<div align="center">
UNIT-I
ELECTROCHEMISTRY & CORROSION
</div>

- Electrochemistry is a branch of chemistry which deals with inter conversion of electrical energy to chemical energy vice versa.
  For ex:
  i)   In a battery light chemical energy is converted to electrical energy
  ii)   In electroplating / electrolysis electrical energy is converted to chemical energy
- Electric current is a flow of electrons. Substances that allow electric current to pass through them are known as conductors.
  For ex: the metals, graphite, fused salts, aq soln. of acids, bases & salts.
- While insulator or non conductor is a substance which does not allow electric current to pass through it.
  For ex : wood, plastic;

Q) What are conductors .How are they classified? Differentiate metallic conductors from electrolytic conductors.

Conductors are of two types :

Metallic conductors: These are substances which conduct electricity through electrons.
<u>For eg</u>: all metals, graphite etc; Na, K, alkaline metals Cu, Ag, Au, transition metals.

<u>Electrolytic conductors</u> : Are the substance which in aqueous solution (or) in fused state liberate ions & conduct electricity through these ions, there by resulting in chemical decomposition:
<u>For eg</u>: Acids, bases & salt soln. etc.

S.No	Metallic conductors	Electrolytic conductors
1	Conductance is due to the flow Of free mobile electrons.	Conductance is due to the movement Of ions in a solution of fused electrolyte.
2	The chemical properties of metallic Conductor does not change.	The conductance involves the chemical Reactions of the electrolyte at the two electrodes
3	There is no transfer of matter during conductance.	Transfer of electrolyte in the form of ions takes place.
4.	The resistance of the conductor increases with increasing temperature.	The resistance of the conductor decreases with increasing temperature.

- **CONDUCTANCE** : Reciprocal of resistance (k) is called conductance
  $\therefore$ C = 1/R.

- For metallic conductors, resistance is the characteristic property. [Resistance can easily be measured]. Whereas electrolytes are characterized by conductance [conductance can be measured easily] rather than by resistance.
- The resistance of a conductor [metallic] is directly proportional to its length & inversely proportional to its cross sectional area[ohm's law]

$$i.e; \quad R = \rho \, \frac{l}{A}$$

R = Resistance in ohms

ρ = specific resistance

l = Length in cm.

A = area of cross section in cm^2

➔ Thus, when l = 1cm & A = $1cm^2$ then R = ρ
Thus, the specific resistance is defined as the resistance of a 1 centimeter cube.

Q) Define following terms and explain their relationship.
A. Specific conductance B. Equivalent conductance C. Molar conductance.(2010-R)

➔ **SPECIFIC CONDUCTIVITY**: (K) is the reciprocal of specific resistance of an electrolytic solution.

$$i.e, \quad K = \frac{1}{\rho} = \frac{l}{AR}$$

Hence specific conductivity is the conductance of $1cm^3$ of a solution.

UNITS: $K = \dfrac{l}{AR} = \dfrac{cm}{cm^2 \, \Omega} = cm^{-1}\Omega^{-1}$ (or) $ohm^{-1} cm^{-1}$ (or) Scm^{-1} (ie means) where

$$Ohm^{-1} = S$$

- **EQUIVALENT CONDUCTIVITY** :[$^\wedge$eq] is the conductance of all the ions liberated by 1gm equivalent of the electrolytic in the solution at a given dilution. If 1gm equivalent of electrolyte is present in v ml, then

$$^\wedge eq = V \times sp \text{ conductivity(of } 1cm^3 \text{ solution)}$$

= V x K (v is known as dilution 'V' contains of 1gm equivalent of electrolyte)

Otherwise, if the normality of electrolytic solution is N then

$$V = \left(\frac{1}{N}\right) L \quad (N = \text{concentration})$$

$$= \frac{1000}{N} \text{ ml}$$

$$= \frac{1000}{N} \text{ cm}^3$$

$$\therefore \Lambda_{eq} = \frac{1000}{N} \times K$$

UNITS : Λ_{eq} = V x K

$= cm^3 \times ohm^{-1} cm^{-1} eq^{-1}$

$= ohm^{-1} cm^2 eq^{-1}$ (or) $scm^2 eq^{-1}$

- **MOLAR CONDUCTIVITY or MOLECULAR CONDUCTIVITY:** ($\wedge$ m) is defined as the conductance of all the ions present is 1 mole of electrolyte in solution.
  Suppose 1 mole of electrolyte is present in V ml of solution, then

  $\wedge$ m $=$ V x K (where V contains 1 mole of the electrolyte)

  Whereas M is molar concentration is mol l^{-1} then

$$\wedge m = \frac{1000 \quad x \quad k}{M}$$

  UNITS: $ohm^{-1} cm^2 mol^{-1}$ (or) $S cm^2 mol^{-1}$

Relationship between equivalent and molar conductivities:-

$\lambda/\mu = 1/z$ where z is the total charge carried by cations or anions liberated on dissociation.

$\lambda/\mu = M/N$ where, M= molarity and N=normality.

For ex., $KCl = K^+ + Cl^-$; z=1 ie., $\lambda=\mu$

$ZnCl_2 = Zn^{+2} + 2Cl^-$; z= 2, $2\lambda=\mu$.

IONIC MOBILITIES : The absolute ionic mobility or absolute velocity of an ion is its velocity in cm/sec under a potential gradient of one volt per cm.

For example if the velocity of an ion at infinite dilution is u cm/sec,

It has been showed that

$\lambda_a \propto u_a \rightarrow \lambda_a \propto ku_a$

$\lambda_c \propto u_c \rightarrow \lambda_c \propto ku_c$

Where, Where, K is proportionality constant & U_c and U_a are the ionic velocities of cation & anion at infinite dilution ie., the charge on 1gm equivalent of the ion ie., faraday ie., 96500 coulombs.

$u_a = \underline{\lambda_a}$ and $u_c = \underline{\lambda_c}$

$$\frac{96500 \qquad\qquad 96500}{}$$

$$\text{Ionic mobility} = \frac{\text{Ionic conductivity}}{96500}$$

$$u_a + u_c = u_\alpha$$

96500

Hence the absolute ionic mobility is obtained by dividing ionic conductance by 96500 ie., Faraday.

$$\lambda_\infty = u_\infty \times 96500$$

- CALUCLATED IONIC MOBILITIES OF FEW COMMON IONS AT 25°c :

Cations - υ_+ (cms^{-1})	Anions - υ_- (cms^{-1})
H^+ - 36.2 x 10^{-4}	OH^- - 20.5 x 10^{-4}
K^+ - 7.61 x 10^{-4}	SO_4^{2-} - 8.27 x 10^{-4}
Ba^{2+} - 6.60 x 10^{-4}	Cl^- - 7.91 x 10^{-4}
Na^+ - 5.91 x 10^{-4}	NO_3^- - 7.40 x 10^{-4}

IONIC CONDUCTANCE:

After observing the variation of specific and equivalent conductivities at infinite dilution (that is specific conductivity increases with dilution). **Kohlrausch** put forward a law.

According to the law at infinite dilution, when dissociation is complete & all the inter ionic effects disappear, each ion moves independently of its co-ion & contributes a definite share to the total molar conductance's of the electrolyte, which depends only on its own nature thus, molar conductivity at infinite dilution $\wedge_\infty$ of an electrolyte is equal to the sum of the molar conductivities of its cation & anion.

Thus, $\wedge_\infty (CH_3COOH) = \lambda_\infty (H^+) + \lambda_\infty (CH_3COO^-)$

$$\wedge_\infty (MgCl_2) = \lambda_\infty (Mg^{2+}) + 2\lambda_\infty (Cl^-)$$

The ionic conductance of cations and anions remain same, let them be in combination with other ion.

Ionic conductance ∞ transport number

Suppose, $\lambda_a \propto V$ (ionic mobility of anion)

$\lambda_c \propto U$ (ionic mobility of cation)

$\lambda_a = KV$, $\lambda_c = KU$

A/C Kohlraucsh law,

$\lambda_\infty = \lambda_c + \lambda_a$ $\lambda_\infty = K(U+V)$

$\dfrac{\lambda_a}{\lambda_\infty} = \dfrac{KV}{K(U+V)} = \dfrac{V}{U+V} = n_a$ (transport no. of anion)

$\dfrac{\lambda_c}{\lambda_\infty} = \dfrac{KU}{K(U+V)} = \dfrac{U}{U+V} = 1-n_a = n_c$ (transport no. of cation)

since, $n_a + n_c = 1$

$\dfrac{\lambda_a}{\lambda_c} = \dfrac{n_a}{1-n_a}$

or $\lambda_a = n_a \lambda_\infty$, $\lambda_c = (1-n_a) \lambda_\infty$.

DEGREE OF IONISATION : The ratio of equivalent conductance at any concentration (λc) to that at infinite dilution(λ_∞) is called as Degree of ionization or Degree of Dissociation or Conductivity ratio.

An increase of molar conductance with increasing dilution can be attributed to the increase in the degree of ionization of an electrolytic substance. So at infinite dilution the degree of ionization is unity. Thus, the degree of ionization (α_c) is given by expression

λ_c equivalent conductance at any given concentration

$\alpha_c = \text{-----} = \text{--}$

λ_∞ equivalent conductance at infinite dilution.

μ_v molar conductance at given volume

$\Rightarrow$ $\text{-------} = \text{--}$

μ_∞ molar conductance at infinite solution.

- **PROBLEM 1:** The resistance of N/50 kcal solution at 20^OC present a conductivity cell is 350Ω. Calculate its cell constant given the electrolytic conductivity of N/50 kcal at 25^OC is 0.0002765 Scm^{-1}

                        Specific conductivity (k)

Sol: Cell constant (x) = ---------------------------------------

                         Observed conductance

            K   I

$$= \frac{}{C} \Rightarrow \frac{}{A\ R}$$

(distance between the electrodes)

L = length of the cell, a = area of cell

Since Resistance (R) is the reverse of conductance

∴ X (Cell constant) = K x R

= 0.0002765 x 350

= 0.9678 Cm^{-1}

- **PROBLEM 2:** The resistance of 0.1N solution is 40Ω. If the distance between the electrodes is 1.2 cm & area of cross section is 2.4 cm^2. Calculate the eq conductivity.

Sol: Given L = 1.2 cm, A = 2.4cm^2; R = 40Ω; concentration (N) = 0.1 N

$$\text{Equivalent conductivity } (\wedge) = \frac{1000}{N} \times K$$

$$K \text{ (electrolytic conductivity) } = \frac{I}{A\ R}$$

$$K = \frac{1.2}{40 X 2.4} = 0.0125\ \Omega^{-1}cm^{-1}$$

$$\wedge = \frac{1000\ x\ 0.0125}{0.1} = 125\ scm^2\ eq^{-1}$$

- **PROBLEM 3:** A conductance cell has two parallel electrodes of 1.25sq.cm area placed 10.5 cm apart; when filled with a solution of an electrolyte the resistance was found to be 1995 Ω. Calculate cell constant and specific conductance.

Sol: Given l= 10.5cm, A= 1.25sqcm, cell constant=l/A= 10.5/1.25= 8.4cm^{-1}.

Observed conductance= 1/1995mho.

Specific conductance= cell constant x observed conductance.

$$k = 8.4 \times 1/1995= 0.00421 \, \Omega^{-1}cm^{-1}.$$

ELECTROCHEMICAL CELL : The device used for converting chemical energy to electrical energy & electrical energy into chemical energy are known as electrochemical cells they contain two electrodes in contact with an electrolyte, they are mainly of two types

1) Galvanic cells 2) Electrolytic cells.

1) *Galvanic cells:* It is an electrochemical cell in which the free energy of chemical reaction is converted into electrical energy i.e electricity is produced from a spontaneous chemical reaction. Ex. Daniel cell
2) *Electrolytic cell:* It is an electrochemical cell in which external electrical energy is used to carry out a non- spontaneous chemical reaction.

DANIEL CELL

- It is designed to make use of the spontaneous redox reaction between zinc and cupric ions to produce an electric current.
- It consists of two half-cells. The half-cells on the left contains a zinc metal electrode dipped in $ZnSO_4$ solution.
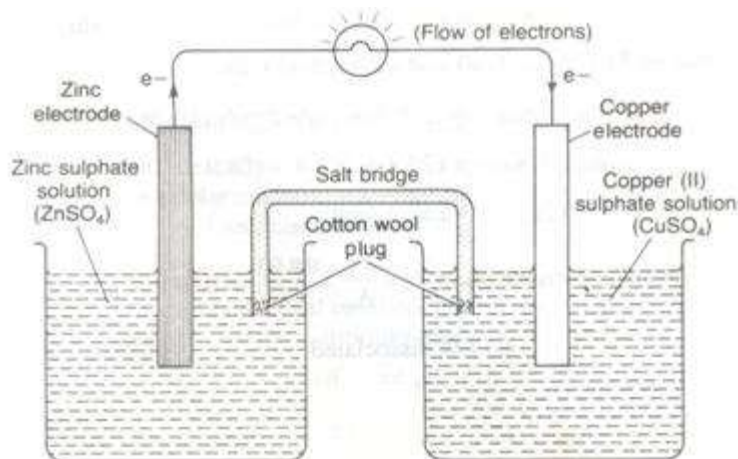
Fig. 12.7   Daniell cell

- The half-cell on the right consists of copper metal electrode in a solution $CuSO_4$.
- The half-cells are joined by a salt bridge that prevents the mechanical mixing of the solution.
- When the zinc and copper electrodes are joined by wire, the following observations are made:

(i) There is a flow of electric current through the external circuit.

(ii) The zinc rod loses its mass while the copper rod gains in mass.

(iii) The concentration of $ZnSO_4$ solution increases while the concentration of copper sulphate solution decreases.

(iv) The solutions in both the compartments remain electrically neutral.

- During the passage if electric current through external circuit, electrons flow from the zinc electrode to the copper electrode. At the zinc electrode, the zinc metal is oxidized to zinc ions which go into the solution. The electrons released at the electrode travel through the external circuit to the copper electrode where they are used in the reduction of Cu^{2+} ions to metallic copper which is deposited on the electrode. Thus, the overall redox reaction is:

$Zn(s) + Cu^{2+} \rightarrow Cu(s) + Zn^{2+}(aq)$
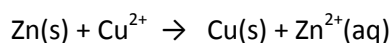
Thus, indirect red-ox reaction leads to the production of electrical energy.

- At the zinc rod, oxidation occurs. It is the anode of the cell and is negatively charged while at copper electrode, reduction takes place; it is the cathode of the cell and is positively charged.

Thus, the above points can be summed up as:

(i)   Voltaic or Galvanic cell consists of two half-cells. The reactions occurring in half-cells are called half-cell reactions. The half-cell in which oxidation taking place in it is called oxidation half-cell and the

reaction taking place in it is called oxidation half-cell reaction. Similarly, the half-cell occurs is called reduction half-cell and the reaction taking place in it is called reduction half-cell reaction.

(ii) The **electrode where oxidation occurs is called anode** and the **electrode where reduction occurs is termed cathode.**

(iii) Electrons flow from anode to cathode in the external circuit.

REPRESENTATION OF AN ELECTROCHEMICAL CELL (GALVANIC CELL)

The following universally accepted conventions are followed in representing an electrochemical cell:

(i) The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.

(ii) A vertical line or semicolon (;) indicates a contact between two phases. The anode of the cell is represented by writing metal first and then the metal ion present in the electrolytic solution. Both are separated by a vertical line or a semicolon. For example,

$Zn|Zn^{2+}$ or $Zn;Zn^{2+}$
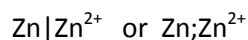
The molar concentration or activity of the solution is written in brackets after the formula of the ion. For example:

$Zn|Zn^{2+}(1 M)$ or $Zn | Zn^{2+}(0.1 M)$
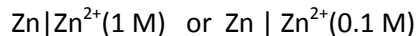
(iii) The cathode of the cell is represented by writing the cation of the electrolyte first and then metal. Both are separated by a vertical line or semicolon. For example,

$Cu^{2+}|Cu$ or $Cu^{2+};Cu$ or $Cu^{2+}(1 M)|Cu$
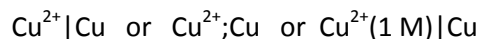
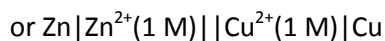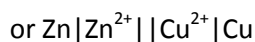(iv)The salt bridge which separates the two half-cells is indicated by two parallel vertical lines.

(v) Sometimes negative and positive signs are also put on the electrodes.

The Daniell cell can be represented as:

$^-Zn|ZnSO_4(aq)||CuSO_4(aq)|Cu^+$

Anode   Salt bridge   Cathode

Oxidation half-cell   Reduction half-cell

or $Zn|Zn^{2+}||Cu^{2+}|Cu$

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

Electrolytic Cells

The concept of reversing the direction of the spontaneous reaction in a galvanic cell through the input of electricity is at the heart of the idea of electrolysis. See for a comparison of galvanic and electrolytic cells.
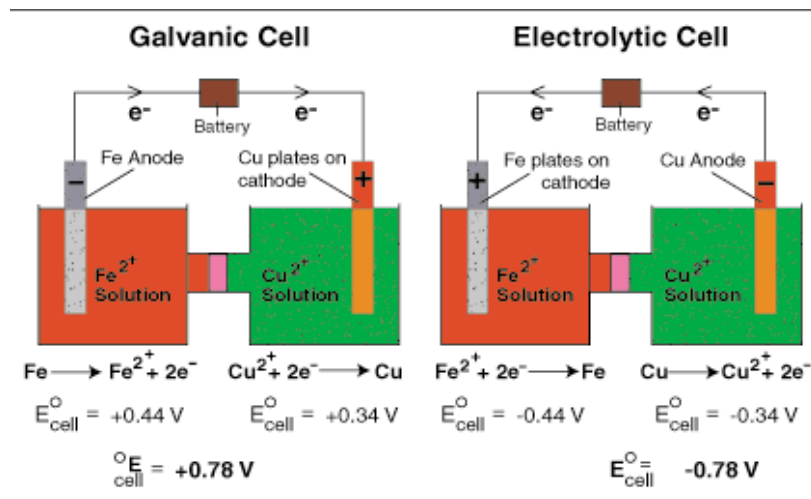
Galvanic Cell   **Electrolytic Cell**

e⁻   Battery   e⁻   e⁻   Battery   e⁻

Fe Anode   Cu plates on cathode   Fe plates on cathode   Cu Anode

Fe²⁺ Solution   Cu²⁺ Solution   Fe²⁺ Solution   Cu²⁺ Solution

$Fe \longrightarrow Fe^{2+} + 2e^-$ $Cu^{2+} + 2e^- \longrightarrow Cu$ $Fe^{2+} + 2e^- \longrightarrow Fe$ $Cu \longrightarrow Cu^{2+} + 2e^-$

$E^\circ_{cell} = +0.44\ V$ $E^\circ_{cell} = +0.34\ V$ $E^\circ_{cell} = -0.44\ V$ $E^\circ_{cell} = -0.34\ V$

$E^\circ_{cell} = +0.78\ V$ $E^\circ_{cell} = -0.78\ V$

Figure : Comparison of Galvanic and Electrolytic Cells

Electrolytic cells, like galvanic cells, are composed of two half-cells--one is a reduction half-cell, the other is an oxidation half-cell.

Though the direction of electron flow in electrolytic cells may be reversed from the direction of spontaneous electron flow in galvanic cells, the definition of both cathode and anode remain the same--reduction takes place at the cathode and oxidation occurs at the anode.

When comparing a galvanic cell to its electrolytic counterpart, as is done in, occurs on the right-hand half-cell. Because the directions of both half-reactions have been reversed, the sign, but not the magnitude, of the cell potential has been reversed.

Note that copper is spontaneously plated onto the copper cathode in the galvanic cell whereas it requires a voltage greater than 0.78 V from the battery to plate iron on its cathode in the electrolytic cell.

The differences between electrolytic and galvanic cell are as follows:

Electrolytic cell	Galvanic cell
1. Electrical energy is converted into chemical energy.	Chemical energy is converted into electrical energy.
2. Anode is positive electrode. Cathode	Anode is negative electrode. Cathode

negative electrode.	positive electrode.
3. Ions are discharged on both the electrodes.	Ions are discharged only on the cathode.
4. If the electrodes are inert, concentration of the electrolyte decreases when the electric current is circulated.	Concentration of the anodic half-cell increases while that of cathodic half-cell decreases when the two electrodes are joined by a wire.
5. Both the electrodes can be fitted in the same compartment.	The electrodes are fitted in different compartments.

Q)Nernst equation is applicable for determination of emf of concentration cell. Explain.

Electromotive force (EMF): The difference in potentials of half cells or electrodes which is responsible for conducting electricity is known as emf of the cell. Electric current passes from the electrode with higher electrode potential to the lower electrode potential

Q)What do you understand by electrochemical series? How is it useful in determination of corrosion of metals?
ELECTROCHEMICAL SERIES

When elements are arranged in increasing order (downwards) of their standard electrode potentials. That arrangement is called as electrochemical series.

Electrode potential: The tendency of a metal to loose or gain electrons when it is in contact with its own salt solution of unit molar concentration at 25^0C is known as electrode potential. The tendency of loosing e^0s when a metal is in contact with its own salt solution is known as oxidation potential.
The tendency of gaining e^0s when a metal is in contact with its own salt solution is known as reduction potentials.
The value of reduction potential of a metallic electrode is –ve of its oxidation potential & vice versa.
Suppose the oxidation potential of an electrode =   +   x   volts
The reduction potential of an electrode =   -   x   volts.

Metal ion   ------------   standard
                                                 Reduction
                                                 Potential.

Li^+	$+ e^-$	$\rightarrow$	Li	---------------	-3.05
k^+	$+ e^-$	$\rightarrow$	K	---------------	-2.93
Ca^+	$+ 2e^-$	$\rightarrow$	Ca	---------------	-2.90
Na^+	$+ e^-$	$\rightarrow$	Na	---------------	-2.71
Mg^+	$+ 2e^-$	$\rightarrow$	Mg	---------------	-2.37
Al^{+3}	$+3 e^-$	$\rightarrow$	Al	---------------	-1.66
Zn^{+2}	$+ 2e^-$	$\rightarrow$	Zn	---------------	-0.76
Cr^{+3}	$+ 3e^-$	$\rightarrow$	Cr	---------------	-0.74
Ni^{+2}	$+2 e^-$	$\rightarrow$	Ni	---------------	-0.23
Sn^{+2}	$+2 e^-$	$\rightarrow$	Sn	---------------	-0.14
Pb^{+2}	$+ 2e^-$	$\rightarrow$	Pb	---------------	-0.73
Fe^{+3}	$+ 3e^-$	$\rightarrow$	Fe	---------------	-0.04
H^+	$+ e^-$	$\rightarrow$	½ H	---------------	0.00
Cu^{+2}	$+2 e^-$	$\rightarrow$	cu	---------------	+0.34
Ag^+	$+ e^-$	$\rightarrow$	Ag	---------------	+0.80
pb^{+4}	$+4 e^-$	$\rightarrow$	Pb	---------------	+0.86
Au^+	$+ e^-$	$\rightarrow$	Au	---------------	+1.69
$½ F^+$	$+ e^-$	$\rightarrow$	F^-	---------------	+2.87

Applications of electrochemical series :

1) **Ease of oxidation/reduction**: In these series a system with high reduction potential has a great tendency to under got reduction , where as a system with a low reduction, potential tend to oxidize more easily. For eg standard reduction potential of F_2 / F^- is the highest , so F^- ions are easily reduced to F_2.

On the other hand standard reduction potential of Hi^+ / li is least , so Li^+ is reduced with great difficulty to Li.

2) **Replacement tendency** : In electrochemical series the metals having lower reduction potential can displace another metal having higher reduction potential from its salt solution spontaneously.
For eg : Zn with displace Cu from the solution of Cu^{2+}

$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu.$

3) **Predicting Spontaineity of red-ox reactions:** Positive value of E of a cell reaction indicates that the reaction is spontaneous/feasible and if the value of E is negative, the reaction is not feasible.

4) **Displacement of H_2:** All metals above Hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of Hydrogen

5) **Corrosion of metals:** Corrosion is defined as the deterioration of a substance because of its reaction with its environment. This is also defined as the process by which metals have the tendency to go back to their combined state, i.e., reverse of extraction of metals.

Ordinary corrosion is a red-ox reaction by which metals are oxidized by oxygen in presence of moisture. Oxidation of metals occurs more readily at points of strain. Thus, a steel nail first corrodes at the tip and head. The end of a steel nail acts as an anode where iron is oxidized to Fe^{2+} ions.

$Fe \dashrightarrow Fe^2 + 2e^-$ (Anode reaction)
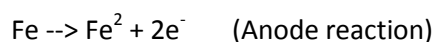
The electrons flow along the nail to areas containing impurities which act as cathodes where oxygen is reduced to hydroxyl ions.

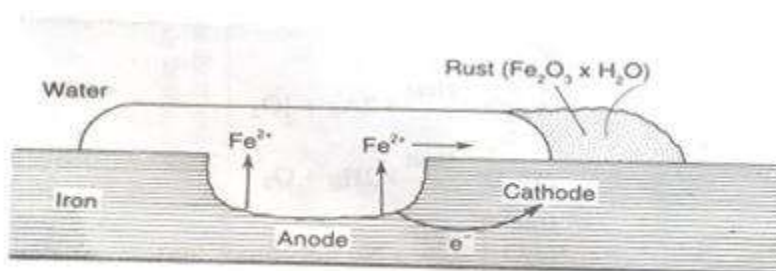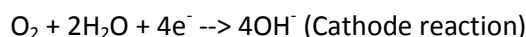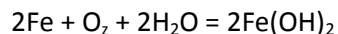$O_2 + 2H_2O + 4e^- \dashrightarrow 4OH^-$ (Cathode reaction)

Fig. 12.16   Corrosion of iron

The overall reaction is

$2Fe + O_z + 2H_2O = 2Fe(OH)_2$

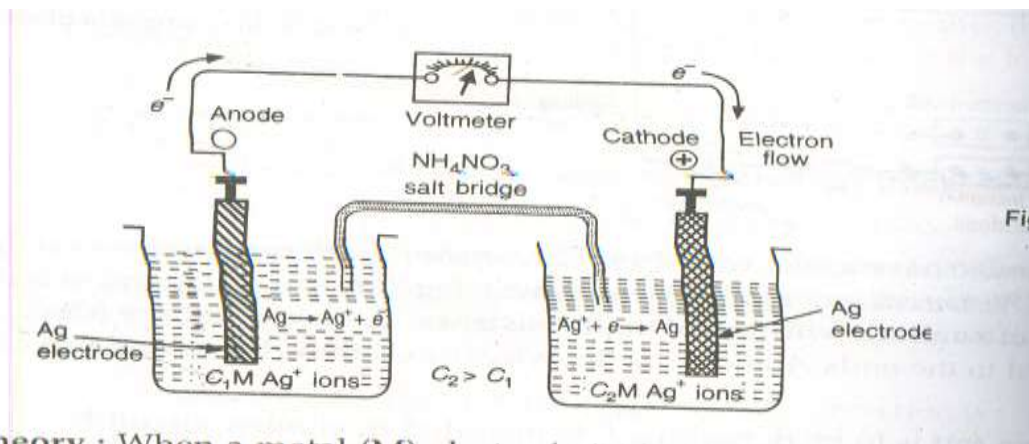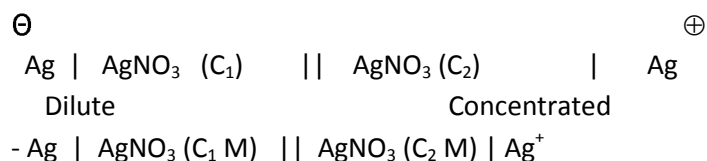$Fe(OH)_2$ may be dehydrated to iron oxide, FeO, or further oxidised to $Fe(OH)_3$ and then dehydrated to iron rust, Fe_2O_3.

Several methods for protection of metals against corrosion have been developed. The most widely used are (i) plating the metal with a thin layer of a less easily oxidised metal (ii) allowing a protective film such as metal oxide (iii) galvanising-steel is coated with zinc (a more active metal).

Q)What are concentration cells. How can EMF of a concentration cell be evaluated?
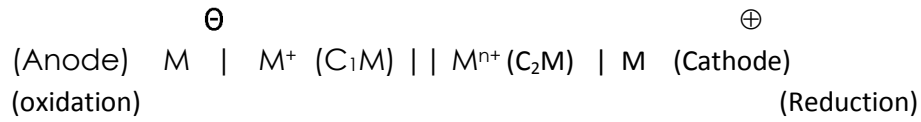
CONCENTRATION CELLS :

In concentration cells, the emf arises due to the change in the concentration of either the electrolytes or the electrodes. This is in contrast to galvanic cell where the emf arises form the decrease in the free energy of the chemical reaction taking place in the cell. However in a concentration cell, there is no net chemical reaction. The electrical energy in a concentration cell arises from the transfer of a substance from the solution of lower concentration (around the other electrode) a concentration cell is made up of 2 half cells having identical electrodes, except that he concentration of the reactive ions at the tow electrodes are different. The half cells may be joined by a salt bridge.

$\ominus$ $\oplus$

Ag | $AgNO_3$ (C_1) || $AgNO_3$ (C_2) | Ag

    Dilute   Concentrated

- Ag | $AgNO_3$ $(C_1 M)$ || $AgNO_3$ $(C_2 M)$ | Ag^+

THEORY: when a metal(M) electrode is dipped in a solution containing its own ions (M^{n+}) , then a potential (E) is developed at the electrode, the value of which varies with the concentration(C) of the ions in accordance with the nernst's equation.

$$E = E^0 + \frac{2.303\ RT}{nF}\ \log c$$

let us consider a general concentration cell represented as

                $\ominus$ $\oplus$

(Anode)   M | M^+ $(C_1 M)$ || M^{n+} $(C_2 M)$ | M   (Cathode)

(oxidation)   (Reduction)

C_1 and C_2 are the concentrations of the active metal ions (M^{n+}) in contact with the 2 electrodes respectively and emf of cell is
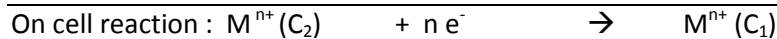
$$= E_{right} - E_{left}$$

$$= \left(E^0 + \frac{0.0592}{n} \log C_2 \right) - \left(E^0 + \frac{0.0592}{n} \log C_1 \right)$$

or

$$E_{cell} = \frac{0.0592 \text{ v}}{n} \log (C_2 / C_1) \text{ at } 25^0 C$$

And at any temp., the general equation is

$$E_{cell} = \frac{2.303 \text{ RT}}{nF} \log (C_2 / C_1)$$

At anode : M $\rightarrow$ $M_{(C1)} + n e^-$

At cathode : $M^{n+} (C_2)$ $+ n e^-$ $\rightarrow$ M

On cell reaction : $M^{n+} (C_2)$ $+ n e^-$ $\rightarrow$ $M^{n+} (C_1)$

Evidently the emf so developed is due to the more transference of metal ions from the soln. of higher concentration (C_2) to the solution of lower concentration (C_1).

Problem: Calculate the emf of the following concentration cell which contains two Zinc electrodes dipped in two solutions of 0.05M and 0.5M concentrations.

Sol: Zn |ZnSO$_4$ | | ZnSO$_4$ | Zn
    0.05   0.5
    (C_1)   (C_2)
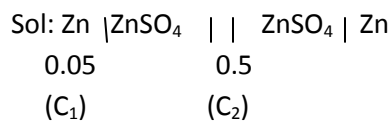
$$E_{cell} = \frac{0.0591}{n} \log (C_2 / C_1) \text{ at } 25^0 C$$

= 0.0591/2 log 0.5/0.05

= 0.02955V.

Q) What are potentiometric titrations. How do you determine end point by using potentiometer?

Potentiometric titrations : The electrode potential of an electrode depends upon the concentration of its ions in solution. Hence the potential of an indicator electrode goes on changing with respect to a standard electrode (calomel electrode) by changing the concentration of ions during titration. In simple words, determination of difference of potential of the indicator electrode can be used as indication in volumetric titrations. The equivalence point is indicated by fairly a large change of potential. Thus the

determination of equivalence point of titrations on the basis of potential measurements is called potentiometric titrations.

DETECTION OF END POINT : In potentiometric titration, a suitable electrode is immersed in the solution to be titrated as the indicator. The indicator electrode is paired with a reference electrode and the electrodes are connected with an electronic voltmeter. Since the reference electrode potential has a constant value, any change in the indicator electrode potential is reflected by a similar change in the cell potential. Therefore the equivalence point can be found by plotting a graph between the cell emf and the volume of titrant added from the burette

1) *ACID – BASE TITRATIONS :* In acid – base titrations, quinhydrone electrode is employed as the indicator saturated calomel electrode.

Fig. 17. Acid-alkali potentiometric titrations.
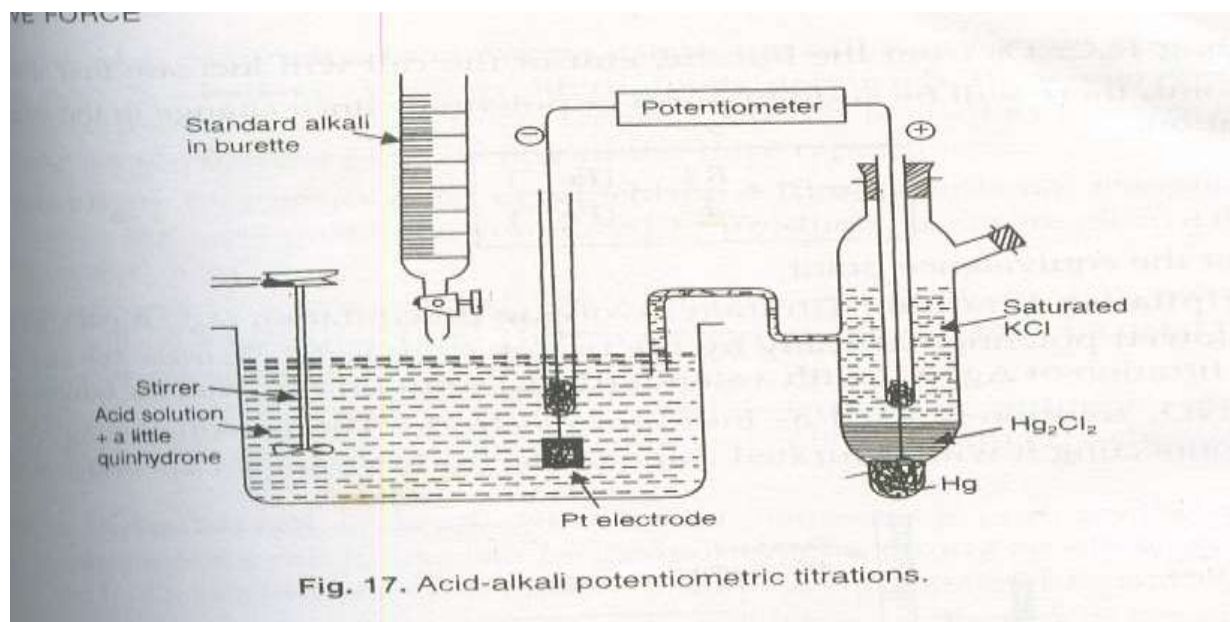
A definite volume of a given acid solution is taken in a large beaker. To it a pinch of quinhydrone is added. A stirrer and a Pt electrode are dipped in it. This electrode is then connected to a saturated electrode through a potentiometer. On adding standard alkali soln. form the burette, the e.m.f of the cell increases at first gradually, but at the end point the rate of change of potential will be suddenly

raised largely. The end point of titration is taken treated by plotting ΔE/ΔV verses V and the maximum point in the curve gives the end point.
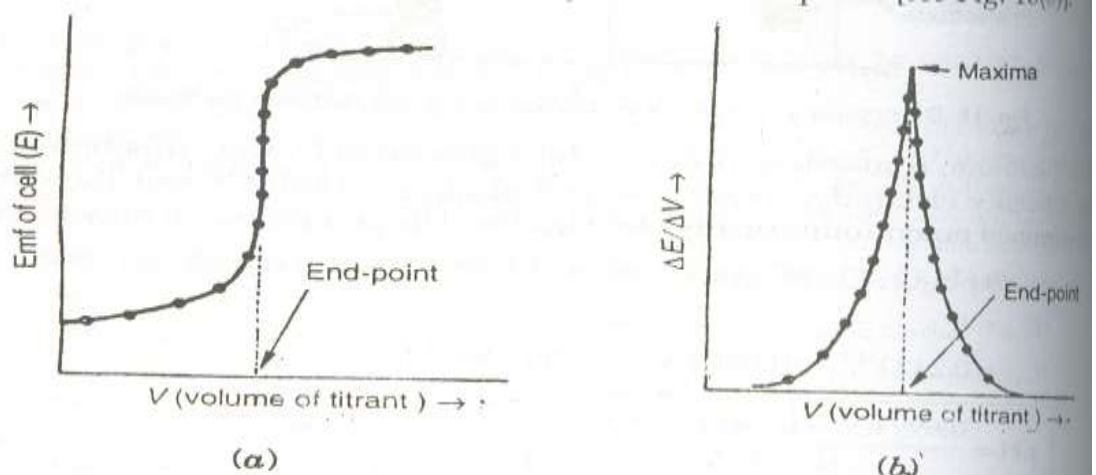

Fig. 16. (*a*) In potentiometric titration, the point of inflection is the end-point.
(*b*) Plot of ΔE/ΔV against volume (*V*). Maxima gives the moe accurate end-point.

ADVANTAGES OF POTENTIOMETRIC TITRATIONS :

1. These titrations can be used even for colored solutions in which an ordinary indicator would be useless.
2. These titrations give highly accurate results.
3. Even weak acid – weak base titrations are possible by this method.
4. These can be found carried out on a micro real.

CORROSION AND ITS CONTROL

INTRODUCTION:- Many metals exist in nature in combined forms as their oxides, carbonates, sulphides, chlorides and silicates(except noble metals) such as Au (gold), Pt (Platinum) etc. During extraction process these are reduced to their metallic states from their ores and during extraction of ores considerable amount of energy is required.

⇨ Compounds are in lower energy state than the metals. Hence when metals are put into use in various forms, they get exposed to environment such as dry gases, moisture, liquids etc. and slowly the exposed metals surface begin to decay by conversion into a compound.

DEFINITION :- Any process of deterioration or destruction and consequent loss of a solid metallic material through an unwanted chemical or electrochemical attack by its environment at its surface is called corrosion thus corrosion is a reversal process of extraction of metals.

Examples:-

i)   Rusting of iron – when iron is exposed to the atmospheric conditions, a layer of reddish scale and powder if Fe_3O_4 is formed.

ii)   Formation of green film of basic carbonate- [$CuCO_3$ + $Cu(OH)_2$] on the surface of copper when exposed to moist air containing CO_2.

DISADVANTAGES OF CORROSION: The process of corrosion is slow and occurs only at surface of metals but the losses incurred are enormous. Destruction of machines equipments, building materials and different types of metallic products, structures etc., thus the losses incurred are very huge and it is estimated that the losses due to corrosion are approximately 2 to 2.5 billion dollars per annum all over the world.

THEORIES OF CORROSION:- Corrosion can be explained by the following two theories .

1. Dry or chemical corrosion.
2. Wet or electrochemical corrosion.
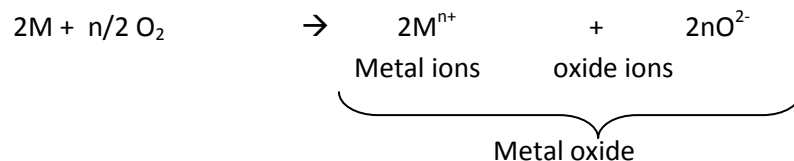
Dry or Chemical corrosion: -

This type of corrosion occurs mainly by the direct chemical action of the environment i.e., by the direct attack of atmospheric gases such as O_2, halogens, H_2S, SO_2, N_2 or anhydrous inorganic liquids on the metal surface with which they are in contact. There are 3 main types of chemical corrosion.
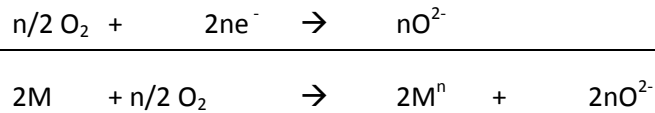
1) Corrosion by oxygen (or) oxidation corrosion.
2) Corrosion by other gases like SO_2, CO_2, H_2S and F_2 etc.
3) Liquid metal corrosion.

Oxidation corrosion:-

➔ It is brought about by direct action of oxygen at low (or) high temperatures, usually in the absence of moisture.

➔ At high temperatures all metals are attacked by oxygen and are oxidized – except noble metals like Ag, Au, Pt.

➔ At ordinary temp generally all the metals are slightly attacked. However alkali metals – Li, Na, K, Rb etc. and alkaline earth metals – Be, Ca , Sr etc. are attacked very rapidly and get oxidized readily.
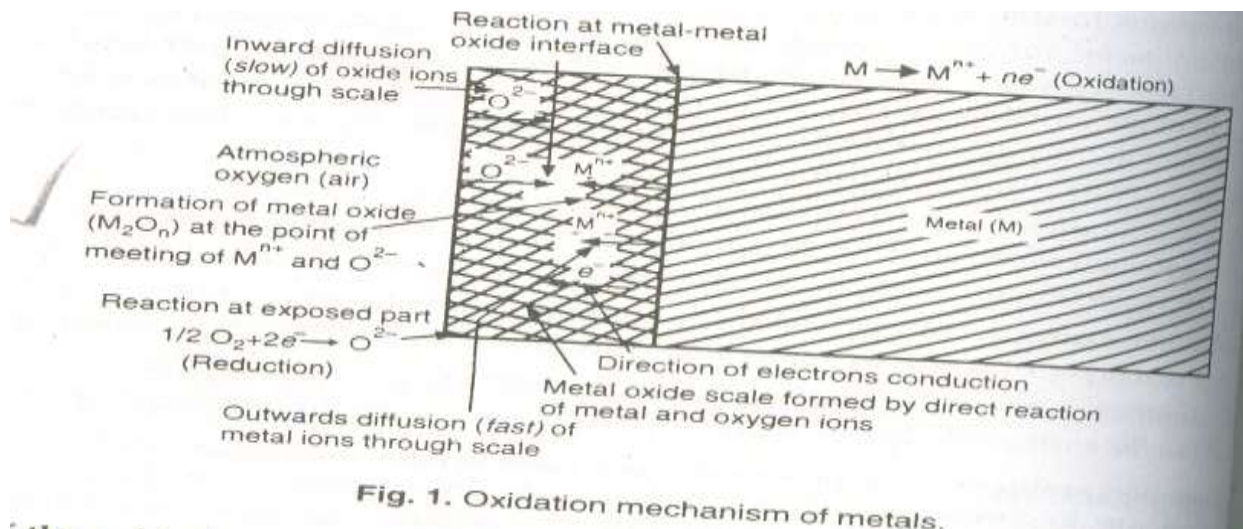
The reactions in the oxidation corrosion are

$$2M + n/2\ O_2 \qquad \rightarrow \qquad 2M^{n+} \qquad + \qquad 2nO^{2-}$$

Metal ions   oxide ions

Metal oxide

$$2M \qquad\qquad \rightarrow \qquad 2M^{n+} \qquad + \qquad 2ne^-$$

$$n/2\ O_2\ +\quad 2ne^-\quad \rightarrow\quad nO^{2-}$$

$$2M\quad +\ n/2\ O_2\quad \rightarrow\quad 2M^n\ +\quad 2nO^{2-}$$

MECHANISM OF OXIDATION CORROSION:- 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.

.:for oxidation to continue either the metal must diffuse outwards through the scale to the surface or the oxygen must diffuse inwards through the scale to the underlying metal. Both transfers occur, but the outward diffusion of the metal is generally much more rapid than the inward diffusion of oxygen, since the metal ion is appreciably smaller than the oxide ion, therefore the metal ion has much higher mobility.

Fig. 1. Oxidation mechanism of metals.

NATURE OF THE OXIDE FORMED :- It plays an important role in further oxidation corrosion process.

Metal + oxygen $\rightarrow$ metal oxide (corrosion product)

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. from 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.

Fig. 2. Unstable oxide layer.

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.

Fig. 3. Volatile oxide 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 continuous until the entire metal is converted to its oxide.
Eg: Iron when attacked by H_2S at high temperature forms porous FeS layer.

Fig. 4. Porous oxide layer.

PILLING – BEDWORTH RULE: According to it- the oxide acts as protective or non – porous, if the volume of the oxide is at least as great as the volume of the metal form which it is formed .

On the other hand -if the volume of the oxide layer is les than the volume of metal, the oxide layer is porous and hence non-protective. Because it cannot prevent the access of oxygen to the fresh metal surface below.

For eg: alkali and alkaline earth metals like Li, Na, K, Mg forms oxides of volume less than volume of metals.

.: these layers are porous and non-protective. On the other hand metals like Al forms oxide whose volume is greater than the volume of the metal.

.: Al forms a tightly – adhering non-porous protective layer.

CORROSION BY OTHER GASES :- Like SO_2, CO_2, Cl_2, H_2S, F_2 etc. The extent of corrosion mainly depends on the chemical affinity between the metal and the gas involved.

The degree of attack depends on the nature of the layer formed.

    i)   For e.g. when Ag metal is attacked by Cl_2 gas, they form AgCl layer, which is protective. Hence further corrosion of Ag by Cl_2 will be stopped.

    ii)   When Sn is attacked by dry Cl_2 gas, they form volatile $SnCl_4$ which evaporates immediately thus leaving the fresh metal for further attack.

LIQUID METAL CORROSION :- is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. Such corrosion occurs in nuclear power devices. The corrosion reaction involves either.

    i)   Dissolution of a solid metal by a liquid metal (or)

    ii)   Internal penetration of the liquid metal into the solid metal.

    Both these types of corrosion cause weakening of the solid metal.

      For eg in nuclear reactors liquid sodium corrodes Cd rods.

WET (OR) ELECTROCHEMICAL CORROSION :-

      This type of corrosion is observed when

➔ I) a conducting liquid is in contact with a metal (or)

➔ Ii) when two dissimilar metals (or) alloys are either immersed (or) dipped partially in a solution.

➔ The corrosion occurs due to the existence of separate anodic and cathodic areas or parts between which current flows through the conduction soln.

➔ In the anodic area oxidation reaction takes place so anodic metal is destroyed by dissolving (or) forming a compound such as an oxide.

➔ Hence corrosion always occurs at anodic areas

    .: At Anode

$$M \rightarrow M^{n+} + ne^-$$
$$M^{n+} \rightarrow \text{dissolves in solution.}$$

    (Metal ion) ➔ forms compound such as oxide.

➔ In cathodic area, reduction reaction (gain of e^- s) takes place. The metal which is acting as cathode is in its reduced form only. Therefore it cannot be further reduced. Therefore cathodic reactions do not affect the cathode.

➔ So at cathodic part dissolved constituents in the conducting medium accept the electrons to form some ions like OH^-, O_2^- etc.

➔ The metallic ions from anodic part and non- metallic ions from cathodic part diffuse towards each other through conducting medium and form a corrosion product some where between anode and cathode.

➔ The e⁻s which are set free at anodic part flow through the metal and are finally consumed in the cathodic region.

➔ Thus we may sum up that electrochemical corrosion involves:

   i)   The formation of anodic and cathodic areas.
   ii)   Electrical contact between the cathodic and anodic parts to enable the conduction of electrons.
   iii)   An electrolyte through which the ions can diffuse or migrate this is usually provided by moisture.
   iv)   Corrosion of anode only
   v)   Formation of corrosion product some where in between cathode and anode.

MECHANISM OF WET OR ELECTROCHEMICAL CORROSION:-

In wet corrosion the anodic reaction involves- the dissolution of metal as corresponding metal ions with the liberation of free electrons :

$$M \rightarrow M^{n+} \quad + \quad ne^-$$

➔ Where as the cathodic reaction consumes e⁻s either by a) evolution of hydrogen b)or by absorption of oxygen depending on the nature of the corrosive environment.

   a) **EVOLUTION OF HYDROGEN**: occurs

➔ In acidic environments.

➔ For eg in the corrosion of iron metal the anodic reaction is dissolution of Fe as ferrous ions with liberation of e⁻s.

$$Fe \quad \rightarrow \quad Fe^{+2} \quad + \quad 2e^- \quad \rightarrow oxidation.$$

➔ These e⁻s flow through the metal from anode to cathode (acidic region) where H^+ ions are eliminated as H_2 gas.

$$2H^+ \quad + \quad 2e^- \quad \rightarrow \quad H_2\uparrow \quad \rightarrow \quad reduction.$$

➔ The overall reaction is

$$Fe \quad + \quad 2H^+ \quad \rightarrow \quad Fe^{2+} \quad + \quad H_2\uparrow \quad \rightarrow \quad reduction$$
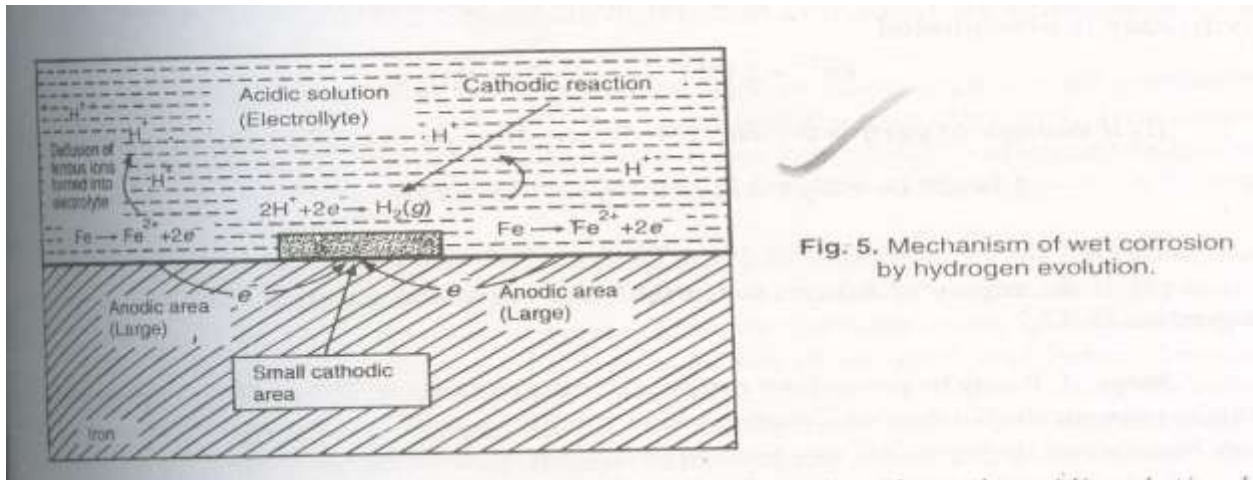
Fig. 5. Mechanism of wet corrosion by hydrogen evolution.

➔ This type of corrosion causes " displacement of hydrogen ions from the acidic solution by metal ions.

➔ In hydrogen evolution type corrosion, the anodes are very large areas, where as cathodes are small areas.

➔ All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

b) **ABSORPTION OF OXYGEN TYPE CORROSION :** Rusting of Fe in neutral aqueous solution of electrolytes like NaCl in the presence of atmospheric oxygen is a common example of this type of corrosion.
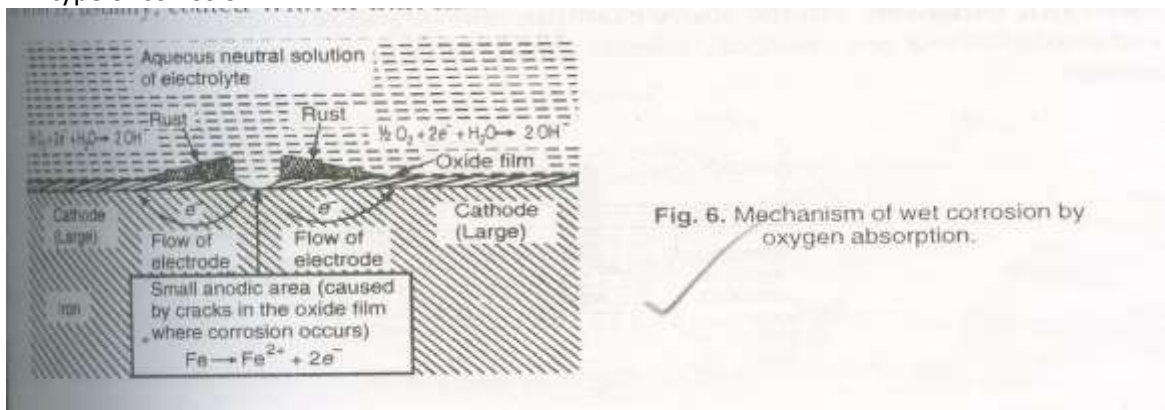

Fig. 6. Mechanism of wet corrosion by oxygen absorption.

➔ The surface of iron will be usually coated with a thin film of iron oxide. However if this oxide film develops some cracks, anodic areas are created on the surface.

➔ While pure metal parts act as cathode.

➔ Thus anodic areas are very small surface parts.

➔ The rest of the surface of the metal forms cathodes.

➔ Thus at the anodic part iron metal dissolves as Fe^{+2} ions with the liberation of e^- s.

$$Fe \rightarrow Fe^{+2} + 2e^-$$

➔ The liberated e^- s flow from anodic to cathodic areas through iron metal during which they interact with dissolved oxygen and moisture.

$$\frac{1}{2} O_2 \quad + H_2O \quad + \quad 2e^- \quad \rightarrow \quad 2OH^-$$

→ The Fe^{+2} ions and OH^- ions diffuse and form ferrous hydroxide precipitate when they meet with each other
$$Fe^{+2} \quad + 2OH^- \rightarrow \quad Fe(OH)_2$$
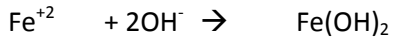
→ If enough O_2 is present $Fe(OH)_2$ is easily oxidized to $Fe(OH)_3$ (ferric hydroxide)
$$4\,Fe(OH)_2 \quad + O_2 \quad + \quad 2H_2O \quad \rightarrow \quad 4Fe(OH)_3$$
The product called yellow rust actually corresponds to $Fe(OH)_3.H_2O$

→ If the supply of O_2 is limited, the corrosion product may be even black

→ anhydrous magnetite Fe_3O_4.

S.No	Dry/Chemical Corrosion	Wet/Electrochemical Corrosion
1.	This corrosion occurs at dry conditions	This corrosion occurs in wet conditions in presence of electrolyte medium.
2.	Corrosion is uniform	Corrosion is not uniform
3.	It is a slow process	It is rapid process
4.	It involves direct chemical attack of the metals 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 in heterogeneous solutions
7.	Corrosion products are developed at the place where corrosion takes place.	Corrosion occurs at the anode and corrosion product occurs at cathode.

GALVANIC SERIES:-

In the electrochemical series (where metals are arranged down in the increasing order fo their reduction potentials) a metal high in the series is more anodic and undergoes corrosion faster than the metal below it.

Electrochemical series   galvanic series.

Li/Li$^+$ reactive metals   Mg

K/K$^+$ Mg alloys

Ca/Ca^{+2} zn

Active   anode

Na/Na$^+$	Al
Mg/Mg^{+2}	Al Alloys
Al/Al^{+3}	low carbon
Zn/Zn^{+2}	cast iron
Mn/Mn^{+2}	stainless steel (active)
Cr/Cr^{+3}	Pb – Sn alloys
Fe/Fe^{+2}	Pb
Cd/Cd^{+2}	Sn
Co/Co^{+2}	Brass
Ni/Ni^{+2}	copper
Sn/Sn^{+2}	Bronze
Pb/Pb^{+2}	Cu- Ni alloys
H$_2$/2H$^+$ reference	Ag
Cu/Cu^{+2}	Stainless steel (possive)
Hg/Hg$^+$	Monel
Ag/Ag$^+$	graphite
Hg/Hg^{+2}	titanium
Pd/Pd^{+2}	gold
Pt/Pt^{+2} s	platinum
Au/Au^{+3} Noble metals	

Noble / Cathodic

For eg: Li corrodes faster than Mg, Zn corrodes faster than Fe, Fe corrodes faster than Sn, Cu corrodes faster than Ag and so on. However some exceptions are there for e.g. Ti above silver is less reactive than Ag similarly Zn – Al couple. Zn below Al in electro chemical series is corroded and acts as anode while Al acts as cathode and is protected. These observations opposite to the predictions by emf series can be explained as metals like Ti and Al develop strongly adhering oxide layers on their surfaces thereby making their effective electrode potential more positive (or less negative)

.: it is clear that electro chemical series does not account for the corrosion of all the metals and alloys consequently a more practical series , called galvanic series have been framed in which metals as well

as alloys are arranged in their reactivity order. Thus move reactive metals and alloys are at the top of the series and they are anodic and get corroded faster where as less reactive metals are at the bottom and they are cathodic and noble.

The differences between Galvanic series and Electrochemical series are as follows:

S.No	Electrochemical Series	Galvanic Series
1.	This series was developed by studying corrosion of metals and alloys in their salt solution of 1M concentration without any oxide film on them.	This series is developed by studying corrosion of metals and alloys in unpolluted sea water without their oxide film.
2.	The position of metal is fixed	The position of metal may shift
3.	There is no information regarding position of alloys.	The corrosion of alloys can be studied in this series.
4.	The position of the metal is permanently fixed.	The position of metal when present in form of alloy is different from that of pure metal.
5.	This series predicts the relative displacement tendencies.	This series predicts the relative corrosion tendencies.
6.	This series comprises of metals and non-metals.	This series comprise of metals and alloys.

FACTORS INFLUENCING CORROSION:

i)   Nature of metals
ii)   Nature of the corroding environment.

<u>**Position in galvanic series**</u> :-
The metal higher in series is more active and suffers corrosion. The rate and extent of corrosion is directly proportional to electrode potential difference between them.

<u>**Over voltage**</u> : - when a metal , which occupies a high position in galvanic series (say Zinc), is placed in IN H_2SO_4 , it undergoes corrosion forming a film and hydrogen gas.

The initial rate of reaction is quite slow, because of high over voltage (0.70 v) of the zinc metal, which reduces the effective electrode potential to a small value. However, if few drops of copper sulphate

($CuSO_4$) are added, the corrosion rate of zinc is accelerated, because some copper gets deposited on the zinc metal forming minute cathodes, where the hydrogen over voltage is only 0.33v, thus, reduction in over voltage of the corroding metal/ alloy accelerates the corrosion rate.

Purity of metal : - Impurity of a metal generally causes heterogeneity and form minute electrochemical cells and the anodic parts gets corroded. For eg: Zn metal containing impurity such as Pb (or) Fe undergoes corrosion .

The rate and extent of corrosion increases with extent of impurities.

Nature of the surface film: - when metals are exposed to atmosphere, practically all metals get covered with a thin surface film of metal oxide. The ratio of the volume of metal oxide to the metal is known as specific volume ratio. Greater the specific volume ratio, lesser is the oxidation corrosion rate. For eg: the specific volume ratio of Ni, Cr, W are 1.6, 2.0 and 3.6 respectively. Consequently the rate of oxidation corrosion is least for (w) tungsten.

Nature of the corrosion product

a)Solubility of corrosion products : If the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate otherwise if it is insoluble, corrosion will be suppressed e.g: $PbSO_4$ formation in case of Pb in H_2SO_4.

b)Volatility of corrosion products : -   If the corrosion product is volatile , it evaporates as soon as it is formed, there by leaving the underlying metal surface exposed for further attack.

This causes rapid and continuous corrosion.

For eg: Mo forms MoO_3 volatile oxide.

NATURE OF THE CORRODING ENVIRONMENT :-

i)   **Temperature**: With increase of temperature, the corrosion rate also increases because the reaction as well as diffusion rate of ions in the corrosion medium increases.

ii)   **Humidity :** The higher the humidity of the atmosphere the greater is rate and extent of corrosion because the moisture acts as medium for O_2 in air and behaves as an electrolyte.
        For eg: atmospheric corrosion of iron is slow in dry air compound to moist air. Iron combines with O_2 and water to form ferrous hydroxide which combines with atmospheric CO_2 to form ferrous bicarbonate.
        $2Fe \quad + \quad O_2 \quad + \quad 2H_2O \rightarrow 2Fe(OH)_2$
 $Fe(OH)_2 \quad + \quad CO_2 \quad \rightarrow \quad Fe(HCO_3)_2$
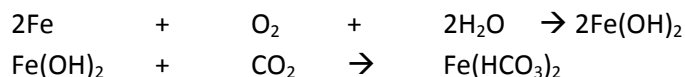
iii)   **Effect of pH :-** Generally acidic media are more corrosive than alkaline and neutral media. Hence metals may be virtually classified according to pH range in which they will be affected (or) resistant. However atmospheric metals like Al, Pb etc. are corroded in alkaline medium and the corrosion rate of iron in O_2 free water is slow, until the pH is below Zn is rapidly corroded in weakly acidic solutions.

CORROSION CONTROL

1) <u>**Cathodic protection**</u> : The principle involved in this method is to force the metal to be protected to behave like a cathode thereby corrosion doesn't occur. There are two types of cathodic protection.

i) **Sacrificial anodic protection method** :- In this method the metallic structure to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal implies the more active metal itself gets corroded slowly. While the parent structure which is cathodic is protected .The more active metal so employed is called " sacrificial anodic" when ever the sacrificial anode is consumed completely. It is replaced by a fresh one metal commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys, sacrificial anodes are used for the protection of buried pipe lines underground cables, marine structures, ship hulls, water tanks etc.
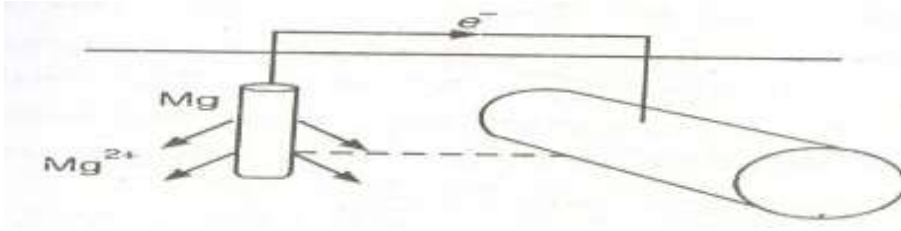
IMPRESSED CURRENT – CATHODIC PROTECTION :- In this method an impressed current is applied in opposite direction to nullify the corrosion current and current the corroding metal from anode to cathode. Usually the impressed current is derived from a direct current source (like battery or rectifier on ac line) with an insoluble anode, like graphite, high silica iron, scrap iron, stainless steel or platinum. Usually a sufficient d.c is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected.

Fig. 2.21: Protection given to underground pipeline by impressed current cathodic protection
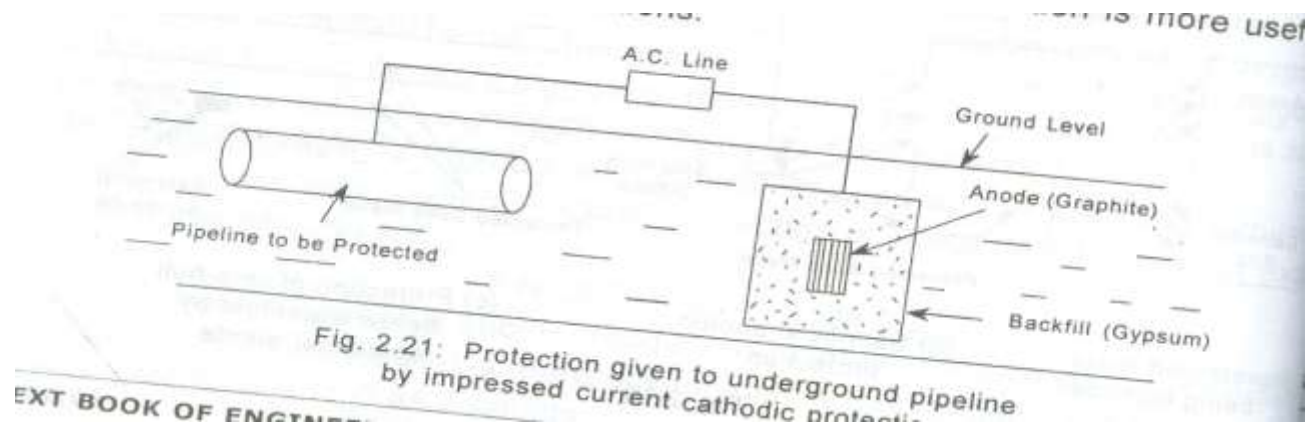
The anode is buried is a backfill such as coke breeze or gypsum to increase the electrical contact between itself and the surrounding soil.

Applications:- This type of protections is used in buried structures such as tanks and pipelines, transmission lime towers, marine piers, laid up ships etc.,

Advantages:- They can be automatically controlled which reduce maintenance and operational costs.

Surface Preparation and methods of application of coatings on metals:

If the metal surface has not been properly prepared, the protective coatings will not stick to the surface and hence, severe corrosion results at points exposed to corrosive environment.

1. Mechanical cleaning:- If the surface is not smooth, it is made smooth by mechanical polishing or by electro polishing or by mechanical rubbing with a wire brush.
2. Alkali cleaning: The surface imperfection may be due to the presence of oil or grease and rust or scale. Oil/grease is removed by washing with soap or alkali in water.
3. Acid pickling: Rust/scale is removed by dipping material in dilute (5-10%) H_2SO_4.
4. Solvent cleaning: A surface may also be cleaned by solvents such as turpentine, kerosene, etc.
5. Sand blasting: A stream of sand is blowed in steam to make the surface clean from other impurities.

The clean surface catches dirt and gets corroded quickly by applying protective coats on the surface by selecting suitable methods of application from the following methods ie., anodic, cathodic, metal cladding and electroplating.

Protective metallic coatings:- Coating of the surface of a metal by protective metallic coating is one of the oldest procedures used for preventing corrosion. A coating isolates the underlying metal from the corroding environment the protective coating should possess the following quantities to act effectively.

i) The coating applied must be chemically insert to the environment under particular conditions of temp and pressure.

ii) The coating must prevent the penetration of the environment into the metal.

Two important protective coatings are

i) Anodic coating   ii) Cathodic coating

i**) Anodic coatings** are produced from coating metals which are anodic to the base metal (which is to be protected) for e.g.: coating of Zn, Al and cd on steel are anodic because their electrode potentials are lower than that of the base metal, Iron.

If any pores, breaks occur in such an anodic coating, a galvanic cell is formed between the coating metal and the exposed part of base metal.

For e.g. in case of galvanized steel, zinc the coating metal develops any cracks, then a galvanic cell is formed between Zn and exposed iron metal. Then zinc dissolves anodic ally, where as the iron is protected. Thus zinc coating protects iron sacrificially.

ii) **Cathodic coatings** are produced from coating metals which are more cathodic to the base metal implies that they have higher electrode potential than the base metal.

They protect the base metal since they have higher corrosion resistance then the base metal. But they provide effective protection as long as there are no pores and breaks are developed once the coating is punctured, the underlying metal will be corroded at a faster rate.

For e.g. when iron is coated with tin metal iron acts as anode and tin acts as a cathode and a galvanic cell is developed and an intense localized attack at the small exposed part occurs resulting in severe pitting corrosion.

S.No	Anodic coating	Cathodic Coating
1.	Involves coating of an anodic metal on the surface of base metal	Involves coating of noble metal on the surface of base metal.
2.	Protects the underlying base metal 'sacrificially'	Protects the underlying base metal due to its noble character and higher corrosion resistance.
3.	Electrode potential of coating metal is lower than that of base metal.	Electrode potential of coating metal is higher than that of base metal.
4.	If pores, breaks or discontinuities occur in such a coating, the base metal is not corroded, till all the coating metal is consumed.	If pores, breaks or discontinuities occur in such a coating, the base metal is not corroded, till all the coating metal is speeded up.
5.	Ex. Coating of Zn on Iron	Ex. Coating of Sn on Iron.

Methods of applications of metal coatings:-

i) Hot dipping   ii) Metal cladding   iii) Electro plating

i) **Hot dipping** is used for producing a coating of low melting metal such as Zn with mp 419^0C, Sn with mp 232^oC pb, Al etc. on iron, steel and copper which have relatively higher melting points. Two widely used hot dipping methods are

a) Galvanising   b) Tinning.

Galvanizing is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting. For carrying out galvanizing firstly the iron or steel article such as sheet, pipe or wire is cleaned by pickling with dil H_2SO_4 solution for 15-20 mts at 60-90^0C. In pickling any scale, dirt, oil, grease or rust and any other impurities are removed from the metal surface. The article is washed well and then dried.
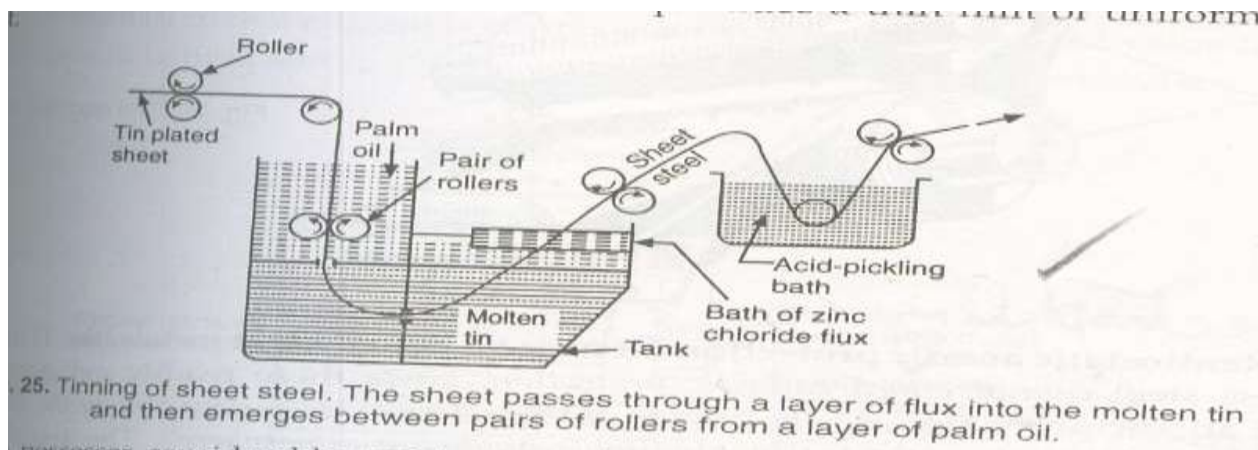
It is then dipped in bath of molten zinc maintained at 425-430°C. The surface of bath is kept covered with ammonium chloride – flux to prevent oxide formation. The article is covered with a thin layer of zinc when it is taken out of bath. It is then passed through a pair of hot rollers, which removes any excess of zinc and produces a thin film of uniform thickness then it is annealed at a temperature of 650°C and finally collected slowly.

Fig. 24. Galvanizing of sheet steel.
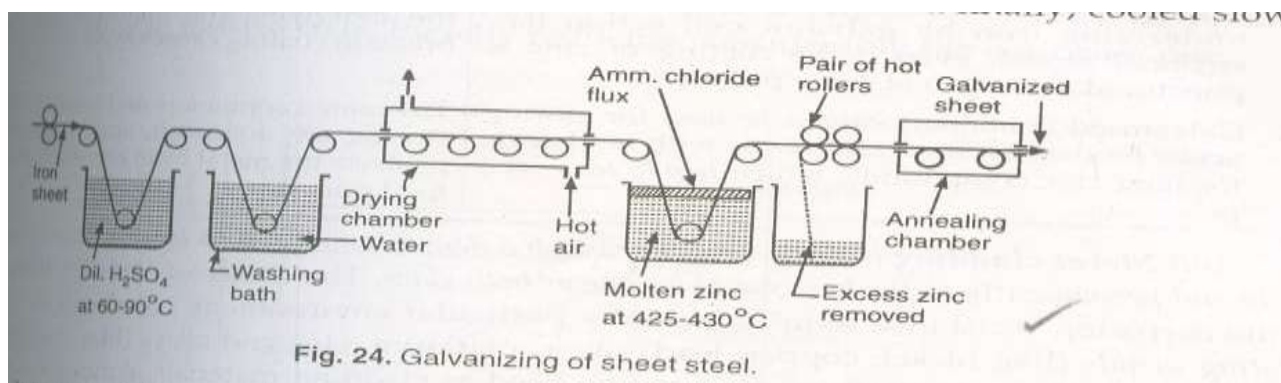
Uses: - Roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes etc. which are made of iron are protected from atmospheric corrosion by galvanizing them. But galvanized utensils cannot be used for preparing and storing food stuffs, especially acidic ores since zinc gets dissolved in all acids forming highly toxic compounds.

Tinning: - Tinning is coating of tin metal over the iron or steel articles. Tinning is carried out by pickling the article in dil H_2SO_4 to remove any oxide film, dirt, grease, oil or scales etc. then it is passed through a molten tin, which is covered with zinc chloride flux. This flux prevents the oxidation of molten tin and also keeps the molten metal to adhere to the metal sheet. Next the sheet passes through a tank of molten tin and finally through a series of rollers from underneath the surface of a layer of palm oil. The palm oil protects the hot tin coated surface against oxidation. The rollers remove any excess of tin and produce a thin film of uniform thickness on the steel sheet.

Uses: - Tin possesses considerable resistance against atmospheric corrosion. Tinning is widely used for coating steel brass and copper sheets used for manufacturing containers for storing food stuffs, ghee, oils and packing food materials, since tin is non toxic in nature. Tinned Cu sheets are employed for making cooking utensils and refrigeration equipments.

25. Tinning of sheet steel. The sheet passes through a layer of flux into the molten tin and then emerges between pairs of rollers from a layer of palm oil.

S.No	Galvanization	Tinning
1.	The process of coating Zn on the surface of Iron or Steel is called Galvanization	The process of coating tin on the surface of iron or steel is called Tinning.
2.	Zn is anodic to the base metal iron or steel	Tin is cathodic to the base metal iron or steel.
3.	Zn protects iron sacrificially	Tin protects iron due to its noble nature.
4.	Since Zn is more electropositive than iron, it does not permit iron to pass into the outside solution ie., corrosion doesnot occur to iron	Since tin is less electropositive than iron, it protects the iron till coating is perfect.
5.	Any break in the protective Zn layer do not cause corrosion to the base metal iron, because iron is cathodic to Zn.	Any break in the protective Sn layer cause severe corrosion to the base metal iron, because iron is anodic to Sn.
6.	Galvanized containers cannot be used for storing food stuffs, because Zn reacts with the acids that are present in the food materials and produces toxic compounds.	Tin coated containers are used for storing food materials because tin produces non toxic protective layer on the surface of metal and avoids any food poisoning.
7.	After galvanization, the galvanized sheet is subjected to annealing process.	No annealing process
8.	Galvanized articles are good engineering materials.	Tinned articles are used majorly in food processing industries.

Metal cladding:- Is the process by which a dense, homogeneous layer of coating metal is bonded firing and permanently to the base metal on one or both sides. Nearly all existing corrosion resisting metals like Nickel, Copper, Lead, Silver, Pt etc. and alloy like stainless steel, Ni alloys, Copper alloys, Lead alloys etc can be used as lading materials the base metals on which cladding is done are mild steel, Al, Cu, Ni and their alloys.

Generally cladding is carried out by arranging thin sheets of the coating metal and base metal sheet in the form of a sandwich, which are then passed through rollers under the action of heat and pressure, very wide use of metal cladding is used in the aircraft industry of 'alclad' sheeting in which a plate of Duralumin is sandwiched between two layers of 99.5% pure aluminum.

Electroplating:- Is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal.

Theory of electroplating:- suppose the anode is made up of coating metal (M) itself, during electrolysis the concentration of the electrolytic bath remains unaltered since the metal ions deposited from the bath are replenished continuously by the reaction of the free anions of the electrolyte with the anode metal. Thus for e.g. if $CuSO_4$ solution is used as an electrolyte is ionizes as

$$CuSO_4 \rightleftharpoons Cu^{+2} + SO_4^{-2}$$

On passing current Cu^{+2} ions go to the cathode (the article to be plated) and get deposited there.

$$Cu^{+2} + 2e^- \rightarrow Cu \qquad \text{(at cathode)}$$

The free sulphate ions migrate to the Cu anode and dissolve an equivalent amount of the Cu to form $CuSO_4$

$$Cu + SO_4^{-2} \rightarrow CuSO_4 + 2e^- \qquad \text{(at anode)}$$
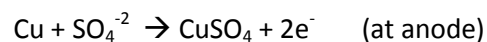
The $CuSO_4$ thus formed dissolves in the electrolyte thus there is continuous replenishment of electrolytic salt during electrolysis.

Procedure:- The article to be electroplated is first treated with organic solvent like tetrachloro ethylene to remove oil, grease etc. then it is treated with dil HCl or H_2SO_4 to remove surface scales, oxides etc. For Ni and Cu HCl is used while for Cr plating H_2SO_4 is used. The cleared article is then made as cathode of an electrolytic cell. The anode is either the coating metal itself or an inert material of good electrical conductivity like graphite. The electrolyte is a solution of a soluble salt of the coating metal. When direct current is passed coating metal ions migrate to the cathode and get deposited there. Thus a thin layer of coating metal is obtained on the article made as cathode. For brighter and smooth deposits, favorable conditions such as low temp, medium current density and low metal ion concentrations are used.
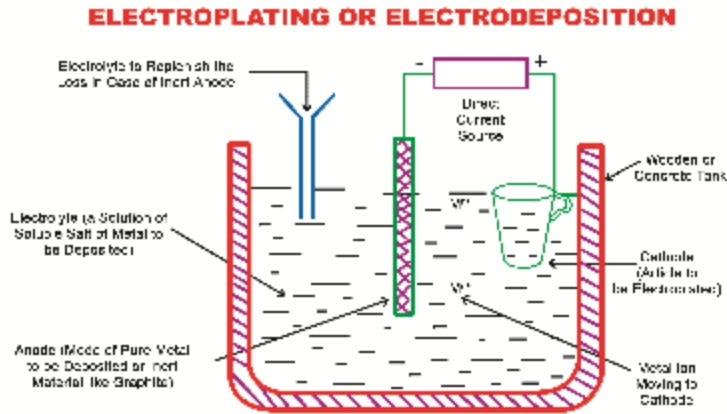
Fig. 2.27 : Electroplating

Factors affecting electroplating:-

1. Concentration of electrolyte: Low concentration of metal ions produce coherent uniform metal deposition.
2. Thickness of the deposit: It should be minimised in order to get a strong adherent coating.
3. Current density: It is the current per unit area of the object being plated. It should have minimum optimum value.
4. Additives: These are added to the electrolytic bath in order to get a strong adherent and mirror smooth coating. Ex. Gelatine, glue, glycine etc.
5. Electrolyte: the electrolyte taken should have good conductivity.
6. pH of electrolyte: It must be maintained properly to get the deposition effectively.

Objectives of Electroplating:-

1. To improve the surface appearance.
2. To increase the wear resistance.
3. To improve the surface hardness.

Applications/ Uses of electroplating:-

1. It is used in automobile, aircraft, refrigerator and electrical appliances.
2. It is also used as coatings in electrical iron, fans, locks, jewellery, type writers, watches, etc,.

Organic coatings:-

Organic coatings are inert organic barriers like paints,varnishes, lacquers and enamels applied on metallic surfaces and other constructional materials for both corrosion protection and decoration. A good organic coating should process the following qualities.

i) Should be chemically inert to the corrosive environment.

ii) Should have good surface adhesion.

iii) Should be impermeable to water, salts and gases.

iv) Should possess good spreading capability.

Paints:-

Paint is a mechanical dispersion mixture of one or more pigments in a vehicle. The vehicle is a liquid consisting of non-volatile film forming material, drying oil and a highly volatile solvent thinner, when a paint is applied to a metal surface the thinner evaporates, while the drying oil slowly oxidize forming a dry pigmented film.

Constituents of paints:- pigment is a solid substance which is an essential constituent of paint it provides

i) Capacity to paints ii) Strength to paint iii) desired color to paint iv) Aesthetical appeal to the paint film. (v) Protection to the paint film by reflecting harmful ultra violet light (vi) Resistance to paint film against abrasion/wear (vii) impermeability of paint film to moisture (viii) increases the weather resistance of the film.

Important pigments used are i) whites – such as white lead, Zinc Oxide, litho phone, titanium oxide.

Red colored – red lead, ferric oxide, Venetian red, chrome red etc.

Green colored: - Chromium Oxide

Blue colored: - Prussian blue

Black colored: - Carbon black

Brown colored: - Brown umber etc.

Vehicle or Drying Oil: is a filon forming constituent of the paint. These are glyceryl esters of high molecular-weight fatty acids generally present in animal and vegetable oils. The most widely used drying oils are linseed oil, soya bean oil and castor oil.
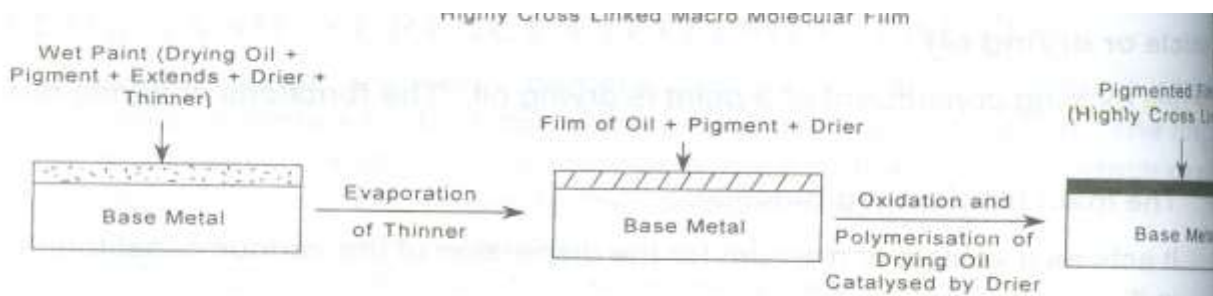
Fig. 2.28 : Drying of paint film

Example of drying oils are

Functions of drying oil: Drying oil supplies i) Main Film-forming constituent   ii)Vehicle or medium iii)Toughness iv)adhesion V)Durability Vi) and water proof ness.

Thinners: i) Reduce the viscosity of the paint to suitable consistency, so that it can easily be handled and applied.

ii)Dissolves the vehicle and the additions increases the penetration power of the vehicle

iii) helps the drying of the paint film, as they evaporate.

Common thinners are turpentine , benzene, dipentene, naptha, kerosene etc…

Driers: are oxygen carrier catalysts, they accelerate the drying of the oil film through oxidation, polymerization and condensation. Thus they improve the drying quality of the oil film.

The most effective driers are resonates, lenoleates, tungstates of Co,Mn,Pb and Zinc.

Extenders or fillers: They are added in limited quantities to the oil paints for adjusting the working quantities of the paint they help to present the setting of heavier pigments.

i) They also increases the mechanical strength of the paint film.

ii) They reduce the cost of the paint eg.s are aluminium silicate, barium carbonate, barium sulphate.

Plasticizers: some times plasticizes are added to the paint. They do not evaporate like thinners and they permanently remain in paints.

i)They improve flexibility and elasticity of the paint film.

ii) They minimize its cracking

Eg. High molecular weight esters like triphenyl phosphate tributyl phosphate, tricresyl phosphate etc.

Anti Skinning agents: They are sometimes added to paints to prevent gelling and skinning of the paint film.

Eg. poly hydroxy phenols.