

# CHAPTER 1

## ELECTROCHEMISTRY AND CORROSION

### 1.1 INTRODUCTION

Electrochemistry is the branch of chemistry which deals with the relation between chemical energy and electrical energy. It is the study of solutions of electrolytes. Also it deals with the chemical reactions produced by passing electric current through an electrolyte solution. In order to have an electric current, charge carriers as well as driving force are essential. These charge carriers can be either electrons or ions. A battery or some other suitable source of electrical energy can be used to provide the necessary driving force. Substances which allow the passage of electric current through them are called conductors while those which do not allow electric current to pass through are called insulators. Conductors are of two different types.

1. Electronic conductors or metallic conductors which allow the conduction of electricity by the movement of electrons. (e.g. Fe, Cu, Al, Ag etc.)
2. Electrolytic conductors where conduction takes place by the movement of ions produced as a result of the decomposition of electrolytes (e.g. acids, bases, salt solution etc.)

The major differences between electronic and electrolytic conductors are given in the following Table 1.1

Table 1.1 Comparison between metallic and electrolytic conductors

No.	Metallic conductor	Electrolytic conductor
1	Conduction takes place by movement of electrons.	Conduction takes place by the movement of charged ions.
2	No chemical or physical changes and new products.	Chemical changes take place by the formation of new products.
3	Do not involve any transfer of matter.	Involves transfer of matter.
4	Resistance of the conductor increases with rise in temperature.	Resistance of the conductor decreases with rise in temperature.

### Electrolytes

Are substances which allow the passage of electric current through it, either in molten stage or in solution (e.g. acids, bases, salt solution etc.). We know that on passing electric current through an electrolyte solution, a chemical reaction takes place. In other words, an electric current can cause a chemical reaction to take place under suitable conditions. This phenomenon is called electrolysis. The reverse is also true i.e. we can generate electric current by chemical reaction. Hence, depending upon these two types of chemical processes, there are two types of cells such as:

1. Electrolytic cells
2. Electrochemical cells

#### Electrolytic Cells

It is a device in which electrical energy from an external source can be used to bring about chemical reactions. In other words, in electrolytic cells, electrical energy is converted into chemical energy. In an electrolytic cell, the redox reaction in the cell is non-spontaneous and occurs as long as the external emf is applied. The electrodes used in such type of cell may be of the same or different materials, the electrodes are set up in one vessel and only single electrolyte is used. In such a cell the anode is connected to a positive terminal and the cathode to the negative terminal of a battery. The refining of metals, electroplating with silver, gold or chromium or production of many chemical substances such as chlorine, sodium hydroxide, hydrogen peroxide etc., are carried out in electrolytic cells.

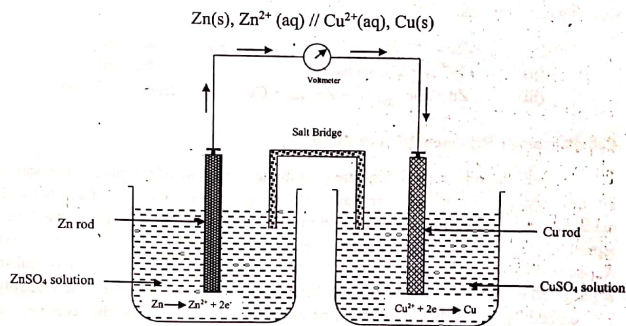
#### 1.2 ELECTROCHEMICAL CELL

It is a device which converts chemical energy in to electrical energy. It is also known as voltaic or galvanic cell. A cell is an arrangement of two electrodes and an electrolytic solution capable of producing electricity due to chemical reaction within the cell or producing chemical action due to the passage of electricity through the cell e.g. Daniel cell. An electrochemical cell is made up of two electrodes. At one electrode, oxidation takes place, i.e. electrons are evolved. At the other electrode, reduction takes place, i.e. electrons are taken up. The anode is defined as that electrode at which electrons leave the cell and oxidation occurs. The cathode is defined as that electrode at which electrons enter the cell and reduction occurs. Each electrode may become either the anode or the cathode depending on the direction of current flow through the cell.

Table 1.2 Comparison between Electrolytic Cells and Electrochemical Cells

No	Electrolytic Cells	Electrochemical Cells
1	It requires a source of external energy	It is a source of energy
2	It converts electrical energy in to chemical energy	It converts chemical energy in to electrical energy
3	The redox reaction is not spontaneous	The redox reaction is spontaneous and is responsible for the production of energy.
4	Both the electrodes are placed in the same container in the electrolytic solution	Two half-cells are set up in different containers being connected through salt bridge.
5	Salt bridge is not required	Salt bridge is required
6	Involves oxidation at anode and reduction at cathode	Involves oxidation at anode and reduction at cathode
7	Here the anode is positive and cathode is the negative electrode	Here the anode is negative and cathode is the positive electrode.

**Daniel Cell:** Daniel cell is an electrochemical cell consisting of a zinc electrode dipped in  $ZnSO_4$  (anode where oxidation takes place) and a copper electrode dipped in  $CuSO_4$  solution (cathode where reduction takes place). The two solutions are separated by a salt bridge and each electrode is referred to as a half cell. The cell can be represented as





The zinc metal has a greater tendency for oxidation than copper. Hence oxidation occurs in Zinc and Zn atoms leaves its electrons to the Zn electrode and goes to the solution as  $Zn^{2+}$  ions.

At the anode,  $Zn \rightarrow Zn^{2+} + 2e^-$  (oxidation).

In the copper compartment,  $Cu^{2+}$  ions have a tendency for reduction, by accepting electrons.

At the cathode,  $Cu^{2+} + 2e^- \rightarrow Cu$  (reduction)

The overall reaction can be written as,  $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$  (cell reaction)

### Redox Reactions

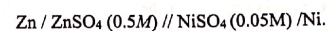
Various chemical reactions occur through redistribution of electrons among the reacting substances. Oxidation is a process, which involves loss of electrons by a substance; while reduction is a process, which involves gain of electrons by a substance. Any substance that loses electrons is said to be oxidized and the one which gains electrons is said to be reduced. However, in a chemical reaction, substance can lose electrons only if there is another substance, which can gain electrons. This implies that oxidation can take place only if reduction also occurs at the same time or vice-versa. These reactions in which reduction and oxidation take place simultaneously are called redox reactions. Thus, if we place zinc metal in a solution of copper sulphate, immediate precipitation of Cu takes place. In this change, the zinc atom (Zn) is oxidized to zinc ion ( $Zn^{2+}$ ), since it loses electrons; while the copper ion ( $Cu^{2+}$ ) is reduced to copper atom, since it gains electrons.

- |       |   |                  |
|-------|---|------------------|
| (i)   | $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$          | (oxidation).     |
| (ii)  | $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$          | (reduction)      |
| (iii) | $Zn + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu$ | (redox reaction) |

### Cell diagram or Representation of a Cell

A cell diagram is an abbreviated symbolic depiction of an electrochemical cell. For this purpose, we will consider that a cell consists of two half-cells. Each half-cell is made of a metal electrode in contact with metal ions in solution. A single vertical line (|) represents a phase boundary between metal electrode and ion solution (electrolyte). Anode half-cell is written on the left and cathode half-cell on the right. The physical state is indicated in bracket. For anode, the electrode is written first and then the electrolyte. For cathode, the electrolyte is written first and then the electrode. In the complete cell diagram, the two half-cells are separated by a double vertical line (|| salt bridge) in

between. The symbol of an inert electrode like the platinum electrode is often enclosed in a bracket. Concentrations of electrolytes and pressures of gases are mentioned. A cell constructed by coupling Zn electrode dipped in 0.5 M  $ZnSO_4$  and Ni electrode dipped in 0.05 M  $NiSO_4$  can be represented as



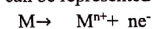
The Hydrogen electrode is represented,  $Pt | H_2(g) (1 atm) | H^+ (1M)$

### 1.3 SINGLE ELECTRODE POTENTIAL

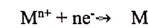
When a strip of metal (M) is brought in contact with the solution containing its own ions ( $M^{n+}$ ) a half cell or single electrode is formed due to its tendency to gain or lose electrons. The electrical potential difference set up between the metal and solution of its ions is known as half cell electrode potential or Single electrode potential. It can be determined relative to the standard hydrogen electrode. It is represented as E.

**Origin of electrode Potential:** When a metal is dipped in a solution containing its own ions, the metal may undergo oxidation by losing electrons or the metal ions may undergo reduction and get deposited on the metal surface.

Consider a metal M, dipped in a solution containing its ions  $M^{n+}$ . The tendency of metal to pass in to solution (oxidation) can be represented as,



Similarly, the metal ions from the solution tend to deposit on the metal as metal atoms (reduction).



The above two opposite tendencies will result in equilibrium as follows

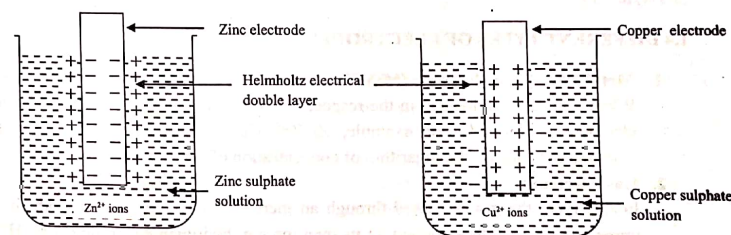
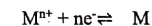


Figure 1.2 Helmholtz Electrical Double Layer

When a metal undergoes oxidation it loses positive ions into solution leaving behind a layer of negative charges on its surfaces. This layer attracts positive charges and forms an electric double layer (EDL). This electrical double layer is known as Helmholtz Electrical Double Layer, because of the formation of EDL electrode potential arises. When metal ions undergo reduction by depositing atoms on the metallic surfaces, the metal surface becomes positively charged. The accumulated positive charge on the metal surface attracts a layer of -ve charges and forms Helmholtz Electrical Double Layer which causes the origin of electrode potential

#### Factors affecting Electrode Potential or emf of Cell

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

#### Standard Electrode Potential ( $E^0$ )

It is a measure of the tendency of the metal electrode to lose or gain electrons, when a metal electrode is in contact with its own salt solution of unit concentration (1M or 1N) at 25°C. With gases at 1 atmospheric pressure is a standard condition. For a Zn-Cu voltaic cell, the standard emf,  $E^0$ , is 1.10 V. This means that the emf of the cell operated with  $[Cu^{2+}]$  and  $[Zn^{2+}]$  both at 1 M and 25°C is 1.10 V. Standard emf of a cell is represented by the symbol  $E^0$ . It is not possible to determine the single electrode potential of an electrode since half cell reactions cannot take place independently. However, the difference in potential between two electrodes can be measured from a complete cell. Generally standard hydrogen electrode, whose potential is zero, is taken to complete the cell. In short, Standard electrode potential is defined as the equilibrium potential difference between the metal electrode and its surrounding ions of unit concentration (1M or 1N) at 25°C.

#### 1.4 DIFFERENT TYPES OF ELECTRODES

##### 1. Metal/Metal Ion electrode ( $M/M^{n+}$ )

When a metal is immersed in the respective metal salt solution, Metal/Metal Ion electrode is formed. For example,  $Zn/Zn^{2+}$ ,  $Cu^{2+}/Cu$  etc. Here the electrode potential depends on the logarithm of concentration of the metal ion.

##### 2. Gas Electrode

In this type, the gas is passed through an inert electrode like platinum which is immersed in a solution containing its own ion e.g. hydrogen electrode ( $Pt/H_2/H^+$ ),

Chlorine electrode ( $Pt/Cl_2/Cl^-$ ). Here the electrode potential depends on the logarithm of concentration of the ion and the pressure at which gas is bubbled.

##### 3. Metal/Insoluble metal salt/Common ion electrode

In this type, the metal is covered with paste of its insoluble metal salt which is in contact with a solution containing a common ion with the insoluble salt. Calomel electrode ( $Hg/Hg_2Cl_2/KCl$ ), Silver-silver chloride electrode ( $Ag/AgCl/Cl^-$ ). Here the electrode potential depends on the logarithm of the concentration of the common ion.

##### 4. Redox Electrode

In this type of electrodes, an electrode like platinum is in contact with a redox system, e.g.  $Pt/Fe^{2+}/Fe^{3+}$ ,  $Pt/Ce^{4+}/Ce^{3+}$ . Here the electrode potential depends on the logarithm of concentration of all ionic species involved in the redox reaction.

##### 5. Ion selective electrode

In this type of electrodes, the sensing part of the electrode is usually made up of an ion-specific membrane. The membrane can be glass membrane, crystalline membrane or an ion exchange resin membrane. E.g. glass electrode. Here the glass membrane is made of an ion-exchange type of glass which are sensitive to specific ions like  $H^+$ ,  $Na^+$ ,  $Ag^+$  etc.

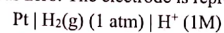
#### Reference Electrodes

These are the standard electrodes with reference to these, the electrode potentials of any other electrode can be determined. The Reference Electrodes are of two types.

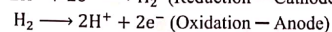
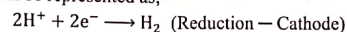
- i) Primary reference electrodes e.g. Standard Hydrogen Electrode
- ii) Secondary reference electrodes e.g. Calomel Electrode

#### 1.5 STANDARD HYDROGEN ELECTRODE (SHE)

The standard hydrogen electrode is a primary reference electrode. It is a gas electrode consisting of a platinum foil connected to platinum wire sealed in a glass tube. The platinum foil is dipped in 1M HCl. Hydrogen gas at 298K and 1 atmospheric pressure is passed through the side arm of glass tube as shown in Fig.1.3. The standard electrode potential of SHE is taken as zero. The electrode is represented as



The electrode reactions can be represented as,





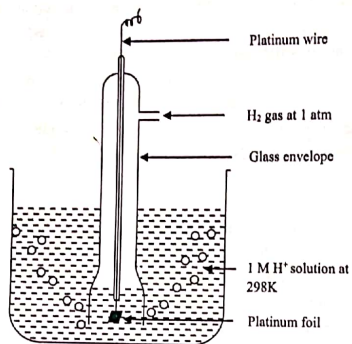


Figure 1.3 Standard Hydrogen Electrode (S.H.E.)

**Advantages of Standard hydrogen electrode (SHE)**

Standard Hydrogen Electrode is a primary reference electrode. The standard Electrode potential ( $E^0$ ) of this electrode has been arbitrarily fixed as zero. SHE has a number of advantages

1. Shows no salt error, negligible internal resistance.
2. It can be used over the entire  $p^H$  range
3. Highly accurate
4. It is a primary reference electrode.

**Limitations of S.H.E**

1. It is difficult to get pure  $H_2$ .
2. The pressure of  $H_2$  is to be maintained at 1 atmosphere all the time.
3. It is difficult to set up and transport.
4. The electrode potential changes with pressure.
5. A large volume of test solution is required.
6. It cannot be used in solutions of redox systems.
7. The solution may poison platinum surface.
8. It cannot be used in solutions having metal ions lower in the Electrochemical Series.

**1.6 MEASUREMENT OF ELECTRODE POTENTIAL**

By single electrode potential, we mean the emf of an isolated half-cell or its half-reaction. Practically it is not possible to measure the emf of a single half-cell directly. However it can be determined by coupling the given half-cell with another standard half-cell. The emf of the newly constructed cell,  $E_{cell}$ , is determined with a voltmeter. The emf of the unknown half-cell, can then be calculated from the expression,

$$E_{cell} = E_R - E_L \quad \text{or} \quad E_{cell} = E_{cathode} - E_{anode}$$

The electrode potentials of any metal electrode can be determined by using reference electrodes like standard hydrogen electrode (SHE) or calomel electrode. The SHE is coupled with the electrode whose electrode potential is to be determined and the electrode potential of the electrode is determined by fixing the electrode potential of SHE as zero. For example, for the determination of Single electrode potential of Zinc electrode, it is coupled with Standard Hydrogen electrode as follows. The emf of the cell is determined (say 0.76V). That value can directly give the electrode potential (as explained below)

The electrode potential of Zinc electrode can be calculated as

$$E_{cell} = E_{cathode} - E_{anode} \quad \text{or} \quad E_{cell} = E_R - E_L$$

$$E_{cell} = E_{SHE} - E_{Zn^{2+}/Zn}$$

$$0.76 = 0 - E_{Zn^{2+}/Zn}$$

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

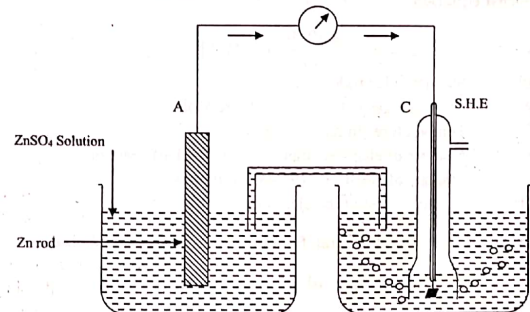


Figure 1.4 Measurement of electrode potential

**Relation between emf and free energy**

When a cell produces current, the current can be used to do work for example to run a motor. Thermodynamic principles can be employed to derive a relation between electrical energy and the maximum amount of work,  $W_{\max}$  obtainable from the cell. The maximum amount of work obtainable from the cell is the product of charge flowing per mole and maximum potential difference,  $E$ , through which the charge is transferred.

$$W_{\max} = -nFE \dots \dots \dots (1)$$

Where,  $n$  is the number of moles of electrons transferred and is equal to the valence of the ion participating in the cell reaction.  $F$  stands for Faraday and is equal to 96,500 coulombs and  $E$  is the emf of the cell. According to thermodynamics, the maximum work that can be derived from a chemical reaction is equal to the free energy ( $G$ ) for the reaction.

$$W_{\max} = \Delta G \dots \dots \dots (2)$$

Therefore, from (1) and (2), we can write,  $\Delta G = -nFE$

**1.7 THE NERNST EQUATION**

We know that the potential of a single electrode or half-cell varies with the concentration of ions in the cell. In 1889 Walter Nernst derived a mathematical relationship to calculate the electrode potential,  $E$ , from the standard electrode potential,  $E^{\circ}$ , the temperature of the cell and the concentration of the electrolyte. This relation known as the **Nernst equation** and can be stated as

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

Where	$E^{\circ}$	= Standard electrode potential
	$R$	= Universal gas constant (8.314 J/K/Mol)
	$T$	= Temperature (In Kelvin scale).
	$n$	= Number of electrons transferred in the half-reaction
	$F$	= Faraday of electricity (96500 Coulombs)
	$[M^{n+}]$	= Concentration of the electrolyte

**Derivation of Nernst Equation:** In general, for a reversible cell the equation is,



The electrical energy of a reversible cell can be measured by the decrease in free energy ( $-\Delta G$ ) of the reaction taking place in the cell. In the cell, if the reaction involves the transfer of  $n$  number of electrons, then  $n$  Faradays of electricity will flow. If  $E$  is the emf

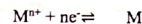
of the cell, then the total electrical energy produced in the cell is

$$-\Delta G = nFE, \text{ where, } -\Delta G = \text{Decrease in free energy change.}$$

At standard conditions,

$$-\Delta G^{\circ} = nFE^{\circ}, \text{ where, } -\Delta G^{\circ} = \text{standard free energy change.}$$

Standard free energy change is the change in free energy when the concentration of reactants and products are unity.  $E^{\circ}$  is the standard emf of the cell in which the reactants and products are kept at 1 molar concentration at 298K. In the reversible electrode reaction,



The equilibrium constant  $K_c$  can be written as,

$$K_c = \frac{[\text{concentration of products}]}{[\text{concentration of reactants}]} = \frac{[M]}{[M^{n+}]}$$

$K_c$  and  $\Delta G$  are related according to Vant Hoff's reaction isotherm of Thermodynamics,

$$\Delta G = \Delta G^{\circ} + RT \ln K_c \dots \dots \dots (1)$$

But  $\Delta G = -nFE$  and  $\Delta G^{\circ} = -nFE^{\circ}$  substituting the value of  $K_c$  in (1)

$$-nFE = -nFE^{\circ} + RT \ln \frac{[M]}{[M^{n+}]} \dots \dots \dots (2)$$

Dividing the above equation (2) by  $-nF$

$$E = E^{\circ} - \frac{RT}{nF} \ln [M] - \frac{RT}{nF} (-\ln [M^{n+}]), \text{ since } [M] = 1, \text{ we have } \ln [M] = 0$$

$$E = E^{\circ} + \frac{RT}{nF} \ln [M^{n+}] \text{ converting } \ln [M^{n+}] \text{ to } \log [M^{n+}]$$

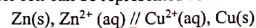
$$E = E^{\circ} + 2.303 \frac{RT}{nF} \log [M^{n+}] \text{ (Nernst equation)}$$

At 298K,  $R = 8.314 \text{ J/K/mol}$ ,  $F = 96500 \text{ coulombs}$ . Nernst equation becomes,

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

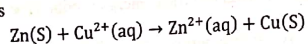
**Variation of emf of Daniel cell with Temperature and Concentration**

The temperature and concentration dependence of emf can be explained with a Daniel cell as shown below. Daniel cell can be represented as





The cell reaction can be written as



Substituting in Nernst equation, we have

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

**Case 1:** When  $[\text{Zn}^{2+}] = [\text{Cu}^{2+}]$ , the logarithmic term become zero, i.e.  $E_{\text{cell}} = E_{\text{cell}}^0$ . This means that the emf of the cell will be independent of temperature.

**Case 2:** When  $[\text{Zn}^{2+}] > [\text{Cu}^{2+}]$ , the logarithmic term becomes negative, i.e.  $E_{\text{cell}} < E_{\text{cell}}^0$ . This indicates that the emf of the cell decreases with rise in temperature.

**Case 3:** When  $[\text{Zn}^{2+}] < [\text{Cu}^{2+}]$ , the logarithmic term becomes positive, i.e.  $E_{\text{cell}} > E_{\text{cell}}^0$ . This indicates that the emf of the cell increases with rise in temperature.

#### Applications of Nernst Equation

- To calculate electrode potential of unknown metal.
- To study the effect of concentration of electrolytes on electrode potential.
- Determination of  $p^{\text{H}}$  of a solution from the measurement of electrode potential.
- Determination of valency of an ion in an electrochemical reaction.
- Calculation of equilibrium constant for a cell reaction.
- Corrosion tendency of metals can be predicted.

**Problem 1:** Calculate the emf of the cell  $\text{Fe} / \text{Fe}^{2+} (0.01) // \text{Ag}^+ (0.1) / \text{Ag}$  at 298K, if standard electrode potential of Fe and Ag electrodes are  $-0.42$  and  $0.8$  V respectively.

**Solution:**  $E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = E_{\text{Ag}^+/\text{Ag}}^0 - E_{\text{Fe}^{2+}/\text{Fe}}^0 = 0.8 - (-0.42) = 1.22\text{V}$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Ag}^+]^2}{[\text{Fe}^{2+}]}$$

$$E_{\text{cell}} = 1.22 - \frac{0.0591}{2} \log \frac{[0.1]^2}{[0.01]}$$

$$E_{\text{cell}} = 1.22 - 0.02955 \log 1 = 1.22\text{ V}$$

**Problem 2:** Calculate the equilibrium constant of Daniel cell reaction given,  $E_{\text{cell}}^0 = 1.1\text{V}$

**Solution:** We know from Nernst equation of Daniel cell that,

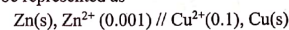
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log K$$

Under equilibrium condition,  $E_{\text{cell}} = 0$ , substituting the value of  $E_{\text{cell}}^0$  and simplifying,

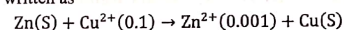
We have  $1.1 = 0.02955 \log K$  or  $\log K = 37.22$  i.e  $K = 1.67 \times 10^{37}$

**Problem 3:** Calculate the emf of a Daniel cell at  $25^\circ\text{C}$ , when the concentration of  $\text{ZnSO}_4$  and  $\text{CuSO}_4$  are  $0.001\text{M}$  and  $0.1\text{ M}$  respectively. (Given  $E_{\text{cell}}^0 = 1.1\text{V}$ )

**Solution:** Daniel cell can be represented as



The cell reaction can be written as

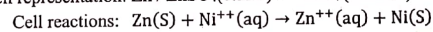


Substituting in Nernst equation, we have

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} = 1.1 + 0.02955 \log \frac{0.1}{0.001} = 1.1 + 0.0591 = 1.1591\text{ V}$$

**Problem 4:** A cell is constructed by coupling Zn electrode dipped in  $0.5\text{ M ZnSO}_4$  and Ni electrode dipped in  $0.05\text{M NiSO}_4$ . Write the cell representation, cell reaction. Calculate the EMF of cell, given  $E^0$  of Zn and Ni as  $-0.76$  and  $-0.25$  volt respectively.

**Solution:** Cell representation:  $\text{Zn} / \text{ZnSO}_4 (0.5\text{M}) // \text{NiSO}_4 (0.05\text{M}) / \text{Ni}$ .



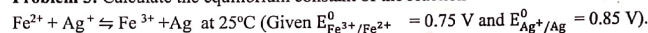
$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = E_{\text{Ni}}^0 - E_{\text{Zn}}^0 = -0.25 - (-0.76) = 0.51\text{V}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Zn}^{2+}]}$$

$$E_{\text{cell}} = 0.51 + \frac{0.0591}{2} \log \frac{[0.05]}{0.5}$$

$$= 0.51 + 0.02955 \log 0.1 = 0.4805\text{ V}$$

**Problem 5:** Calculate the equilibrium constant of the reaction



**Solution:**  $E_{\text{cell}}^0 = E_{\text{Ag}^+/\text{Ag}}^0 - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.85 - (0.75) = 0.1\text{V}$

We know from Nernst equation that,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{1} \log K. \text{ Where, } K \text{ is the equilibrium constant.}$$

Under equilibrium condition,  $E_{\text{cell}} = 0$ , substituting the value of  $E_{\text{cell}}^0$  and simplifying,

$$E_{\text{cell}}^0 = \frac{0.0591}{1} \log K \text{ or } \log K = \frac{E_{\text{cell}}^0 \times 1}{0.0591} = \frac{0.1}{0.0591} = 1.69 \therefore K = \text{Antilog } 1.69 = 48.97$$

**Problem 6:** At  $25^\circ\text{C}$  the standard emf of a cell having reaction involving 2 electrons are found to be  $0.295\text{ V}$ . Calculate the equilibrium constant of the reaction. (KTU June 2016)

**Solution:** We know from Nernst equation that,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log K, \text{ where } K \text{ is the equilibrium constant}$$

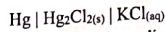
Under equilibrium condition,  $E_{\text{cell}} = 0$ , substituting the value of  $E^{\circ}_{\text{cell}}$  and simplifying,

$$E^{\circ}_{\text{cell}} = \frac{0.0591}{2} \log K \text{ or } \log K = \frac{E^{\circ}_{\text{cell}} \times 2}{0.0591} = \frac{2 \times 2.95}{0.0591} = 9.983$$

$$\therefore K = \text{Antilog } 9.983 = 9.6 \times 10^9$$

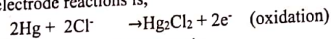
**1.8 CALOMEL ELECTRODE (Secondary Reference Electrode)**

It consists of a glass tube containing pure mercury at the bottom. A paste of mercurous chloride ( $\text{Hg}_2\text{Cl}_2$ -calomel) covers the mercury. A solution of potassium chloride is placed over the paste. A platinum wire, dipping in to the mercury layer, is used for making electrical contact. There is a side-tube containing KCl solution - the salt bridge, for coupling the electrode to any other electrode (for electrical contact). The electrode is represented as,



The calomel electrode acts as anode or cathode depending upon the other electrode used.

When it acts as anode, the electrode reactions is,



When it acts as cathode, the electrode reaction is

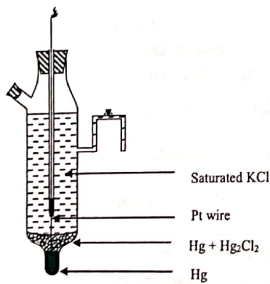
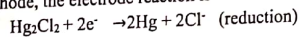


Figure 1.5 Saturated Calomel Electrode

Electrode potential of the cell is reversible with respect to the chloride ions and depends on the concentration of KCl used.

$$E_{\text{calomel}} = E^{\circ}_{\text{calomel}} - \frac{2.303RT}{nF} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$E_{\text{calomel}} = E^{\circ}_{\text{calomel}} - \frac{2.303RT}{2F} \log \frac{[\text{Hg}]^2 [\text{Cl}^-]^2}{[\text{Hg}_2\text{Cl}_2]}$$

Since the concentrations of the solids are unity, the above equation can be written as

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

On simplification, the above equation becomes,

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

Table 1.3 Variation of emf with KCl concentration in Calomel Electrode

KCl concentration	0.1N	1N (NCE)	Saturated (SCE)
Electrode potential	0.335	0.2810	0.2422

**Advantages of Calomel Electrode**

1. Easy to set up.
2. Easily transportable
3. Long shelf life
4. Reproducibility of emf
5. Low temperature coefficient
6. Electrode can be used in a variety of solutions.
7.  $E^{\circ}$  value is accurately known.

**Electrode Potential Using Calomel Electrode**

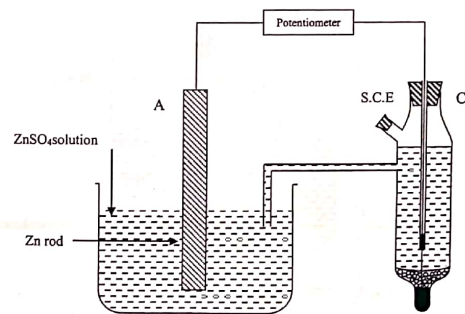


Figure 1.6 Determination of Electrode Potential



In order to determine the unknown potential of an electrode (say Zn electrode), the calomel electrode is coupled with that electrode and the emf of the resulting cell is determined using a potentiometer. By normal convention we can write,

$$E^{\circ}_{cell} = E^{\circ}_{calomel} - E^{\circ}_{Zn}$$

When we use saturated calomel electrode and Zn electrode, from the measured value of the emf of the resultant cell, (for instance measured value of emf is 1.0) we can write,

$$1.0 = 0.2422 - E^{\circ}_{Zn}$$

$$E^{\circ}_{Zn} = 0.2422 - 1 = -0.76 \text{ Volt}$$

### 1.9 GLASS ELECTRODE

Glass electrode is commonly used as secondary reference electrode. Its emf is determined by coupling with a saturated calomel electrode (SCE). The glass electrode provides one of the easiest methods for measuring the pH of a given solution. It consists of a thin walled glass bulb containing AgCl coated Ag electrode or simply a Pt electrode in 0.1 M HCl. The glass has low melting point and high electrical conductivity. The glass electrode can be represented as

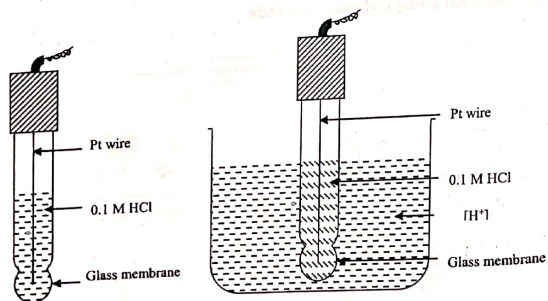
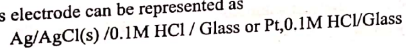


Fig. 1.7 Glass electrode

**Principle:** When two solutions of different pH values are separated by a thin glass

membrane, there develops a difference in potential between the two surfaces of the membrane. The potential difference developed is proportional to the difference in pH value. The glass membrane functions as an ion exchange resin and an equilibrium is attained between the Na<sup>+</sup> ions of glass and H<sup>+</sup> ions in solution. The potential of the electrode E<sub>G</sub> is given by,

$$E_G = E_G^{\circ} + 0.0591 \log[H^+]$$

$$E = E_G^{\circ} - 0.0591 \text{ pH}$$

### Determination of pH of a solution using Glass Electrode

Glass electrode is used as an internal reference electrode. To determine pH of unknown solution the glass electrode is combined with secondary reference electrode such as calomel electrode. The two electrodes are connected to potentiometer. The cell formed is represented as

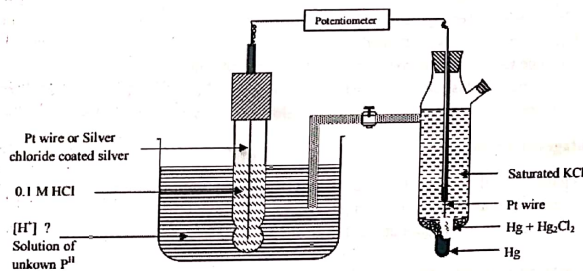
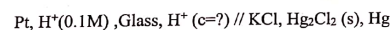


Fig. 1.8 Determination of pH using Glass Electrode

It is clear that E<sub>G</sub> of the glass electrode depends on the pH of the solution in which the glass electrode is dipped. The potential of the electrode E<sub>G</sub> is given by

$$E_{Glass} = E_G^{\circ} - 0.0591 \text{ pH} \text{ ----- (1)}$$

Where, E<sub>G</sub><sup>0</sup> is the standard electrode potential of the glass electrode. By using a potentiometer, the resultant emf of the coupled cell is measured. Knowing the value of

$E^0_G$  of glass electrode and potential of saturated calomel electrode ( $E_{SCE}$ ), the pH of the solution can be calculated as follows:

$$E_{cell} = E_{cathode} - E_{anode} \text{ or } E_{right} - E_{left}$$

$$E_{cell} = E_{SCE} - E_{Glass} \text{----- (2)}$$

But we know that  $E_{SCE} = 0.2422$ , substituting this and the value of  $E_{Glass}$  from eqn.1 in equation 2 we have

$$E_{cell} = 0.2422 - (E^0_G - 0.0591 \text{ pH}) \text{----- (3)}$$

Rearranging and simplifying equation 3,

$$0.0591 \text{ pH} = E_{cell} + E^0_G - 0.2422$$

Hence, pH can be determined using the formula  $\text{pH} = \frac{E_{cell} + E^0_G - 0.2422}{0.0591}$

The  $E^0_G$  value of glass electrode can be determined using a buffer solution of known pH.

#### Advantages of Glass Electrode

- It is used in colored, turbid and colloid solutions
- Results are accurate
- Electrode is not easily poisoned
- Equilibrium is quickly attained
- It can be used in strong oxidizing solutions and alkaline solutions
- Using special glass electrode, pH can be measured from 0 to 12.
- It can be used in chemical, industrial, biological and agricultural laboratories.

#### Disadvantages or Limitations

- Glass has high resistance. So special electronic potentiometer must be used.
- It cannot be used if the solution  $\text{pH}$  is more than 12
- It cannot be used in pure ethanol or in acetic acid.

### 1.10 LITHIUM ION CELLS

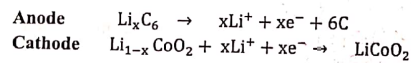
Lithium ion cell is a type of a battery composed of Lithium, the lightest metal and the metal that has the highest electrode potential. Because of its lightness and high energy density, Lithium-Ion batteries are ideal for portable devices, such as notebook computers. In addition, Lithium ion batteries have no memory effect and do not use heavy metals, such as lead, mercury or cadmium. The only disadvantage to Lithium-Ion batteries is that they are currently more expensive than NiCad and NiMH battery packs. Lithium metal cannot be used safely in secondary batteries. For this reason, various lithium compounds have been made, which are used in rechargeable batteries, commonly known as lithium

ion cells. These are the most energetic rechargeable batteries available. Lithium ion battery is regarded as a new generation battery since it can give an emf varying from 3.5 – 4 V (depending upon the electrode material). Lithium ion battery (LIB) consists of an anode, cathode and an electrolyte, for which a variety of materials may be used. Lithium ion batteries are common in modern consumer electronics.

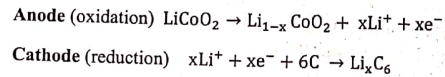
Three primary functional components of a lithium ion battery are

- Anode:** Consisting of lithiated graphite (lithium ions are inserted in between the layers of carbon atoms).
  - Cathode:** Is a mixed metal oxide like  $\text{LiCoO}_2$ ,  $\text{LiMnO}_2$ ,  $\text{LiFeO}_2$  etc.
  - Electrolyte:** Is a lithium salt like  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiClO}_4$  etc.
- The lithium ions move from the anode to the cathode during discharging and from cathode to anode while charging. Lithium is extracted from anode and inserted to cathode during discharging. Various chemical reactions taking place during charging and discharging can be written as follows,

**Discharging:** During discharging, the cell act as an electrochemical cell where the chemical energy is converted to electrical energy. When the cell acts as an electrochemical cell,  $\text{LiCoO}_2$  acts as cathode and the graphite act as anode.



**Charging:** Charging is done by applying a higher voltage than the voltage of the battery across the electrodes. The charging involves exactly the reverse process of the normal cell reaction. The various reactions during charging operations can be written as



During charging an external voltage source pulls electrons from the cathode through an external circuit to the anode and causes Li-ions to move from the cathode to the anode by transport through a liquid electrolyte. During discharge the processes are reversed. Li-ions move from the anode to the cathode through the electrolyte while electrons flow through the external circuit from the anode to the cathode and produce power. Depending on the choice of material for anode, cathode and electrolyte, the voltage, capacity, life and safety of a lithium ion battery can change drastically.



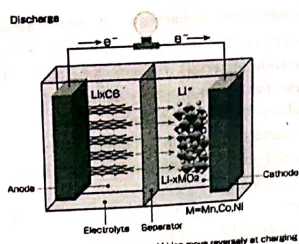


Fig. 1.9 Lithium ion battery

#### Advantages of lithium ion batteries

1. They are usually much lighter than other types of rechargeable batteries.
2. Lithium-Ion batteries have no memory effect.
3. Lithium-Ion batteries can handle hundreds of charge / discharge cycles.
4. Lithium-Ion batteries can be formed in to a wide variety of shapes and sizes so as to efficiently fill the available space in the device they power.
5. Lithium-Ion battery pack loses only 5% of its charge per month, compared to 20% loss per month for other batteries.
6. Since Li-ion batteries contain no toxic metals (unlike other types of batteries which may contain lead or cadmium) they are generally categorized as non-hazardous waste.
7. Lithium-ion is a low maintenance battery, an advantage over other batteries.
8. The load characteristics are reasonably good and behave similarly to nickel-cadmium in terms of discharge. The high cell voltage of 3.6 volts allows battery pack designs with only one cell. Most of today's mobile phones run on a single cell. A nickel-based pack would require three 1.2-volt cells connected in series.

#### Limitations of lithium ion batteries

1. Requires protection circuit to maintain voltage and current within safe limits.
2. Transportation restrictions - shipment of larger quantities may be subject to regulatory control. This restriction does not apply to personal carry-on batteries.
3. Expensive to manufacture - about 40 percent higher in cost than nickel-cadmium.
4. They are extremely sensitive to high temperatures. Heat causes lithium - ion battery pack to degrade much faster than they normally would.
5. If lithium ion battery gets completely discharged, then it is ruined.

#### Applications of Lithium Ion Batteries

1. Lithium-Ion batteries are ideal for portable devices, such as notebook computers.
2. Lithium -Ion batteries find application in many long-life, critical devices, such as artificial pacemakers and other implantable electronic medical devices.
3. Lithium batteries also prove valuable in oceanographic applications.
4. Small lithium batteries are very commonly used in small, portable electronic devices, such as PDAs, watches, camcorders, digital cameras, thermometers, calculators etc.
5. Digital cameras and consumer electronics.

#### 1.11 POTENTIOMETRIC TITRATIONS

Potentiometric titration makes use of the measurement of change in electrode potential upon the addition of the titrant against the volume of titrant added. In this method, a cell is constructed in which at least one of the electrodes is reversible with respect to one of the ions taking part in the titration reaction.

**Theory:** From Nernst equation, we know that the potential of an electrode dipped in an electrolyte depends upon the concentration of active ions which changes the electrode potential.

$$E = E^{\circ} + \frac{RT}{nF} \log C$$

A small change in active ion concentration in the solution changes the electrode potential correspondingly. During the course of titration, the concentration of active ion decreases, thereby electrode potential of the indicator electrode decreases. Thus the measurement of indicator electrode potential can give indication about the end point or equivalence point of the titration. The potential of the indicator electrode is, usually measured potentiometrically by coupling it with a reference electrode like Saturated Calomel Electrode (SCE).

**Advantages of Potentiometric Titrations:** There are many situations where potentiometric titrations have an advantage over "classical" visual indicator methods.

1. No indicators are required for potentiometric titrations.
2. Potentiometric titrations can be used for the determination of end points with colored, turbid or fluorescent solutions.
3. Potentiometric titrations are widely used since the apparatus used are not expensive and freely available.
4. Potentiometric titrations are more accurate
5. Prior information about the relative strength of titrants are not required.
6. Redox and precipitation reactions can be followed.

**Types of Potentiometric Titrations:** There are three types of potentiometric titrations

1. Oxidation-reduction (Redox) titrations
2. Acid-base titrations
3. Precipitation titrations

**Oxidation-Reduction Titrations**

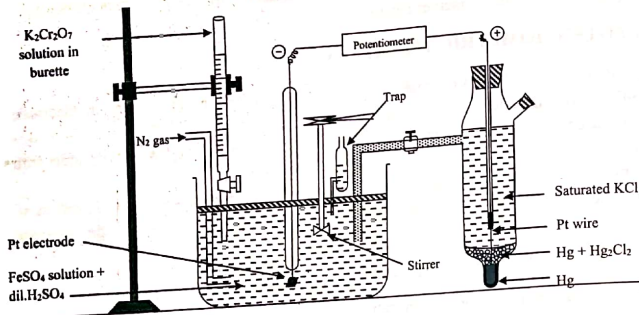


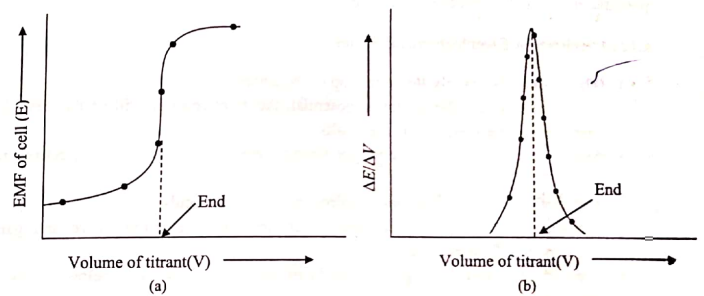
Fig. 1.10 Oxidation - reduction potentiometric titration

Titration involving oxidizing agents ( $K_2Cr_2O_7$  or  $KMnO_4$ ) and reducing agents (like ferrous salts) can be followed potentiometrically by using platinum indicator electrode. The apparatus for the titration of a ferrous salt with acidified  $K_2Cr_2O_7$  is shown in Figure 1.10. In this case an inert platinum electrode is immersed in a solution containing both oxidized and reduced forms of ions. It acts as a redox electrode which is coupled with a calomel electrode. On adding  $K_2Cr_2O_7$  from the burette, emf of the cell will increase first slowly. However, at the equivalence point, there will be a sudden jump in potential due to the rapid change in ratio of  $Fe^{2+}/Fe^{3+}$  ion concentration.

$$E = E^0 + \frac{RT}{F} \ln \frac{(Fe^{2+})}{(Fe^{3+})}$$

The titration curve is an S-shaped curve and the inflexion point corresponds to end point. But in most of the cases, the curve may not give a sharp inflexion and hence analytical (or derivative) method is preferred for more accurate results. In analytical method, the

first derivative  $\frac{\Delta E}{\Delta V}$  is plotted against V. The end point can be detected from the peak of the curve.



- (a) In potentiometric titration, the point of inflexion represents the end point
- (b) Graph of  $\Delta E/\Delta V$  against volume (V) of titrant. Maxima gives more accurate end point

**1.12 ELECTROCHEMICAL SERIES (ECS)**

Table 1.4 Electrochemical Series

Metal	Electrode	Electrode Potential
Li	Li, Li <sup>+</sup>	-3.05
K	K, K <sup>+</sup>	-2.93
Ca	Ca, Ca <sup>2+</sup>	-2.90
Mg	Mg, Mg <sup>2+</sup>	-2.37
Al	Al, Al <sup>3+</sup>	-1.66
Zn	Zn, Zn <sup>2+</sup>	-0.76
Fe	Fe, Fe <sup>2+</sup>	-0.44
Ni	Ni, Ni <sup>2+</sup>	-0.23
Pb	Pb, Pb <sup>2+</sup>	-0.13
H <sub>2</sub>	H <sub>2(g)</sub> , H <sup>+</sup>	0.00
Cu	Cu, Cu <sup>2+</sup>	+0.34
Ag	Ag, Ag <sup>2+</sup>	+0.80
Pt	Pt, H <sup>+</sup>	+0.86
Au	Au, Au <sup>+</sup>	+1.69

A series which represents an arrangement of various electrodes in the increasing order of their standard reduction potentials or decreasing order of their standard oxidation potential are called electrochemical series.

#### Characteristics of Electrochemical Series

1. The most active metals are on the top of the series.
2. The more negative the reduction potential, the more reactive will be the metal in displacing other metals from their salts.
3. Metals near the top of the series are strongly electropositive and lose electrons to give cations.
4. Metals above hydrogen displace hydrogen from dilute acids.
5. Elements near the bottom of the series are highly electronegative and gain electrons readily to form anions.
6. Metals lying above hydrogen are easily rusted, while those lying below hydrogen are not rusted.
7. Various oxidizing agents are arranged in the increasing order
8. Various reducing agents are arranged in the decreasing order.
9. The emf of a galvanic cell can be readily calculated from the relation

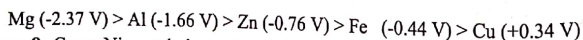
$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{cathode}} - E_{\text{anode}}$$

#### Applications of Electrochemical Series

1. To know the relative ease of oxidation and reduction. Greater the reduction potential, more easily the substance undergoes reduction.
2. To predict whether a metal reacts with acid to liberate hydrogen gas.
3. To calculate the standard emf of a cell.
4. Calculation of equilibrium constant.

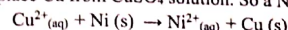
**Problem 7:** Arrange the following metals in the order in which they displace each other: Al, Cu, Fe, Mg, Zn. The standard reduction potentials of these metals are -1.66 V, +0.34 V, -0.44 V, -2.37 V, and -0.76 V respectively.

**Solution:** When the reduction potential becomes low the metal shows more tendencies to lose electrons and can be displaced and deposited easily. Thus the arrangement is



**Problem 8:** Can a Ni spatula be used to stir  $\text{CuSO}_4$  solution? Give valid reason for the answer.  $E_{\text{Ni}}^{\circ} = -0.23 \text{ V}$ ,  $E_{\text{Cu}}^{\circ} = 0.34 \text{ V}$  (KTU May 2017)

**Solution:**  $E^{\circ}$  of Ni is lower than that of Cu. Hence if a Ni spatula is used to stir  $\text{CuSO}_4$  solution, it will displace Cu from  $\text{CuSO}_4$  solution. So a Ni spatula cannot be used to stir.

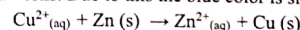


**Problem 9:** Can we use a copper vessel to store 1M  $\text{AgNO}_3$  solution? ( $E_{\text{Cu}}^{\circ} = +0.34 \text{ V}$ ,  $E_{\text{Ag}}^{\circ} = +0.80 \text{ V}$ )

**Solution:** The reduction potential ( $E_{\text{Ag}}^{\circ}$ ) of silver is higher than that of ( $E_{\text{Cu}}^{\circ}$ ) copper. Hence, Cu is incapable of displacing silver from silver nitrate solution. Thus, we can use a copper vessel to store 1M  $\text{AgNO}_3$  solution.

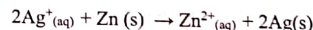
**Problem 10:** When a zinc rod ( $E_{\text{Zn}}^{\circ} = -0.76 \text{ V}$ ) is dipped in a copper sulphate solution ( $E_{\text{Cu}}^{\circ} = +0.34 \text{ V}$ ), the blue color of  $\text{CuSO}_4$  is slowly discharged. Explain the phenomenon.

**Solution:**  $E^{\circ}$  of Zn is lower than that of Cu. Hence when a Zn rod is dipped in  $\text{CuSO}_4$  solution, it will displace Cu from  $\text{CuSO}_4$  solution. This will result in the decrease in concentration of  $\text{Cu}^{2+}$  ions. Due to this the blue color is slowly discharged.



**Problem 11:** A zinc wire is dipped in silver nitrate solution taken in beaker A and a silver wire is dipped in zinc sulphate solution taken in beaker B. Predict in which beaker the ions present will get reduced. Given that the standard reduction potential of zinc and silver are -0.76 V and 0.80V respectively. (KTU January 2016)

**Solution:** In beaker A the ions present will get reduced.  $E^{\circ}$  of Zn is lower than that of Ag. Hence when a Zn rod is dipped in  $\text{AgNO}_3$  solution, it will displace Ag from the electrolyte solution.



### 1.13 CORROSION

Corrosion is the process of gradual deterioration of a metal from its surface due to the unwanted chemical or electrochemical reaction of metal with its environment. Even though it is a natural phenomenon in which the gases present in the atmosphere react chemically with metals to convert them into their salts, it results in loss of material and money. Metals and alloys are used as construction and fabrication materials in engineering. If the metal or alloy structure is not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. This phenomenon of metals and alloys to undergo destruction by the act of environment is known as corrosion. Corrosion is defined as the destruction or deterioration of a metal or its alloy and consequent loss of metal, caused due to direct chemical action or electrochemical reactions with its environment.



### Causes of Corrosion

Metals occur in nature as their oxides, sulphides carbonates etc. The chemically combined state is thermodynamically more stable. When we extract a metal from its ore, the metal is in a higher energy state, which is thermodynamically unstable. So it tries to go back to the stable state by chemical or electrochemical interaction with the environment.

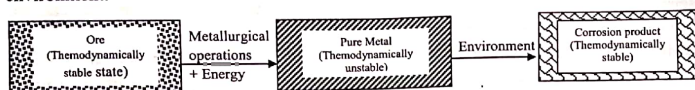


Fig. 1.11 Causes of corrosion

### Consequences or Effects of Corrosion

Due to corrosion the useful properties of a metal such as malleability, ductility and electrical conductivity are lost. The most familiar example of corrosion is rusting of iron when exposed to atmospheric conditions. During this, a layer of reddish scale and powder of oxide ( $\text{Fe}_2\text{O}_3$ ) is formed and the iron becomes weak. Another example is the formation of green film or basic carbonate [ $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$ ] on the surface of copper when exposed to moist air containing  $\text{CO}_2$ . It has been roughly assessed that the amount of iron wasted due to corrosion is one fourth of world production. The direct loss due to corrosion in India amounts to Rs. 200 crore/annum while the money spent annually in controlling corrosion is of the order of Rs. 50 crore. It is better to control rather than to prevent corrosion, since it is impossible to eliminate corrosion. Effects of corrosion are briefly given below.

1. Efficiency of the machine decreases.
2. Plant has to be shut down due to failure.
3. Product is contaminated.
4. The toxic products of corrosion cause health hazards.
5. There is a necessity to over design to allow for corrosion

### Factors affecting corrosion

Metal corrosion is a slow process of destruction of metal surface by its environment. It is due to various chemical reactions that occur on the surface of metals and alloys under the action of the environment. There are two factors influencing the rate of corrosion process.

1. Nature of Metal (Internal factors of corrosion)
2. Nature of corrosive Environment (External factors of corrosion)

Primary factors related to the metal and secondary factors related to the environment. Various factors affecting corrosion are outlined in Table.1.5

Table.1.5 Factors affecting corrosion

No.	Nature of the metal	Nature of the environment
1.	Position in the Galvanic Series	Temperature
2.	Relative anodic and cathodic area.	Humidity
3.	Purity of the metal	$\text{p}^{\text{H}}$ of the medium
4.	Physical state of the metal	Conductance of the corroding medium
5.	Nature of surface film	Formation of oxygen concentration cells
6.	Solubilities of products of corrosion	Nature of impurities
7.	Volatility of corrosion products	Flow velocity of process stream
8.	Overvoltage	Presence of impurities

### Mechanism or Theories of Corrosion

1. Dry or Chemical Corrosion
2. Wet or Electrochemical Corrosion

**1. Dry or Chemical Corrosion:** It is due to the attack on metal surface by atmospheric gases like  $\text{O}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$  etc. (e.g.) tarnishing of silver by  $\text{H}_2\text{S}$ . There are three types of dry corrosion.

- 1) Oxidation Corrosion
- 2) Corrosion by Hydrogen
- 3) Liquid Metal Corrosion

**2. Wet or Electrochemical Theory of Corrosion:** It is a common type of corrosion of metal in aqueous corrosive environment. This type of corrosion occurs when the metal comes in contact with a conducting liquid or when two dissimilar metals are immersed or dipped partly in a solution. According to this theory, there is the formation of a galvanic cell on the surface of metals. Some parts of the metal surface act as anodic area and rest as cathodic area. The chemicals in the environment and humidity act as an electrolyte. Oxidation of anodic part takes place and it results in corrosion at anode, while reduction takes place at cathode. The corrosion product is formed on the surface of the metal between anode and cathode. To explain the wet theory, let us take the example of corrosion of iron. Depending on the nature of the environment, it may occur in two different ways.

- 1) **In acidic environment by evolution of hydrogen:** In this case, metals react in the acidic environment and are dissolved (undergo corrosion) to release H<sub>2</sub> gas. All metals above hydrogen in electrochemical series shows this type of corrosion. In hydrogen evolution type of corrosion, anodic area is large as compared to its cathodic area (See Fig 1.12)

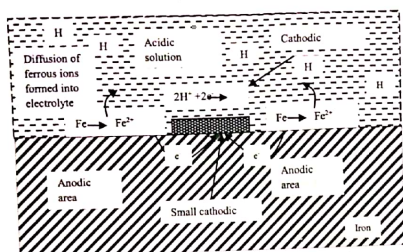
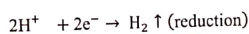


Fig. 1.12 Mechanism of wet corrosion by Hydrogen evolution

**At anode:** Oxidation occurs.



**At cathode:** The hydrogen ions (H<sup>+</sup>) are formed due to the acidic environment and the following reaction occurs in the absence of oxygen

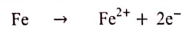


The overall reaction is,

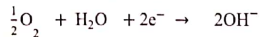


- 2) **In neutral or alkaline environment by Absorption of oxygen:** This type of corrosion takes place in neutral or basic medium in the presence of oxygen. The oxide of iron covers the surface of the iron. The small scratch on the surface creates small anodic area and rest of the surface acts as cathodic area. The following chemical reactions occur at anode and cathode.

**At anode,** oxidation occurs,



**At cathode,** reduction can occur,



The Fe<sup>2+</sup> ions (at anode) and OH<sup>-</sup> (at cathode) diffuse and when they meet, ferrous hydroxide is precipitated.



Ferric hydroxide is actually hydrated ferric oxide, Fe<sub>2</sub>O<sub>3</sub>.H<sub>2</sub>O, which is yellowish rust. Anhydrous magnetite, Fe<sub>3</sub>O<sub>4</sub> [a mixture of (FeO + Fe<sub>2</sub>O<sub>3</sub>)], is also formed, which is

brown-black in color. It is to be noted that the corrosion occurs at anode but the corrosion product is formed near cathode. It is because of the rapid diffusion of Fe<sup>2+</sup> as compared to OH<sup>-</sup> (see Fig.1.13). Hence corrosion occurs at anode, but rust is deposited in between anode and cathode.

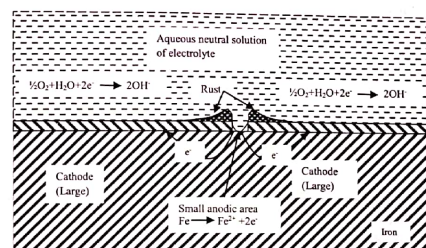


Fig.1.13 Mechanism of wet corrosion by oxygen absorption

#### Types of Electrochemical Corrosion

- Galvanic corrosion (Bimetallic corrosion):** This type of electrochemical corrosion occurs when two dissimilar metals are connected and exposed to an electrolyte. These dissimilar metals will form a galvanic cell. The anodic metal will be oxidized and it will undergo corrosion. For instance, Zinc and copper metals connected with each other in an electrolyte medium form a galvanic cell. Zinc acts as anode and undergoes corrosion while cathode (copper) will be unaffected.
 

**Examples:** (i) Steel screws in a brass marine hardware; (ii) Lead-antimony solder around copper wire (iii) steel propeller shaft in bronze bearing (iv) steel pipe connected to copper plumbing.
- Differential aeration corrosion (Concentration Cell Corrosion):** Differential aeration corrosion is the most common type of electrochemical corrosion. This type of corrosion is more common whenever a metal or alloy structure is partially dipped in an electrolyte. The portion dipped in water is poor in oxygen, works as anode which gets corroded and the portion above water acts as cathode which is protected. The system will act as a concentration cell.
 

**Examples:** (i) Half-immersed iron plate in aqueous solution (ii) Ocean going ships (iii) Steel storage tanks (iv) steel pipe carrying any liquid exposed to atmosphere.

### Corrosion Control

There are various corrosion control techniques as the corrosion depends on the nature of the environment. Some of the corrosion control methods are

1. Corrosion inhibitors
2. By cathodic protection
3. Using corrosion Inhibitor
4. By proper designing
5. By the application of protective coating

#### 1.14 CATHODIC PROTECTION

Cathodic protection is an electrochemical method of mitigating corrosion on metallic structures that are exposed to electrolytes such as soils and waters. The corrosion of metal takes place at the anodic region whereas at the cathodic region, metal is unaffected. The principle of cathodic protection involves the elimination of anodic sites and conversion of the entire metal into cathodic site. In other words, the principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur. This can be achieved by providing electrons from an external source so that the specimen always remains cathode. This technique of offering protection to a metal against corrosion by providing electrons from an external source is called cathodic protection. There are two types of cathodic protections:

##### 1. Sacrificial Anodic Protection Method

In this protection method, the metallic structure (to be protected) is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly; while the parent structure (cathodic) is protected.

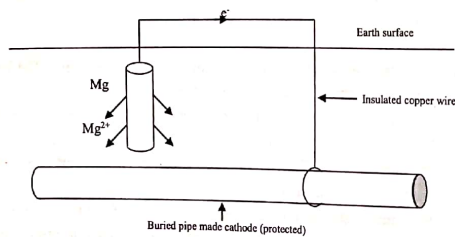


Fig. 1.14 Sacrificial anodic protection

The more active metal so-employed is called "sacrificial anode". The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anodes are magnesium, zinc, aluminium and their alloys.

#### Applications of sacrificial anodic protection

Important applications of sacrificial anodic method include:

1. Protection of buried pipelines and distribution systems
2. Protection of underground cables
3. Protection of marine structures, ship-hulls etc.
4. Protection of water heaters and boilers
5. Protection of water-tanks, piers etc.

#### Advantages of sacrificial anodic protection systems.

1. No external power is required.
2. No regulation is required.
3. Easy to install.
4. Minimum cathodic interference problem.
5. Anodes can be readily added.
6. Minimum maintenance required.
7. Uniform distribution of current.
8. Efficient use of protective current.
9. Installation can be inexpensive if installed at the time of construction.

#### Limitations of Sacrificial Anodic Protection.

1. Limited driving potential.
2. Poorly coated structures may require many anodes.
3. Lower/ limited current output.
4. Can be ineffective in high - resistivity environments.
5. Installation can be expensive if installed after construction.

#### 2. Impressed Current Cathodic Protection

Corrosion occurs in metals depending on the environment to which it is exposed. The corrosion current always flows from the anodic area to the cathodic area of the metal. In impressed current cathodic protection method, a current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode. Usually, the impressed current is derived from a direct current source (like battery or rectifier on A.C. line) with an insoluble anode (like graphite, high silica iron, scrap iron,



stainless steel etc.). Usually, a sufficient D.C. current is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium), and connected to the metallic structure to be protected (see Fig.1.15). The anode is usually, in a backfill (composed of coke breeze or gypsum) so as to increase the electrical contact with the surrounding soil.

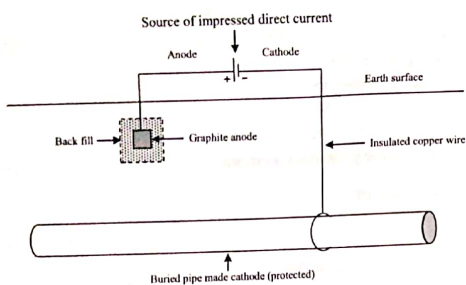


Fig.1.15 Impressed Current Cathodic Protection

Table. 1.6 Comparison of Sacrificial Anodic and Impressed Current Cathodic methods

No	Sacrificial Anodic Protection	Impressed Current Cathodic Protection
1	No external power supply required	External power supply required
2	Economical for short term protection.	More suitable for long term operations.
3	Investment is less	High investment required
4	Suitable when the current requirements and the resistivity of the electrolytes are relatively low	Suitable when the current requirements and the resistivity of the electrolytes are relatively high
5	Requires periodical replacement of anodic material.	Anodes are relatively stable and do not corrode.

**Applications of Impressed current cathodic protection**

Impressed current cathodic protection is generally applied in

1. Protection of buried pipelines and distribution systems
2. Protection of underground oil pipelines, marine piers etc.

3. Protection of transmission line towers.
4. Protection of condensers, laid-up ships etc.
5. Protection of large structures for long-term operations.

**Advantages of impressed current cathodic protection systems**

1. Can be designed for a wide range of voltage and current.
2. High ampere output is available from single ground bed.
3. Large areas can be protected by single installation.
4. Variable voltage and current output.
5. Applicable in high – resistivity areas.
6. Effective in protecting un coated and poorly coated structures.

**Disadvantages of impressed –current cathodic protection systems**

1. Are subjected to power failure and vandalism.
2. Require periodic inspection and maintenance.
3. Requires external power, resulting in monthly power costs.
4. Overprotection can cause coating damage.

**1.15 GALVANIC SERIES**

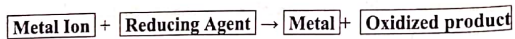
Galvanic series indicates the relative corrosion tendency of a metal or alloy when exposed to the seawater at a specific temperature for a specified period of time. The electrochemical series (ECS) give useful information regarding the reactivity of metals, but it does not provide sufficient information in predicting the corrosion behavior. In electrochemical series, the metals having lower reduction potential in the series are more anodic and undergo corrosion faster. However, as a result of passivity some metals exhibit noble behavior, due to the change of electrode potential more positive. So a more practical series called galvanic series have been prepared. A series obtained by arranging metals and alloys in the order of corrosion tendencies is known as galvanic series. Galvanic series is a more practical series which give real and useful information regarding the corrosion behavior of metals and alloys in a given environment. It predicts the corrosion tendencies of both metals and non metals in actual environments. It is developed by studying corrosion of metals and alloys in unpolluted sea water without their oxide films. In galvanic series electrode potentials are measured using calomel electrode as the reference electrode. The position of a particular metal may be changed in the galvanic series. The position of a metal when present in the form of an alloy is different from that of pure metal.

Table 1. 7 Comparison of electrochemical Series and Galvanic Series

Electrochemical Series	Galvanic Series
1. Is an arrangement of various metal electrodes in the increasing order of their standard reduction potentials.	Is a series obtained by arranging metals and alloys in the order of corrosion tendencies.
2. ECS predicts the relative displacement tendencies of metals in electrolytes.	It predicts the corrosion tendencies in actual environments.
3. In ECS, electrode potentials are measured by using SHE as the reference electrode.	In galvanic series electrode potentials are measured by using calomel electrode as the reference electrode.
4. The position of a particular metal is fixed in the electrochemical series.	The position of a particular metal may be changed in the galvanic series.
5. Alloys of metals are not included in the electrochemical series.	Position of a metal when present in alloy form is different from that of pure metal.
6. Electrode potential is measured by dipping pure metals in 1M salt solution	Electrode potential is measured by dipping metals and alloys in unpolluted sea water.

### 1.16 ELECTROLESS PLATING

Electroless plating (also known as **autocatalytic plating**) is a method of depositing a metal from its salt solution on a catalytically active surface of the metal to be plated using a suitable reducing agent without using electrical energy. The reducing agent reduces the metal ion in to metal which gets plated over the catalytically activated surface giving a thin uniform coating. The process is a chemical reaction and is autocatalytic. The decrease in free energy involved in the redox reaction is responsible for the plating. In this plating, metal is deposited evenly long edges, inside holes, and over irregularly shaped objects that are difficult to plate evenly with electroplating. Electroless plating is also used to deposit a conductive surface on a non-conductive object to improve its electroplating. This technique was introduced by Brenner and Riddell in 1946.



### ELECTROLESS PLATING OF NICKEL

In electroless plating of Nickel, following steps are followed.

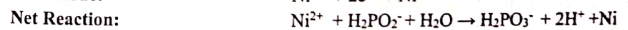
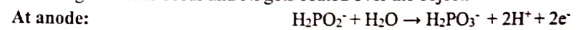
- Pretreatment and activation of the surface:** The surface to be plated is first degreased by using organic solvents or alkali followed by acid treatment.
  - Surface of stainless steel is activated by dipping in hot solution of 50% dil. H<sub>2</sub>SO<sub>4</sub>.
  - Mg alloy surface is activated by thin coating of zinc and copper over it.
  - Metals like Cu, Al and alloys like brass can be directly Ni plated without activation.
  - Non-metallic articles like plastics, glasses are activated by dipping them in the solution containing SnCl<sub>2</sub> and HCl followed by dipping a PdCl<sub>2</sub> solution. A thin layer of palladium will be formed on the surface upon drying.

#### Plating Bath

Table.1.8 various ingredients in plating bath

No	Ingredient type	Ingredient	Function	Qty. (g/l)
1	Coating solution	NiCl <sub>2</sub>	Coating	20
2	Reducing agent	Sodium hypophosphite	Metal deposition	20
3	Complexing agent	Sodium succinate	Quality improvement	15
4	Buffer	Sodium acetate buffer	pH maintenance	10

**Procedure:** The pretreated object is immersed in the plating bath for required time. The following reactions occur and Ni gets coated over the object.



#### Applications of Electroless Plating

- Electroless Ni plating is extensively used in electronic applications.
- It is used in domestic (e.g. Jewellery, perfume bottle top etc.)
- Automotive fields ( Car trims)
- Electroless Ni plated polymers (like ABS plastics) are used in decorative as well as functional applications.

**Advantages**

1. No electricity required.
2. Electroless plating can be carried out on insulators and semiconductor materials.
3. Electroless plating can be used to obtain uniform coating on irregular shaped objects.
4. The deposits are more compact and highly adherent
5. No elaborate arrangements are required

**ELECTROLESS PLATING OF COPPER**

Copper is an ideal material in electroless plating due to its outstanding electroconductive properties and the possibility of coating on various materials including non-conductors. Non-conductive surfaces may be metalized by employing electroless baths, since the baths contain their own source of electrons.

**Components of electroless plating bath of copper**

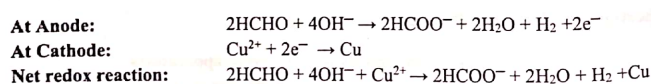
Electroless plating bath for copper consists of the following components:

1. Copper sulphate as source for copper.
2. Formaldehyde as reducing agent.
3. Caustic-basic medium
4. Chelating agents (amines, gluconates, glucoheptaonates, various EDTAs, and tartarates).

These agents govern the plating rate and have a marked influence on the properties of the deposit and the bath stability.

**Chemical reactions during electroless copper plating**

By maintaining a pH of 11-12 using a buffer solution (NaOH 12-15 g/l and Rochelle salt 14 g/l) and at an optimum temperature of around 25°C the following redox reactions takes place.



However, the reduction proceeds through a cuprous state. An excess of cuprous oxide formation will cause the reduction reaction to proceed out of control. To inhibit the

formation of cuprous oxide, air is bubbled slowly through the electroless copper solution and small complexing agents are added to the solution.

**Disadvantages of electroless copper plating**

1. The chelating agent creates difficulties and interferes with waste water treatment
2. The reducing agent, formaldehyde, is a human health hazard.
3. The instability of the electroless copper bath creates difficulties in process control.

**Applications of Electroless plating of Copper**

1. Widely used for metalizing printed circuit boards
2. For producing through-hole connections (through hole connections are necessary when double sided printed circuit boards are fabricated. The electrical connections between two sides of the board are made by drilling hole and then plating through holes by electroless plating.).
3. For plating on non-conductors
4. As a base for subsequent conventional electroplating
5. Applied on wave guides and for decorative plating on plastics.

**1.17 CONDUCTIVITY**

The flow of electricity through a conductor involves the transfer of charges from a higher negative potential to one of lower positive potential. The resistance of an electric conductor to current passage can be determined by applying Ohm's law. According to this law

$$I = \frac{E}{R}$$

Where, I is the strength of current in amperes flowing through a resistance R in Ohms under an applied potential difference E. This equation indicates that current strength is directly proportional to the difference in potential and inversely proportional to the resistance in electronic conduction. The term conductance (C) is frequently used in electrochemistry instead of resistance. This term implies the ease which the current flows through a conductor. It is therefore defined as the reciprocal of resistance, i.e.

$$C = 1/R$$

Conductance is expressed in the unit  $\text{Ohm}^{-1}$  or mho. In SI system the unit of conductance is Siemens S. In an ionic solution the cations and anions are free to move and both can transport charge. When a current is passed through an ionic solution the ions carry current. The ability of an ion in a solution to carry current is called conductivity. The



conductivity of a solution depends upon the number of cations and anions present in it and the readiness of ions to move.

**Specific conductance:** The conductivity of a solution is measured by a cell, known as conductivity cell. The conductivity of a solution of 1 cm length and 1 cm<sup>2</sup> area of cross section is the specific conductance K.

**Cell Constant:** The electrodes in a conductivity cell may not be exactly one cm apart and may not have an area of one sq.cm. Thus the measured conductivity value using the conductivity cell will not be equal to the specific conductivity, but a value proportional to it. It is therefore essential to calculate a factor for the conductivity cell, called the cell constant, which when multiplied by the observed conductance gives the value of specific conductance. This factor is known as the cell constant. Cell constant is a factor, which must be multiplied by the observed conductivity to get the specific conductivity. It is the ratio of distance between the two electrodes and the area of the electrodes in the conductivity cell

$$\text{Specific conductance } K = \left[ \frac{l}{a} \right] C$$

Where  $\frac{l}{a}$  is the cell constant, expressed in cm<sup>-1</sup>

$$K = \text{Cell constant} \times \text{conductance}$$

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Measured conductance}}$$

#### Conductivity Cell

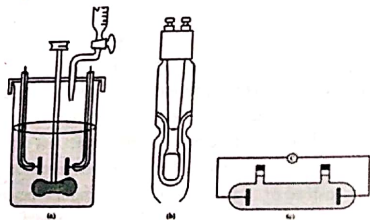


Fig.1.16. Various types of conductivity cells (a), (b) cup type and (c) dip type

Various types of cells are used for the measuring the conductance which differ in shape and structure. Two main types of cells are commonly used one is called the cup type and the other is the dip type. They are made of highly insoluble glass such as Pyrex or quartz with two platinum electrodes fused in to the glass. The relative positions of the

two electrodes are fixed. For accurate work solutions are prepared in conductivity water (absolutely pure water with no impurity). The solution whose conductance has to be measured is taken in cup type cell, where as the dip type cell is kept dipped in to the solution taken in a beaker.

#### Measurement of conductivity of a solution

Measurement of solution conductance is a classical electro analytical technique that finds application in a variety of chemical and biochemical studies. The electrical conductivity of ionic solutions can be measured by using a conductometer. The electrolytic conductance measurements usually involve the determination of the resistance of a segment of a solution between the parallel electrodes. The measurements are made based on the principle of Wheatstone bridge. To measure the conductance of a solution, it is placed in a conductivity cell carrying a pair of platinum electrodes which are firmly fixed in position. The platinum electrodes are generally electroplated with platinum black. The measurements are made by connecting the conductance cell to a conductivity bridge, which is made up of a uniform resistance wire AB. A resistance R is introduced into the circuit and the sliding contact D is moved along the wire AB till a null point is obtained as detected by the head phone or any other detector. The balancing length AD and DB are measured from the scale fixed below the wire AB. Since R is known, the resistance of the solution can be calculated. Reciprocal of this resistance gives conductance of the solution.

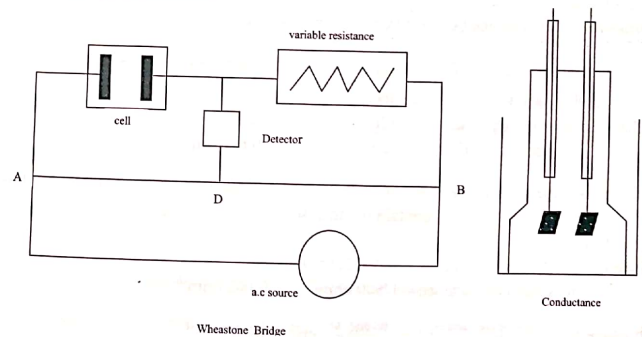


Fig. 1.17 Measurement of Conductivity using Wheatstone Bridge

$$\frac{\text{Resistance of the solution}}{\text{Resistance } R} = \frac{DA}{DB}$$

**Applications of conductance measurements**

- Study of strong and weak electrolytes
- Determination of degree of dissociation
- Determination of solubility of sparingly soluble salts
- Determination of concentration of solutions by conductometric titration

**Problem 12:** The resistance of N/2 solution of an electrolyte in a cell was found to be 45 ohms. Calculate the specific conductance of the solution, if the electrodes in the cell are 2.2 cm apart and have an area of 3.8 cm<sup>2</sup>.

**Solution:** We know that the cell constant  $= \frac{l}{a} = \frac{2.2}{3.8} = 0.5789 \text{ cm}^{-1}$

The conductance of the solution  $C = 1/R = 1/45 \text{ mhos} = 0.0222 \text{ ohm}^{-1}$

Specific conductance of the solution  $k = \text{Cell constant} \times \text{conductance}$   
 $= 0.0222 \times 0.5789 = 0.01286 \text{ ohm}^{-1} \text{ cm}^{-1}$

**Problem 13:** The specific conductance of a decinormal solution of KCl at 18°C is 0.0112 mhos. The resistance of a cell containing the solution at 18°C was found to be 55 ohms. What is the cell constant?

**Solution:** Sp. Conductance (k) = Cell constant  $\times$  conductance

But conductance = 1/Resistance, i.e. Sp. Conductance (k) =  $\frac{\text{Cell constant}}{\text{Resistance}}$

$\therefore$  Cell constant = Sp. Conductance (k)  $\times$  Resistance

We have Sp. Conductance (k) = 0.0112 ohm<sup>-1</sup> cm<sup>-1</sup> and Resistance = 55 ohm

$\therefore$  Cell constant = 0.0112 ohm<sup>-1</sup> cm<sup>-1</sup>  $\times$  55 ohm = 0.616 cm<sup>-1</sup>.

**Problem 14:** Specific conductivity of an N/50 KCl solution at 25°C is 0.0002765 mhos cm<sup>-1</sup>. If the resistance of cell containing this solution is 500 ohms, calculate its cell constant. (KTU May 2016)

**Solution:** Specific conductance = 0.0002765 ohm<sup>-1</sup> cm<sup>-1</sup>

Measured conductance = 1/500 ohms = 0.002 ohm<sup>-1</sup>

Cell constant =  $\frac{\text{Specific conductance}}{\text{Measured conductance}} = \frac{0.0002765}{0.002} \text{ cm}^{-1} = 0.138 \text{ cm}^{-1}$

**Problem 14:** A conductivity cell has two parallel plates of 1.25 cm<sup>2</sup> area placed at 10.5 cm apart, when filled with a solution of an electrolyte, the resistance was found to be 2000 ohms. Calculate the cell constant and the specific conductance of the solution.

**Solution:** Cell constant =  $\frac{l}{a} = 10.5 \text{ cm} / 1.25 \text{ cm}^2 = 8.4 \text{ cm}^{-1}$

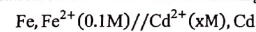
Measured conductance = 1/2000 ohms = 0.0005 ohm<sup>-1</sup>

Specific conductance = cell constant  $\times$  measured conductance

Specific conductance = 8.4 cm<sup>-1</sup>  $\times$  0.0005 ohm<sup>-1</sup> = 4.2  $\times$  10<sup>-3</sup> ohm<sup>-1</sup> cm<sup>-1</sup>

**SOLVED PROBLEMS**

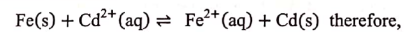
- Determine the concentration of Cd<sup>2+</sup> ions in the following electrochemical cell,



Assuming that activities equal concentrations,

Given the EMF of the cell  $E = -0.02\text{V}$  and  $E^0 = 0.04\text{V}$  and 25°C.

**Solution:** Over all cell reaction:



$$E = E^0 - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{Cd}^{2+}]}$$

$$-0.02 = 0.04 - \frac{0.0591}{2} \log \frac{0.1}{x}$$

$$X = 0.00093 \text{ or } X = 0.001\text{M (approx)}$$

- Two electrodes are given with their reduction potentials Pb<sup>2+</sup>, Pb (-0.126V) and Ag<sup>+</sup>, Ag (0.799V), combine the two electrodes to form an electro-chemical cell that works spontaneously. Write the cell reaction and calculate potential.

**Solution:** The cell formed is Pb, Pb<sup>2+</sup>/Ag<sup>+</sup>, Ag

Oxidation at the anode  $\text{Pb} \rightarrow \text{Pb}^{2+} + 2\text{e}$

Reduction at the cathode  $\text{Ag}^+ + \text{e} \rightarrow \text{Ag}$

Cell reaction,  $\text{Pb} + 2\text{Ag}^+ \rightarrow \text{Pb}^{2+} + 2\text{Ag}$

$$E_{\text{cell}} = E_{\text{Ag}} - E_{\text{Pb}} = 0.7999 - (-0.126) = 0.9259 \text{ V}$$

3. Calculate the voltage of the cell  $Zn, Zn^{2+}(0.0004)/Cd^{2+}(0.02), Cd$ . The standard reduction potential of zinc and cadmium are  $-0.763$  and  $-0.403$  V respectively.

**Solution**

$$E_{cell} = E_R - E_L = E_{Cd} - E_{Zn}$$

$$E_{Cd} = E_{Cd}^0 + \frac{0.0591}{2} \log[Cd^{2+}]$$

$$= -0.403 + \frac{0.0591}{2} \log[0.02] = -0.4532$$

$$E_{Zn} = E_{Zn}^0 + \frac{0.0591}{2} \log[Zn^{2+}]$$

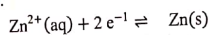
$$= -0.763 + \frac{0.0591}{2} \log[0.0004] = -0.8634$$

$$E_{cell} = E_{Cd} - E_{Zn} = -0.4532 - (-0.8634) = 0.4102V$$

4. A Zinc rod is placed in a 0.1M solution of zinc sulphate at 25°C. Calculate the potential of the electrode at this temperature, assuming 96% dissociation of  $ZnSO_4$  and  $E^0(Zn^{2+}/Zn) = 0.76V$ .

**Solution:** Concentration of  $Zn^{2+}$  (with 96% dissociation)  $= 0.1 \times \frac{96}{100} = 96 \times 10^{-3} M$

The electrode reaction:



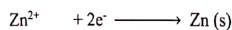
According to the Nernst equation, the potential of the electrode is

$$E = E^0 - \frac{RT}{nF} \ln\left(\frac{1}{[Zn^{2+}]}\right)$$

$$= (-0.76) - \frac{8.314 \times 298}{2 \times 96500} \ln\left(\frac{1}{96 \times 10^{-3}}\right) = -0.79 V$$

5. A Zinc electrode is dipped in a 0.1 M solution at 25°C. Assuming that salt is 20% dissociated, calculate the reduction potential (Given,  $E^0_{Zn^{2+}/Zn} = -0.76 V$ ).

**Solution:**



$$[Zn^{2+}] = \frac{0.1 \times 20}{100} = 0.02 M; \text{ From Nernst equation we have,}$$

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} + \frac{0.0591}{n} \log [Zn^{2+}] = -0.76 + \frac{0.0591}{2} \log 0.02 = -0.81$$

### IMPORTANT QUESTIONS

- 1) Nernst equation derivation. (Amaravati Dec.2000, Tripura,2000)
- 2) Construction and working of a fuel cell with an example and its advantages.
- 3) Write note on the characteristics of Electrochemical Series
- 4) Briefly explain the applications of Electrochemical Series
- 5) Explain the working and applications of lithium ion battery.
- 6) (a) How will you determine the  $P^H$  of a solution, using calomel electrode.  
(b) Write note on calomel electrode. (KTU Jan 2015)
- 7) Derive Nernst equation for electrode potential (K.U.2014) KTU 2015 Jan
- 8) What is Helmholtz electrical double layer? (K.U.April.,2014)
- 9) What is reference electrode? Explain the working of one such electrode.
- 10) Draw neatly a labeled diagram of saturated calomel electrode. Also give the redox reaction involved. (KTU 2015 Jan)
- 11) What is electrode potential? Explain Helmholtz double layer theory for its origin. (K.U.April.,2014)
- 12) Write a short note on fuel cells. (M.G.U 2006) (KTU 2015 Jan)
- 13) Derive Nernst equation for the electrode potential.
- 14) Give an experiment to find out the emf of an unknown cell.
- 15) Describe the experimental determination of single electrode potential.
- 16) What are fuel cells? Write the chemical reaction of  $H_2-O_2$  fuel cell.
- 17) Explain glass electrode and describe the determination of  $P^H$  using glass electrode.
- 18) Why can glass electrode not be used for a solution of high alkalinity? (Anna,05)
- 19) Compare electronic and electrolytic conductors. (Dibrugarh June, 2000)
- 20) What is meant by single electrode potential? How is it measured?
- 21) Differentiate the terms: Single electrode potential and standard electrode potential.
- 22) Explain the terms electrode potential and electromotive force of a cell.
- 23) State and explain Nernst equation. What are its applications?
- 24) Using Nernst equation calculate the  $E_{red}$  of the following electrode.  
 $Pt, Cl_2(1.5atm) | 2Cl^{-}(0.01M); E^0_{Cl_2/Cl} = 1.36V$
- 25) What is cell constant? (KTU 2016)
- 26) What is a conductivity cell? Explain the different forms.
- 27) What are the applications of conductance measurements?
- 28) Explain the procedure for conductivity measurements.
- 29) Explain the term specific conductance
- 30) Explain the mechanism of electrochemical corrosion (wet corrosion) (K.U. 2007)
- 31) Write note on Corrosion inhibitors. (K.U.2014)
- 32) Distinguish between Galvanic series and Electro Chemical Series (K.U.2010)



- 33) What are inhibitors? Explain with examples. (KU.2006,2009,2014,2011,May)
- 34) Discuss electrochemical corrosion and action of inhibitors. (KU.2008,June)
- 35) What are the advantages of electroless plating
- 36) Write any five important applications of electroless plating.
- 37) Explain the theory behind electroless plating.
- 38) Describe in detail electroless plating.
- 39) Explain how pH is determined using glass electrode.
- 40) Write down the procedures for the measurement of conductivity (KTU 2019June)
- 41) Describe i) Cell constant ii) Specific conductance iii) Conductivity (KTU 2019)
- 42) What are the various types of electrodes? (KTU 2019June)
- 43) If you take a mixture of  $ZnSO_4$  and  $CuSO_4$  solutions in a beaker and a Zn rod and a Cu rod are inserted in it, will you get electricity? Give reason (KTU 2019 June)
- 44) Discuss the variation in emf of a Daniel cell with respect to temperature at different concentration ratios of  $Zn^{2+}$  and  $Cu^{2+}$  (KTU 2019 June)