this kind of an electrode is Quinhydrone electrode.

Calomel electrode (secondary reference electrode):

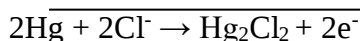
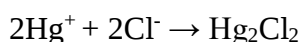
- It is a metal- metal insoluble salt electrode, and a secondary reference electrode for potential measurements.
- The calomel or mercury/mercurous chloride electrode is a member of a group of electrodes in which a mercurous salt is in equilibrium with a soluble anion.
- Such anions have included bromide, iodide, phosphate, iodate, acetate, and hydroxide.
- But mercury type electrodes with chloride ion as the anion in the salt are the most commonly available.
- The mercurous chloride paste is called calomel, hence the name of the electrode.

Construction:

- Calomel electrode consists of tube in the bottom of which is a layer of mercury, over which is placed a paste of $\text{Hg} + \text{Hg}_2\text{Cl}_2$.
- The remaining portion of cell is filled with a solution of normal or decinormal or saturated solution of KCl.
- A platinum wire dipping into the mercury layer is used for making electrical contact.
- The side tube is used for electrode is formulated as; $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{KCl}$.
- The electrode can be coupled with the hydrogen electrode of unknown pH.

Half reaction:

When it acts as anode:



When it acts as cathode:

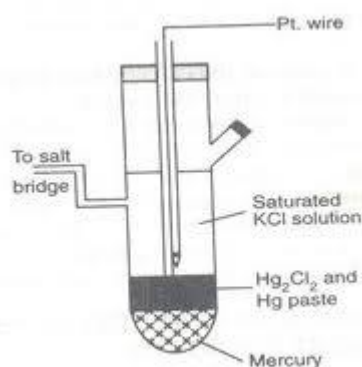
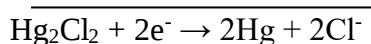
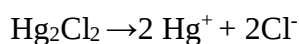
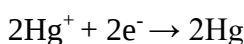


Fig. 12.15 Calomel electrode

The Nernst equation for the electrode: The potential of the electrode depends on the chloride ion concentration obtained from potassium chloride in the solution. This effect is illustrated as follows:

$$E = E^\circ - \frac{2.303RT}{2F} \log[\text{Cl}^-]^2$$

$$E = E^\circ - \frac{2.303RT}{F} \log[\text{Cl}^-]$$

At 298K

$$E = E^\circ - 0.0591 \log[\text{Cl}^-]$$

Calomel electrode prepared in saturated KCl, 1M KCl and 0.1M KCl has potentials of:

- However, once it is prepared in either one of these solutions it has a definite constant potential.
- When the KCl solution is saturated, 1N, 0.1N, it is called saturated calomel electrode (SCE), Normal calomel electrode (NCE), Decinormal calomel electrode (DNCE).

KCl	E volt
Saturated	0.241
1N	0.280
0.1N	0.334

Advantages:

- ✓ It is simple to construct
- ✓ Results of cell potential measurements are reproducible, stable, & do not vary with temperature.

Glass electrodes for pH-measurements:

- This is the most used one for measuring the pH. It is one of the ion selective electrodes, which is specific for hydrogen ion
- When two solutions of different PH values are separated by a thin glass membrane, there develops a difference of potential between the two surfaces of the membrane.
- The potential difference developed is proportional to the difference in pH value.
- The glass membrane acts as an ion-exchange resin, & an equilibrium is set up between the Na^+ ions of the glass[glass contains Na_2O -22%, CaO -6%, SiO_2 -72%] and H^+ ions in solution.
- For a particular type of glass the potential difference varies with the H^+ ion concentration, and is given by the expression

$E_{\text{Glass}} = \text{glass potential}$

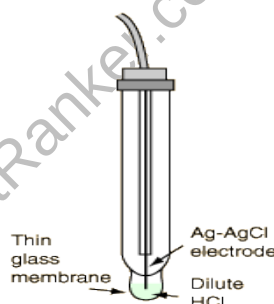
$E^0_{\text{G}} = \text{standard glass electrode potential}$

$E_{\text{Glass}} = E^0_{\text{G}} + 0.0592 \text{ V pH.}$

Over a range of pH of the test solution 0-10.

Construction:

- Glass electrode consists of a thin walled glass tube or bulb containing AgCl coated Ag electrode or simply a platinum electrode in 0.1M HCl.
- Schematic representation of glass electrode is
 $\text{Ag}/\text{AgCl}_{(\text{s})}, \text{HCl (0.1M)}/ \text{Glass or Pt, 0.1M HCl}/ \text{Glass}^+$



- HCl in the bulb furnishes a constant H^+ ion concentration.
- Thus, it is a silver- silver chloride electrode reversible with respect to chloride ions.
- Glass electrode is used as “internal reference electrode” for determining the pH of solutions, especially colored solutions containing oxidizing or reducing agent.
- Usually calomel electrode is used as the second electrode.
- In order to determine the pH of the solution, the glass electrode is placed in the solution under test, and this half cell is coupled with the saturated calomel electrode& EMF of the cell is measured.
- Since resistance is very high, special electron-tube voltmeters are used to measure the EMF of the above cell.
- The EMF of the complete cell is given by

$E_{\text{Cell}} = E_{\text{Right}} - E_{\text{Left}}$

$$=0.02422V-[E_G^0 + 0.0592 V \text{ pH}]$$

$$\text{pH} = \frac{0.02422V - E_{\text{Cell}} - E_G^0}{0.0592 V}$$

- The E_G^0 value of a glass electrode can be determined by using a solution of known pH.

Advantages of glass electrode:

- It can be used in presence of oxidizing, reducing, complexing and catalytic poisonous substances. Also in reactions involving volatile constituents' noble metals....
- It is simple and can be easily used.
- Equilibrium is rapidly achieved.
- The results are accurate.

Disadvantage:

1. Delicate, it can't be used in presence of dehydrating agent e.g. conc. H_2SO_4 , ethyl alcohol....
2. It can be used in the solutions with pH range 0-10.
3. Interference from Na^+ occurs above pH 12 i.e. Na^+ exchange together with H^+ above pH 12 and higher results are obtained.
4. Above pH 12 cations of the solution affect the glass interface and render the electrode useless.
5. Although glass membrane of the electrode is very thin, yet it's resistance is extremely high, which cannot be measured by ordinary potentiometers.

Concentration cells:

- Concentration cell is a galvanic cell in which electrical energy is produced by the transfer of material from a system of high concentration to a system of low concentration.
- There are two types of concentration cells.
 1. Electrode concentration cell,
 2. Electrolyte concentration cell.
- 1) **Electrode concentration cell:** In these cells emf arises as a result of two like electrodes at different concentrations dipped in the same solution of electrolyte.
 - E.g.: Two Hydrogen electrodes at unequal gas pressures P_1 and P_2 immersed in the same solution of H^+ ion.
 - The following cell reactions take place.
 Oxidation reaction: $\text{H}_2 (P_1) \rightarrow 2\text{H}^+ + 2\text{e}^-$
 Reduction reaction: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(P_2)$
 Total reaction: $\text{H}_2(P_1) \rightarrow \text{H}_2(P_2)$
 - It is clear that in this there is no overall chemical change and there is only transfer of H_2 gas from the electrode with pressure P_1 to the electrode with pressure P_2 .
 - The emf depends only on the two pressures and independent of the concentration of electrolyte solutions Hydrogen ions, in which the electrodes are dipped.

$$E = \frac{RT}{2F} \log \frac{P_1}{P_2}$$

- In amalgam cells two amalgams of same metal at two different concentrations are dipped in the same solution of metal ions.
- E.g.: two unequal concentrations of Zinc amalgam dipped in a solution of ZnSO_4 .
 $\text{Zn (Hg) } C_1 / \text{Zn}^{2+} / \text{Zn (Hg) } C_2$
 Overall reaction: $\text{Zn (Hg) } C_1 \rightarrow \text{Zn (Hg) } C_2$

$$E = \frac{RT}{2F} \log \frac{C_1}{C_2}$$

2) Electrolyte concentration cells:

- These cells consist of two identical electrodes dipped in a two electrolyte solutions of different concentrations, due to which a difference in the potential at the electrode and the electrolyte solution in which it is dipped.
- The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration.
- The emf of the concentration cell falls to zero, when the two concentrations of the electrolyte become identical.
- A concentration cell with two zinc electrodes dipped into two solutions of ZnSO_4 with different concentrations C_1 & C_2 joined through a salt bridge can be represented as follows.
 $(+)\text{cathode Zn} / \text{Zn}^{+2} (C_1) // \text{Zn}^{+2} (C_2) / \text{Zn} (-)\text{anode}.$
- The concentration $C_2 > C_1$, the electrode reaction on the left is oxidation.
 $\text{Zn} \rightarrow \text{Zn}^{+2}(C_2) + 2e^- (-)\text{ anode (oxidation)}$
 $\text{Zn}^{+2}(C_1) + 2e^- \rightarrow \text{Zn} (+)\text{ cathode. (Reduction)}$
- The emf of such cell can be calculated by the following expression based on Nernst equation.
- $E = \frac{0.0591}{n} \log \frac{C_2}{C_1}$
- The EMF of the cell is maximum in the beginning, slowly decreases as the reaction proceeds and becomes zero when the concentration of $C_1 = C_2$.

Applications of concentration cells:

- To determine the solubility of a sparingly soluble salt.
- To calculate the valency of cations.
- To determine the transition point.
- To calculate the extent of corrosion in metals.

Batteries:

Battery is an electrochemical cell or often, several electrochemical cells are connected in series that can be used as a source of direct electric current at a constant voltage.

Principle: A battery is a device which converts chemical energy into electrical energy, it is

- ✓ An electrochemical cell
- ✓ A source of direct electric current at constant voltage.
- ✓ Operating on the basis of the principle of galvanic cell.

Batteries are of three types.

1. Primary battery or A Primary cell:

- In this type of batteries cell reaction is not reversible.
- In these electrical energy can be obtained by at the expense of chemical energy, only as long as the active materials are present.
- Thus, when all the reactants are converted into products, no more electricity is produced and the battery becomes dead.
- These are non rechargeable and are meant for a single usage and are meant to be discarded after use.
- These cells are used in ordinary gadgets like torch light, watches & toys.
- Eg: dry cell.

2. Secondary battery or A Secondary cell:

- It is one in which the cell reaction can be reversed by passing direct electric current in opposite direction.
- Once used, a secondary battery can be recharged.
- The redox reaction gets reversed during recharge. They are also known as storage cells.
- These are rechargeable and are meant for multy cycle use.

3. Flow battery or fuel cells:

- These are ones in which materials pass through the battery this is simply an electrochemical cell.

Primary cells:

Dry cell (Leclanche cell):

Anode: cylindrical Zinc container.

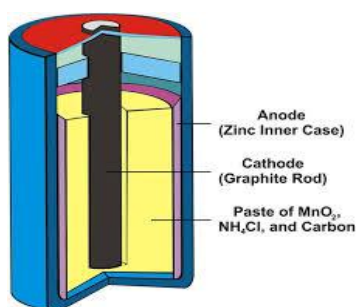
Cathode: Graphite rod placed in the centre (but not touching the base).

Electrolyte: paste of NH_4Cl and ZnCl_2

- Graphite rod is surrounded by powdered MnO_2 and carbon.
- The cell is called dry cell because of the absence of any liquid phase.

The electrolyte consists of NH_4Cl and ZnCl_2 and MnO_2 Mixed with starch to make a paste to prevent leakage.

- The graphite rod is fitted with a metal cap and the cylinder is sealed at the top with a pitch.
- The dry cell (Zn-MnO₂) is represented as $\text{Zn}/\text{Zn}^{+2}, \text{NH}_4^+/\text{MnO}_2/\text{C}$
- EMF is 1.5 V.
At anode: $\text{Zn}_{(\text{s})} \rightarrow \text{Zn}^{+2} + 2\text{e}^-$ (Oxidation)
At cathode: $2\text{MnO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^-$
The net cell reaction is: $\text{Zn}_{(\text{s})} + 2\text{MnO}_2 + \text{H}_2\text{O} \rightarrow \text{Zn}^{+2} + \text{Mn}_2\text{O}_3 + 2\text{OH}^-$



- The resulting OH⁻ ions react with NH₄Cl to produce NH₃ which is not liberated as gas but immediately combines with the Zn⁺² and Cl⁻ ions to form a complex salt [Zn(NH₃)₂Cl₂] Diammine dichloro Zinc.
 $2\text{NH}_4\text{Cl} + 2\text{OH}^- \rightarrow 2\text{NH}_3 + 2\text{Cl}^- + 2\text{H}_2\text{O}$
 $\text{Zn}^{+2} + 2\text{NH}_3 + 2\text{Cl}^- \rightarrow [\text{Zn}(\text{NH}_3)_2\text{Cl}_2]$

Advantages:

- These cells have voltage ranging from 1.25 V -1.50 V
- Primary cells are used in torches, radios, transistors, hearing aids, pacemakers, watches, etc...
- Price is low.

Disadvantages:

- These cells do not have a long life, because the acidic NH₄Cl corrodes the container even when the cell is not in use.

Lithium cells:

- These are primary cells.
- Lithium is used as anode, cathode may differ.
- Lithium is used as anode because of its light weight, high standard oxidation potential (>3V) and good conductivity.
- As the reactivity of lithium in aqueous solution is more, lithium cells use nonaqueous solvent as electrolyte. Lithium cells are classified into two categories.
 - Lithium cells with solid cathodes.

b. Lithium cells with liquid cathodes.

a) Lithium cells with solid cathode:

Anode: Lithium metal

Cathode: MnO_2 as an active metal.

Electrolyte: LiBF_4 salt in a solution of propylene carbonate and dimethoxy ethane.

- MnO_2 is heated to 300°C to remove water from it so as to work efficiently before keeping it in the cathode.
- Cell potential is 3V.

Reactions: At anode: $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$

At cathode: $\text{MnO}_2 + \text{e}^- \rightarrow \text{MnO}_2^-$

Net reaction: $\text{Li} + \text{MnO}_2 \rightarrow \text{LiMnO}_2$

Applications:

- Coin type cells are used in watches and calculators.
- Cylindrical cells are used in fully automatic cameras.

Lithium cells with liquid cathode:

Li-SOCl_2 cells are example for this.

Anode: Li metal

Cathode: SOCl_2 adsorbed on to high surface area carbon cathode.

Electrolyte: SOCl_2

Cell reactions: At anode: $4\text{Li} \rightarrow 4\text{Li}^+ + 4\text{e}^-$

At cathode: $4\text{Li} + 4\text{e}^- + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{SO}_2 + \text{S}$

Net reaction: $4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{SO}_2 + \text{S}$

In this cell discharging voltage is 3.3V – 3.5V.

Uses:

- They are used for military and space applications.
- In medicinal devices such as neuro stimulators, drug delivery systems.

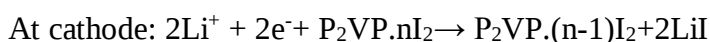
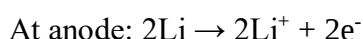
- Electrical circuit boards for supplying fixed voltage for memory protection and stand by functions.

Solid electrolyte lithium cells:

Anode: Li metal

Cathode: poly-2-vinyl pyridine (P₂VP)

Electrolyte: solid lithium iodide (LiI)



Uses:

- Because of low current applications and long shelf life

Lithium ion cells – Secondary battery:

Anode: Carbon compound, Graphite.

Cathode: Lithium oxide.

- Cathode consists of a layered crystal (graphite) into which the lithium is intercalated.
- Experimental cells have also used lithiated metal oxides such as LiCoO₂, NiNi_{0.3}Co_{0.7}O₂, LiNiO₂, LiV₂O₅, LiV₆O₁₃, LiMnO₉, LiMn₂O₄, LiNiO_{0.2}CoO₂.

Electrolyte: usually LiPF₄, although this has a problem with aluminum corrosion, and so LiBF₄ is also used.

- Lithium metal batteries have safety disadvantages. These are overcome in lithium ion batteries.
- In these batteries, membranes are necessary to separate the electrons from the ions. Currently the batteries in wide use have micro porous poly ethylene membranes.
- Intercalation in the cathode keeps the small ions (such as Li⁺, Na⁺ & the other alkali metals) into the interstitial spaces in a graphite crystal.
- This makes the graphite conductive, dilutes the Li for safety, reasonably cheap. & does not allow dendrites or other unwanted crystal structures of Li to form.

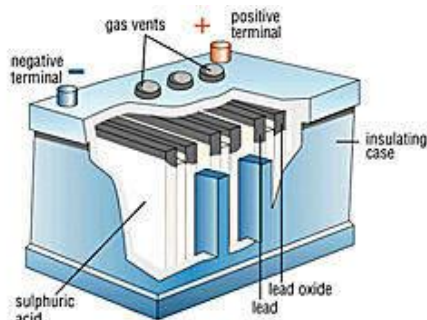
Lead Acid Storage Battery:

The electrodes are lead grids.

Anode grid: filled with spongy lead.

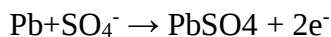
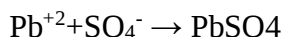
Cathode grid: lead dioxide (PbO₂)

- A number of electrode pairs with inert porous partitions in between, are dipped in approximately 20% H₂SO₄.
- The battery is encased in a plastic container.

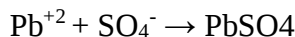


Electrode reactions for discharging reaction:

- At anode: $\text{Pb} \rightarrow \text{Pb}^{+2} + 2\text{e}^-$



- At cathode: $\text{PbO}_2(\text{s}) + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{+2} + 2\text{H}_2\text{O}$



- Net reaction : $\text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + \text{Energy}$
- The potential of lead storage cell depends on the concentration of H₂SO₄
- When the density of H₂SO₄ falls below 1.2 gm/cc the battery needs charging.

Charging: during charging / recharging of the battery an external emf greater than 2V is passed, so that the cell reactions are reversed as shown below.

Electrode reactions for charging reaction:

- At cathode: $\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$
- At anode: $\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{PbO}_2(\text{s})$
- Net reaction: $2 \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l}) + \text{Energy} \rightarrow \text{Pb}(\text{s}) + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq})$

Applications:

- They are extensively used in automobiles, electric supply in telephone exchanges, railway trains, and hospitals.

Advantages:

- The lead storage battery is both a voltaic cell and an electrolytic cell. During discharge process it acts as voltaic cell, during charging process it acts as electrolytic cell.
- It has relatively constant voltage of 12V.
- It is portable and inexpensive.

Nickel- Cadmium Cells:

Anode: Cadmium

Cathode: NiO(OH)_(s)

Cell reactions:

At anode: $\text{Cd}_{(s)} + 2\text{OH}^- \rightarrow \text{Cd(OH)}_{2(s)} + 2\text{e}^-$

At cathode: $2\text{NiO(OH)} + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Ni(OH)}_{2(s)} + 2\text{OH}^-_{(aq)}$

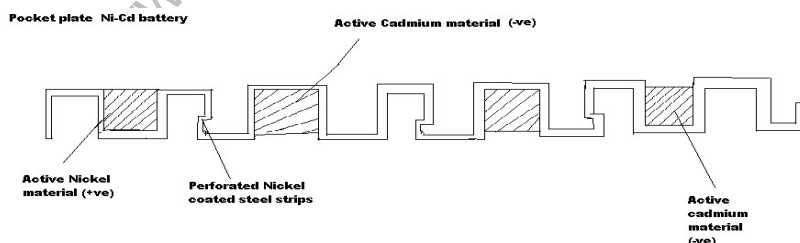
Net reaction: $2\text{NiO(OH)} + 2\text{H}_2\text{O} + \text{Cd}_{(s)} \rightarrow \text{Cd(OH)}_{2(s)} + 2\text{Ni(OH)}_{2(s)}$.

Recharging Ni-Cd Battery:

- The reaction can be easily reversed because the reaction products $2\text{Ni(OH)}_{2(s)}$ & $\text{Cd(OH)}_{2(s)}$ adhere to the electrode surface.
- Ni-Cd cell gives a 1.4V and they can be connected in series to give Ni-Cd storage battery.
- There are two types of Ni-Cd batteries.

A. Pocket plate Ni-Cd Battery:

- Two perforated Nickel coated steel strips act as pocket plates here.
- Anodic and cathodic materials are filled in these pocket plates, and connected in series as shown below.



- These cells have long shelf life >20 years with capacities between 10 – 1000 ampere and maintain voltage of 1.4 – 1.45 V.

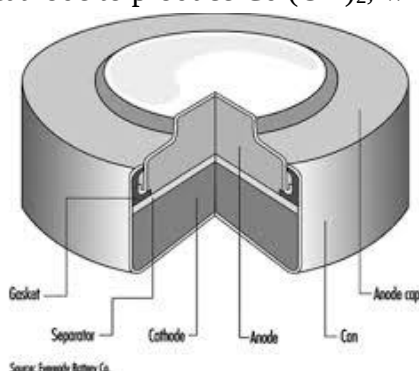
B. Sintered – plate Ni –Cd battery:

Anode: fine Ni sintered in a mold around a Nickel screen impregnated with Nickel Nitrate and processed to produce Nickel hydrate in the pores.

Cathode: the molds are impregnated with Cadmium salt processed to get hydrated oxides inside the pores.

Electrolyte: KOH solution with specific gravity 1.24 -1.3.

- Anode And cathode are assembled with suitably placed separators such as porous polymer membrane.
- The oxygen liberated during electrolysis, liberated through the porous membrane to Cd cathode to produce $\text{Cd}(\text{OH})_2$, which helps in charging.



- The sealed cells are made in three different designs – plates, button cells, & spirally wound cylindrical cells.

Advantages:

- The potential of Cd anode is below the Hydrogen potential. Hence, the Cd electrode is comparatively inert to electrolyte. It requires no float current to keep charged. The water consumption and float charge currents are extremely low.
- These are suitable to very high rate discharge and low temperature operations.
- They have long shelf life without any maintenance.

Applications:

- The Ni –Cd batteries are used for aircraft and diesel engine starting, lighting of trains, emergency power supply and for many military applications.

Fuel cells:

Definition: It is an electrochemical cell, which converts chemical energy contained in readily available fuel oxidant system into electrical energy.

Principle: The basic principle of the fuel cell is same as that of an electrochemical cell. The only difference is that the fuel and the oxidant are stored outside the cell. Fuel & the oxidant are supplied continuously and separately to electrodes at which they undergo redox reactions.

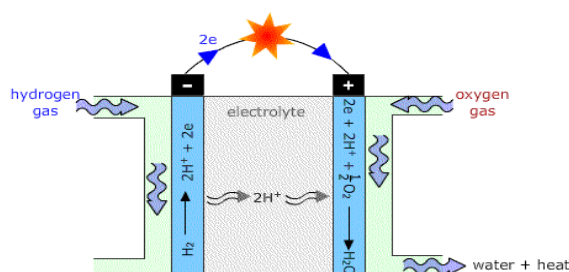
Fuel cells are capable of supplying current as long as reactants are replenished.

Fuel + oxidant → oxidation products + electricity.

Eg: H₂ – O₂ fuel cells, methanol – O₂ fuel cells.

Hydrogen – Oxygen Fuel Cells:

- This is similar to a galvanic cell.
- Both the half cells have porous graphite electrode with a catalyst (Pt, Ag, or a Metal oxide.)
- The electrodes are placed in the aqueous solution of NaOH or KOH, which acts as an electrolyte.



- Hydrogen and Oxygen are supplied at anode & cathode respectively, at about 50 atm pressure.
- The gases diffuse at respective electrodes.

Cell reactions:

At anode: $2\text{H}_{2(g)} \rightarrow 4\text{H}^+ + 4\text{e}^-$

$4\text{H}^+ + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O}$

$2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$

At cathode: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$

Net reaction: $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

- EMF of the cell is 1V.
- In place of NaOH or KOH phosphoric acid is also used as electrolyte.
- The fuel cells are used at temperatures above 100°C.

Uses:

- They are used as auxiliary source of energy in space vehicles, submarines etc...
- Because of light weight, these are used in space crafts.

Advantages:

- Product water is used as drinking water source for astronauts.
- The energy conversion is very high (75 – 82%)
- Noise and thermal pollution are low.
- Fuel cells offer excellent method for use of fossil fuels.
- Maintenance cost is low.

Disadvantages:

- Life time of a fuel cell is not accurately known.
- Initial cost is high.
- Pure Hydrogen is also costly; liquefaction of hydrogen requires 30% of storage energy.

Methyl Alcohol – Oxygen Fuel Cell:

Anode: Porous Nickel electrode impregnated with Pt/Pd catalyst.

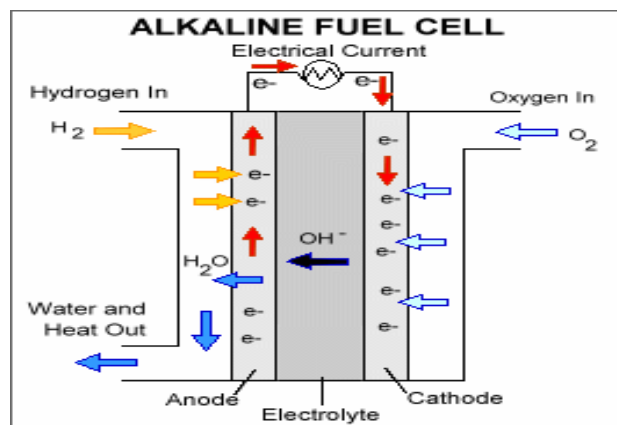
Cathode: Porous Nickel electrode coated with silver catalyst

Electrolyte: KOH

Fuel: Methanol

Oxidant: Oxygen.

CH₃OH, O₂ are sent continuously into their respective electrodes.



Cell reactions:

At anode: $\text{CH}_3\text{OH} + 6\text{OH}^- \rightarrow \text{CO}_2 + 5\text{H}_2\text{O} + 6\text{e}^-$

At cathode: $\frac{3}{2} \text{O}_2 + 3\text{H}_2\text{O} + 6\text{e}^- \rightarrow 6\text{OH}^-$

Overall reaction: $\text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

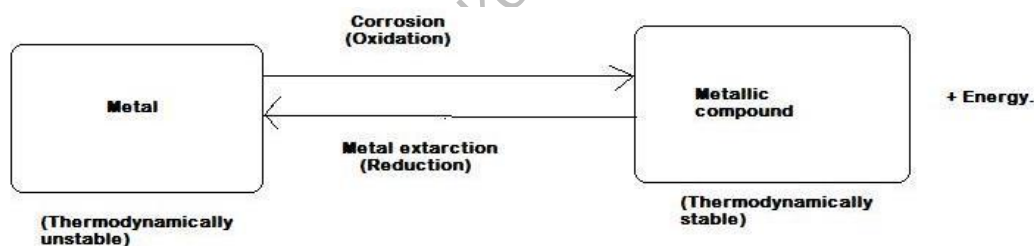
Advantages:

- Methanol fuel cells are reasonably stable at all environmental conditions.
- Easy to transport.
- Do not require complex steam forming operations.
- These are targeted to portable applications.
- Because of high Hydrogen concentration in methanol it is an excellent fuel.
- Methanol possesses less risk to aquatic plants, animals and human beings than gasoline.
- Methanol has lower inflammability limit than gasoline. Hence, possess fewer fire risks than gasoline.
- There is zero emission by the cells hence are eco friendly.

Applications: These cells are fuel for fuel cell motor vehicles like NECAR – 5 in Japan, USA etc...

CORROSION AND ITS CORROSION CONTROL

- Most metals (except noble metals like Au, Pt etc) exist in nature in combined forms as their Oxides, Carbonates, Sulphides, Chlorides and Silicates.
- These are generally known as metallic ores.
- During their extraction processes metallic ores are converted to pure metals.
- The pure metals are unstable due to their higher energy state than the corresponding ores.
- They have the natural tendency to revert back to combined state, i.e; lower energy state.



- Extraction of a metal from the metallic ore is an endothermic process.

Definition: Corrosion is defined as destruction or disintegration of a metal or alloy by chemical or electrochemical reaction with its environment.

- But, physical or mechanical wearing away of a metal is not called corrosion, but, it is called erosion.
- If corrosion and erosion takes place together, the destruction of the metal takes place very much faster.

Causes:

- All metals and alloys are susceptible to corrosion.

- Corrosion is a spontaneous process which always results in decrease of free energy.
- Eg: corrosion of Iron is known as rusting. During corrosion metal is converted to its compounds.
- Therefore the process of corrosion the metal passes from a thermodynamically less stable state to more stable state, releasing energy. This is the basic trigger for corrosion.
- Eg: Gold (Au) has excellent resistance to corrosion under atmospheric conditions but get readily corroded by mercury at ambient temperature.
- Therefore the secret of effective engineering lies in controlling rather than preventing corrosion, because it is impracticable to eliminate corrosion.

CONSEQUENCES OR EFFECTS OF CORROSION:

- Plant shutdown due to failure
- Replacement of corroded equipment
- Preventive maintenance (such as painting)
- Necessity for over design to allow for corrosion.
- Loss of efficiency
- Contamination or loss of the product (e.g. from a corroded container)
- Safety (e.g. from a fire hazard or explosion or release of a toxic product or a collapse of construction because of a sudden failure)
- Health (e.g. from pollution due to a corrosion product or due to an escaping chemical from a corroded equipment).

THEORIES OF CORROSION:

Two theories were proposed to explain the mechanism of corrosion.

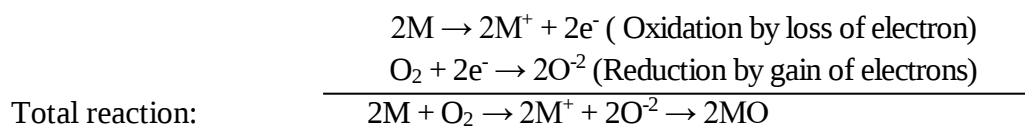
- a. Chemical corrosion (or) Dry corrosion.
- b. Electrochemical (or) Wet corrosion.

CHEMICAL CORROSION:

- Direct chemical attack by gases such as Oxygen, Halogen, Hydrogen Sulphide, Sulphur dioxide, Nitrogen, or anhydrous inorganic liquid with metal surfaces in immediate proximity at atmospheric temperature results in corrosion.
- Chemical corrosion is of 3 types.
 - a. Oxidation corrosion
 - b. Corrosion by other gases
 - c. Liquid metal corrosion

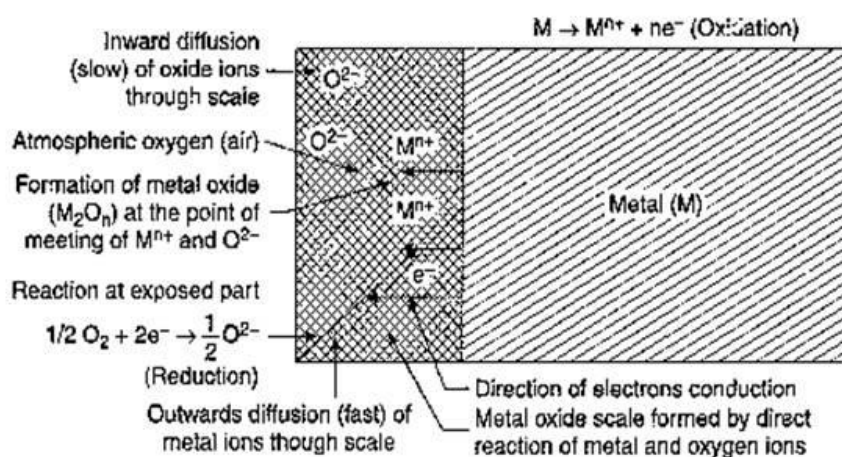
A. OXIDATION CORROSION:

- In dry conditions or in the absence of moisture attack of oxygen on the metal surface at low or high temperatures results in this type of corrosion.
- Generally metals are oxidised to a small extent.
- But, alkali metals (Li, Na, K, Rb etc...) and alkaline earth metals (Be, Ca, Sr, etc...) are rapidly oxidised at low temperatures.
- Except Au, Ag, and Pt all metals are oxidised at high temperatures.



Mechanism of Oxidation corrosion:

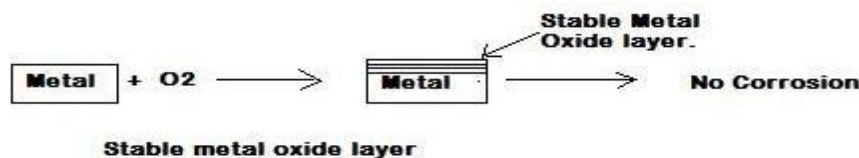
- The oxidation of the metal occurs at the surface first, there the metal oxide scale is formed, which restricts further oxidation.
- After the formation of the metal oxide scale, further corrosion may occur in two ways
 - a. Metal diffusion out of the scale.
 - b. Oxygen diffusion through the scale to the underlying metal.
- Of the two types of diffusion metal diffusion takes place rapidly, because the size of the metal ion is smaller than the size of the oxygen ion, hence higher mobility to metal ion.



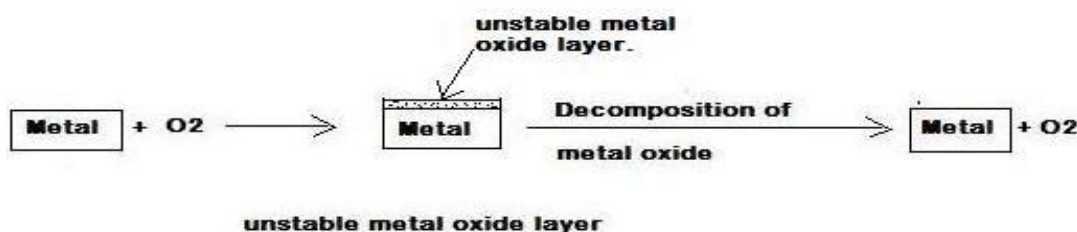
Nature of the metal oxide formed plays an important role in oxidation.

1. If stable metal oxide layer is formed, it protects the underlying metal from further oxidation. Stable metal oxide film is with fine grained structure, adheres tightly to the metal surface and impermeable to the attacking oxygen. E.g. the oxide film on Al, Sn, Pb, Cu, Cr, W etc... Iron

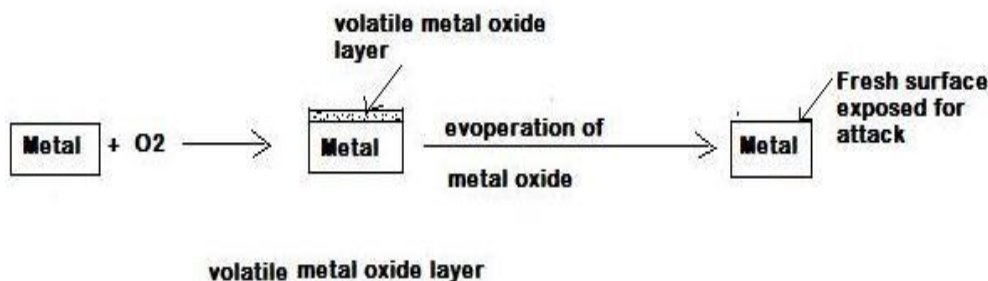
corrodes faster than aluminium because Al forms non-porous, tightly adhering protective Al_2O_3 film on the Al metal surface.



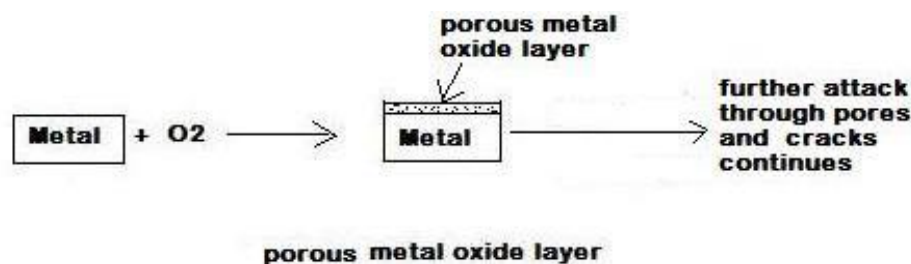
2. If unstable metal oxide film is formed it decomposes back to the metal and oxygen. In such cases oxidation corrosion is not possible. E.g. Ag, Au, Pt do not undergo oxidation corrosion.



3. If a volatile oxide layer is formed it evaporates as soon as it is formed and the metal surface is exposed for further attack. In such cases rapid and continuous corrosion occurs. E.g. molybdenum oxide (MoO_3) is volatile.



4. If porous metal oxide layer is formed, it contains pores & cracks in it, through which oxygen can diffuse thereby causing underlying metal to corrode till entire metal gets converted into its metal oxide. E.g. alkali & alkaline earth metals form such type of oxide film.



Pilling Bedworth rule:

- This rule was postulated to express the extent of protection given by metal oxide to the underlying metal.
- It states that, the smaller the specific volume ratio (volume of metal oxide/ volume of metal), the greater is oxidation corrosion.
 - i. If the volume of the metal oxide layer is at least as greater as the volume of the metal from which it is formed is non-porous and becomes protective layer by tightly adhering to the base metal from which it is formed. No corrosion occurs as the oxidation of the metal reaches to zero. For example, the specific volume ratio of W, Cr, and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in tungsten (W).
 - ii. If the volume of the metal oxide is less than the volume of the metal, the oxide layer is porous, non continuous, non protective and faces strains. Hence, cracks and pores are developed in the layer, creating access to the atmospheric oxygen to reach the underlying metal. In this case corrosion is continuous and rapidly increases. For example Li, Na, and K.

B. CORROSION BY OTHER GASES:

- The gases like SO_2 , Cl_2 , CO_2 , H_2S and F_2 also cause chemical corrosion.
- The extent of corrosion depends on the chemical affinity between the metal and the gas involved.
- The degree of attack depends on the formation of the metal compound films.
- If the film is protective in nature the degree of attack decreases. E.g. Cl_2 on Ag forms AgCl. This film protects the film from further attack.
- If the film formed is not protective in nature, the surface of the complete metal is gradually destroyed. E.g. $\text{Cl}_2 + \text{Sn} \rightarrow \text{SnCl}_2$. This film is volatile, as soon as it is formed it gets evaporated and the metal surface is exposed. Hence, lead to rapid corrosion of the metal.

C. LIQUID METAL CORROSION:

- This is due to chemical action of the flowing liquid at high temperature on solid metal or alloy.
- E.g. corrosion in devices used for nuclear power generation.
- This corrosion reaction involves
 - i. Dissolution of solid metal by liquid metal
 - ii. Internal penetration of the liquid metal into the solid metal.

ELECTROCHEMICAL CORROSION (OR) WET CORROSION:

- Electrochemical corrosion takes place in wet or moist conditions.
- Wet corrosion is more common than dry corrosion.
- Electrochemical cell is developed during this type of corrosion, hence name electrochemical corrosion.

Essential requirements for the formation of the electrochemical corrosion are:

1. Cathodic and anodic areas separated by conducting medium.
2. At anode oxidation takes place and electrons are liberated. $M \rightarrow M^{n+} + ne^{-}$
3. Electrons liberated at anodic area are transported to cathodic area through the metal.
4. During the cathodic reaction H_2O and either H^{+} or O_2 are consumed electrons and generates non metallic ions like OH^{-} or O^{2-} either by evolution of H_2 gas or absorption of O_2 .
5. Through the conducting medium metal ions and non metallic ions (OH^{-} or O^{2-}) diffuses towards each other, and formation of metallic product takes place in between the anodic and cathodic areas. Without conducting medium no corrosion takes place.
6. Mechanism of Electrochemical corrosion can be explained by taking corrosion Iron as an example.

CORROSION (or) RUSTING OF IRON:

- ❑ In Iron wet corrosion takes place.
- ❑ Whenever Iron is in contact with water and if any damage occurs to the metal, electrochemical cell formation takes place.
- ❑ Anodic area and cathodic area are formed, water acts as an electrolyte (conducting medium).
- ❑ In the process of rusting iron has higher oxidation state, Iron is converted to hydrated ferric oxide.
- ❑ Rusting is considered as an oxidative process.

At anode: Anode reactions:

- ❑ The metal atoms lose electrons to the environment and pass into the solution (water) as ferrous ions.
- ❑ At anode oxidation takes place.
- ❑ $Fe \rightarrow Fe^{+2} + 2e^{-}$
- ❑ Above reaction takes place in Iron in the presence of moisture.
- ❑ If metal ions and electrons are not removed from the environment the forward reaction will stop and corrosion will not proceed.
- ❑ When corrosion is taking place, the ferrous ions move away and react with hydroxyl ions of the solution and form less soluble ferrous hydroxide.
- ❑ $Fe^{+2} + 2OH^{-} \rightarrow Fe(OH)_2 \downarrow$
- ❑ In an oxidizing environment ferrous hydroxide oxidizes to ferric hydroxide, which is insoluble & appears as oxides of iron found in Iron rust.
- ❑ $4 Fe(OH)_2 + O_2 + 2 H_2O \rightarrow 2Fe_2O_3.3 H_2O$

- ❑ Rust formula is $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

At cathode: Cathodic reactions:

- ❑ The electrons released at anode are conducted to the cathode.
- ❑ At cathode two types of reactions takes place. Hydrogen evolution type reactions and Oxygen absorption type reactions.

Evolution of Hydrogen:

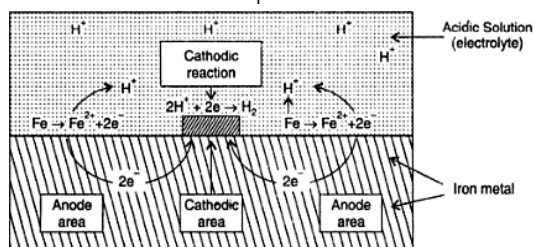
Evolution of hydrogen takes place in the absence of Oxygen.

a) In Acidic media:

- ❑ In acidic media protons are available. Hence, hydrogen ions acquire electrons and generate H_2 gas.
- ❑ $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \uparrow$

b) In neutral and alkaline media:

- ❑ In neutral media and alkaline media H_2O is available; hence water takes up electrons' and liberates hydrogen gas.
- ❑ $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 \uparrow + 2\text{OH}^-$



Diagrammatic representation of the mechanism of wet corrosion by hydrogen evolution.

Absorption of Oxygen:

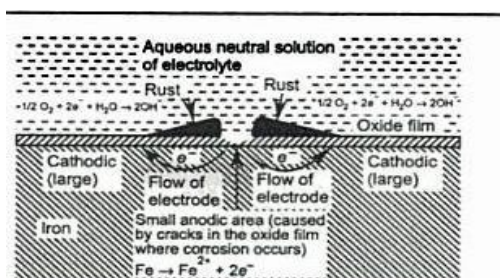
Absorption of oxygen type of reactions take place in the presence of dissolved oxygen, either in acidic media or in neutral or alkaline media.

a) In acidic medium:

- ❑ Protons from acidic media takes up electrons react with oxygen to generate water molecules.
- ❑ $4\text{H}^+ + 4\text{e}^- + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

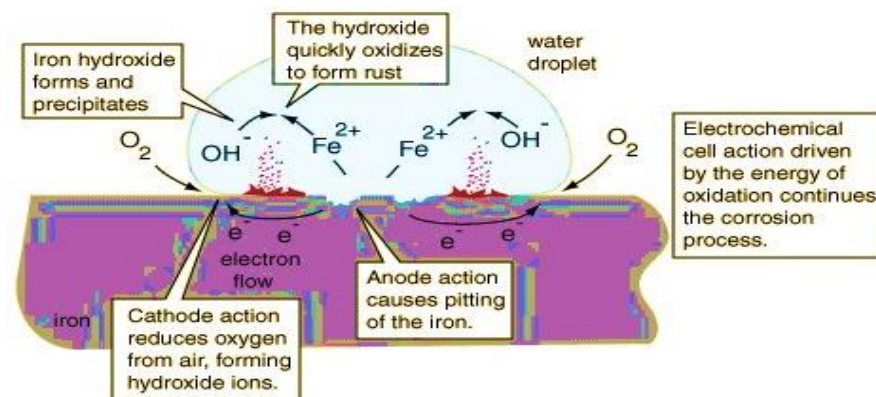
b) In neutral and alkaline medium:

- ❑ H_2O in the neutral and alkaline media acquires electrons and react with oxygen to give hydroxyl ions.
- ❑ $2\text{H}_2\text{O} + 4\text{e}^- + \text{O}_2 \rightarrow 4\text{OH}^-$



Mechanism of wet corrosion by oxygen absorption

- Corrosion occurs at anode, rust formation takes place in between the cathodic and anodic areas as the metal ions and OH^- ions move towards opposite electrodes from where they are formed.
- $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \rightarrow 2Fe_2O_3 \cdot 3H_2O$



COMPARISON OF CHEMICAL CORROSION WITH ELECTROCHEMICAL CORROSION:

S.No	Dry or Chemical Corrosion	Wet or Electrochemical Corrosion
1.	It occurs in dry conditions.	It occurs in wet conditions in presence of electrolyte medium.
2.	Corrosion is uniform	Corrosion is not uniform if the anodic area is small, pitting is more frequent.
3.	It is a slow process	It is a rapid process.
4.	It involves direct chemical attack of the metal by environment.	It involves the formation of large number of electrochemical cells.
5.	It is explained by absorption mechanism.	It is explained by mechanism of electrochemical reactions.
6.	It occurs both on homogeneous and heterogeneous solutions.	It takes place only on heterogeneous process.
7.	Corrosion products are produced at the place of corrosion	Corrosion occurs at anode & corrosion product occurs in between anodic and cathodic areas.

Basic requirements of rusting of Iron:

- ❑ Oxygen and water are essential for rusting. Iron will not undergo rusting in dry conditions or water that is completely free from oxygen.
- ❑ Rusting of Iron is accelerated by
 - i. Rust itself
 - ii. Presence of acids and electrolytes
 - iii. Contact with less corrosion active metals like Cu, Ag etc...
- ❑ Production of anodic and cathodic areas on the metal surface.

Types of corrosion:

Several types of corrosion are often distinguished as follows.

(1) Galvanic Corrosion :

- Galvanic corrosion may take place when two different metals contact (or) (connected by an electrical conductor) are exposed to an electrolytic solution.
- The difference in electrical potential between the two metals provides the driving force to pass current through the corroder and results in corrosion of the anodic metal.
- The larger the potential difference between the two metals, the greater may be the galvanic corrosion. The relative areas of the cathodic and anodic metals are also important.
- A much larger area of the more noble metal compared to the active metal, accelerates the attack.
- E.g. when Zn, Cu are connected and provided electrical environment following reactions take place.
- At Anode: $\text{Zn}_{(s)} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ (oxidation)
- Cathode: $\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}_{(s)}$ (reduction)

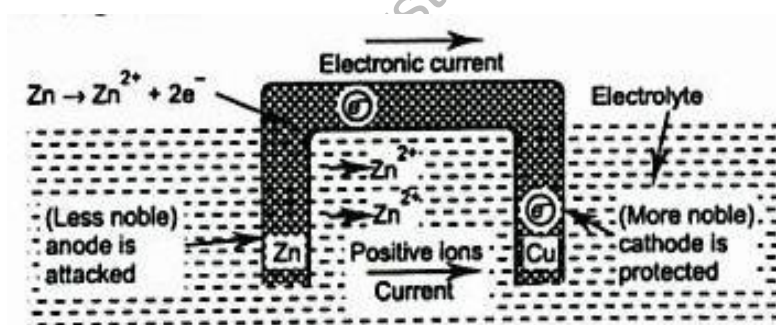
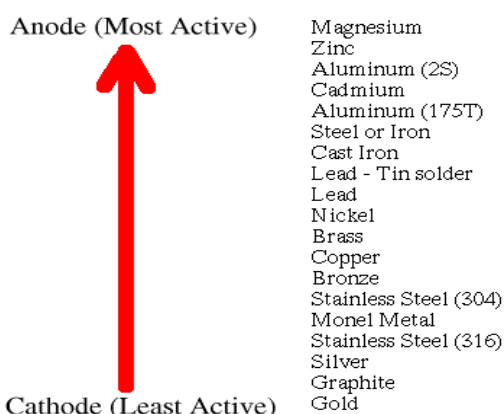


Fig. 3.12. Galvanic corrosion

Galvanic series:

- Electrochemical series may not provide sufficient information about the metal which undergoes corrosion when two different metals are in contact with each other.
- This is because several side reactions taking place may influence the corrosion reactions.

- Hence, oxidation potentials of several metals and alloys are measured using standard calomel electrode as the reference electrode and immersing the metals and alloys in sea water.
- Decreasing order of activity of the oxidation potentials of metals and alloys is known as galvanic series.
- Galvanic series gives more practical information about the corrosive tendency of metals and alloys.



- And corrosion takes place always at the metal which acts as anodic part, and cathodic part is protected.

Examples of galvanic corrosion:

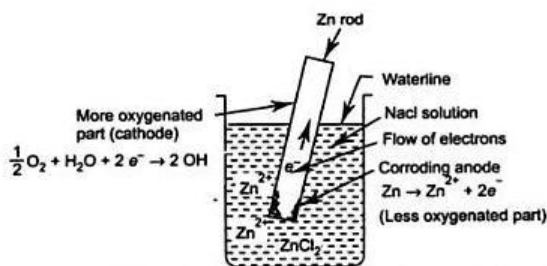
1. A steel screw is a brass marine hardware.
2. Lead antimony solder around copper wire (lead, antimony solder becomes anodic).
3. A steel propeller shaft in bronze bearing (steel becomes anodic).
4. Steel pipe connected to bronze plumbing (steel becomes anodic).

Difference between Galvanic and Electrochemical series:

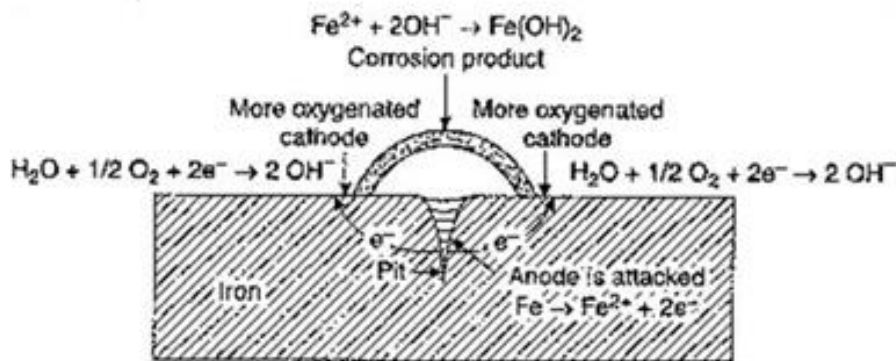
S.No	Galvanic series	Electrochemical series
1.	It predicts the corrosive tendencies of metals and alloys.	It predicts the relative displacement tendencies.
2.	Calomel electrode is used as the reference electrode.	Standard hydrogen electrode is used as reference electrode.
3.	Position of a metal or alloy may change. The metals and alloys are immersed in the sea water for study.	Position of a metal is fixed, it cannot be changed.
4.	Electrode potentials are measured for both metals and alloys.	The electrolyte contained particular concentration of salts of the same metal that was being used.
5.		Electrode potentials are measured only for metals and non-metals.

2) Water line corrosion:

- It is a type of concentration cell corrosion.
- Concentration cell corrosion may arise due to
 - i. Difference in the concentration of the metal ions or
 - ii. Difference in the exposure to air/Oxygen (differential aeration corrosion) or
 - iii. Difference in temperature or
 - iv. Inadequate agitation or
 - v. Different diffusions of metal.
- Waterline corrosion is a best example for differential aeration corrosion.
- It is when a metal is exposed to different air concentrations or concentration of salts etc...
- It has been found that the poorly oxygenated metallic part becomes anodic and well oxygenated part becomes cathodic.
- Difference of potential is created, which causes the flow of electrons between the two differently aerated parts of the same metal.



- E.g. Zn rod immersed deep in NaCl: - anodic solution; Zn rod above NaCl solution: - cathodic part.
 - The flow of electrons takes place from anodic part to cathodic part through the metal.
 - Migration of ions takes place through the electrolyte.
 - The Zn starts corroding in the anodic area immersed in sodium chloride solution.
 - Other examples are ship hulls, storage tanks, iron pole immersed in water etc
- ## 3) Pitting corrosion:
- ❖ A cavity, pinholes, pits, and cracking of the protective film developed on the metal surface creates the formation of small anodic areas in the less oxygenated parts and large cathodic areas in well oxygenated parts.
 - ❖ The flow of electrons takes place from anodic part to cathodic part through the metal.



- ❖ Migration of ions takes place through the medium (atmospheric moisture).
 - ❖ The corrosion product is formed between anodic and cathodic areas.
 - ❖ Damage of the protective film may be due to
 - i. Surface roughness or non uniform stresses
 - ii. Scratches or cut edges
 - iii. Local strain of metal
 - iv. Alternating stress
 - v. Sliding under load
 - vi. Impingement attack
 - vii. Chemical attack
- a) **Carry over in boiler causing corrosion to turbine plates:**
- ❖ The boiler water concentrated with dissolved salts, is carried along the steam or in the form of droplets of water and deposits on the turbine plates.
 - ❖ The metal under the drop becomes anodic due to high concentration of dissolved salts and starts corroding while the remaining large area of the turbine plates becomes cathodic.
 - ❖ The flow of electrons takes place through the metal and ions through the medium.
 - ❖ The electrochemical corrosion due to concentration cell occurs to the metal.
- b) **Corrosion due to Caustic embrittlement:**
- ❖ Boiler water contains certain amount of sodium carbonate which decomposes to sodium hydroxide under the high pressure of the boiler, which deposits in the hair cracks, pits, etc... of the boiler plate creating a concentration cell.
 - ❖ The metal deposited with NaOH becomes anodic while the metal surround the drop becomes cathodic.
 - ❖ $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{CO}_2$
 - ❖ The concentrated alkali in the anodic areas dissolves the metal as sodium ferrite (Na_2FeO_2), which decomposes a short distance away from the point of formation as magnetite and sodium hydroxide thereby enhancing corrosion.
 - ❖ $6 \text{Na}_2\text{FeO}_2 + \text{H}_2\text{O} + \text{O}_2 \rightarrow 12 \text{NaOH} + 2\text{Fe}_3\text{O}_4$.

- ❖ The concentration cell formed can be represented as
[Iron (-) anodic/ Concentrated NaOH/Dilute NaOH/Iron (+) (Cathodic)].

4) Intergranular corrosion:

This corrosion occurs along the grain boundaries. The main reason for the corrosion of grain boundaries is

- ⇒ Grain boundaries where the metal is sensitive to corrosive attack
- ⇒ The corrosive attacking liquid/reagent possesses the character of only attacking at the grain boundary.

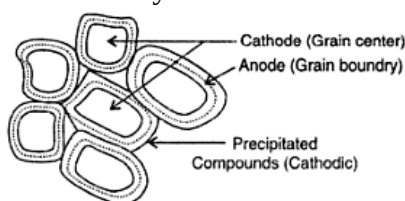


FIGURE 9.17 Intergranular corrosion.

- ⇒ The grain boundary contain a material which shows electrode potential more anodic at the grain boundary and
- ⇒ The precipitation of certain compounds at grain boundary producing a solid solution depleted in one constituent, making the grain boundary anodic.
- ❖ Grain boundary behaves as anodic and centre of the body behaves cathodic.
- ❖ Electrons flow from anode to cathode through metal.
- ❖ Corrosion product is formed in between anodic and cathodic areas.
- ❖ E.g. welding of stainless steel is done by deposition of chromium carbide at the grain boundaries which makes the grain boundaries anodic and corrosion occurs.

FACTORS INFLUENCING CORROSION:

The rate of extent of corrosion depends on the following factors.

- A. Nature of metal
- B. Nature of corroding environment.

NATURE OF THE METAL:

1. Position in the galvanic series:

- ❖ When two metals or alloys are in electrical contact in presence of an electrolyte, the metal with higher oxidation potential suffers corrosion.
- ❖ The rate and severity of corrosion depends upon the difference in their positions in electrochemical series and greater is the difference, the faster is the corrosion of the anodic metal.

2. Over voltage:

- ❖ If a pure Zn is placed in 1N H_2SO_4 , it undergoes corrosion, forms a film with liberation of H_2 gas on the immersed metal surface, initial rate of reaction is very slow due to high voltage i.e. 0.70V.
- ❖ But corrosion of zinc can be accelerated by adding a drop of CuSO_4 or a drop of platinic chloride.
- ❖ Because, some copper gets deposited on the Zn, forming minute cathodes where hydrogen over voltage reduces to 0.33. Thus accelerates corrosion.

3. Relative areas of the anodic and cathodic parts:

- ❖ When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the areas of the cathodic and anodic parts.
- ❖ E.g. corrosion is more rapid, severe and highly localized if the anodic area is small.
- ❖ E.g. a small pipe made of steel fitted in a large copper tank.
- ❖ Due to smaller anodic areas the current density at a smaller anodic area is much greater.
- ❖ The large cathodic area demands more electrons, which should be met by smaller anodic areas only by undergoing corrosion rapidly.

4. Purity of the metal:

- ❖ As the extent of exposure and impurity increases, the extent of corrosion increases with the increasing exposure and impurities.
- ❖ E.g. Zn metal containing impurity such as Pb or Fe undergoes corrosion due to formation of local electrochemical cells.
- ❖ When impurities are present heterogeneity is produced which forms tiny electrochemical cells.

5. Nature of surface film:

- ❖ if the “specific volume ratio” is more, the rate of corrosion is less, because the surface of the metal is completely covered by the film, offering protection to the metal surface.
- ❖ E.g. the specific volume ratio of W, Cr, and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in tungsten (W) even at elevated temperatures.

6. Physical state of metal:

- ❖ The grain size, orientation of crystals, stress etc. of the metals influence the rate of corrosion.
- ❖ The smaller the grain size of the metal or alloy greater will be the rate of corrosion, because of its high solubility.
- ❖ The areas under stress become anodic and corrosion takes place in these areas.

7. Passive character of the metal:

- ❖ Metals like Ti, Al, Cr, Mg, Ni, & Co are passive and they exhibit much higher corrosion resistance than expected from their position in the electrochemical series.
- ❖ This is because the metals form very thin, highly protective corrosion film, by reacting with atmospheric oxygen.
- ❖ If the film is broken, it compensates the film by re-exposure to oxidizing conditions.
- ❖ Thus they produce “self healing film”.

- ❖ This property is called passive character of the metal.
- ❖ E.g. corrosion resistance of “stainless steel” is due to passivating character of chromium present in it.

8. Volatility of corrosion product:

- ❖ If a volatile oxide layer is formed it evaporates as soon as it is formed and the metal surface is exposed for further attack. In such cases rapid and continuous corrosion occurs. E.g. molybdenum oxide (MoO_3) is volatile.

9. Solubility of corrosion product:

- ❖ The corrosion product acts as a physical barrier between the metal and environment.
- ❖ If the oxide film formed as corrosion product is soluble in corroding medium, the corrosion proceeds at a faster rate.
- ❖ E.g. PbSO_4 film formed by Pb on sulphuric acid medium.

NATURE OF THE CORRODING ENVIRONMENT:

1. Temperature:

- ❖ The rate of corrosion reaction and diffusion rate increases with increases in temperature, causing the increase in rate of corrosion.

2. Humidity of air:

- ❖ The humidity of air is a deciding factor for rate of corrosion.
- ❖ The relative humidity above which, the rate of corrosion increases sharply is called “critical humidity”.
- ❖ The value of critical humidity depends on the physical characteristics of the metal and the nature of corroding atmosphere.
- ❖ The moisture or vapor present in atmosphere furnishes water to the electrolyte, essential for setting up an electrochemical cell.
- ❖ The oxide film formed has the tendency to absorb moisture, which creates other electrochemical cell corrosion.
- ❖ The rain water not only supplies necessary moisture for electrochemical attack but also wash away a good amount of oxide film from the metal surface, leading to enhanced atmospheric attack, unless the oxide film is exceptionally adherent.

3. Presence of impurities in atmosphere:

- ❖ Gases like CO_2 , SO_2 , H_2S , etc., and fumes of H_2SO_4 , HCl etc, suspended particles of chemical activity/inactive by nature like NaCl , $(\text{NH}_4)_2\text{SO}_4$ and charcoal are present in atmosphere.
- ❖ The gases and acidity of the atmosphere increases the electrical conductivity, thereby increases corrosion.

- ❖ In marine atmosphere the presence of sodium and other chlorides lead to increased conductivity there by increased corrosion.
- ❖ The suspended particles absorb moisture and act as strong electrolytes increasing the rate of corrosion.
- ❖ These suspended impurities also absorb both gases and moisture and slowly enhance the rate of corrosion.

4. Nature of ions present in the medium:

- ❖ The presence of ions like silicates in the medium leads to the formation of “insoluble reaction products” like silica gel, on the metal surface which inhibit further corrosion.
- ❖ On the other hand chloride ions, if present in the medium destroys the protective film on the surface of the metal, there by exposing the metal surface for fresh corrosion attack.
- ❖ Presence of traces of copper in marine waters enhances the corrosion of the Iron pipes or steel body of the ships.

5. Conductance of the corroding medium:

- ❖ For the conductance of underground or submerged structures of the corroding medium place an important role.
- ❖ The conductance of dry sandy soil is lower than the conductance of clayey and mineralized soils.
- ❖ Hence the rate of corrosion is more in clayey and mineralized soils, causing severe damage to metallic structures buried.

6. Amount of oxygen in atmosphere:

- ❖ As the % of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell.
- ❖ The decay of the metal occurs at the anodic part and the cathodic part of the metal is protected.
- ❖ Anodic reaction for iron: $\text{Fe} \rightarrow \text{Fe}^{+2} + 2\text{e}^-$
- ❖ Cathodic reactions: $2\text{H}_2\text{O} + \text{O}_2 + 2\text{e}^- \rightarrow 4\text{OH}^-$
- ❖ Corrosion product: $2\text{Fe}^{+2} + 4\text{OH}^- \rightarrow 2\text{Fe}(\text{OH})_2$
- ❖ $2\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{Fe}(\text{OH})_3 \rightarrow \text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

7. Velocity of ions which flow in the medium:

- ❖ As the velocity of the diffusion of ions in the medium increases, the rate of corrosion increases.

8. p^H value of the medium:

- ❖ It has greater effect on corrosion. When the P^H value is lowered, the corrosion is increased.

CORROSION CONTROL METHODS:

Corrosion of a metal leads to many practical problems. Hence, it is necessary to control corrosion. There are different types of corrosion control methods.

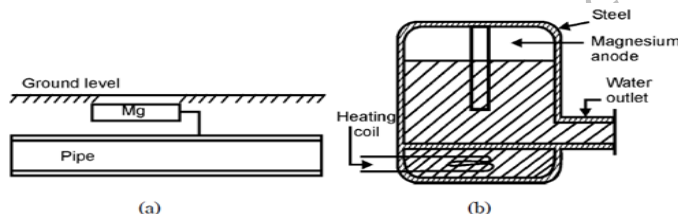
CATHODIC PROTECTION:

The principle involved in this method is “to force a metal to behave as a cathode”. If metal behaves as a cathode it is unaffected. There are two types of cathodic protection

- i. Sacrificial anodic protection
- ii. Impressed current cathodic protection.

A. Sacrificial anodic protection:

- In this method the metal to be protected is called “base metal “converted into cathode by connecting it to more active metal(less noble)
- The active metal acts as auxiliary anode, Zn, Mg, Al, are commonly used anodes.
- These metals being more active acts as anode, and undergo preferential corrosion, protecting the base metal.
- Since the anodic metals are sacrificed to protect the base metal, it is known as sacrificial anodic protection.
- Exhausted anode metals are replaced by new ones as and when required.
- E.g. a Mg block connected to a buried oil storage tank. Mg bars are fixed to the sides of ocean going ships; Mg blocks are connected to buried pipelines.



Advantages:

- Method is simple
- Low installation cost
- Does not require power supply

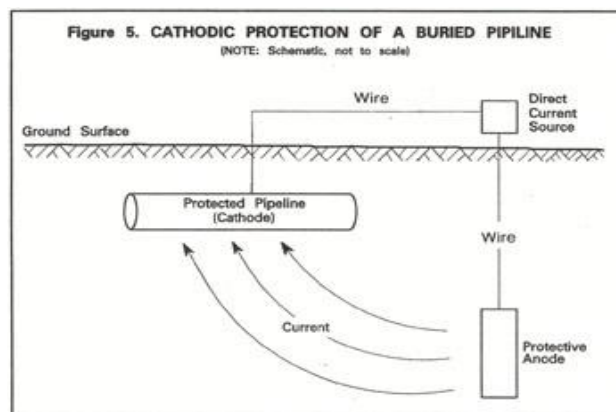
Disadvantages:

- Recurring expenditure for replacement of consumed anode.

B. Impressed current cathode protection:

- It is carried out by applying direct current little more than corrosion current in opposite direction to nullify the corrosion current producing a reverse cell reaction.
- The impressed current source may be a battery or rectified A.C. line.

- The anode is usually insoluble anode like graphite, high silica iron, scrap iron, stainless steel, or platinum.
- In this case base metal behaves as cathode hence does not undergo corrosion.
- E.g. water tanks, open water box coolers, buried water or oil pipelines, condensers, transmission line towers, marine pipes.



Advantages:

- One installation can protect large area of metal
- Low maintenance cost

Disadvantages:

- Expensive, it needs high current
- If impressed current is not uniform, localized corrosion takes place.
- May suffer hydrogen embrittlement.

Disadvantages of cathodic protection:

1. The cathodic protection may be efficient in protecting a pipeline but it may increase the corrosion of the adjacent pipelines or metal structure because of stray current.
2. Capital investment and maintenance costs are more.
3. Special care must be taken that the metal is not over protected, i.e. the use of much higher potential than the open circuit voltage for the metal/ metal ion couple in case of impressed current method and the higher anodic metal in the series must be avoided. Otherwise problems related to cathodic reactions like evolution of H_2 or formation of OH^- will take place.

METALLIC COATINGS:

- Metallic coatings are produced by coating one metal on the surface of another metal.
- The metal which is protected is called "base metal".

- The metal which is coated on the surface of the base metal is called “coating metal”.
- Metallic coatings are broadly divided into two types:
 1. Anodic coatings
 2. Cathodic coatings

Anodic coatings:

- ⇒ These types of coatings are produced by coating metals whose reduction potentials are lower than that of base metal.
- ⇒ E.g. Zn, Al, and Cd are coated over Iron.
- ⇒ If any pores, breaks, or discontinuation in metallic coating, & the base metal is exposed, there develops a galvanic cell.
- ⇒ The coated metal acts as anode and gets corroded, base metal acts as cathode and protected till all the coated metal is consumed.

Cathodic coatings:

- ⇒ These types of coatings are produced by coating metals whose reduction potentials are higher (noble metal) than that of base metal.
- ⇒ Coated metal protects the base metal due to their higher corrosion resistance than the base metal.
- ⇒ But, in these type of coatings if any pores, breaks or discontinuation occurs to the coated metal corrosion occurs severely and the base metal is damaged.
- ⇒ This is because when damage occurs to the coated metal, base metal exposes to the environment and a galvanic cell is developed, base metal acts as anode and coated metal acts as cathode.
- ⇒ E.g. coating of tin over Iron.

Comparison of anodic and cathodic coatings:

S.No	Anodic coatings	Cathodic coatings
1.	These coatings involve coating of anodic metal on the surface of base metal.	These coatings involve coating of noble metal on the surface of base metal.
2.	Protects the underlying base metal “sacrificially”	Protects the underlying base metal by their noble character and higher corrosion resistivity.
3.	Reduction potential of the coating metal is lower than that of base metal.	Reduction potential of the coating metal is higher than that of base metal.
4.	Even If any damage occurs to the coating metal, base metal is protected.	If any damage occurs to the coating metal, base metal is corroded.
5.	e.g. galvanization.	e.g. tinning.

Objectives of coating:

- ⇒ To prevent corrosion
- ⇒ To enhance wear and scratch resistance
- ⇒ To increase hardness
- ⇒ To insulate electrically, thermally
- ⇒ To impart decorative color.

METHODS OF APPLICATION OF METALLIC COATINGS:

Following are the methods for application of metallic coatings.

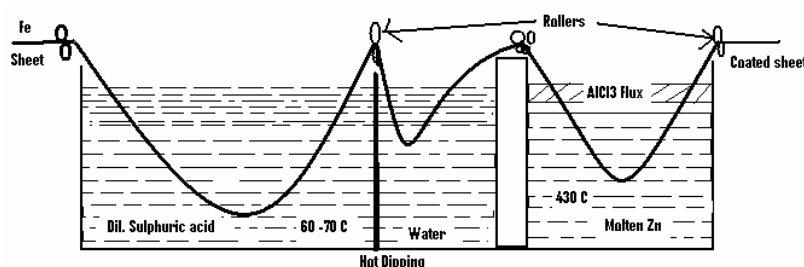
1. Hot dipping, 2. Metal cladding, 3. Electroplating, 4. Electroless plating, 5. Cementation

1. Hot dipping:

- Coating a low melting metal such as Zn, Sn, Pb, Al on the surface of high melting metal such as Iron, steel etc.. is hot dipping.
- The metal to be coated is dipped in the molten bath of the coating metal for efficient time and then removed along with the adhering film.
- Two widely used hot dipping methods are:
 - A. Galvanization
 - B. Tinning.

A. Galvanization:

- It is a process of coating Iron or steel with a thin coat of Zinc to prevent Iron from rusting.
- Process:
- The base metal Iron or Steel is cleaned with H_2SO_4 by acid pickling method at $60\text{-}90^\circ\text{C}$ for 15-20 minutes.
 - The steel is then washed and dried.
 - It is dipped in molten Zn bath maintained at $425\text{-}430^\circ\text{C}$.
 - The surface of the bath is covered with aluminum chloride flux to prevent oxide formation.
 - The sheet is taken out and excess Zn is removed by passing it between a pair of hot rollers.
 - Then the sheet is subjected to annealing process at 650°C and cooled slowly.
 - An alloy of Zn and Iron are formed at the junction of the base metal coating.



Applications:

- It is mostly used to protect the iron used for roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes.

Limitations:

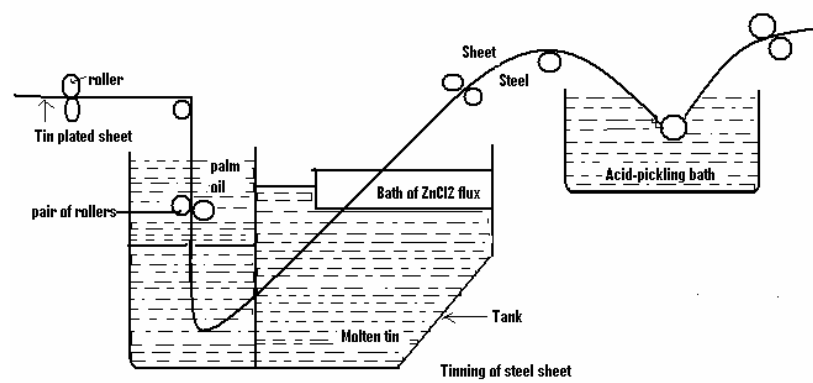
- Galvanized utensils cannot be used for preparing and storing food stuffs especially acidic in nature, because Zn dissolves to form highly toxic or poisonous compounds.

B. Tinning:

- ❖ It is the process of coating tin over Iron or Steel.
- ❖ Tin is a nobler metal than iron, therefore, it is more resistance to chemical attack.

Process:

- ❖ Iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film if present.
- ❖ A cleaned Iron sheet is passed through a bath molten flux. Like Zinc chloride, then through molten tin and finally through a suitable vegetable oil.
- ❖ Tinning of mild steel plates is done mostly for the requirements of the foodstuff industry. Tin is a nobler metal than iron, therefore, it is more resistant to chemical attack.
- ❖ if the coating formed does not cover the surface completely during use and leaves iron exposed, more rapid corrosion of iron will take place.
- ❖ A cleaned iron sheet is passed through a bath of molten flux, like zinc chloride, then through molten tin and finally through a suitable vegetable oil. Lastly it is passed between rolls to adjust the thickness of the tin layer, which may be about 0.002 mm thick.

Applications:

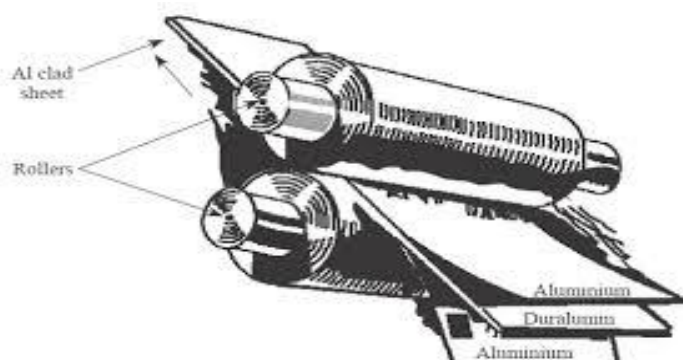
- ❖ Tin metal possess good resistance against atmospheric corrosion.
- ❖ Tin is non toxic and widely used for coating steel, copper, and brass sheet.
- ❖ The containers coated with tin are used for storing food stuffs, ghee, oils etc. and packing food materials.
- ❖ Tinned copper sheets are used for making cooking utensils and refrigeration equipment.

Comparison of galvanization and tinning:

<u>S.No</u>	<u>Galvanization</u>	<u>Tinning</u>
1.	A process of covering iron with a thin coat of 'Zinc' to prevent it from rusting.	A process of covering iron with a thin coat of 'tin' to prevent it from Corrosion.
2.	Zinc protects the iron sacrificially.(Zinc undergo corrosion)	Tin protects the base metal without undergo any corrosion (nonsacrificially)
3.	Zinc continuously protects the base metal even if broken at some places.	A break in coating causes rapid corrosion of base metal.
4.	Galvanized containers cannot be used for strong acidic food stuffs as Zinc becomes toxic in acidic medium.	Tin is non-toxic in nature of any medium.
5.	After galvanization process the sheet is subjected to annealing process.	No annealing process.
6.	Galvanized articles are good engineering materials.	Tinned articles are used majorly in food processing industries.

2. Metal cladding:

- ⇒ Coating of a thin homogeneous layer of a coating metal on a base metal and fused so that it strongly binds permanently either on one side or on both sides and passed through rollers under heat and pressure is called metal cladding.
- ⇒ The metal clad is called cladding metal.
- ⇒ Only plain surfaces can be cladded.
- ⇒ The process of metal cladding is a kind of “metal sandwiching”.
- ⇒ The surface to be protected is sandwiched between two thin layers of coat metal and pressed between rollers.



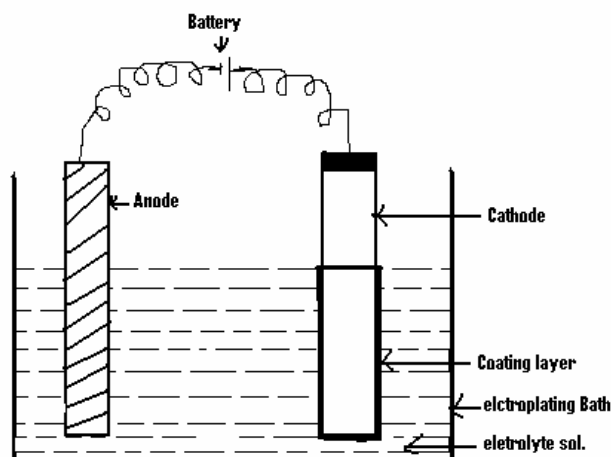
- ⇒ The finished product may be welded at the edges or riveted at some points.
- ⇒ The coat metal has to be anodic to the base metal.
- ⇒ This method is used for coating Al, Cr, Ni, Duralumin, etc.
- ⇒ All corrosion-resistant metals like Ni, Cu, Ag, Au & Pt, and alloys like steel nickel alloys can be used as cladding materials.
- ⇒ Base metals on which cladding is done are mild steel, aluminium, copper, nickel and other alloys.
- ⇒ E.g. A 99.5% pure Al is subjected to cladding to protect duraluminium to produce 'alclad', which is widely used in air craft industry.

Applications:

- ⇒ This method is widely adopted in aircraft industry and automobile industry.

3. Electroplating or Electrodeposition:

- ✓ The process of deposition of coating metal over base metal/non metal by electrolysis is called electroplating.
- ✓ Base metal is anodic to coating metal.
- ✓ The article to be electroplated is cleaned with trichloroethylene to remove oil, grease etc...
- ✓ Then it is subjected to acid pickling with dil. HCl or H₂SO₄ to remove scales, oxide films.
- ✓ The base metal is made cathodic and coating metal is made anodic with graphite, and the electrodes are dipped in the electrolytic solution containing metal ions of coating metal which becomes an electrolytic cell.
- ✓ The electrolytic salt is added continuously to maintain the proper concentration in the electrolytic bath.
- ✓ D.C (direct current) is passed through the electrolyte.
- ✓ The coating metal ions migrate to the cathode and deposit on the surface of the base metal article as a thin layer.
- ✓ For brighter and smooth deposits, conditions like low temperatures, medium current density, and low metal ion concentrations are used.



- ✓ E.g. electroplating of copper on iron article, the following are maintained
- Electrolyte: Copper sulphate.
 - Temperature: 40-70°C
 - Current density: 20-30mA /cm².
 - Anode: 99% pure copper pellets taken in a titanium mesh basket or graphite.
 - Cathode: base metal article.

Applications:

1. Plating for protection from corrosion and chemical attack, hardness, wear resistance.
2. Plating for decoration.
3. Plating for special for special surface and engineering effects.
4. Electroforming
5. Plating on non-metallic materials.

Therefore, this process is widely used in automobiles, aircrafts, refrigerators, jewelry, radios, cameras, type-writers, umbrellas, watch etc.

4. Electroless plating:

- ❖ The method of deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy is called Electroless plating.
- ❖ This process is also called chemical plating or autocatalytic plating.
- ❖ The metal ions (M^+) are reduced to the metal with the help of reducing agents(R^-).
- ❖ When the metal (M) is formed, it gets plated over a catalytic surface.
- ❖ $M^+ + R^- \rightarrow M + R$
- ❖ The metal surface to be subjected to electroplating is prepared by
 - Etching (acid treatment)
 - For non conducting surfaces like plastics or printed circuit boards, treatment with stannous chloride and palladium chloride alternatively used.
 - To get an active surface, electroplating followed heat treatment is adopted.
 - For Ni surface treatment of organic solvents followed by acid treatment is used.

The following are the requirements for Electroless plating:

- Soluble electro active metal in the form of metal chlorides or sulphate.
- The reducing agents like formaldehyde, hypophosphite.
- Complexing agents like citrate, tartarate and succinate.
- Exaltants like succinates, glycinate, and fluorides to improve the rate of plating.
- Stabilizers which prevent decomposition of bath. E.g. Pb^{+2} , Ca^{+2} , Th^{+2} ions and thio urea.
- To control p^H of the bath buffer solution was added.

Electroless plating of Nickel:

- ❖ The base object, plastic materials like acrylonitrile-butadiene styrene (ABS) can be coated with Nickel.

- ❖ Preparation of base metal surface is by stannous chloride followed by palladium chloride, to get the layer of Pd and the surface is dried.
- ❖ The base metal is dipped in the following solutions
 - Metal ions solution : Nickel chloride
 - Reducing agent: sodium hyposulphite
 - Buffer: sodium acetate
 - Complexing agent and exalt: sodium succinate
 - pH : 4.5
 - Temperature: 93°C
- ❖ The following reactions take place and Ni is plated electrolessly on the surface of base object.
- ❖ $\text{Ni}^{+2} + \text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \rightarrow \text{Ni} + \text{H}_2\text{PO}_3 + 2\text{H}^+$

Properties:

- ❖ Electroless plated Ni objects has better corrosion resistance, deposits are pore free, hard and wear resistant.

Applications:

- ❖ Electroless Ni plating is extensively used in electronic application providing a non magnetic underlay in magnetic components.
- ❖ ABS plastics coated objects are used for decorative applications automotive, electronic, domestics of industry like knobs in hi-fi equipment, tops on perfume bottles costume jewelry and car decorative.
- ❖ They are also used in digital and electronic instruments for electromagnetic interference shielding.

5. Cementation of diffusion coatings:

- This type of coating is obtained by heating the base metal in a revolving drum containing powdered coating metal.
- Diffusion of the coating metal into the base metal takes place, resulting in the formation of layers of alloy of varying composition.
- The layer adjacent to the base metal is solid solution and the outer layers are richer in coating metal.
- There are different types of cementation
 - Sherardizing
 - Colorizing
 - Chromising
 - siliconizing

i. Sherardizing:

- ✓ It was developed by Sherad Cowpercoles in 1890.
- ✓ Coating metal is Zinc powder.
- ✓ Base metal is Iron.

- ✓ The Iron article to be coated is cleaned by acid pickling method and rotated for 2-3 hours in the drum containing Zn dust is maintained at 350-370°C.
- ✓ Zn diffuses into Iron.
- ✓ Fe-Zn alloy is formed at the junction of base metal and coating metal.
- ✓ Thin layer of Zn is deposited over Iron.
- ✓ This method is used for coating small articles like nails, nuts, bolts, screws, threaded parts, washers, valves and gauge tools.
- ✓ Advantage of this metal is coating is uniform and there is no change in the dimension of the article.

ii. Colorizing:

- ✓ It is coating Aluminium over Iron.
- ✓ The base metal article is cleaned by sandblasting and heated in a drum tightly packed with a mixture of aluminium powder and aluminium oxide together with trace of aluminium chloride as flux in a reducing atmosphere of hydrogen.
- ✓ The layer formed has the approximate composition of Al_2Fe_3 containing about 25% by weight of aluminium.
- ✓ This method is used for the protection of furnace parts.

iii. Chromising:

- ✓ The base metal is heated with a mixture of 55% Cr, and 45% alumina powder to 1300-1400°C for 3-4 hours.
- ✓ A mixture of volatile chromous chloride and hydrogen with steel parts produced the protective layer of chromium diffused into Iron surface.
- ✓ This method is fairly used for the protection of turbine blades.

iv. Siliconizing:

- ✓ Coating silicon on the surface of molybdenum is called siliconizing.
- ✓ Silicon tetrachloride is used as coating metal.

ORGANIC COATINGS – PAINTS:

PAINTS: Paint may be defined as the mechanical dispersion mixture of pigments and fillers which are in a liquid medium and later becomes film forming oil. The volatile liquids such as thinners are again added to these liquids.

Requisites of a good paint :

CONSTITUENTS OF PAINT:

- a. Pigment
- b. Vehicle or drying oil
- c. Thinners d. Driers
- d. Fillers or extenders
- e. Plasticizers
- f. Anti-skinning agents

a) Pigment:

It is solid constituent present in paint which provides a decorative color effect to protect it from ultraviolet rays. Pigment is one of the essential constituents of paint.

The essential functions of pigments are-

- ☐ ☐ To provide desired color, opacity and strength to the paint.
- ☐ ☐ To give aesthetical appeal to the paint film,
- ☐ ☐ To give protection the paint film by reflecting harmful ultraviolet light,
- ☐ ☐ To provide resistance to paint film to moisture and
- ☐ ☐ To increase the weather-resistance of the film.

The following are the common pigments used:

S.No	Common pigment	Color imparted by the pigment
1.	White lead, Zinc oxide, Lithophone etc...	White
2.	Red lead, ferric oxide, chrome red etc...	Red
3.	Chromium oxide	Green
4.	Prussian blue	Blue
5.	Carbon black	Black
6.	Umbre brown	Brown

Characteristics of a good pigment:

- ✓ A good pigment must be opaque, chemically inert, non toxic, freely mixable and cheap.

b) Vehicle (or) drying oil :

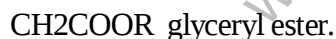
It is a film forming constituent of the point. These are glyceryl esters of high molecular – weight fatty acids generally, present in animal and vegetable oils. The most widely used drying oil, are linseed oil, soyabean oil, and dehydrated castor oil.



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The important functions of vehicle oil are:

- ☐ They hold the pigment on the metal surface
- ☐ They form the protective film,
- ☐ They impart water-repellency, durability and toughness to the film, and
- ☐ They give better adhesion to the metal surface.

c) Thinners:

- Viscosity (or consistency) of the paints are reduced by the addition of thinners. So paints easily applied on the metal surface.

The important functions of thinners are:

- ☐ Thinners reduce the viscosity of the paint to suitable consistency, so that it can be easily handled and applied to the metal surface.
- ☐ They dissolve the film-forming material and also the other desirable additives in the vehicle.
- ☐ They evaporate rapidly and help the drying of the paint film.
- ☐ They suspend the pigments in the paint film.
- ☐ They increase the elasticity of the paint film,
- ☐ They also increase the penetration power of the vehicle.

d) Driers:

- The drying of the oil is accelerated or catalyzed by driers. They do this by oxidation, polymerization and condensation. In fact, driers are oxygen carrier catalysts. The important functions of the driers are-Linoleates, borates, naphthalene's, resonates and tungstates of heavy metals like Pb, Zn, Co and Mn.
- ☐ Surface driers: Cobalt substances,
- ☐ Bottom- driers: Lead substances,
- ☐ Through driers: Manganese substances.

e) Fillers or extenders:

- Fillers are inert materials which are used to improve the properties and reduce the cost of the paint.

The important functions of fillers are:

- ☐ They reducing the cost of the paint.(Expensive pigments which have excellent hiding power (Like TiO_2 and ZnSO_4) are used in a admixture with cheap extenders for reducing the costwithout reducing the efficiency),
- ☐ They serve to fill the voids in the film,
- ☐ They increase random arrangement of the primary pigment particles, and act as carriers for the pigment color,
- ☐ They improve the durability of the film by reducing the cracking of the paints after drying.

f) Plasticizers:

- Plasticizers are added to the paint film to give elasticity to the paint film and to prevent cracking of the film, to increase the elasticity to the film.

Ex: Tri cresyl phosphate, triphenyl phosphate, dibutyl tartarate, and tributyl phthalate.

g) Antiskinning agents:

- Antiskinning agents prevent the gelling and skinning of the paint film. E.g.Polyhydroxy phenols

Requirements of a Paint:

1. The adhesion capacity of the paint should be high to the material on which it is to be used.
2. The paint should spread easily over the surface to be protected.
3. On drying, the paint film should not be cracked.
4. The paint film should have high corrosion resistance property so as to protect the painted surface from the corrosion environment.
5. The paint film should be stable.
6. The paint film should be prepared such a way as to be applicable easily by spraying or brushing.
7. The paint film should yield a smooth and uniform surface.
8. The paint film obtained on the surface should be tough, uniform and adherent.
9. The color of the film should be stable and should not get affected by the environment conditions.
10. The covering power of the paint should be high.

QUESTIONS:-

- (1) (a) What are concentration cells? How can the EMF of a concentration cell be evaluated?
(b) Write short notes on single electrode potential and its significance.
- (2) (a) What do you understand by electrochemical series? How is this series useful in the determination of corrosion of metals.
(b) The resistance of a 0.1N solution of an electrolyte of 40 ohms. If the distance between the electrodes is 1.2 cm and area of cross section is 2.4 cm². Calculate equivalent conductivity.
- (3) (a) Give reasons for the following statements:-
 - i. When a zinc rod is dipped in a solution of aq. copper sulphate, copper is precipitated out.
 - ii. Nernst equation is applicable for the determination of emf of a concentration cell.(b) State and explain the Kohlrausch's law and its applications.
- (4) (a) Define the terms specific, equivalent and molar conductivities. How do they vary with dilution.
(b) Calculate the cell constant of a cell having a solution of concentration N/30 gm

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c) Constant

d) none of the above

QUESTIONS:-

- (1) (a) What are the factors that lead to caustic embrittlement in boilers? How can this be prevented?
- (b) Distinguish between Zeolite process and Ion-Exchange process.
- (2) (a) Discuss the influence of following factors on corrosion:-
- i. Over voltage
 - ii. Nature of the metal
 - iii. Nature of environment.
- (b) Explain the nature and role of constituents of organic paints
- (3) (a) Explain the electrochemical theory of corrosion of metals with special reference to rusting of iron.
- (b) Write a note on galvanizing and metal cladding.
- (4) (a) How are metals protected by impressed current method?
- (b) Explain the galvanization and tinning processes of metals.
- (5) (a) Outline the electrochemical theory of corrosion and explain the mechanism of rust formation in acidic and neutral medium.
- (b) Write a brief account of cathodic protection.
- (6) (a) Explain sacrificial anodic protection method of controlling corrosion.
- (b) Write a note on anodic protection and the nature of corrosion product.
- (7) Write notes on the following:-
- (a) Hot dipping
 - (b) Galvanizing
 - (c) Tinning

(d) Electroplating.

OBJECTIVE QUESTIONS

- The rusting of iron is catalyzed by (d)
a) Fe b) O₂
c) Zn d) Hydrogen ion
- Corrosion is an example of (a)
a) Oxidation b) reduction
c) electrolysis d) erosion
- The metal at the top of electrochemical series is (d)
a) most stable b) best protective
c) most noble d) most active
- During galvanic corrosion the more noble metal acts as (b)
a) anode b) cathode
c) anode as well as cathode d) corroding metal
- The process of cementation with Zn powder is known as (c)
a) galvanizing b) zincing
c) sheradizing d) tinning
- Anodic coating protects the underlined metal due to (b)
a) noble character b) sacrificial
c) higher electrode potential d) none of the above
- Drying oil supply to paint film (d)
a) main film forming constituent b) medium or vehicle
c) water proof ness d) all of these
- The process of covering steel with tine to prevent it from corrosion is called (b)
a) galvanizing b) tinning
c) metal cladding d) electroplating
- Sand blasting is used for removing the following from the metal surface (a)
a) oxide scale b) oils

