UNIT – II – ELECTROCHEMISTRY & CORROSION

Introduction: “Electrochemistry is the study of the processes involved in the inter conversion of electrical energy and chemical energy”.

ELECTROCHEMICAL CELL: An electrochemical cell is a device in which the chemical energy is spontaneously converted into electrical energy through redox reaction. Example: Daniel cell. It is a reversible cell. It consist of Zn electrode, dipped in 1 M ZnSO₄ solution (where oxidation takes place) and Cu electrode, dipped in 1 M CuSO₄ solution (where reduction takes place). i.e. Each electrode may considered as a half-cell.

The electrode reactions are:
At anode: \[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^- \] (oxidation)
At cathode: \[ \text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu} \] (reduction)

Cell reaction: \[ \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu} \]

The two solutions are separated by a salt bridge and they slowly pass through the salt bridge, and so come in contact with each other. The tendency of Zn to form Zn²⁺ is greater than that of Zn²⁺ to Zn metal and hence, Zn metal acquires a negative charge. Similarly, the tendency of Cu to form Cu²⁺ is lesser than that of Cu²⁺ to Cu metal and hence, Cu metal acquires a positive charge. The e.m.f. of a cell is 1.1 Volt. It can be represented by IUPAC convention as follows,

\[ \text{Zn}, \text{Zn}^{2+}_(1 \text{M}) // \text{Cu}^{2+}_(1 \text{M}), \text{Cu}; \quad E^0 = 1.1 \text{ V} \]

Uses of salt bridge:
1. It maintains electrical neutrality.
2. It eliminates liquid junction potential.
3. It produces connectivity between two half cells.
4. It allows migration of ions from one half cells to another.

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>ELECTROCHEMICAL CELL</th>
<th>ELECTROLYTIC CELL</th>
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<tbody>
<tr>
<td>1</td>
<td>It is a device producing electrical Energy from chemical energy.</td>
<td>It is a device producing chemical Reaction from electrical energy.</td>
</tr>
<tr>
<td>2</td>
<td>Anode carries negative charge.</td>
<td>Anode carries positive charge.</td>
</tr>
<tr>
<td>3</td>
<td>Cathode carries positive charge.</td>
<td>Cathode carries negative charge.</td>
</tr>
<tr>
<td>4</td>
<td>Electrons move from anode to cathode through the external circuit.</td>
<td>Electrons move towards cathode and come out through anode.</td>
</tr>
<tr>
<td>5</td>
<td>The emf produced by the cell is Measured using potentiometers.</td>
<td>The amount of electricity passed During electrolysis is measured By coulometer.</td>
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</tbody>
</table>
The emf of the cell depends on the concentration of the electrolytes & the chemical nature of the electrode. The extent of chemical reaction is governed by Faraday’s law.

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<tbody>
<tr>
<td>6</td>
<td>It contain two different electrode &amp; two different electrolytes.</td>
</tr>
<tr>
<td>7</td>
<td>It contain one type of electrolyte &amp; two different/same electrode.</td>
</tr>
<tr>
<td>8</td>
<td>It is reversible.</td>
</tr>
<tr>
<td></td>
<td>It is irreversible.</td>
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**REVERSIBLE & IRREVERSIBLE CELLS:**

**Thermodynamic conditions:**
1. If the cell is connected to an external source of emf = 1.1 V, no current flows and no chemical reaction takes place in the cell.
2. If the external emf < 1.1 V, small current flows in the forward direction.
3. If the external emf > 1.1 V, the current flows in the opposite direction.

**Reversible cells:** Those cells which obey the following three conditions of thermodynamic reversibility are called reversible cells. Eg. Daniel cell.

**Irreversible cells:** Those cells which do not obey the conditions of thermodynamic reversibility are called irreversible cells. Eg. Dry cell. A cell consisting of Zn and cu electrodes dipped in sulphuric acid solution is irreversible. The cell reaction is \( \text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{Zn}_2\text{SO}_4 + \text{H}_2 \).

If the applied emf of the external source is slightly greater than that of the cell, Cu goes into the solution, Hydrogen gas is liberated at the other electrode and the cell reaction is \( \text{Cu} + \text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{H}_2 \). Such a cell is said to be irreversible because in each case different sets of products are formed.

**ELECTRODE POTENTIAL:** When a metal is in contact with its own salt solution, two types of chemical reactions are possible: (1) \( \text{M} \rightarrow \text{M}^{n+} + e^- \) (2) \( \text{M}^{n+} + e^- \rightarrow \text{M} \). The rate of the above two reactions depends on the nature of the metal, temperature and concentration of metal ions in solution.

**Electrode potential** is defined as, “the tendency of a metallic electrode to gain or lose electrons, when it is in contact with its own salt solution”. It is also called single electrode potential. Consequently, two types of electrode potential can be arisen.

1. **Oxidation potential:** The tendency of a metallic electrode to lose electrons when it is in contact with its own salt solution.
2. **Reduction potential:** The tendency of a metallic electrode to gain electrons when it is in contact with its own salt solution.

**Standard electrode potential (SEP):** The tendency of a metallic electrode to gain or lose electrons, when it is in contact with its own salt solution of unit molar concentration at 25\(^\circ\)C.

**EMF of an electrochemical cell:** “The difference of potential which causes flow of current from higher potential electrode to lower potential electrode” is called EMF and is expressed in Volts.

\[ E_{\text{Cell}} = E_R - E_L \]

Where, \( E_{\text{Cell}} \) = EMF of a cell

\( E_R \) and \( E_L \) are the reduction potentials of right & left hand side electrodes respectively.
**Measurement of emf of a cell:** The emf of a cell can be measured accurately by potentiometric method, which is based on Poggendorff’s compensation principle.

![Diagram of a potentiometric measurement setup]

It consists of a uniform wire AB of high resistance. A storage battery of constant emf, which should be larger than the emf of the cell to be measured, is connected at the ends A and B of the wire as in the figure. The cell X, for which the emf to be determined is included in the circuit by connecting the positive pole at the same point. The end A at which that of the battery is connected and then through a galvanometer G to a sliding contact D. The sliding contact is moved along the wire AB till no current flows through the galvanometer. The position of D is then noted. The emf of the cell, \( E_x \) is proportional to the distance, \( AD \). The cell X is now replaced by a standard cell S, the emf of which, \( E_s \) is known. The position of the sliding contact is re-adjusted by moving it over the wire AB, as before, till the point of no current in galvanometer, i.e. the null point, is reached again, say at D’ as shown in the figure. Then \( E_s \) is proportional to \( AD' \). Therefore \( E_x = (AD/AD') \times E_s \), knowing the value of \( E_s \), the value of \( E_x \) can be calculated.

**ELECTROCHEMICAL SERIES:** A series in which various electrodes are arranged in the increasing order of their standard reduction potential values based on Hydrogen scale is called electrochemical series. The standard reduction potential value of Hydrogen electrode is arbitrarily fixed as zero. The electrodes above hydrogen have negative reduction potential, while those placed below it have positive reduction potentials.

**Applications:**

1. **To predict the relative oxidizing and reducing powers:** A system with high reduction potential has a greater tendency to undergo reduction. For example, \( E^{0}_{F_2/F^-} = + 2.87 \text{ V} \), So F ions are easily reduced to F. \( E^{0}_{Li^+/Li} = - 3.05 \text{ V} \), So Li\(^+\) is reduced with greater difficulty to Li or Li is very easily oxidized to Li\(^+\). In general, Oxidizing agents have positive electrode potential and reducing agents have negative reduction potentials.

2. **To predict whether a metal will react with acid to give hydrogen gas or not:** Metals with negative reduction potentials have greater tendency to displace hydrogen gas from acids.

3. **To predict the spontaneity of a redox reaction:**
   If \( E_{\text{Cell}}^{0} \) is + ve, the cell reaction is spontaneous & \( E_{\text{Cell}}^{0} \) is - ve, the cell reaction is non-spontaneous.

4. **Calculation of equilibrium constant:** \( \ln K = nF E^{0} / 0.0591 \), So that by knowing the value of \( E^{0} \), it is enables to calculate the value of equilibrium constant of a cell reaction.
5. **Replacement tendency:** Higher the value of reduction potential, greater the replaceable tendency. For Example, $E^0_{\text{Cu}} = +0.34 \text{ V}$ and $E^0_{\text{Zn}} = -0.76 \text{ V}$, $\text{Cu}^{2+}$ has a greater tendency to form $\text{Cu}$ than $\text{Zn}^{2+}$ to $\text{Zn}$. Hence $\text{Zn}$ will displace $\text{Cu}$ from copper sulphate.

**NERNST EQUATION:**

Consider a general reversible redox reaction, $\text{M}^{n+}_{(aq)} + n \text{e}^- \leftrightarrow \text{M}_{(s)}$ ........ (1)

Now for a reversible reaction the free energy change ($\Delta G$) and its equilibrium constant (K) are interrelated as,

$$\Delta G = -RT \ln K + RT \ln \left\{ \frac{[\text{Products}]}{[\text{Reactants}]}) \right\}$$

We know that

$$\Delta G^0 = -RT \ln K$$

Apply the equation (3) in (2), We get

$$\Delta G = \Delta G^0 + RT \ln \left\{ \frac{[\text{Products}]}{[\text{Reactants}]}) \right\}$$

where $\Delta G^0$ is the standard free energy change. The eqn (4) is known as Van’t Hoff reaction isotherm.

In a reversible reaction, the electrical energy is produced is the same as decrease in free energy.

i.e. $\Delta G = nEF$ and $-\Delta G^0 = nE^0F$ .... (5)

where, $E =$ electrode potential, $E^0 =$ standard electrode potential and $F =$ Faraday (96,500 C).

Apply the equations (1) and (5) in equation (4), we get

$$-nEF = -nE^0F + RT \ln \left\{ \frac{[\text{M}]}{[\text{M}^{n+}]} \right\}$$

Since the $[\text{M}]$is unity, we have

$$-nEF = -nE^0F + RT \ln \left\{ 1 / [\text{M}^{n+}] \right\}$$

$$-nEF = -nE^0F - RT \ln [\text{M}^{n+}]$$

Divide this equation by $-nF$, we get

$$E = E^0 + \frac{RT}{nF} \ln [\text{M}^{n+}]$$

$$E = E^0 + \frac{2.303 RT}{nF} \log [\text{M}^{n+}]$$

Applying $R = 8.314 \text{ J/K/mol}$, $T = 298 \text{ K}$ and $F = 96495 \text{ C}$, We get

$$E = E^0 + \frac{(0.0592/ n) \log [\text{M}^{n+}]}{\text{... (6)}}$$

This equation (6) is known as Nernst’s equation for the calculation of reduction potential.

Similarly Oxidation potential-Nernst Equation, $E = E^0 - \frac{(0.0592/ n) \log [\text{M}^{n+}]}{\text{... (7)}}$

**Significance:**

1. As the concentration of the solution $[\text{M}^{n+}]$ increases, the electrode potential also increases.
2. If temperature increases, the electrode potential also increases and vice versa.

**Applications:**

1. To study the effect of electrolyte concentration on electrode potential.
2. To calculate the electrode potential of a cell under non-standard conditions.
3. To determine unknown concentration of one of the ionic species in a cell provided standard electrode potential and concentration of other ionic species are known.
4. The pH of a solution can be calculated from the emf and Nernst equation.
5. It is used for finding the valency of an ion or the number of electrons involved in the electrode reaction.

**Corrosion:** The gradual destruction of metal/alloys due to the chemical/electrochemical reaction with the environment is called corrosion. Example: Rusting of iron.

**Consequences of corrosion:**
1. Decrease in malleability, ductility and electrical conductivity.
2. Loss of efficiency.
3. Production of toxic corrosion product.
4. Increase in maintenance and production cost.

**Methods to control corrosion:**
1. Pure material selection.
2. Alloying.
3. Cathodic protection.
4. Protective coating.

**Types of Corrosion**

**Chemical corrosion (dry corrosion):** The corrosion occurs due to the direct attack of atmospheric gases (O\(_2\), X\(_2\), SO\(_2\), H\(_2\)S,...) with the metal is called chemical corrosion.

**Electrochemical corrosion (wet corrosion):** The corrosion occurs due to the flow of electron between the anodic and cathodic areas in corrosive environment.

<table>
<thead>
<tr>
<th>Chemical corrosion</th>
<th>Electrochemical corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 It occurs in dry condition.</td>
<td>It occurs in wet condition.</td>
</tr>
<tr>
<td>2 It is a slow process.</td>
<td>It is a fast process.</td>
</tr>
<tr>
<td>3 Corrosion is uniform.</td>
<td>Corrosion is not uniform.</td>
</tr>
<tr>
<td>4 It is explained by adsorption mechanism.</td>
<td>It is explained by electrochemical reaction.</td>
</tr>
<tr>
<td>5 It involves the direct chemical on metal by environment.</td>
<td>It involves the arrangement of no of galvanic cells.</td>
</tr>
</tbody>
</table>

**Mechanism of chemical corrosion:** The corrosion occurs due to the direct attack of atmospheric gases (O\(_2\), X\(_2\), SO\(_2\), H\(_2\)S,...) with the metal is called chemical corrosion.

- At ordinary temperature the metals are slightly oxidized. However, alkali and alkaline earth metals are rapidly oxidized even at low temperature and almost all the metals (except Ag, Au and Pt) are oxidized at high temperature.

**Mechanism of corrosion:**

\[
\text{At anode: } \text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{e}^- \quad \text{(oxidation)} \\
\text{At cathode: } \frac{1}{2} \text{O}_2 + 2 \text{e}^- \rightarrow \text{O}^{2-} \quad \text{(reduction)}
\]

Net reaction: \( \text{Fe} + \frac{1}{2} \text{O}_2 \rightarrow \text{Fe}^{2+} \text{O}^{2-} \) or \( \text{FeO} \)

- Oxidation occurs first at the Fe metal surface and the resulting FeO scale.
The oxidation process continues, either by the outward diffusion of Fe metal or the inward diffusion of oxygen through the oxide scale.

Usually the outward diffusion of metal is much faster than inward diffusion of oxygen and tends to increases the corrosion.

**Corrosion by oxygen:**

\[
\begin{align*}
\text{Fe metal} & \rightarrow \text{Fe}^{2+} + 2e^- \\
\text{FeO} & \leftarrow O^2- \\
\end{align*}
\]

(anode reaction Fe $\rightarrow$ Fe$^{2+} + 2e^-$) (cathode reaction $\frac{1}{2} O_2 + 2 e^- \rightarrow O^2-$)

**Nature of Oxide film:**

1. **Stable oxide layer:** It is finely grained in structure and gets adsorbed tightly to the metal surface. This layer stops further oxygen attack through diffusion and behaves as a protective coating. Example. Oxides of Al, Sn, Pb and Cu, etc.

2. **Unstable oxide layer:** This layer mainly produced on the surface of noble metals, which decomposes back into the metal and oxygen. Example. Oxides of Pt, Ag, etc

3. **Volatile oxide layer:** The oxide layer volatilizes as soon as it is formed on the metal surface for further corrosion. Example. Molybdenum oxide.

**Pilling Bedworth Rule:**

(i) If $V_{MO} > V_M$ then the metal oxide film is protective & non-porous. Example. Al & Cu

(ii) If $V_{MO} < V_M$ then the metal oxide film is non-protective & porous. Example. Na, K & Ca.

**Pilling Bedworth Ratio:** Pilling – Bedworth Ratio = Volume of MO formed / volume of M consumed

- Iron corrodes faster than Al, even though iron is placed below Al in the electrochemical series. This is because Al forms a non-porous and protective film ($Al_2O_3$) on its surface and this film prevents the further corrosion.

**Corrosion by Cl$_2$:**

- The extent of corrosion is depends on the chemical affinity between the metal and the gas involved.

- The AgCl layer formed on the Ag metal is stable and non-porous, hence it prevents further corrosion. $\text{Ag} + \text{Cl}_2 \rightarrow \text{AgCl}$

- The SnCl$_4$ layer formed on the Sn metal is volatile, hence it leads to further corrosion. $\text{Sn} + 2 \text{Cl}_2 \rightarrow \text{SnCl}_4$

**Liquid Metal corrosion:**

- The corrosion due chemical action of flowing liquid metal at high temperature on solid metal or alloy.

- This types of corrosion occurs in nuclear power plant. i.e. Liquid Na metal corrodes the Cd control rods.
Mechanism of Electrochemical reaction: The corrosion occurs due to the flow of electron between the anodic and cathodic areas in corrosive environment. This type of corrosion occurs when a metal or two dissimilar metals immersed fully or partially in an electrolyte. There are two types of mechanism proposed based on the environment, i.e. either acidic or basic/neutral.

1. **Hydrogen gas evolution type corrosion:** This type of corrosion occurs in acidic environments. Consider the Fe metal in HCl environment.

   ![Anodic and Cathodic Reaction Diagram](image)

   The following reactions occur during corrosion.
   - **At anode:** \( \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \) (oxidation)
   - **At cathode:** \( 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \) (reduction)

   **Net reaction:** \( \text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \)

   At anode Fe metal oxidizes to give \( \text{Fe}^{2+} \) ion and 2e. These liberated electrons are gained by the \( \text{H}^+ \) ions of the acid environment to carry out the reduction reaction at cathode. As a result the corrosion takes place with evolution of hydrogen gas.

2. **Absorption of oxygen type corrosion:** This type of corrosion occurs in neutral/basic environments. Consider the Fe metal in neutral solution.

   ![Anodic and Cathodic Reaction Diagram](image)

   **Net reaction:** \( \text{Fe} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{O}^2- \) (cathode reaction)

   Oxide film
The following reactions occur during corrosion.

At anode: \( \text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{e}^- \) (oxidation)

At cathode: \( \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 2 \text{OH}^- \) (reduction)

Net reaction: \( \text{Fe} + 2 \text{OH}^- \rightarrow \text{Fe(OH)}_2 \downarrow \)

- At anode Fe metal oxidizes to give Fe\(^{2+}\) ion and 2e. These liberated electrons flows from anodic to cathodic areas, through the Fe metal, where the electrons are gained by the dissolved oxygen to give hydroxide ion.
- The Fe\(^{2+}\) ion and hydroxide ion is combining to give ferrous hydroxide, which further oxidizes in excess of oxygen to form ferric hydroxide.

\[
\text{Fe(OH)}_2 + \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 4 \text{Fe(OH)}_3
\]

Factors influencing rate of corrosion:

1. **Purity of metal:** As the purity of metal decreases the rate of corrosion tremendously increases. Example: Consider the corrosion rate of Zn metal.

<table>
<thead>
<tr>
<th>% Purity</th>
<th>99.999</th>
<th>99.990</th>
<th>99.950</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion rate</td>
<td>1</td>
<td>2650</td>
<td>5000</td>
</tr>
</tbody>
</table>

2. **Physical state of the metal:**
   As the grain-size of the metal decreases the rate of corrosion is increases.

3. **Nature of the oxide film:**
   As the specific volume ratio decreases the rate of corrosion is increases. \((\text{SVR} = \frac{\text{V}_{\text{MO}}}{\text{V}_\text{M}})\)

4. **Position of the metal in emf series:** The metal placed above the hydrogen in emf series, becomes anodic and undergoes corrosion faster.

5. **Temperature:** As the temperature increases the rate of corrosion is also increases.

6. **pH:** As the pH decreases the rate of corrosion is increases.

7. **Humidity:** As the amount of humidity in the atmosphere increases, the corrosion rate is also increases.

Wet corrosion (Electrochemical corrosion):

**Galvanic corrosion:** When two different metals are in contact in presence of an electrolyte, the metal at higher potential in emf series become anode and undergoes corrosion. This is called galvanic corrosion.

![Galvanic corrosion diagram](image-url)
example: in zn – cu cell, zn behaves as anode where oxidation takes place and corrosion occurs; and cu behaves as cathode and it is protected from corrosion.

- bolt and nuts made of the same metal is preferred in practice to avoid galvanic corrosion.
- a steel screw in a brass marine hardware corrodes due to galvanic corrosion. iron has larger negative reduction potential than that of brass. hence it become anodic and is attacked and corroded.

pitting corrosion: it is a non-uniform corrosion resulting from a localized accelerated attack and results in the formation of pits, cavities and pin-holes in the metal. example: consider a drop of water on the surface of fe metal. the metal surface covered by the drop of water has low oxygen concentration and become anode and suffers corrosion where as the uncovered metal surface has high oxygen concentration and become cathode.

![cathode drop of water anode Fe metal](image)

the following reactions occur during pitting corrosion.

at anode: \( \text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{e}^- \) (oxidation)

at cathode: \( \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 2 \text{OH}^- \) (reduction)

\[ \text{Fe} + 2 \text{OH}^- \rightarrow \text{Fe(OH)}_2 \rightarrow \text{Fe(OH)}_3 \]

differential aeration corrosion: when a metal rod is partly immersed into an electrolyte, the part of the rod above the water-line is more oxygenated and hence, becomes cathodic; while the lower part of rod immersed in water is less oxygenated and hence, become anodic. due to the difference in potential created, the corrosion starts at the bottom. this is called differential aeration corrosion. the following reactions occur during corrosion.

![anode Zn rod cathode electrolyte](image)

at anode: \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^- \) (oxidation)

at cathode: \( \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 2 \text{OH}^- \) (reduction)

\[ \text{Zn} + 2 \text{OH}^- \rightarrow \text{Zn(OH)}_2 \]

crevise corrosion: it is an accelerated attack at the junction of two different metals in presence of corrosive environment. crevice area has lack of oxygen; it becomes anodic and the exposed area acts as cathode. thus corrosion takes place at anode. example: bolts, nuts, rivets, etc in contact with an electrolyte.
Electrochemical protection:
Material Selection & Design of the material:

1. Selection of the metal: The selection of right type of metal is the main factor for corrosion control. Thus, noble metals are used in ornaments and in surgical instruments, as they are most resistant to corrosion.
2. Using pure metal: Pure metals have higher corrosion resistance. The rate of corrosion is more even in presence of very small amount of impurity.
3. Alloying: The corrosion resistance of metals increased by alloying. For example, Nichrome containing Ni, Cr and Fe shows excellent resistance against corrosion due to the formation of oxide layer on the surface.
4. Proper Design:
   a) When to different metals joined, galvanic corrosion will occur, but this can be avoided by choosing the two different metals which are close in the electrochemical series.
   b) Providing smaller cathodic area and larger anodic area controls corrosion.
   c) Avoiding sharp corners, bends, edges, .. in pipe lines, which avoid the corrosion.

Cathodic Protection: The method in which an article to be prevented from corrosion is forced to act as cathode is called cathodic protection.
It has two types. (i) Sacrificial anodic protection (ii) Impressed current cathodic protection.

Sacrificial Anodic Protection method:
- In this method, the metal structure (Fe) in the corrosive environment to be prevented from corrosion is connected to the more active metals like Zn ($E^0 = -0.76 \, V$), Mg ($E^0 = -2.37 \, V$), etc through an insulated wire.
• Since Mg has large negative reduction potential \( E^0 = -2.37 \text{ V} \) than that of Fe \( E^0 = -0.44 \text{ V} \), it becomes anodic and more active. Hence it undergoes corrosion by oxidation reaction and the corrosion current released is passed in opposite direction to prevent the oxidation of Fe.

• Thus the corrosion of Fe is prevented. Here the more active metal (Mg) sacrifices its life to save the cathode, so it is called sacrificial anode.

![Diagram of sacrificial anode system]

**Anode:** More active metal (Mg or Zn)

**Cathode:** The metal structure to be prevented from corrosion (Ship hull or pipeline)

**Electrolyte:** Sea water or Soil

**Applications:**
1. To protect the underground cable and pipelines from soil corrosion.
2. To prevent the formation rusty water in boilers by the insertion of Mg rods.
3. To protect the ship and boat hulls from marine corrosion.

**Impressed current cathodic protection:**

• In this method, an impressed current is applied in the opposite direction of the corrosion current to nullify it, and the corroding metal is converted from anode to cathode.
• This can be done by connecting negative terminal of the battery to the metallic structure (article) to be protected and positive terminal is connected to an inert anode (graphite, platinised titanium).
• The anode is buried in a backfill (mixture of gypsum, coke, breeze, sodium sulphate) which provides electrical contact to anode. Thus the corrosion of Fe is prevented.
Applications:
1. To protect the underground cable and pipelines from soil corrosion.
2. To prevent the transmission line towers from corrosion.

Paint: It is a mechanical dispersion of one or more pigments in a vehicle.

Requisites: i) It should possess high covering power ii) It should form a quite tough, uniform, adherent and impervious film iii) The film should not cracked on drying iv) The film should be glossy and good v) The film should be stable vi) It should spread easily to give smooth and uniform surface vii) It should be cheap and available.

Constituents & Functions:
- **Pigment:** It is the colour producing substance in the paint. It should be i) chemically inert ii) non-toxic iii) opaque and high covering power. **Examples:** White pigments – BaSO$_4$, Red – Pb$_3$O$_4$, Green – Cr$_2$O$_3$ and Black – Graphite.

- **Vehicle or drying oil or medium:** The liquid portion of the paint in which the pigment is dispersed is called vehicle. It should be i) hold the pigment particles together on the metal surface ii) to form protective film iii) to impart water repellency, durability and toughness to the film. **Examples:** Linseed oil, soyabean oil and castor oil.

- **Thinners:** The substance added to paints to reduce the viscosity of the paint is called thinner. It should be i) reduce the viscosity of the paint ii) to produce homogeneous mixture ii) to dry the film iv) to increase the penetrating power of the vehicle. **Examples:** turpentine and kerosene.

- **Driers:** The substance used to accelerate the drying of the paint film by oxidation, polymerization and condensation steps is called drier. It should be i) act as oxygen carrier. **Example:** napthalates, tungstates and borates of Pb and Mn.

- **Fillers or extenders:** The substance reduces the cost and increase the durability of the paint is called filler. It should be i) reduce the cracks on the film ii) increase the durability iii) reduce the cost of the paint.

- **Plasticizers:** The substance prevents the cracking of the film and to increase the elasticity to the film is called plasticizer. **Examples:** triphenyl phosphate and tricresyl phosphate.

- **Antiskinning agents:** The substance prevents the skinning or gelling of the paint is called antiskinning agent. **Example:** polyhydroxy phenols.

Electroplating: It is also called electro-deposition. It is the process in which the coating metal is deposited on the base metal by passing a direct current through an electrolyte, containing the soluble salt of the coating metal.

**Purpose of electroplating (Advantages):**
(i) To increase the corrosion resistance of the metal.
(ii) To increase the resistance to chemical attack and wear resistance.
(iii) To improve physical appearance and hardness.
(iv) To improve the surface properties.
(v) To increase the decorative and commercial value of the metal.

**Methods of cleaning articles before electroplating:**
- **Solvent cleaning:** The process of cleaning the metal surface from oils, greases, buffing compounds and fatty acids using organic solvents (toluene) is called solvent cleaning.
- **Alkali cleaning:** The process of removing the old paint coating from metal surfaces using trisodium phosphate and NaOH is called alkali cleaning.
- **Flame cleaning:** The process in which the metal surface is introduced into a hot flame to remove moisture and loosely adhering scales is called flame cleaning.
- **Pickling:** Pickling is the process in which the metal surface is cleaned with warm dil. H₂SO₄ or dil. HCl so that the metal surface becomes clean and smooth which will favours efficient electroplating.

**Electroplating of Copper:** It is the process in which the coating metal (Cu) is deposited on the base metal (article) by passing a direct current through an electrolyte (CuSO₄).

**Process:** The well cleaned object to be copper plated is taken as shown in the figure and the process of electroplating carried out under the following experimental condition, we find the smooth and uniform deposition of copper over the object

- Anode: Cu ; Cathode: Article to be plated
- Electrolyte: Aqueous solution of CuSO₄
- Temperature: 30 - 40°C
- Current density: 20 - 50 mA/cm³

**Reactions:**
- At cathode: Cu²⁺ + 2 e⁻ → Cu
- At anode: Cu → Cu²⁺ + 2 e⁻

**Applications of Copper plating:**
- It is used for electrical and electronic appliances, high quality decoration and highly oxidation resistant coating.
- It is used in printed circuits boards.
- It is coated at the bottom of the stainless steel cooking utensils to effect better heat transfer.

**Electroless Ni plating:** It is a technique of depositing a noble metal (Ni) on a catalytically active surface of a less noble metal (Al, Cu and Fe etc) by employing suitable reducing agents without using electrical energy.
**Principle:**

\[
\text{Metal ions} + \text{Reducing agent} \rightarrow \text{Metal} + \text{Oxidised product}
\]

(Deposited over catalytically active surface)

**Pretreatment:** The article to be electroless plated is first degreased by using organic solvent (toluene) followed by acid-treatment.

**Preparation of plating bath solution:**
- The plating bath solution is prepared in the following composition.
- Coating solution = NiCl\(_2\) solution (20 g/L)
- Reducing agent = Sodium hypophosphite (20 g/L)
- Buffer solution = Sodium acetate (10 g/L)
- Complexing agent (Exaltant) = Sodium succinate (15 g/L)
- pH = 4.5 (acidic)
- Temperature = 93°C

**Reactions:**
- At cathode: \(\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}\)
- At anode: \(\text{H}_3\text{PO}_2^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{PO}_2^- + 2 \text{H}^+ + 2 \text{e}^-\)
- Net redox reaction: \(\text{Ni}^{2+} + \text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \rightarrow \text{Ni} + \text{H}_2\text{PO}_3^- + 2 \text{H}^+\)

**Advantages of electroless Ni plating:**
- Electroless Ni deposits are free from pores and possess better corrosion resistance.
- It gives rise to harder surface with better wear resistance.

**Applications:**
- Electroless Ni-P plating is extensively used in electronic applications (e.g. knobs of hi-fi equipments)
- Electroless Ni plating finds applications in domestic as well as automotive fields (e.g. consume jewellery, car trims, tops of perfume bottles, etc)

**Advantages of Electroless plating over electroplating:**
- Does not require power source.
- It has better throwing power.
- Irregular shapes can be uniformly coated.
- It is applicable to conductors, semiconductors (e.g. plastics).
- It needs no levelers.

**QUESTION BANK**

Part – A

1. What is electrode potential?
2. What is an electrochemical cell?
3. Define reduction potential?
4. Why is salt bridge used in the construction of a cell?
5. Write the mathematical expression for Nernst’s equation for a Daniel cell.
6. Why we use NH\(_4\)NO\(_3\) or KCl for preparing salt bridges?
7. Differentiate between electrolytic cell and an electrochemical cell.
8. Give Nernst equation.
10. What are reversible cells? Give an example.
11. What are irreversible cells? Give an example.
12. Zn reacts with dil. H$_2$SO$_4$ to give H$_2$, but Ag does not. Why?
13. How electrode is potential developed?
15. What is electrochemical series?
16. What is the effect of electrolyte concentration on electrode potential?
17. A Zn rod is placed in 0.1 M ZnSO$_4$ solution at 298 K. Write the electrode reactions and calculate the potential of the electrode. $E^0_{\text{Zn}} = -0.76$ V.
18. How is the free energy change for the cell reaction is related to the cell emf.?
20. Mention the methods to control corrosion.
22. Define chemical and electrochemical corrosion.
24. Bolt and nuts made of the same is preferred in practice. Why?
25. Mention any four factors influences rate of corrosion.
27. Define Pitting corrosion.
29. How temperature and pH does affect the rate of corrosion?
30. Mention the function of a) Pigment b) antiskinning agent c) drier in a paint.

**Part – B**

1. Derive Nernst equation for single electrode potential and write its applications.
2. Explain the construction and functioning of a Daniel cell.
3. What is electrochemical series? Give its applications with suitable examples.
4. Calculate the emf of a Daniel cell at 298 K, when the concentration of ZnSO$_4$ and CuSO$_4$ are 0.001 M and 0.1 M respectively. The standard electrode potential of cell is 1.1 V.
5. Write the half – cell reactions and net cell reactions of the following cell: Zn / Zn$^{2+}$(1M)// Cu$^{2+}$(1M) / Cu. Find the emf of the above cell, given that the SRP of Zn and Cu are -0.76 V and +0.34 V.
6. What is the concentration of Ni$^{2+}$ in the cell at 25$^\circ$C, if the emf is 0.601 V? Ni / Ni$^{2+}$ ( ? )// Cu$^{2+}$(0.75 M) / Cu. Given that Standard reduction potentials of Ni and Cu are 0.25 V and 0.34 V respectively.
7. Cal. the standard free energy change of the following cell reaction: Fe$^{2+} +$ Ag$^+$ $\rightarrow$ Fe$^{3+} +$ Ag. Given that $E^0_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77$ V and $E^0_{\text{Ag}^+/\text{Ag}} = 0.80$ V.
8. Write the half cell reactions and net cell reactions for the cell: Cd / Cd$^{2+}$(0.01M)// Cu$^{2+}$(0.5 M) / Cu. The SRP of Cd and Cu are -0.4 V & 0.34 V respectively. Cal. the emf of the cell.
9. Calculate the standard electrode potential of Cu$^{2+} /$ Cu, if the electrode potential at 298 K is 0.296 V, when the concentration of Cu$^{2+}$ is 0.015 M.
10. Distinguish between chemical and electrochemical corrosion.
11. Discuss the mechanism of chemical and electrochemical corrosions.
12. Discuss the various factors affecting rate of corrosion.
13. Write a note on a) Galvanic corrosion b) Pitting corrosion c) Differential aeration corrosion
14. What is cathodic protection? Explain the techniques of sacrificial anodic protection and impressed current protection in detail.
15. Explain how material selection and design of a material controls corrosion.
16. Explain the electroplating of Copper.
17. Explain the electroless plating of Nickel.
18. What is paint? Explain its constituents with their function and example.