

# Electrochemistry

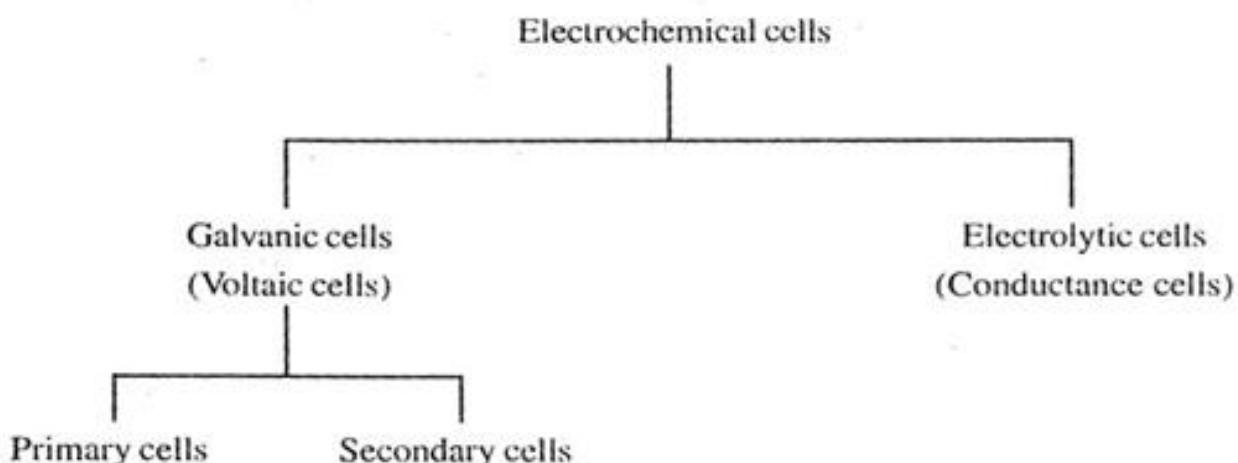
## Introduction

Electrochemistry is an important area of physical chemistry. It plays a dominant role in a vast number of fundamental and applied science such as energy storage, energy conversion, biochemistry, solid state chemistry, materials science and microelectronics. It is basically a consequence of unique combination of different features of electrochemical reactions.

In the academic tradition, electrochemistry deals with interaction between matter and electricity. In other words, it is the study of relationship that exists between chemical reactions and the flow of electricity. It involves spontaneous redox reactions that would supply electrical energy and non-spontaneous changes which are forced to occur by the passage of electricity.

## Electrochemical cells

Electrochemical cells are the devices which converts chemical energy into electrical energy or electrical energy into chemical energy by means of electrochemical redox reactions. These cells consist of two electrodes immersed in a suitable electrolyte. They are broadly classified as follows:



**Galvanic cell or voltaic cell** is a device which converts chemical energy into electrical energy. The free energy change of the redox reaction at the electrodes is transformed into electrical energy. Eg: Daniel cell, Batteries.

Galvanic cells are further classified into two types.

- Primary Cell (Irreversible):** In this, the cell reaction is not reversible. They are rechargeable. Eg: Dry cell, Zn- Ag<sub>2</sub>O cell and Zn-air battery and Li-MnO<sub>2</sub> battery.
- Secondary Cell (reversible):** In this, cell reaction is completely reversible and rechargeable. Therefore we use over and over again. These are also called as storage cells. Eg: Lead storage battery, Ni-Cd battery, Ni - Metal hydride battery & lithium ion battery.

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**Electrolytic Cell** is a device which converts electrical energy into chemical energy. Eg: Electroplating of metals, electrolysis of water.

## Definitions

**Single electrode potential:** *Single electrode potential is the potential developed at the interface between metal and its solution when it is in contact with a solution of its own ions and the two are in equilibrium with each other.* It is denoted by 'E'.

**Standard electrode potential:** *Standard electrode potential is the potential developed when the pure metal electrode is in contact with a solution of its ions of unit concentration at 298 K. If the electrode involves gas, then the gas is at 1 atmospheric pressure.* It is denoted by E°.

**Emf of a cell:** *The potential difference between the two electrodes of a cell which causes the flow of current from one electrode (high reduction potential) to the other (lower reduction electrode) is called electromotive force of the cell.* It is denoted by E<sub>cell</sub>.

$$\text{Emf of cell} = \text{Reduction potential of cathode} - \text{Reduction potential of anode}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Emf of a cell depends upon the

- 1) Nature of the metals which constitutes the two half cells.
- 2) Concentrations of solutions of 2 half cells.
- 3) Temperature.

but, Emf of cell does not depend on the size and area of the electrode.

## Construction and working of a Galvanic cell (Daniel cell)

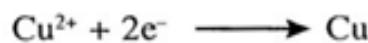
Daniel cell (fig. 1) consists of a Zn rod dipped in 1M solution of  $\text{ZnSO}_4$  forms a half cell and Cu rod dipped in 1M solution of  $\text{CuSO}_4$  forms another half cell. The two half cells are internally connected by a salt bridge (an inverted U-shaped glass tube filled with saturated KCl solution) and the two ends of the salt bridge are plugged with a porous material. The two electrodes are connected externally by a wire through voltmeter.

The two half cell reactions are represented as follows:

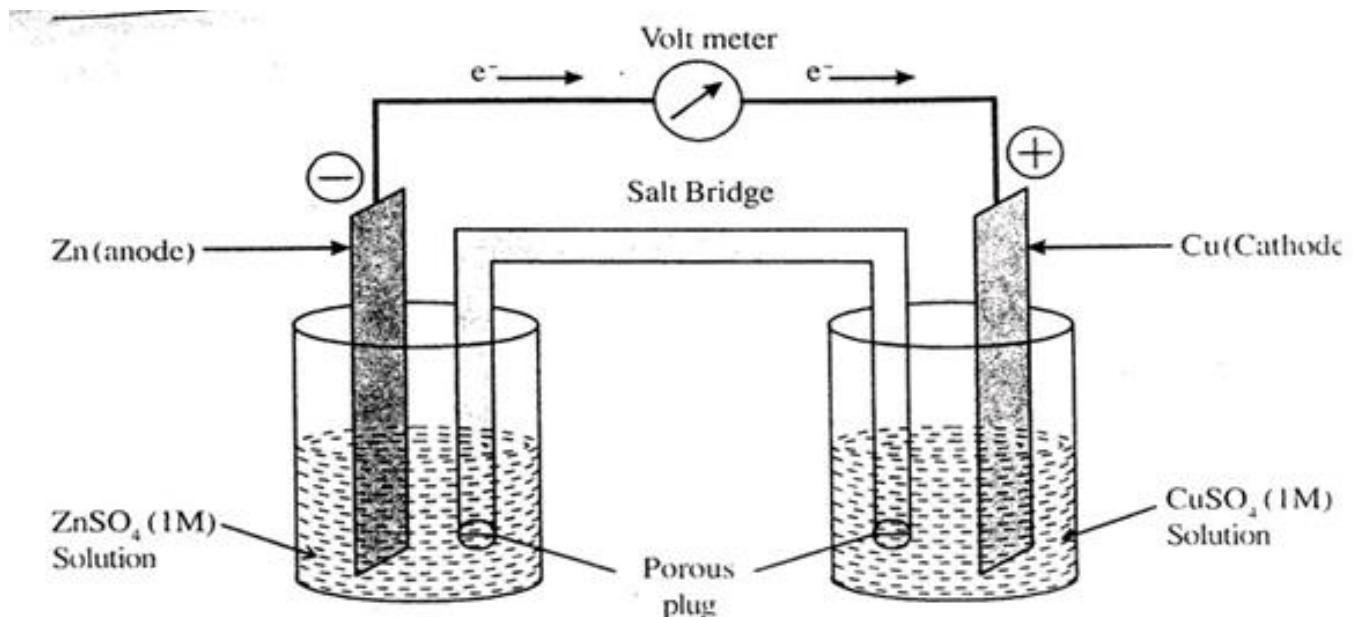
**At Anode :** Zn oxidizes to  $\text{Zn}^{2+}$  liberating two electrons.



**At Cathode:**  $\text{Cu}^{2+}$  ions reduces to Cu by accepting two electrons.



Thus the **Net cell reaction** :  $\text{Zn} + \text{Cu}^{2+}(1\text{M}) \longrightarrow \text{Zn}^{2+}(1\text{M}) + \text{Cu}$



The electron liberated at the zinc half cell builds up an electrical potential difference. i.e., electrons move from the zinc electrode (Anode) to the copper electrode (Cathode) producing a current in the circuit which is indicated by voltmeter. In the galvanic cell, the electrode where oxidation takes place is referred as anode which is assigned with a negative sign and the electrode where reduction takes place referred as cathode which is assigned with a positive sign.

## Functions of salt bridge

A salt bridge helps to,

- Bring about internal contact between the electrodes.
- To minimize liquid junction potential.
- To maintain electrical neutrality
- To minimize polarization.

## Electrochemical conventions

1. There are two electrodes in galvanic cell. Each of these electrodes is referred to as half cell.
2. If reduction occurs at an electrode, it is called a reduction (positive) electrode or cathode. If oxidation occurs at an electrode, it is called an oxidation (negative) electrode or anode.
3. The potential of an electrode is always expressed as reduction potential and is represented as  $E_{M^{n+}/M}$
4. The electrode at which oxidation occurs (anode) is written on the LHS and the electrode at which reduction occurs (cathode) is written on the RHS.
5. The electrode on the left (anode) is written by writing the metal first and then the electrolytic solution. For example,  $Zn|ZnSO_4$
6. The electrode on the right (cathode) is written by writing the electrolytic solution first and then the metal. For example,  $CuSO_4|Cu$ .
7. The single vertical line indicates the phase boundary between the metal and the electrolytic solution and double vertical line indicates the salt bridge.
8. The concentration of corresponding electrolytic solutions is represented in the parenthesis. The arrow mark indicates the direction of flow of electrons i.e., from anode to cathode.

For example, a Daniel cell can be represented as:



9. The EMF of a cell is given by

$$E_{cell} = E_{Cathode} - E_{Anode} \quad \text{or} \quad E_{cell} = E_C - E_A$$

where  $E_C$  and  $E_A$  are the reduction electrode potentials of Cathode and Anode respectively.

## Derivation of Nernst equation for single electrode potential

NOT IN THE SYLLABUS

Nernst derived a thermodynamic equation which relates the change in free energy ( $\Delta G$ ), electrode potential (E) and the concentration of metal ions ( $M^{n+}$ ). He considered a reduction reaction of the type.



The change in the free energy for spontaneous reaction is related to equilibrium constant (K) by Van't Hoff equation:

$$\Delta G = \Delta G^0 + RT \ln K \quad \text{NOT IN THE SYLLABUS} \quad \dots\dots (1)$$

Where  $\Delta G$  is the free energy change,  $\Delta G^0$  is the std. free energy change

R is the Universal gas constant, T is the absolute temperature and K is the equilibrium constant. Equilibrium constant for the reduction reaction of the type,  $M^{n+} + ne^- \rightarrow M$  is given by,

$$K = \frac{[M]}{[M^{n+}]} \quad \text{NOT IN THE SYLLABUS} \quad \dots\dots (2)$$

For a spontaneous reaction, decrease in the free energy ( $-\Delta G$ ) is the maximum amount of work and is given by

$$-\Delta G = W_{\max} \quad \dots\dots (3)$$

But the maximum amount of work done for an electrochemical reaction depends on the number of coulombs of electricity that flow and the energy available per coulomb.

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$$\text{i.e., } W_{\max} = nFE \quad \dots\dots (4)$$

Where. n = number of moles of electrons involved in the reaction.

F = Faraday's constant E = Electrode potential

Then. The relationship between free energy change ( $\Delta G$ ) and electrode potential (E) is given by

$$\Delta G = -nFE \quad \dots\dots (5)$$

Under standard conditions,

NOT IN THE SYLLABUS

$$\Delta G^0 = -nFE^0 \quad \dots\dots (6)$$

On substituting (2), (5), (6) in (1), we get

$$-nFE = -nFE^0 + RT \ln \frac{[M]}{[M^{n+}]} \quad \dots\dots (7)$$

Divide equation (7) by  $-nF$ , on both sides and converting natural logarithm to the base 10.

We get

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[M]}{[M^{n+}]} \quad \dots\dots (8)$$

Under standard conditions  $[M] = 1$ , hence the above equation reduces to

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[I]}{[M^{n+}]} \quad \text{NOT IN THE SYLLABUS}$$

$$E = E^{\circ} + \frac{2.303RT}{nF} \log [M^{n+}] \quad \dots\dots (9)$$

On substituting the values for

$$R = 8.314 \text{ J/K/mol}$$

$$T = 298 \text{ K}$$

$F = 96500 \text{ C/mol}$ , the above equation reduces to

$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$

**NOT IN THE SYLLABUS**  $\dots\dots (10)$

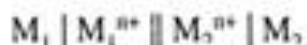
The above equation (10) is known as the Nernst equation for single electrode potential.

## Application of Nernst equation

- The potential of an electrode and EMF of a cell can be calculated at any temperature and concentration.
- Knowing potential of an electrode, the concentration of the electrolyte can be calculated.

**NOTE :** Nernst equation for a cell

Let us consider a cell,



Which is obtained by connecting two half cells

The net cell reaction is given as



The emf of the cell is

$$E_{cell} = E_{cell}^0 + \frac{2.303 RT}{n F} \log \frac{[\text{Metal ion concentration at cathode}]}{[\text{Metal ion concentration at anode}]}$$

$$E_{cell} = E_{cell}^0 + \frac{2.303 RT}{n F} \log \frac{[M_2^{n+}]}{[M_1^{n+}]}$$

$$E_{cell} = E_{cell}^0 + \frac{0.0591}{n} \log \frac{[M_2^{n+}]}{[M_1^{n+}]}$$

$$E_{cell}^0 = E_{cathode}^0 - E_{anode}^0 = E_{M_2^{n+}/M_2}^0 - E_{M_1^{n+}/M_1}^0$$

where,  $[M_i^{n+}]$  = The metal ion concentration at Anode

$[M_j^{n+}]$  = The metal ion concentration at Cathode

For Daniel cell,

$$E_{cell} = E_{cell}^0 + \frac{0.0591}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} \quad \text{Where, } E_{cell}^0 = E_{\text{Cu}^{2+}/\text{Zn}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0$$

- 1. Calculate the standard electrode potential of  $\text{Cu}^{2+}/\text{Cu}$  if its electrode potential at  $25^\circ\text{C}$  is  $0.296\text{V}$  when  $[\text{Cu}^{2+}] = 0.015$**  [VTU, June, 2008]

**Solution :**

$$E = E^\circ + \frac{0.0591}{n} \log [\text{M}^{n+}]$$

$$E^\circ = E - \frac{0.0591}{n} \log [\text{Cu}^{2+}]$$

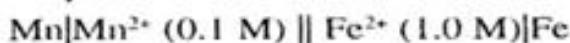
$$E^\circ = 0.296 - \frac{0.0591}{n} \log (0.015)$$

$$E^\circ = 0.349\text{V}$$

- 2. Calculate the voltage generated in the following cell  $\text{Mn}/\text{Mn}^{2+} \parallel \text{Fe}^{2+}/\text{Fe}$  when iron rod is immersed in  $1.0\text{M}$   $\text{FeSO}_4$  solution and Mn rod is immersed in  $0.1\text{M}$   $\text{MnSO}_4$  solution. Given  $E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.40\text{ V}$  and  $E_{\text{Mn}^{2+}/\text{Mn}}^\circ = -1.18\text{ volt}$ . [Feb, 2001]**

**Solution :**

(i) Cell representation :



(ii) Electrode reactions :



(iii) The emf of the cell is

$$E_{\text{cell}} = E_{\text{cell}}^\circ + \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{Mn}^{2+}]}$$

$$E_{\text{cell}} = (E_{\text{Fe}^{2+}/\text{Fe}}^\circ - E_{\text{Mn}^{2+}/\text{Mn}}^\circ) + \frac{0.0591}{2} \log \frac{1.0}{0.1}$$

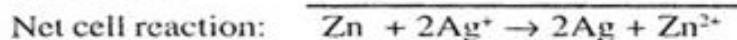
$$= [-0.40 - (-1.18)] + 0.02955 \times \log (10) = 0.78 + 0.02955 \times 1$$

$$E_{\text{cell}} = 0.8095\text{ V}$$

3. Calculate the potential of Ag-Zn cell at 298K if the concentration of  $\text{Ag}^+$  and  $\text{Zn}^{2+}$  are  $5.2 \times 10^{-6} \text{ M}$  and  $1.3 \times 10^{-3} \text{ M}$  respectively.  $E^\circ$  of the cell at 298K is 1.56V. Calculate the change in free energy  $\Delta G$  for the reduction of 1mole of  $\text{Ag}^+$ . [July, 2006]

*Solution :*

We know from electrochemical series that,  $E_{\text{Ag}^+/\text{Ag}}^\circ > E_{\text{Zn}^{2+}/\text{Zn}}^\circ$  so Zn becomes anode and Ag become cathode.



$$\therefore E_{\text{cell}} = E_{\text{cell}}^\circ + \frac{0.0591}{n} \log \frac{[\text{Ag}^+]^2}{[\text{Zn}^{2+}]}$$

$$= 1.56 + \frac{0.0591}{2} \log \frac{[5.2 \times 10^{-6}]^2}{[1.3 \times 10^{-3}]}$$

$$= 1.56 + 0.02955 \log [20.8 \times 10^{-9}]$$

$$= 1.56 + [0.02955 \times -7.6819]$$

$$= 1.56 - 0.2270$$

$$E_{\text{cell}} = 1.3329 \text{ V}$$

$$\Delta G = -nFE$$

$$= -1 \times 1.3329 \times 96.500 \text{ for 1 mole of } \text{Ag}^*$$

$$\Delta G = -128.62 \text{ kJ/mol}$$

4. Calculate the potential of Ag-Cu cell at 298K if the concentration of  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  are  $4.2 \times 10^{-6} \text{ M}$  and  $1.3 \times 10^{-3} \text{ M}$  respectively. Given  $E_{\text{Ag}^+/\text{Ag}}^\circ = 0.80 \text{ V}$ ,  $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.34 \text{ V}$  of the cell at 298K. Calculate the change in free energy  $\Delta G$  for the reduction of 1mole of  $\text{Ag}^+$ .

[Jan, 2004]

*Solution :*



$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Ag}^+]^2}{[\text{Cu}^{2+}]} \\
 &= (0.80 - 0.34) + \frac{0.0591}{2} \log \frac{[4.2 \times 10^{-6}]^2}{[1.3 \times 10^{-3}]} \\
 &= 0.46 + 0.02955 \log [13.56 \times 10^{-9}] \\
 &= 0.46 + [0.02955 \times -7.867] \\
 &= 0.46 - 0.2324 \\
 \mathbf{E}_{\text{cell}} &= \mathbf{0.2275 \text{ V}} \\
 \Delta G &= -nEF \\
 &= -1 \times 0.2275 \times 96.5 \text{ for 1 mole of Ag}^* \\
 \Delta G &= -21.95 \text{ kJ / mol}
 \end{aligned}$$

5. The  $E^{\circ}$  values of  $\text{Li}^+/\text{Li}$ ,  $\text{Zn}^{2+}/\text{Zn}$ ,  $\text{Cu}^{2+}/\text{Cu}$  and  $\text{Ag}^+/\text{Ag}$  are  $-3.0\text{V}$ ,  $-0.76\text{V}$ ,  $+0.34\text{V}$ , and  $+0.80\text{ Volts}$  respectively. Which combination of the electrodes you use to construct a cell of highest emf, if the ionic concentrations are  $0.1\text{M}$ ,  $1.0\text{M}$ ,  $10\text{M}$  and  $0.01\text{M}$  in the same order. Justify your answer. [July, 2005]

*Solution :*

The potential of a half cell is

$$E = E^{\circ} + \frac{0.0591}{n} \log [\text{M}^{n+}]$$

- i) For  $\text{Li}^+/\text{Li}$ , the electrode potential is

$$\begin{aligned}
 E &= -3.0 + \frac{0.0591}{1} \log (0.1) \\
 &= -3.0 + [0.0591 \times -1] = -3.0591 \text{ V}
 \end{aligned}$$

- ii) For  $\text{Zn}^{2+}/\text{Zn}$ , the electrode potential is

$$\begin{aligned}
 E &= -0.76 + \frac{0.0591}{2} \log (1.0) \\
 &= -0.76 \text{ V}
 \end{aligned}$$

- iii) For  $\text{Cu}^{2+}/\text{Cu}$ , the electrode potential is

$$\begin{aligned}
 E &= 0.34 + \frac{0.0591}{2} \log (10.0) = 0.34 + 0.02955 \times 1 \\
 &= 0.3695 \text{ V}
 \end{aligned}$$

iv) For  $\text{Ag}^+/\text{Ag}$ , the electrode potential is

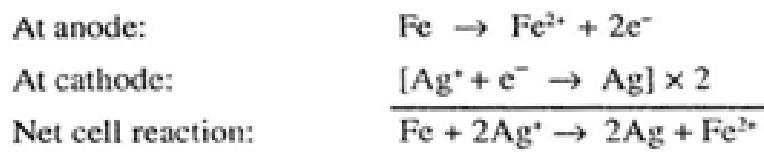
$$\begin{aligned} E &= 0.80 + \frac{0.0591}{1} \log(0.01) \\ &= 0.80 + [0.0591 \times -2] \\ &= 0.80 - 0.1182 \\ &= \mathbf{0.6818 \text{ V}} \end{aligned}$$

From the above E values, if we couple  $\text{Ag}^+/\text{Ag}$  (as cathode) and  $\text{Li}^+/\text{Li}$  (as an anode) the cell generates highest emf.

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ E_{\text{cell}} &= E_{\text{Ag}^+/\text{Ag}} - E_{\text{Li}^+/\text{Li}} = 0.6818 - [-3.0591] \\ &= 0.6818 + 3.0591 \\ E_{\text{cell}} &= \mathbf{3.7409 \text{ V}} \end{aligned}$$

6. Calculate the emf of the cell  $\text{Fe}/\text{Fe}^{2+} (0.01 \text{ M}) // \text{Ag}^+ (0.1 \text{ M})/\text{Ag}$  at 298K, if SRP of Fe and Ag are  $-0.42$  and  $0.8 \text{ V}$  respectively. [VTU, Jan 2008]

*Solution :*



$$E_{\text{cell}} = E_{\text{cell}}^\circ + \frac{0.0591}{n} \log \frac{[\text{Ag}^+]^2}{[\text{Fe}^{2+}]}$$

$$\begin{aligned} E_{\text{cell}} &= (E_{\text{Ag}^+/\text{Ag}} - E_{\text{Fe}^{2+}/\text{Fe}}) + \frac{0.0591}{2} \log \frac{[0.1]^2}{[0.01]} \\ &= [0.8 - (-0.42)] + 0.02955 \log(1) = 1.22 + 0 \\ E_{\text{cell}} &= \mathbf{1.22 \text{ V}} \end{aligned}$$

7. Calculate the voltage of a cell which consists of a iron rod immersed in a 1M solution of  $\text{FeSO}_4$  and manganese rod immersed in a 0.1M solution of  $\text{MnSO}_4$  at 25°C. Write the cell reaction. Given  $E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44 \text{ V}$  and  $E_{\text{Mn}^{2+}/\text{Mn}}^\circ = -1.18 \text{ V}$ .

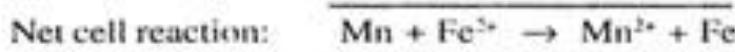
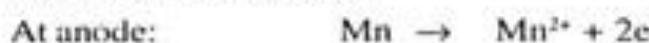
[VTU, July 2011]

**Solution :**

(i) Cell representation :



(ii) Electrode reactions :



(iii) The emf of the cell is :

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.0591}{n} \log \left[ \frac{\text{Fe}^{2+}}{\text{Mn}^{2+}} \right]$$

$$\begin{aligned} E_{\text{cell}} &= (E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} - E_{\text{Mn}^{2+}/\text{Mn}}^{\circ}) + \frac{0.0591}{2} \log \frac{1.0}{0.1} \\ &= [-0.44 - (-1.18)] + 0.02955 = 0.74 + 0.02955 \\ E_{\text{cell}} &= 0.7696 \text{ V} \end{aligned}$$

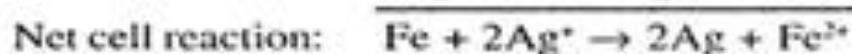
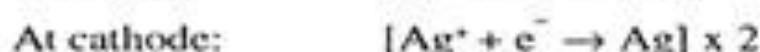
8. An electrochemical cell consists of an iron electrode, dipped in 0.1M  $\text{FeSO}_4$  and silver electrode dipped in 0.05M  $\text{AgNO}_3$  solution. Write cell representation, cell reaction and calculate the emf of the cell at 298K. Given SRP of Fe and Ag are -0.44 and +0.8V respectively.[VTU, Jan 2011]

**Solution:**

(i) Cell representation :



(ii) Electrode reactions :



(iii) The emf of the cell is

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.0591}{n} \log \left[ \frac{[\text{Ag}^+]^2}{[\text{Fe}^{2+}]} \right]$$

$$E_{\text{cell}} = (E_{\text{Ag}^+/\text{Ag}}^{\circ} - E_{\text{Fe}^{2+}/\text{Fe}}^{\circ}) + \frac{0.0591}{2} \log \frac{[0.05]^2}{[0.1]}$$

$$= [0.8 - (-0.44)] + 0.02955 \log (0.025) = 1.24 - 0.0473$$

$$E_{\text{cell}} = 1.1927 \text{ V}$$

9. A galvanic cell is constructed by coupling Ag and Cd electrodes dipped in 0.5M  $\text{AgNO}_3$  and 0.25M  $\text{CdSO}_4$  respectively at 25°C. Write the cell scheme, cell reaction and calculate emf of the cell. Given SRP of Ag and Cd are 0.80 and -0.40V respectively.

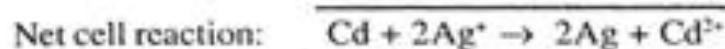
[VTU, June 2010]

*Solution:*

- (i) Cell representation:



- (ii) Electrode reactions:



- (iii) The emf of the cell is

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Ag}^+]^2}{[\text{Cd}^{2+}]}$$

$$E_{\text{cell}} = (E_{\text{Ag}^+/\text{Ag}}^{\circ} - E_{\text{Cd}^{2+}/\text{Cd}}^{\circ}) + \frac{0.0591}{2} \log \frac{[0.5]^2}{[0.25]}$$

$$= [0.8 - (-0.40)] + 0.02955 \times \log 1 = 1.2 + 0$$

$$E_{\text{cell}} = 1.2 \text{ V}$$

10. An electro chemical cell is formed from Ni and Pb electrodes having 0.01 M  $\text{NiSO}_4$  and 0.5M  $\text{PbSO}_4$  electrolytes. The standard electrode potentials of Ni and Pb electrodes are -0.24V and -0.13V respectively. Write the cell scheme, cell reaction and calculate emf of the cell at 298K.

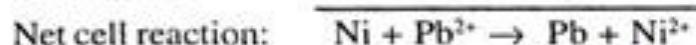
[VTU, Jan 2012]

*Solution:*

- (i) Cell representation :



- (ii) Electrode reactions:



(iii) The emf of the cell is,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} + \frac{0.0591}{n} \log \left[ \frac{[\text{Pb}^{2+}]}{[\text{Ni}^{2+}]} \right]$$

$$E_{\text{cell}} = (E_{\text{Pb}^{2+}/\text{Pb}}^{\circ} - E_{\text{Ni}^{2+}/\text{Ni}}^{\circ}) + \frac{0.0591}{2} \log \frac{[0.5]}{[0.01]}$$

$$= [-0.13 - (-0.24)] + 0.02955 \log 50 = 0.11 + 0.050$$

$$E_{\text{cell}} = 0.16 \text{ V}$$

### Types of electrodes

The following are the six important types of electrode:

- 1) **Metal-Metal ion electrodes:** These are the electrodes where a metal is dipped in a solution containing its own ions. Eg: Cu|CuSO<sub>4</sub>, Zn|ZnSO<sub>4</sub>.
- 2) **Gas electrodes:** These are the electrodes where a gas is in contact with an inert metal like Pt foil which is dipped in an ionic solution of gas molecules. Eg: Hydrogen electrode.
- 3) **Metal-Metal Insoluble salt electrodes:** These are the electrodes where a metal will be in contact with an insoluble salt of the same metal dipped in a solution containing anions of the salt.  
Eg: Calomel electrode (Hg|Hg<sub>2</sub>Cl<sub>2</sub>|Cl<sup>-</sup>), Silver-silver chloride electrode (Ag|AgCl|Cl<sup>-</sup>).
- 4) **Ion selective electrodes:** These are the electrodes which are sensitive to particular ionic species and will develop a potential when a membrane is in contact with an ionic solution. Eg: Glass membrane electrode
- 5) **Redox electrodes:** These are the electrodes, where the inert metal like Pt will be in contact with oxidized and reduced forms of the same metal in solution. The electrode potential arises due to the presence of both oxidized and reduced species of the same metal at an inert electrode like Pt. Eg: Pt/Fe<sup>2+</sup>;Fe<sup>3+</sup>, Pt/Cr<sup>3+</sup>;Cr<sup>6+</sup>, Pt/Sn<sup>2+</sup>;Sn<sup>4+</sup>
- 6) **Amalgum electrode:** An amalgum electrode is a modification of metal-metal ion electrode. Amalgum is the alloy of any metal with mercury. In place of a metal, its solution in mercury is used. Eg. Zinc amalgam electrode Zn (Hg)| ZnSO<sub>4</sub>.

### Reference electrodes

*Reference electrodes are those electrodes which have constant reduction potential and which are used to determine the electrode potential of other electrodes.* There are two types of reference electrodes.

1. Primary reference electrode. Eg: Standard hydrogen electrode (SHE).
2. Secondary reference electrode. Eg: Calomel electrode, Silver-Silver Chloride electrode.

### **Limitation of primary reference electrode**

1. It is difficult to construct hydrogen electrode.
2. It is difficult to maintain  $H^+$  ion concentration at 1M.
3. It is difficult to maintain constant pressure (1 atm) of the  $H_2$  gas.
4.  $H_2$  gas should be pure. If any impurities present in the  $H_2$  gas, the Pt electrode becomes inactive.
5. It cannot be used in the presence of strong oxidising and reducing agents.
6. Presence of arsenic compounds would poison the Pt foil.

**Secondary reference electrodes :** *These are the type of electrodes whose reduction potential remains constant and their potential is measured w.r.t SHE and can be used as reference electrode for measuring potential of other electrodes and for various analytical analysis.*

### **Requirement of secondary reference electrodes**

1. It should be portable.
2. It should not be bulky.
3. It should not be easily poisoned by the impurities.
4. Its electrode potential should not change even with change in pH of the solution.

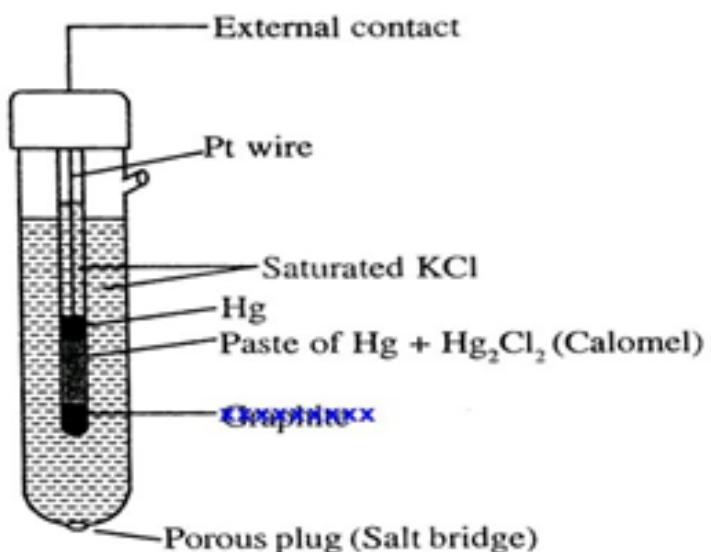
**Secondary reference electrodes :** *These are the type of electrodes whose reduction potential remains constant and their potential is measured w.r.t SHE and can be used as reference electrode for measuring potential of other electrodes and for various analytical analysis.*

### **Requirement of secondary reference electrodes**

1. It should be portable.
2. It should not be bulky.
3. It should not be easily poisoned by the impurities.
4. Its electrode potential should not change even with change in pH of the solution.

### **Construction and working of calomel electrode**

**Construction:** Calomel electrode is a metal-metal insoluble salt electrode. Dipping type calomel electrode is shown in figure 2. It consists of a two glass tubes. ~~xxxxxxxxxxxxxxxxxxxx~~ the bottom of the inner glass tube covered with paste of Hg and mercurous chloride (calomel) and above which mercury is placed. The remaining portion of both inner and outer tube is filled with saturated KCl solution. A platinum wire is dipped in the inner tube and is used to provide external electrical contact. The porous plug at the bottom of the outer tube acts as a salt bridge.



The calomel electrode is represented as :



**Working :** Calomel Electrode can act as anode or cathode depending on the nature of the other electrode.

- a) When it act as anode the electrode reaction is



- b) When it act as cathode the electrode reaction is



The electrode potential is given by

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

From the above equation it is clear that as the concentration of  $\text{Cl}^-$  ion increases, the electrode potential decreases. The electrode potential depends on the concentration of chloride ions and the electrode is reversible with respect to chloride ions. At 298K, the electrode potentials are as follows.

KCl concentration	0.1N	1N	Saturated
Electrode potential (V)	0.3334	0.2810	0.2422

### Advantages

- 1) Calomel electrode is easy to construct and portable
- 2) Cell potential is reproducible.
- 3) Potential is stable over a long period.
- 4) It can be used in the presence of strong oxidizing agent.

### Applications

- 1) It is used as a secondary reference electrode in the measurement of electrode potential of other electrodes.
- 2) It is used as reference electrode in all potentiometric titrations.
- 3) It is used as reference electrode with glass membrane electrode in pH determination.

## Measurement of standard electrode potential using calomel electrode

Eg: Determination of std. electrode potential of zinc electrode

To measure the standard electrode potential of Zn electrode it has to be coupled with calomel electrode. The emf of the cell is determined using an electronic voltmeter (figure 4).

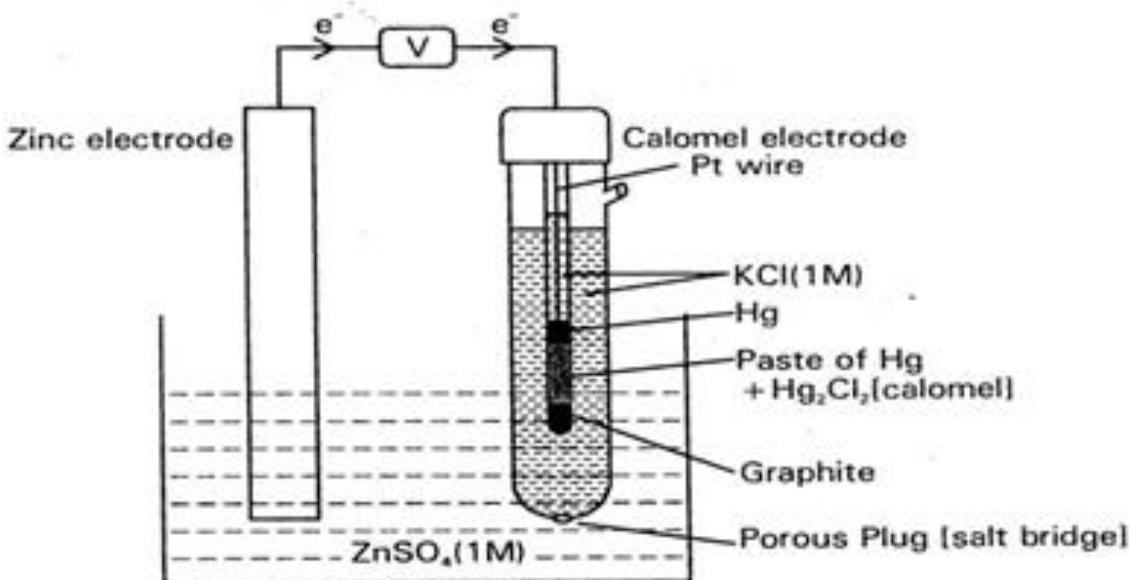


Figure 4. Zinc-calomel electrode cell.

Cell representation



The electrode reactions are:



### b) Assigning sign on electrode

When the two electrodes are connected to voltmeter direction of the current indicates sign of the electrode. In case of Zn electrode it takes negative sign and is assigned as anode. Calomel electrode takes positive sign and assigned as cathode.

### c) Calculation

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{Zn}^{2+}/\text{Zn}}$$

The emf of the cell was found to be 1.040 V.

$E_{\text{calomel}}$  is 0.2810 V for 1N KCl solution.

Therefore,  $1.040 = 0.2810 - E_{\text{Zn}^{2+}/\text{Zn}}$

$$E_{\text{Zn}^{2+}/\text{Zn}} = -0.759 \text{ V} \equiv -0.76 \text{ V} = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

[because  $[\text{Zn}^{2+}] = 1 \text{ M}$ ]

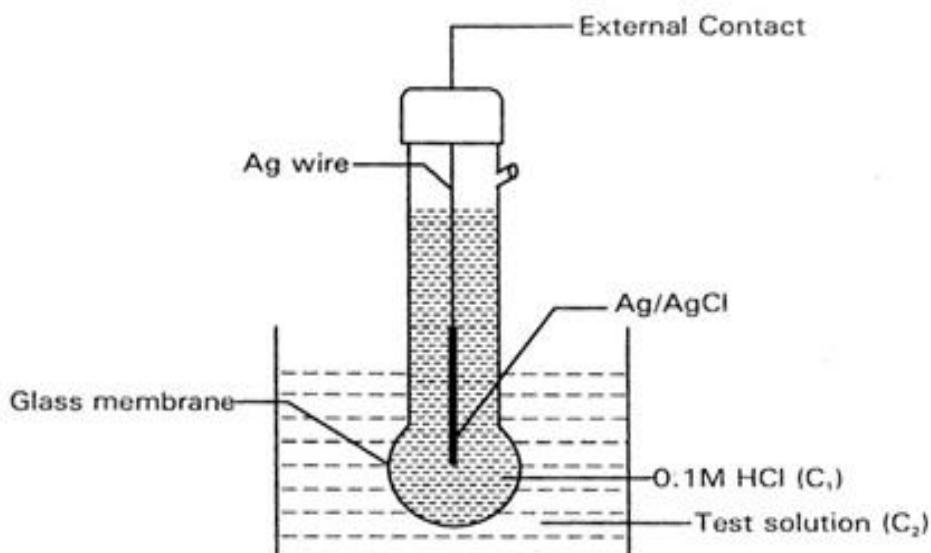
### Ion selective electrodes

*Ion selective electrodes are the electrodes which are sensitive to certain specific ions present in the solution and they develop the potential with respect to that species.* Eg: Glass membrane electrode.

Glass membrane electrode is an ion selective electrode in which a thin membrane present is permeable only to  $\text{H}^+$  ions and not to other ions in the solution. It develops the potential if any change in the  $\text{H}^+$  ion concentration.

### Construction and working of a glass membrane electrode

**Construction:** A typical glass membrane electrode is shown in the figure 5. It consists of a long glass tube with a thin walled (0.01-0.03 mm) bulb at the bottom. This is made up of special corning glass of relatively high electrical conductivity, low melting point and high hygroscopic in nature. The approximate composition of glass membrane is 72%  $\text{SiO}_2$ , 22%  $\text{Na}_2\text{O}$  and 6%  $\text{CaO}$ . It specifically allows only  $\text{H}^+$  ions upto a pH range from 1 to 9. The bulb is filled with 0.1M HCl in which a silver silver chloride electrode is dipped as an internal reference electrode and is connected for external electrical contact.



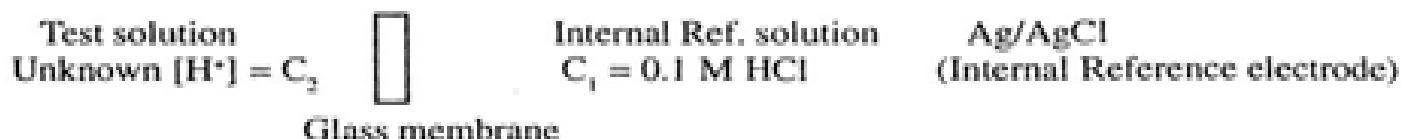
The glass membrane electrode is represented as:



**Working:** When the glass membrane electrode is dipped in the test solution, the  $\text{Na}^+$  ions of the glass membrane is exchanged with  $\text{H}^+$  ions of the test solution.



It can be represented as follows:



Test solution whose concentration is  $C_2$ , and correspondingly it exhibit electrode potential,  $E_2$ , and internal reference solution whose concentration is  $C_1$ , and correspondingly it exhibit electrode potential  $E_1$ . The exchange of ions by the inner and outer membrane gives rise to a boundary potential ( $E_b$ ).

### Determination of boundary potential ( $E_b$ ) & electrode potential of glass membrane electrode ( $E_G$ )

When a thin walled glass tube containing 0.1M HCl solution is immersed in test solution, potential developed across the glass membrane at the interface is called boundary potential.

$$E_b = E_2 - E_1$$

$E_b$  is related to difference in the  $\text{H}^+$  ion concentration of two solutions.

$$E_b = E_2 - E_1 = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

$$E_b = \frac{2.303RT}{nF} \log C_2 - \frac{2.303RT}{nF} \log C_1$$

$$E_b = L + \frac{2.303RT}{nF} \log C_2 \quad \text{where } L = -\frac{2.303RT}{nF} \log C_1$$

Since  $C_2$  is the unknown hydrogen ion concentration we can write

$$E_b = L + \frac{2.303RT}{nF} \log [\text{H}^+]$$

On substituting the values for R, T & F

$$E_b = L + 0.0591 \log [\text{H}^+]$$

since  $n = 1$

$$\boxed{E_b = L - 0.0591 \text{ pH}}$$

since  $\text{pH} = -\log [\text{H}^+]$

It is found that the potential of the glass membrane electrode  $E_G$  has three components:

It is found that the potential of the glass membrane electrode  $E_G$  has three components:

- i)  $E_b$ , boundary potential.
- ii) Potential of the internal reference electrode ( $\text{Ag}/\text{AgCl}$ ) i.e.,  $E_{\text{Ag}/\text{AgCl}}$
- iii) Asymmetric potential  $E_{\text{assy}}$  (This potential arises due to the difference in response of the inner and outer surface of the glass bulb to the change in  $\text{H}^+$  ion activity and strain in the inside and outside the electrode bulb)

Therefore, 
$$E_G = E_b + E_{\text{Ag}/\text{AgCl}} + E_{\text{assy}} \quad \dots\dots (1)$$

Substitute for  $E_b$  in equation (1) becomes,

$$\begin{aligned} E_G &= (L - 0.0591 \text{ pH}) + E_{\text{Ag}/\text{AgCl}} + E_{\text{assy}} \\ \boxed{E_G &= E^0_G - 0.0591 \text{ pH}} \end{aligned} \quad \dots\dots (2)$$

Where  $E^0_G = L + E_{\text{Ag}/\text{AgCl}} + E_{\text{assy}}$ .  $E^0_G$  is the combination of 3 constant terms.

## Advantages and disadvantages of glass membrane electrode

### Advantages

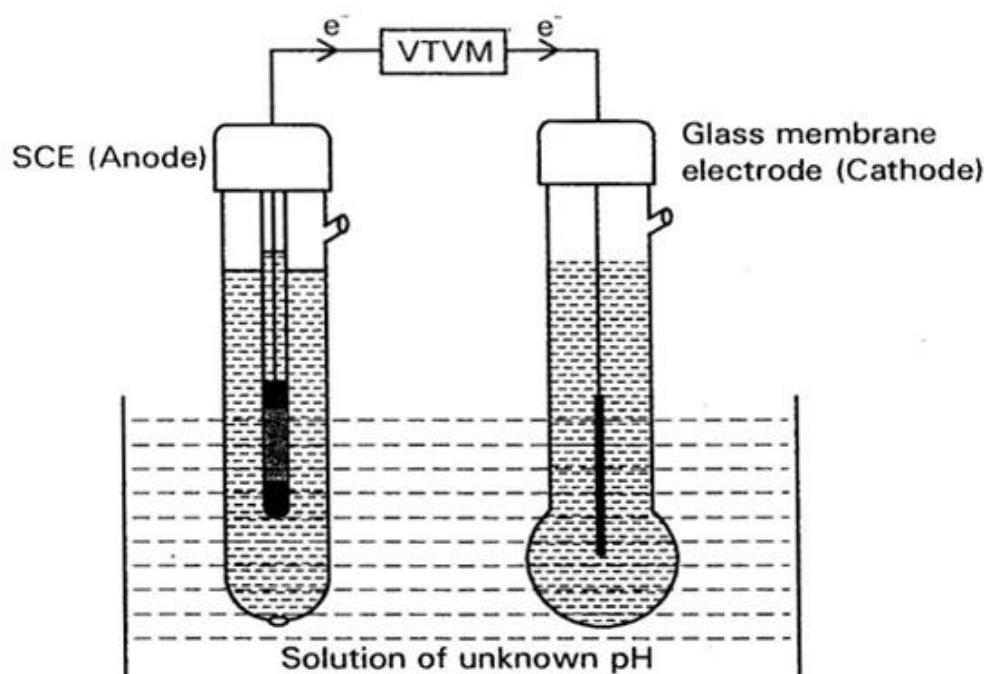
- a) Accurate results are obtained between pH range 1 – 9.
- b) The glass membrane electrode does not get poisoned.
- c) It can be used in the presence of oxidizing and reducing agents.
- d) Glass electrodes are portable and easy to operate.
- e) Equilibrium is attained rapidly.
- f) It can be used for colored, turbid and colloidal solutions.
- g) It does not require the use of salt bridge.

### Disadvantages

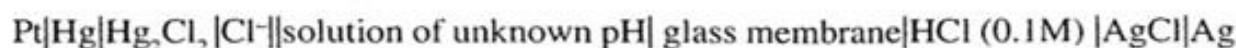
- a) Glass electrode cannot be used in presence of fluoride ions.
- b) Glass electrodes are very thin and fragile, should be handled with care.
- c) It requires special glass membrane for solutions of pH less than 0.5 and more than 10.
- d) Glass membrane has high internal resistance; ordinary potentiometer is not employed and hence requires vacuum tube voltmeter (VTVM). This is relatively costlier when compared to ordinary potentiometers.

## Method to measure pH of unknown solution using glass membrane electrode

To determine the pH of the given unknown solution, the glass membrane electrode is combined with saturated calomel electrode (SCE) and both the electrodes should be immersed in the test solution (figure 6). The emf of the cell is measured using electronic voltmeter-VTVM (vacuum tube voltmeter). By convention glass membrane electrode is taken as cathode and SCE as the anode.



The cell assembly is represented as:



The emf of the cell is given by

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_G - E_{\text{SCE}}$$

$$E_{\text{cell}} = (E_G^0 - 0.0591 \text{ pH}) - E_{\text{SCE}} \quad (\text{Where } E_G = E_G^0 - 0.0591 \text{ pH})$$

$$\boxed{\text{pH} = \frac{E_G^0 - E_{\text{SCE}} - E_{\text{cell}}}{0.0591}}$$

$E_G^0$  value is calculated by dipping the glass membrane electrode in a solution of known pH and measuring the emf of the cell when combined with a calomel electrode.

### Concentration cells

A concentration cell is a galvanic cell which generates electrical energy at the expense of chemical energy. In concentration cells, electrode and electrolyte present in both half cells are same but the concentration of electrode or electrolyte is different. Concentration cells are classified into two types:

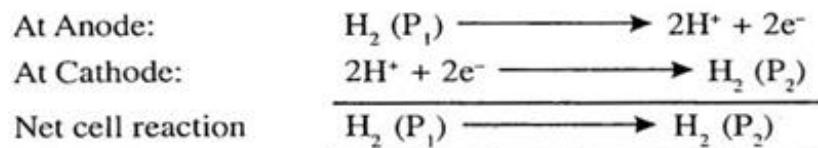
1. Electrode concentration cells and 2. Electrolyte concentration cells

**Electrode concentration cells:** In these cells, the concentration of electrolyte is same. The two electrodes contain the same material but with different concentrations.

Ex: (1) Two hydrogen electrodes having hydrogen gas at different pressures, dipped in the same electrolytic solution. It is represented as: Pt/H<sub>2</sub>(P<sub>1</sub>)/HCl(x M)/H<sub>2</sub>(P<sub>2</sub>)/Pt

Where, P<sub>1</sub> and P<sub>2</sub> are the pressure at which H<sub>2</sub> gas is maintained at anode and cathode respectively. P<sub>1</sub> > P<sub>2</sub>.

The half cell reactions are



According to Nernst's equation

$$E_{\text{cell}} = \frac{2.303RT}{nF} \times \log \frac{P_1}{P_2}$$

[E<sub>cell</sub><sup>0</sup> = 0, since both electrodes are hydrogen electrodes]

(2) Pb(0.5M)(Hg)/PbSO<sub>4</sub>/Pb(0.1M)(Hg) : The electrode with higher concentration of metal will have lower potential and it is taken as anode, whereas electrode containing lower concentration of metal will have higher potential and it is taken as cathode. These type of cells are generally obtained by dissolving different amount of metal in liquid mercury. They are called as amalgam electrode.

### Electrolyte concentration cells

#### (i) Electrolyte concentration cells with transference

In these cells, same electrode material as anode and cathode are dipped in different concentration of the same electrolyte. The two electrodes are connected directly through a diffusion membrane. These types of cells are called **electrolyte concentration cells with transference**. Ex: Pt/H<sub>2</sub>(1 atm)/HCl(a<sub>1</sub> M) || HCl(a<sub>2</sub> M)/H<sub>2</sub>(1 atm)/Pt

The dashed line indicates the direct contact between the electrodes through a membrane.

As there is a direct contact between the electrodes, ions are free to move. H<sup>+</sup> ions move from oxidation electrode to reduction electrode, while Cl<sup>-</sup> ions move in the opposite direction. After the diffusion, the dilute solution of HCl contains excess of H<sup>+</sup> ions which are highly mobile and acquire net positive charge at the junction of the membrane. On the other hand, the concentrated solution will contain an excess of Cl<sup>-</sup> ions which are less mobile and acquire negative charge. As a result, potential difference is developed at the junction of the solution, which is called **liquid junction potential**. Liquid junction potential complicates the measurement of the EMF of the cell. The liquid junction potential can be reduced using salt bridge.

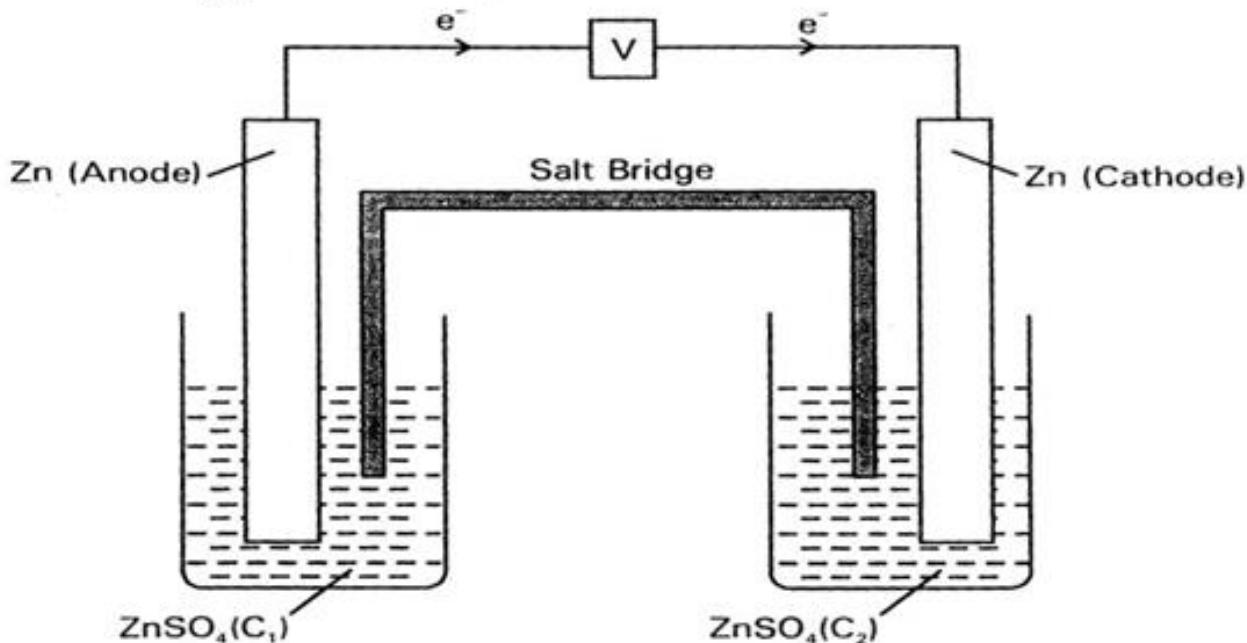
#### (ii) Electrolyte concentration cells without transference

In these cells, two same electrode materials are dipped in the two solutions containing the same electrolyte of different concentrations. The electrodes are connected through a salt bridge (fig. 7). This minimizes the junction potential and the cell works without transference of ions from the electrodes.

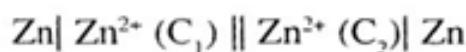
Ex: Zn|ZnSO<sub>4</sub>(C<sub>1</sub>) || ZnSO<sub>4</sub>(C<sub>2</sub>)|Zn

Where C<sub>2</sub> > C<sub>1</sub>

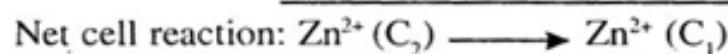
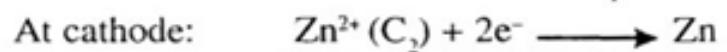
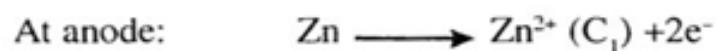
## Expression for emf ( $E_{cell}$ ) of a electrolyte concentration cell



Zinc concentration cell can be represented as



The half cell reactions are



$C_1$  and  $C_2$  are concentrations of  $Zn^{2+}$  in the two half cells respectively and  $C_2 > C_1$ .

Emf of a concentration cell can be calculated using Nernst Equation as follows:

$$E_{\text{anode}} = E_{\text{anode}}^0 + \frac{2.303 RT}{nF} \log C_1$$

$$E_{\text{cathode}} = E_{\text{cathode}}^0 + \frac{2.303 RT}{nF} \log C_2$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= [E_{\text{cathode}}^0 + \frac{2.303 RT}{nF} \log C_2] - [E_{\text{anode}}^0 + \frac{2.303 RT}{nF} \log C_1]$$

$$E_{\text{cell}} = \frac{2.303 RT}{nF} \log \frac{[C_2]}{[C_1]}$$

By substituting the values of R, T and F we get,

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]}$$

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{\text{Metal ion concentration at cathode}}{\text{Metal ion concentration at anode}}$$

### SOLVED PROBLEMS

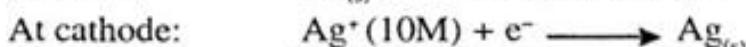
1. A concentration cell was constructed by immersing two silver electrodes in 0.01 M and 10 M  $\text{AgNO}_3$  solutions. Write the cell reactions and calculate the emf of the concentration cell. [VTU, July 2005]

An electrode of higher concentration of  $\text{Ag}^+$  (10M) acts as cathode, while the other silver electrode with  $\text{Ag}^+$  ion concentration (0.01M) acts as anode.

- (i) Cell representation:



- (ii) Electrode reactions:



- (iii) The emf of the concentration cell,

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]}$$

$$E_{\text{cell}} = \frac{0.0591}{1} \log \frac{[10]}{[0.01]}$$

$$= 0.0591 \log 1000$$

$$= 0.0591 \times 3$$

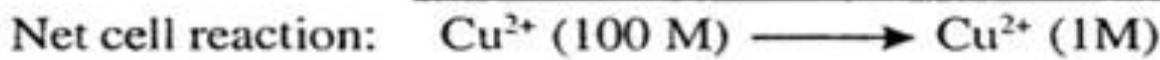
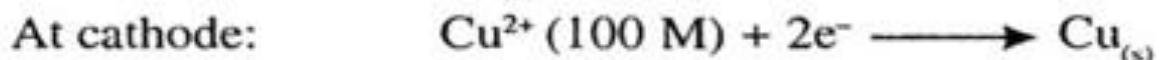
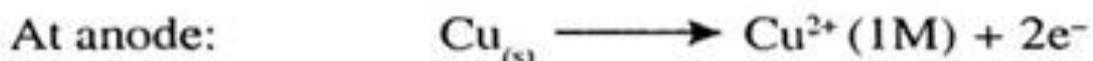
$$E_{\text{cell}} = 0.1773 \text{ V}$$

2. Represent the cell formed by the coupling of two Cu electrodes immersed in  $\text{CuSO}_4$  solutions. Concentration of cupric ions in one electrode system in 100 times more concentrated than other. Write the cell reaction and calculate the potential at 300K. [July 2007]

(i) Cell representation:



(ii) Electrode reactions:



(iii) The emf of the concentration cell,

$$E_{\text{cell}} = \frac{2.303 \text{ RT}}{nF} \log \frac{[C_2]}{[C_1]}$$

$$E_{\text{cell}} = \frac{2.303 \times 8.314 \times 300}{2 \times 96500} \log \frac{[100]}{[1]}$$

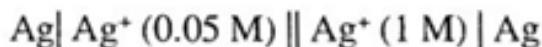
$$= 0.02976 \log 100$$

$$= 0.02976 \times 2$$

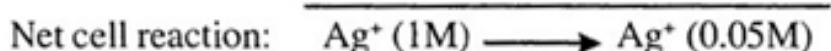
$$E_{\text{cell}} = \mathbf{0.05952 \text{ V}}$$

3. A concentration cell was constructed by immersing two silver electrodes in 0.05 M and 1 M  $\text{AgNO}_3$  solutions. Write the cell reactions and calculate the emf of the concentration cell. (VTU, July 2006)

(i) Cell representation:



(ii) Electrode reactions:



(iii) The emf of the concentration cell,

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]}$$

$$E_{\text{cell}} = \frac{0.0591}{1} \log \frac{[1]}{[0.05]}$$

$$= 0.0591 \log 20$$

$$= 0.0591 \times 1.3010$$

$$E_{\text{cell}} = 0.07689 \text{ V}$$

4. The emf of the cell  $\text{Cd}/\text{CdSO}_4(0.0093 \text{ M}) // \text{CdSO}_4(x \text{ M})/\text{Cd}$  is 0.086V at 25°C. Find the value of x. [Jan 2010]

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]}$$

$$0.086 = \frac{0.0591}{1} \log \frac{[x]}{[0.0093]}$$

$$\log \frac{[x]}{[0.0093]} = 2.910$$

$$\log x - \log 0.0093 = 2.910$$

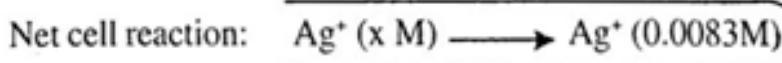
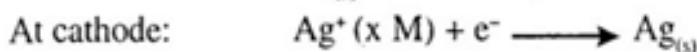
$$\log x - (-1.0315) = 2.910$$

$$\log x = 2.910 - 1.0315 = 0.8785$$

$$x = \text{antilog}(0.8785) = 7.55 \text{ M}$$

- Engineering Chemistry  
[Jan 2015]
5. The emf of the cell  $\text{Ag}/\text{AgNO}_3(0.0083 \text{ M}) // \text{AgNO}_3(x \text{ M})/\text{Ag}$  was found to be 0.074V at 298K. Calculate the value of x and write cell reaction.

Cell reactions:



The emf of the concentration cell,

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[\text{C}_2]}{[\text{C}_1]}$$

$$0.074 = \frac{0.0591}{1} \log \frac{[x]}{[0.0083]}$$

$$\log \frac{[x]}{[0.0083]} = 1.252$$

$$\log x - \log 0.0083 = 1.252$$

$$\log x - (-2.0809) = 1.252$$

$$\log x = 1.252 - 2.0809 = 0.8289$$

$$x = \text{antilog}(0.8289) = 0.1483 \text{ M}$$

6. A spontaneous galvanic cell tin/tin ion (0.024M//tin ion (0.064M) //tin develops an emf of 0.0126V at 25°C. Calculate the valency of tin.

The emf of the concentration cell,

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[\text{C}_2]}{[\text{C}_1]}$$

$$0.0126 = \frac{0.0591}{n} \log \frac{[0.064]}{[0.024]}$$

$$n = \frac{0.0591}{0.0126} \log \frac{[0.064]}{[0.024]}$$

$$= 4.690 \times \log(2.6666)$$

$$= 4.690 \times 0.4259$$

$$n = 1.9972 \sim 2$$

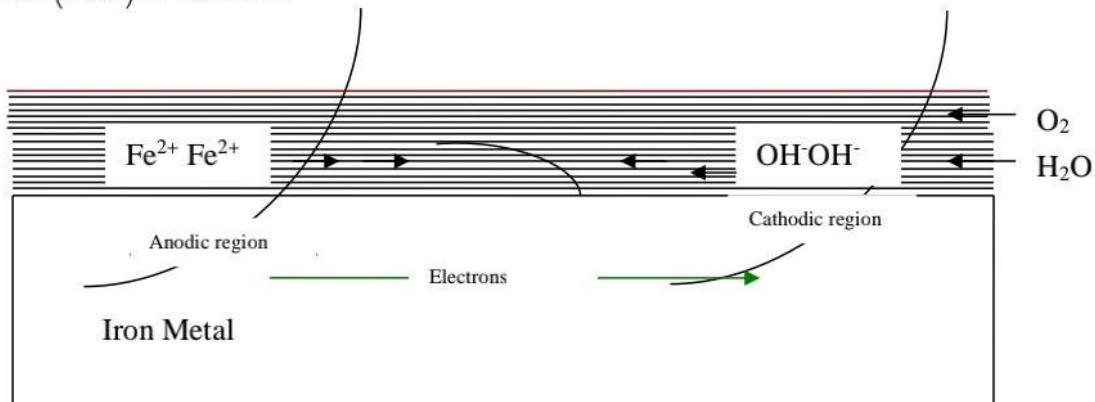
**Valency of tin is 2**

1. What are electrochemical cells? Give the classification with examples?
2. Define (i) single electrode potential and (ii) standard electrode potential?  
(Jan 2013) (Dec 2011)
3. Derive Nernst equation for a single electrode potential? (Jan 2013) (July 2013) (**Jan 2015**)
4. State the different types of electrodes with examples?
5. What are reference electrodes? List the limitations of primary reference electrode?
6. What are secondary reference electrodes? Mention the requirements of secondary reference electrodes?
7. What are the advantages of secondary reference electrodes over primary reference electrodes?
8. Explain the construction, working and applications of calomel electrode?  
(Jan 2011) (Jan 2013) (July 2013) (**Jan 2015**)
9. What are secondary reference electrodes? Explain the construction, working and applications of Ag/AgCl electrode?
10. What are reference electrodes? Explain the determination of electrode potential of an unknown electrode using calomel electrode?  
(Jan 2014) (**Jan 2015**)
11. What are ion selective electrodes?
12. Explain the construction, working and applications of Glass membrane electrode? (Jan 2011)
13. What are the advantages and limitations of glass membrane electrode?
14. Explain how glass membrane electrode can be used in determination of pH of unknown solution?  
(Jan 2011)
15. What are concentration cells? Give its classification with examples?
16. What are electrolyte concentration cells? Deduce an expression for the EMF of a concentration cell?  
(Dec 2011) (Jan 2014)

## CORROSION OF METALS

**Definition of corrosion:** Corrosion is defined as the destruction of metals or alloys by the surrounding environment through chemical or electrochemical reactions.

**Example:** When iron is exposed to air in the presence of moisture, hydrated ferric oxide (rust) is formed.



**Electrochemical theory of corrosion:** According to electrochemical theory, when a metal such as iron is exposed to corrosive environment, following changes occur. There will be formation of tiny galvanic cells on the surface of the metal (i.e., anodic and cathodic regions are formed).

Oxidation of metal takes place at the anodic region. (e.g.  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ ). The  $\text{Fe}^{2+}$  ions dissolve, so corrosion takes place at the anodic region. The electrons travel through the metal from the anodic region to cathodic region. Reduction of  $\text{O}_2$  or  $\text{H}^+$  takes place at the cathodic region. The metal is unaffected at the cathodic region.  $\text{Fe}^{2+}$  and  $\text{OH}^-$  ions travel through the aqueous medium and form corrosion product. The corrosion product may undergo further oxidation to form rust.

### Reactions:

**Reaction at anodic region:** As mentioned above, oxidation of metal takes place at anode.

**Reactions at cathodic region:** At cathode, the reaction is either a) liberation of hydrogen or b) absorption of oxygen.

a) Liberation of hydrogen (in the absence of oxygen)



In neutral or alkaline medium, (in the absence of oxygen) the reaction is



b) Absorption of oxygen (in the presence of oxygen)

In acidic medium, the reaction is



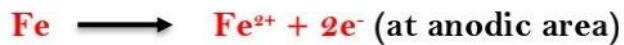
In neutral or alkaline medium, the reaction is



The points to be noted here is :

- \* Oxidation and reduction are simultaneous processes. If the environment is not favor for reduction to occur obviously the oxidation also not possible to occur.  
*That is the reason A metal kept in Vacuum does not corrode easily.*
- \* Metal will corrode at cathodic area as its not involved in any cathodic reaction.

#### Overall reaction:



## **Electrochemical Series:**

The arrangement of elements in their increasing order of their standard reduction electrode potential.

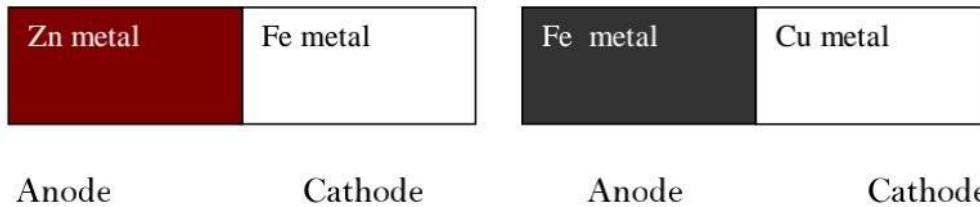
M <sup>n+</sup> /M	E <sup>o</sup> (V)	Mn <sup>+</sup> /M	E <sup>o</sup> (V)
Li <sup>+</sup> /Li	-3.05	H <sup>+</sup> /H <sub>2</sub>	0.0
Mg <sup>2+</sup> /Mg	-2.37	Cu <sup>2+</sup> /Cu	0.34
Zn <sup>2+</sup> /Zn	-0.76	Ag <sup>+</sup> /Ag	0.8
Fe <sup>2+</sup> /Fe	-0.44	Pt <sup>2+</sup> /Pt	1.20
Cd <sup>2+</sup> /Cd	-0.40	Au <sup>3+</sup> /Au	1.38

The electrochemical series does not take passivity of the metals into account. In order to overcome the limitations of electrochemical series, galvanic series was introduced.

**Galvanic Series:** The metals and alloys were arranged in the order of their corrosion tendencies or corrosion resistance.

### **❖ Types of corrosion:**

#### **1. Differential metal corrosion:**



This type of corrosion occurs when two dissimilar metals are in contact with each other and are exposed to a corrosive environment. The two metals differ in their electrode potentials. The metal with lower electrode potential acts as anode and the other metal with higher electrode potential acts as cathode.

The anodic metal undergoes oxidation and gets corroded. A reduction reaction occurs at the cathodic metal. The cathodic metal does not undergo corrosion.

The reactions may be represented as follows:



The reaction may be represented in Zinc :



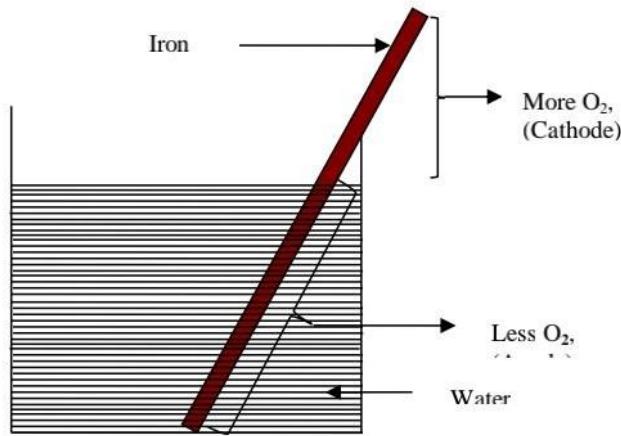
*Higher the potential difference between the anodic and cathodic metals, higher is the rate of corrosion.*

**Example:** When iron is in contact with zinc, iron acts as cathode and zinc acts as anode because zinc has lower electrode potential compared to iron. Therefore zinc undergoes corrosion. On the other hand, when iron is in contact with tin, iron acts as anode because iron has lower electrode potential compared to tin. Hence iron undergoes corrosion.

Other examples:

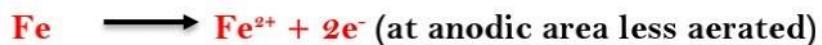
1. Steel screws in copper sheet.
  2. Steel screws with copper washer.
  3. Bolt and nut made of different metals.
-

## 2. Differential aeration corrosion:



This type of corrosion occurs when two different parts of the same metal are exposed to different oxygen concentrations. (e.g. An iron rod partially dipped in water.) The part of the metal which is exposed to less oxygen concentration acts as anode. The part which is exposed to more oxygen concentration acts as cathode. The anodic region undergoes corrosion and the cathodic region is unaffected.

The reactions may be represented as follows:

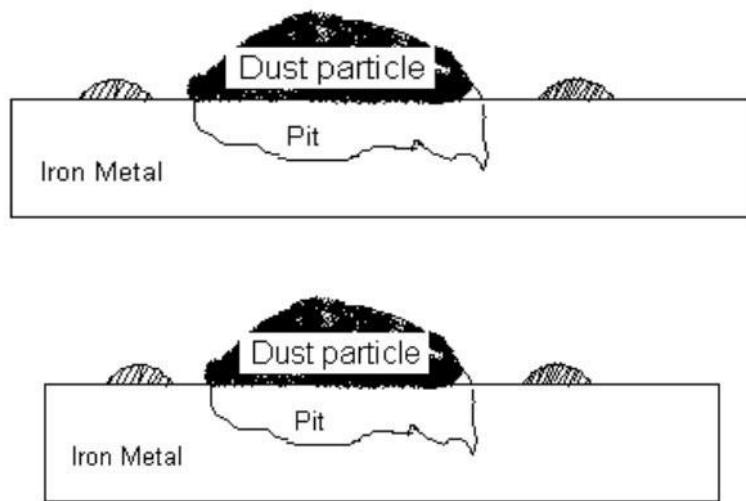


### Other examples:

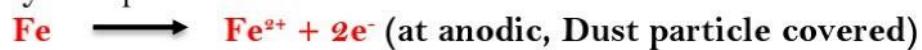
1. Part of the nail inside the wall undergoes corrosion.
2. When a dirt particle sits on a metal bar, the part under the dirt undergoes corrosion.
3. Partially filled iron tank undergoes corrosion inside water.

**Pitting corrosion:** This is an example of differential aeration corrosion.

When a small dust particle gets deposited on a steel surface, the region below the dust particle is exposed to less oxygen compared to the remaining part. As a result, the region below the dust particle acts as anode undergoes corrosion and forms a pit. The remaining region of the metal acts as cathode and is unaffected.

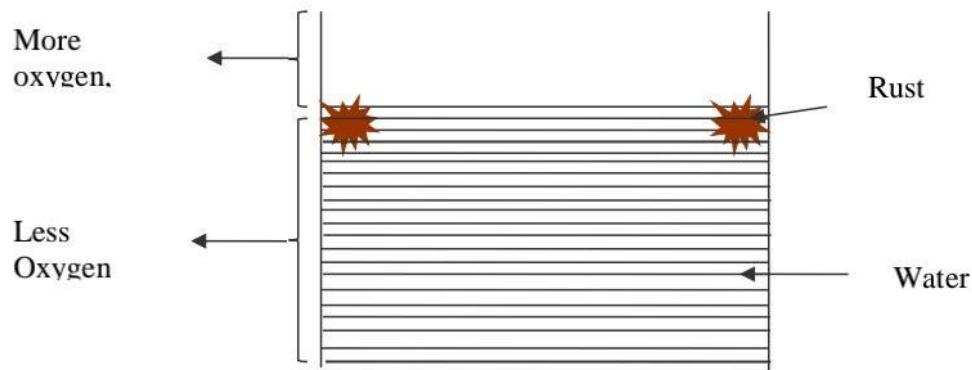


The reactions may be represented as follows:



Formation of a small anodic area and a large cathodic area results in intense corrosion below the dust particle.

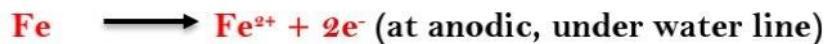
**Water line corrosion:** This is an example of differential aeration corrosion.



When a steel tank is partially filled with water for a long time, the inner portion of the tank below the water line is exposed only to dissolved oxygen, whereas, the portion above the water line is exposed to more oxygen. Thus the portion below the water line acts as anode and undergoes corrosion. The upper portion acts as cathode and is unaffected.

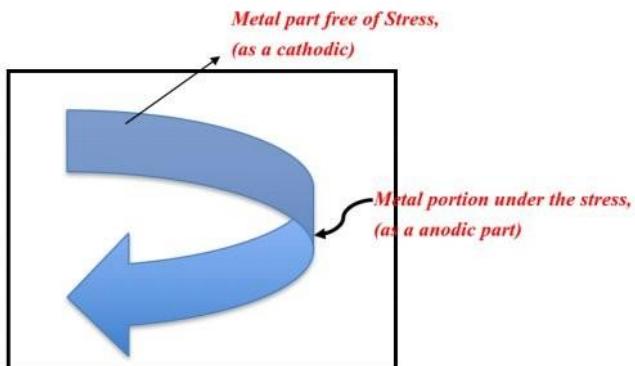
A distinct brown line is formed just below the water line due to the deposition of rust.

The reactions may be represented as follows:



**Other example:** Ships which remain partially immersed in sea water for a long time undergo water line corrosion.

#### 4. Stress corrosion:



Example : Iron rod under the mechanical stress

Stress corrosion occurs when stressed region of metals are exposed to corrosive environments. The stressed region acts as anode and undergoes corrosion. The unstressed region acts as cathode and is unaffected.

Stress corrosion is highly specific in nature. For corrosion to occur, the presence of both stress and a specific corrosive environment are necessary. For example, stressed regions of mild steel undergo stress corrosion in the presence of NaOH solution.

**Caustic embrittlement** in boilers is an example of stress corrosion. Here alkaline (NaOH) water enters the hairline cracks on the boiler wall (mild steel). The water evaporates off leaving behind a concentrated solution of NaOH in the crack. When the concentration of NaOH increases to 10%, an electrochemical cell is set up with the stressed region acting as anode. The iron surrounded by dilute NaOH acts as cathode. The anodic region undergoes corrosion leading to crack propagation which may result in boiler failure.



### **Factors affecting the rate of corrosion:**

1. **Nature of the metal:** Metals with lower electrode potentials are more reactive and are more susceptible to corrosion. For example, elements such as Mg and Zn, which have low electrode potentials, are highly susceptible to corrosion. Noble metal such as gold and platinum, which have higher electrode potentials, are less susceptible to corrosion.

Exceptions: Metals and alloys which show passivity are exceptions for this general trend. Such metals form a protective coating on the surface which prevents corrosion.

2. **Nature of corrosion product:** If the corrosion product is insoluble, stable and non-porous, then it acts as a protective film which prevents further corrosion. The film acts as a barrier between the fresh metal surface and the corrosive environment. On the other hand, if the corrosion product is soluble, unstable and porous, then the corrosion process continues even after the formation of corrosion product.

**Example:** Aluminium, titanium and chromium form a protective film of metal oxide on the surface. Stainless steel forms a protective film of  $\text{Cr}_2\text{O}_3$  on the surface. But in the case of Zn and Fe, the corrosion products formed do not have protective value.

3. **Difference in potential between anodic and cathodic regions:** Larger the potential difference between the anodic and cathodic regions, higher is the rate of corrosion. For example, the potential difference between iron and copper is 0.78 V, and between iron and tin is 0.3 V. Therefore, corrosion is faster when iron is in contact with copper.

The use of dissimilar metals should be avoided wherever possible. Otherwise, the anodic metal gets corroded.

4. **Anodic and cathodic areas:** Smaller the anodic area and larger the cathodic area, more intense and faster is the corrosion. For example, a broken coating of tin on iron surface results in intense corrosion at the broken region. Iron is anodic to tin. Exposed region of iron acts as anode with small area. Tin acts as cathode which has large area.

**5. Anodic and cathodic polarizations:** The polarization at anode and cathode decreases the rate of corrosion.

Anodic polarization occurs due to the accumulation of metal ions in the vicinity of anodic region. This retards the formation of new metal ions by oxidation. Thus the corrosion process is retarded.

Cathodic polarization occurs due to the accumulation of hydroxyl ions in the vicinity of cathodic region. This accumulation retards the movement of cathodic reactant (oxygen) towards the cathodic surface. Hence, the rate of cathodic reaction decreases. A retarded cathodic reaction results in retardation of anodic reaction also. Thus, the corrosion process is slowed down.

**6. Hydrogen over voltage:** When the cathodic reaction is liberation of hydrogen, high hydrogen over voltage retards the cathodic reaction. A retarded cathodic reaction retards the anodic reaction also. Thus, the corrosion process is slowed down.

(Note: Theoretically, certain potential difference between anode and cathode is required for the hydrogen evolution to occur at cathode. But in practice, the potential difference required is more than the theoretical value. This excess potential difference is called hydrogen over voltage.)

**7. pH of the medium:** In general, lower the  $p^H$  of corrosion medium, higher is the corrosion rate. (Exception: Metals like Al, Zn etc. undergo fast corrosion in media with high  $p^H$ .)

Iron does not undergo corrosion at  $p^H$  greater than 10. This is due to the formation of protective coating of hydrous oxides of iron. Between  $p^H$  10 and 3, the presence of oxygen is essential for corrosion. If the  $p^H$  is less than 3, corrosion occurs even in the absence of oxygen.

**8. Temperature:** Higher the temperature, higher is the rate of corrosion.

In general, the rate of a chemical reaction increases with increase in temperature. Corrosion is one such chemical reaction. Therefore, the rate of corrosion increases as the temperature increases.

Increase in temperature increases the ionic conductivity of the corrosive medium. This also contributes to the increase in corrosion rate.

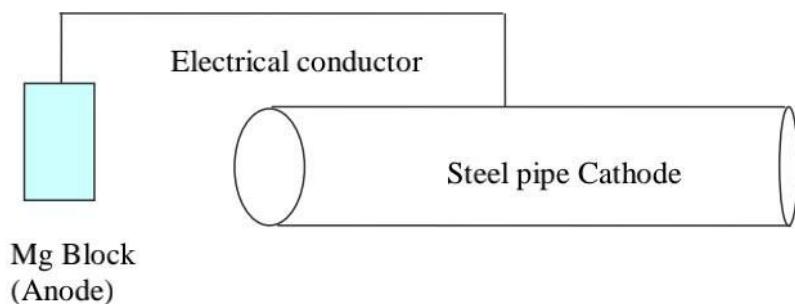
## Corrosion control

**1. Selection of the Material and Design:** Material should be as pure as possible, and the design should be such that there should be minimum residual stress in the structure. Differential aeration should be eliminated and so on.

### **2. Cathodic protection:**

In cathodic protection, the metal to be protected is completely converted into a cathode. Since cathodes do not undergo corrosion, the metal is protected against corrosion.

#### **(i) Sacrificial anode method:**



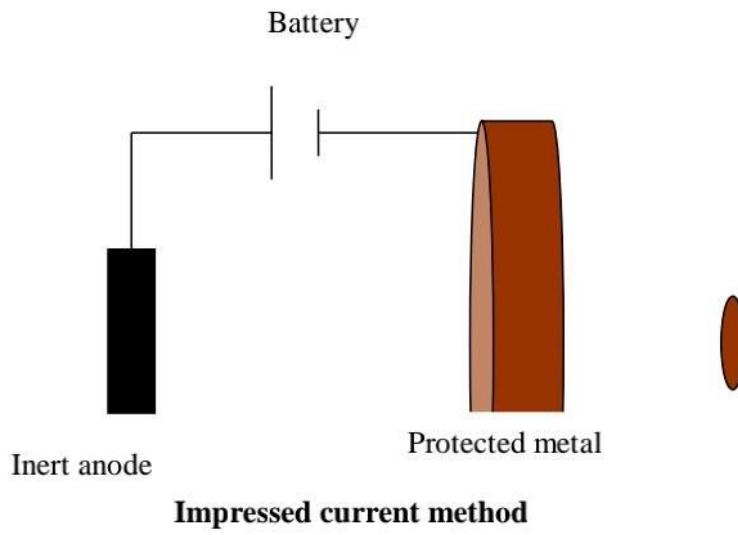
In sacrificial anode method, the metal to be protected is electrically connected to a more active metal. For example, when steel is to be protected, it may be connected to a block of Mg or Zn. In such a situation, steel acts as cathode and is unaffected. Mg and Zn act as anode and undergo sacrificial corrosion. When the sacrificial anode gets exhausted, it is replaced with new ones.

Other examples: Mg bars are fixed to the sides of ships to act as sacrificial anode. Mg blocks are connected to buried pipe lines.

#### **(ii) impressed current method (impressed voltage method)**

In cathodic protection, the metal to be protected is completely converted into a cathode. Since cathodes do not undergo corrosion, the metal is protected against corrosion.

In impressed current method, the metal to be protected is connected to the negative terminal of an external d.c. power supply. The positive terminal is connected to an inert electrode such as graphite. Under these conditions, the metal acts as cathode and hence does not undergo corrosion. The inert electrode acts as anode; but it does not undergo corrosion because it is inert.

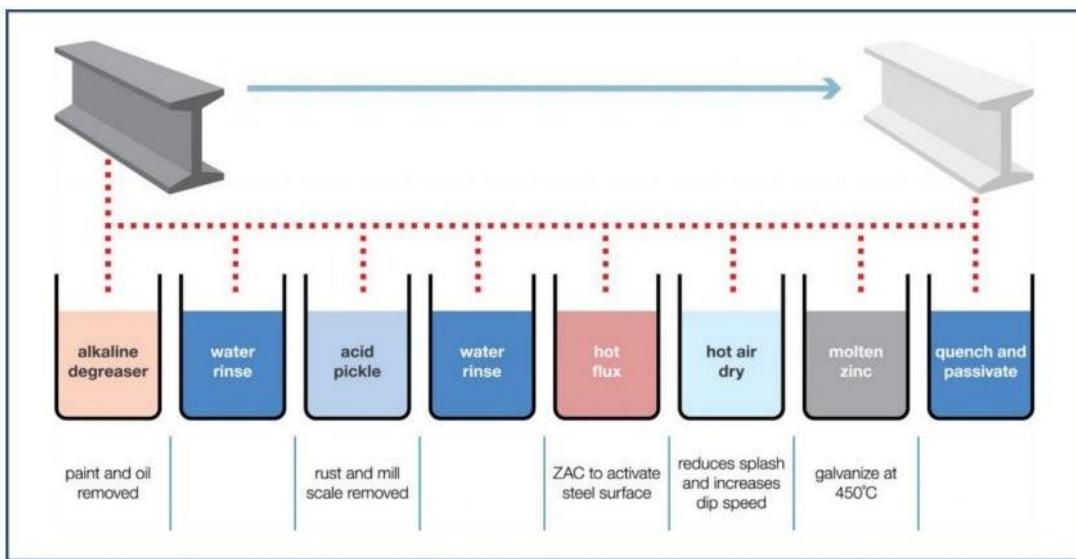


## 2. Metallic coating

(i) **Galvanizing:** Galvanizing is the process of coating a metal surface such as iron with zinc metal. Galvanizing of iron is an example of anodic metal coating on the surface of a cathodic metal.

Galvanization is carried out by hot dipping method. It involves the following steps.

1. The metal surface is washed with organic solvents to remove organic matter on the surface.
2. Rust is removed by washing with dilute sulphuric acid.
3. Finally, the article is washed with water and air-dried.
4. The article is then dipped in a bath of molten zinc. (Molten zinc is covered with a flux of ammonium chloride to prevent the oxidation of molten zinc.)
5. The excess zinc on the surface is removed by passing through a pair of hot rollers.



**Application:** Galvanization of iron is carried out to produce roofing sheets, fencing wire, buckets, bolts, nuts, pipes etc.

(Note: Even if the Zn coating falls off at some places, the base metal (Fe) does not get corroded at those places. This is because the base metal acts as cathode. In corrosion process, the cathodic metal always remains unaffected.)

(Note: Galvanized articles are not used for preparing and storing food because zinc dissolves in dilute acids producing toxic zinc compounds)

(ii) **Tinning:** Tinning is the process of coating the surface of a base metal (such as iron) with tin. Tinning of iron metal is an example of cathodic metal coating on an anodic base metal.

Tinning of iron is carried out by hot dipping method. It involves the following steps.

1. The metal surface is washed with organic solvents to remove organic matter on the surface.
2. Rust is removed by washing with dilute sulphuric acid.
3. Finally, the article is washed with water and air-dried.
4. It is then passed through molten zinc chloride flux. The flux helps the molten tin to adhere strongly on the surface.
5. It is then dipped in a bath of molten tin.

6. The excess tin on the surface is removed by passing through a series of rollers immersed in palm oil. The oil prevents the oxidation of tin coating.

Applications: Tin-coated steel is used for manufacturing containers.

*(Note: In tin-coated iron, if a small crack is formed in the tin coating, an intense and accelerated corrosion of iron occurs at the exposed region because of the formation of a small anodic area (iron) and large cathodic area (tin)).*

*(Note: Copper utensils are coated with tin to prevent contamination of food with poisonous copper salts.)*

### 3. By Inorganic coatings (Or Surface conversion coating)

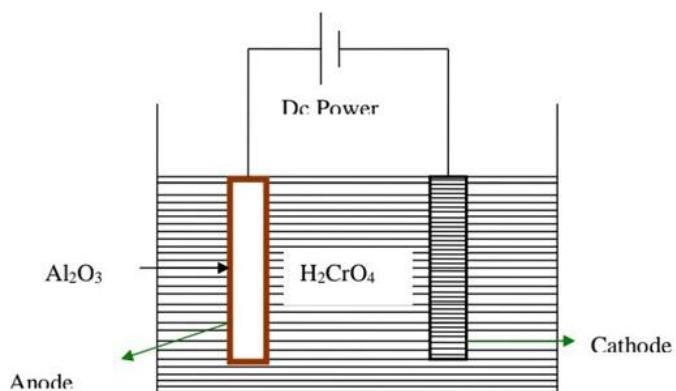
(i) **Anodizing** (Anodizing of aluminum): When aluminum metal is made anodic in an electrolytic bath with sulphuric acid or chromic acid as the electrolyte, a thin layer of aluminium oxide ( $\text{Al}_2\text{O}_3$ ) is formed on the surface. This process is called anodizing of aluminium or anodic oxidation of aluminum.

When anodized aluminium is exposed to a corrosive environment, the  $\text{Al}_2\text{O}_3$  layer on the surface acts as a protective coating. Hence corrosion is prevented.

Other metals such as Mg, Ti etc. can also be anodized.

(Note: On anodizing,  $\text{Al}_2\text{O}_3$  is formed on the surface as a porous layer. The layer may be made compact by sealing, which involves heating with boiling water or steam. During sealing,  $\text{Al}_2\text{O}_3$  is converted into  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$  which occupies higher volume. Therefore, the pores are sealed.)

Applications: Metals such as Al, Mg, Ti etc. are anodized to control corrosion.



(ii) **Phosphating:** Converting the surface metal atoms into their phosphates by chemical or electrochemical reactions is called phosphating.

The phosphating bath contains three essential components: (i) free phosphoric acid, (ii) a metal phosphate such as Fe, Mn phosphate and (iii) an accelerator such as  $\text{H}_2\text{O}_2$ .

Phosphating not only improves the corrosion resistance but also imparts good paint adhesion quality to the surface.

Applications: Phosphate coating is given as an under layer before painting the car bodies, refrigerators and washing machines.

## Metal finishing

### Definition

Metal finishing is a process of coating metal on metal, metal on an alloy or metal on a polymer or forming oxide film to modify surface properties. Major techniques used are electroplating and electroless

plating

### **Technological importance of metal finishing**

- 1) To provide resistance against corrosion Ex; Zn, Cd, Sn, coating on Iron
- 2) To increase the conductivity. This technique have been developed to deposit metal on non conducting materials. Ex; PCB s, Computers, cameras.
- 3) To provide Thermal conducting surface.
- 4) To impart decorative appearance. Ex; Gold Plating, Chromium plating.
- 5) To improve surface hardness. Ex: Hard Chromo Plating on dies and cutting tools.
- 6) To electroforming. Make the object of required size and shape by the growth of the metal form solution. Ex; Aircraft components are made by this method.
- 7) To impart wear resistance.
- 8) To impart chemical resistance.

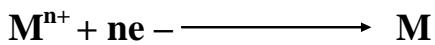
### **Electroplating**

It is a process of deposition of a metal on a conducting surface through the process of electrolysis.

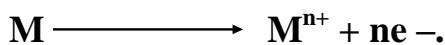
OR

It is a deposition of a metal on a conducting surface by passing direct current, through the solution containing ions to be deposited and making the object cathode.

**Process of electroplating:** It is done in a device called electrolytic cell. The material to be coated is taken as cathode and is connected to the negative terminal, anode is connected to the positive terminal. Both electrodes are dipped in an electrolyte containing the coating metal ion. When current passes through the electrolyte solution, cations will move towards cathode and at cathodic surface, it will be reduced to metal and will get deposited. So the concentration of metal ions in the solution decreases:



Anode can be a dissolvable anode or an inert one. In case of dissolvable anode, the anode reaction is oxidation of metal,



In this case the thickness of the anode gradually decreases and has to be replaced periodically. In case of inert anode, the metal ions in the electrolyte will get reduced and deposited. Hence to maintain the cation concentration, electrolyte should be added occasionally.

## **Surface preparation or cleaning of the object for electroplating**

The impurities present on the metal surface like oil, grease, oxide layer, surface anomalies etc need to be removed before coating. The cleaning methods are:

1. **Solvent cleaning:** Organic solvents (acetone, ether, etc) are used to remove impurities like oil, grease, etc.,
2. **Alkali cleaning:** The minute residue left behind after solvent cleaning is cleared using alkali cleaners. It includes alkali (eg. NaOH, Na<sub>2</sub>CO<sub>3</sub>), soap (eg. sodium lauryl sulphate) and a chelating agent (eg. EDTA).
3. **Mechanical cleaning:** It is used to remove loose rust and other impurities from the surface. Hand cleaning with a brush or polishing using sand paper, sand blasting etc are examples
4. **Pickling:** It is used to remove oxides and other contaminants from the metal surface using an acid. Dil HCl or dil H<sub>2</sub>SO<sub>4</sub> is used for cleaning steel
5. **Electro polishing:** The metal to be coated is made anode in a suitable solution in order to have a polished surface for electroplating and during the cleaning, the surface irregularities also will be removed. The baths used are H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub>, H<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

## **Electroplating of chromium**

There are two types of chromium coating.

Decorative chromium coating and hard chromium coating

	<b>Decorative Cr coating</b>	<b>Hard Cr coating</b>
<i>Thickness</i>	0.25 – 0.75 µM	0.005 – 0.75 mM
<i>Anode</i>	Insoluble anodes like Pb-Sb alloy	Insoluble anodes like Pb-Sb alloy
<i>Cathode</i>	Object to be plated	Object to be plated
<i>Current Density (mA cm<sup>-2</sup>)</i>	145-430	290-580
<i>Temperature</i>	45-55 degree Celsius	45-55 degree Celsius
<i>Current Efficiency (%)</i>	10-15 %	17-20 17-21 %
<i>Bath computation</i>	Chromic acid(250g) , Sulfuric acid (25 g) and trivalent chromium (1g)	Cutting tools, position rings, cylinder lining, bearings. Chromic acid(250g) , Sulfuric acid (25 g) and trivalent chromium (1g)

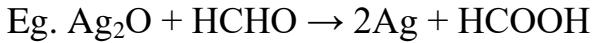
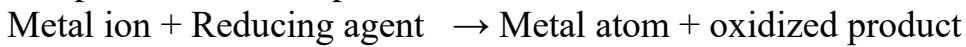
During Chromium plating, chromium rod is not used as anode because

1. Chromium rod get passivized ( i.e. Anode efficiency is five time more than cathode efficiency) and
2. It can cause the increasing in concentration of Cr<sup>3+</sup> ions leading to burnt deposit.

## Electroless plating

The process of depositing a metal or alloy on a catalytically active surface by chemical reduction of metal ions using a reducing agent instead of electrical energy is called as electroless plating. Reducing agent reduces the metal atoms which get deposited over the material and reducing agent is oxidized.

The process can be represented as:



The plating bath contains a metal ion solution of the metal to be coated, reducing agent to reduce the metal ions to metal, a complexing agent to avoid bulk deposition, an exaltant to increase the rate of plating, a stabilizer to increase the stability of the bath and a buffer to maintain the pH.

## **Distinction between Electroplating and electroless plating**

	ELECTRO PLATING	ELECTROLESS PLATING
Driving force	Electrical energy	Autocatalytic redox reaction
Cathode reaction	$\text{M}^{n+} + ne \rightarrow \text{M}$	$\text{M}^{n+} + ne \rightarrow \text{M}$
Site of Oxidation	Separate anode	Catalytic surface of the object
Site of reduction	Object (Cathode)	Catalytic surface of the object
Cause of reduction	Electrical energy	Reducing agent
Applicability	Only to conductors	Conductors and non-conductors

## Electroless Plating of copper

The surface to be coated must be cleaned properly by using organic solvents, followed by acid treatment.

Non-metallic materials like glass, plastics, PCB, etc., are activated by dipping in the solution containing  $\text{SnCl}_2$  and  $\text{HCl}$ , followed by dipping in palladium chloride solution.

pH : 11

Temperature : 25 Degree Celsius.

Plating Bath :  $\text{CuSO}_4$  ( $12\text{g}/\text{dm}^3$ )

Reducing agent : Formaldehyde ( $8\text{g}/\text{dm}^3$ )

Buffer :  $\text{NaOH}$  ( $15\text{g}/\text{dm}^3$ )

Complexing agent : Disodium salt of EDTA ( $20\text{g}/\text{dm}^3$ )

The electrode reactions are:

