

4.1 INTRODUCTION

Electrochemistry is that branch of science which deals with the study of production of electrical energy from chemical energy or production of chemical energy from electrical energy. Electrochemistry plays an important role in our daily life. For example, the cell phones which are used, the source of energy is based on the principle of electrochemistry. When it is in use, actually conversion of chemical energy into electrical energy is taking place. When it is discharged for its charging, electrical energy is supplied to it which gets converted into chemical energy. It is this chemical energy which is stored by the battery of the phone which is later on consumed when it works.

The word cell is very significant in electrochemistry. A cell is actually an arrangement of two electrodes dipped in an electrolytic solution. Out of the two electrodes one behaves as cathode and the other as anode. The cell can be either of two types : Electrolytic cell and Electrochemical cell.

4.1.1 Electrolytic Cell

When electrical energy is supplied to the cell and it leads to chemical change in the cell, this chemical change which is taking place is actually oxidation and reduction on respective electrodes. This type of arrangement is called **Electrolytic cell** as shown in figure 4.1. This cell is very useful arrangement for extraction of metal from the electrolyte. Charging of storage cell battery is another example of the electrolytic cell.

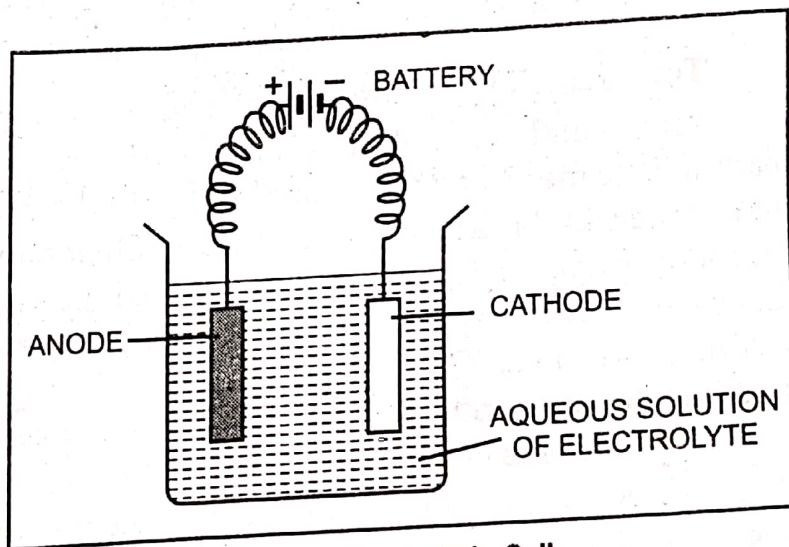


Fig. 4.1 Electrolytic Cell

To explain electrochemical cell, knowledge of redox reactions is must. So, let's first explain redox reactions.

4.2 REDOX REACTIONS

Oxidation and reduction reactions may take place in the same vessel or may take place in separate vessels, called **direct or indirect redox reactions** respectively.

If redox reaction is carried out directly, *i.e.* **oxidation and reduction reactions take place in one vessel** it is called **direct redox reaction**, *e.g.* if Zn rod is dipped in the solution

of CuSO_4 , then Zn rod gradually starts dissolving, copper metal of electrolytic solution either starts setting at bottom of the beaker or depositing on the Zinc rod. This reaction is exothermic and the solution becomes hot. In this case chemical energy has been converted into heat energy. So direct redox reactions lead to conversion of chemical energy into heat energy. In the direct redox reactions, transference of electrons from the reducing agent to oxidising agent occur over very short distance and hence no useful electric work can be obtained.

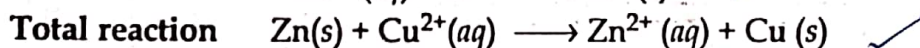
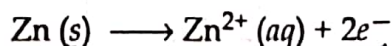
4.3 INDIRECT REDOX REACTIONS—ELECTROCHEMICAL CELL

In the case of indirect redox reactions, the electrodes are placed separately in two separate vessels having electrolytes. Oxidation and reduction take place on the respective electrodes. Electrons get transferred from reducing agent to oxidising agent through metallic wires over large distances. Hence, these reactions are useful in conversion of chemical energy into electrical energy. Such a device for carrying out an indirect redox reaction is called electrochemical cell.

Electrochemical cell or simply a chemical cell is a device to convert chemical energy produced in an indirect redox reaction into electrical energy. Electrochemical cell is also called Voltaic cell or galvanic cell.

4.3.1 Construction of an Electrochemical cell

When Zinc rod is placed in beaker having Copper Sulphate (CuSO_4) solution, the following redox reaction takes place :



Zinc metal gives electrons and Cu^{2+} accept the electrons. The same reaction takes place if Zinc metal and Cu^{2+} ions are not in direct contact. This can be explained by taking two beakers and filling one with 1M CuSO_4 and other with 1M Zinc sulphate i.e. ZnSO_4 . A Cu rod is dipped in CuSO_4 and Zn rod is dipped in ZnSO_4 solution and the two rods which act as electrodes are connected with a copper wire through voltmeter. The ZnSO_4 solution is connected to CuSO_4 solution through salt bridge. Salt bridge is an inverted U-shaped tube having semi-solid paste of agar-agar or gelatin with a strong electrolyte (KCl, KNO_3 , K_2SO_4 etc.). In this case, K_2SO_4 is used. If the electrodes are not connected or salt bridge is not used, no reaction takes place and hence no current will flow.

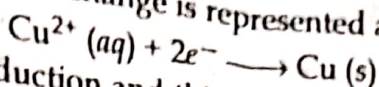
4.3.2 Chemical Reactions

Chemical reactions taking place in the above discussed cell are :

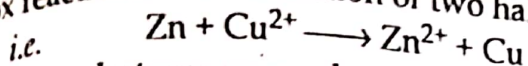
The beaker in which Zn rod is dipped in the ZnSO_4 solution, Zn^{2+} ions are formed from the Zn atom of Zn rod, and move away from the electrode. The electrons so released pass through the metallic wire, voltmeter and ultimately reach at Copper rod. This change may be represented as $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2e^-$. This is called oxidation and the electrode is called **Anode**.

The other beaker in which Cu rod is dipped, electrons (coming from other beaker) combine with Cu^{2+} ions present in the CuSO_4 solution to form neutral Cu atoms, which get

deposited on the Copper rod. This change is represented as :



This reaction is called reduction and this electrode at which reduction takes place is called **Cathode**. That means each beaker makes a half cell and the respective reactions taking place are called **oxidation half reaction** and **reduction half reaction**. The overall redox reaction is a combination of two half cell reactions.



Since electrons are produced at the beaker where Zn rod is dipped in ZnSO_4 solution, this end is rich in electrons and pushes the electrons into external circuit and hence acts as **negative electrode**. The copper electrode is deficient in electrons and reduces Cu^{2+} into Cu and pulls the electrons from the external circuit. So it acts as **positive electrode**. Salt bridge is U-shaped glass tube having electrolyte like K_2SO_4 , KNO_3 , KCl etc. in Agar-Agar/gelatin.

4.3.3 Importance of Salt Bridge

Salt bridge is used to :

1. Allow the movement of the ions from one solution to other without intermixing the two solutions.
2. It completes the inner circuit. (whereas electrons flow in the outer circuit). Hence flow of current takes place. (Current always flow in the direction opposite to the direction of flow of electrons)
3. Salt bridge maintains the electrical neutrality of the solution in two half cells.

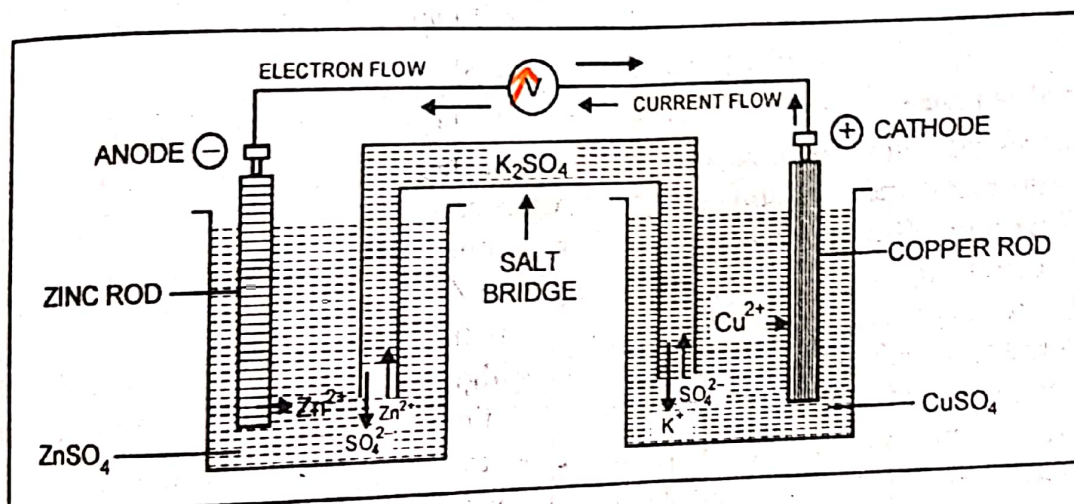


Fig. 4.2 Electrochemical Cell

As copper from the CuSO_4 solution gets deposited on the Copper electrode and sulphate ions migrate to the other side through salt bridge, the conc. of CuSO_4 solution decreases as the cell operates. Hence current falls with the passage of time.

The consequence of above phenomenon is that the weight of the Cu rod increases while weight of Zn rod decreases. The gain and loss in the weights of metal rods is in the ratio of their equivalent weight.

$$\frac{\text{Loss in weight of Zinc rod}}{\text{Gain in weight of Copper rod}} = \frac{\text{Eq. wt. of Zn}}{\text{Eq. wt. of Cu}} = \frac{32.50}{31.75}$$

4.3.4 Working of Salt Bridge

As we know that salt bridge completes the inner circuit by allowing the flow of ions from one side to the other. Now the question arises from where these ions are coming. Actually when oxidation takes place at anode *i.e.* Zinc electrode, Zn^{2+} are formed which get accumulated near the electrode (and electrons flow through the wire to the Copper rod. Due to this loss of electrons, +ve charge develops near Zinc rod). Likewise due to reduction at Cathode, *i.e.* deposition of Cu^{2+} from the solution onto Copper rod, in the form of Cu leaves behind SO_4^{2-} ions near the Copper rod. (Now as Copper rod accepts electrons and it has accumulation of SO_4^{2-} near it so it develops -ve charge around it as shown in diagram 4.3.)

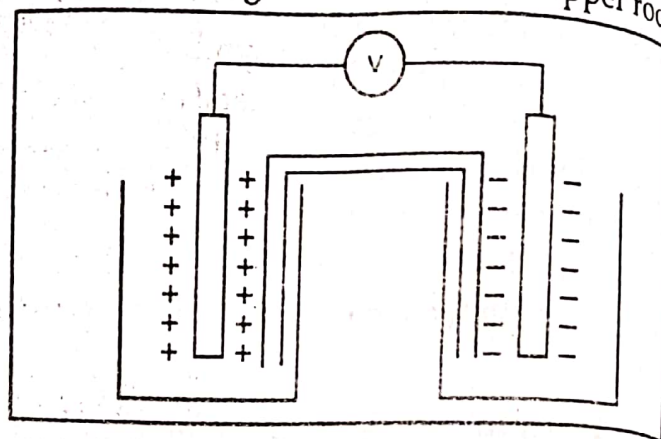


Fig. 4.3 Development of +ve and -ve charge around the electrodes

Due to this reason, Zinc electrode will no longer give electrons and Copper electrode will no longer accept electrons. So cell will stop working. But due to salt bridge, negative ions from the salt bridge move through salt bridge to Zinc rod and neutralize the +ve charge around Zinc rod. Similarly, accumulation of (SO_4^{2-}) -ve charge around Copper rod is neutralized by positive ions from the salt bridge. As a result of which the electric neutrality of the two solutions is maintained and current flows.

The electrochemical cell which we have discussed is also called Daniell cell. It can be illustrated as shown in Fig. 4.4.

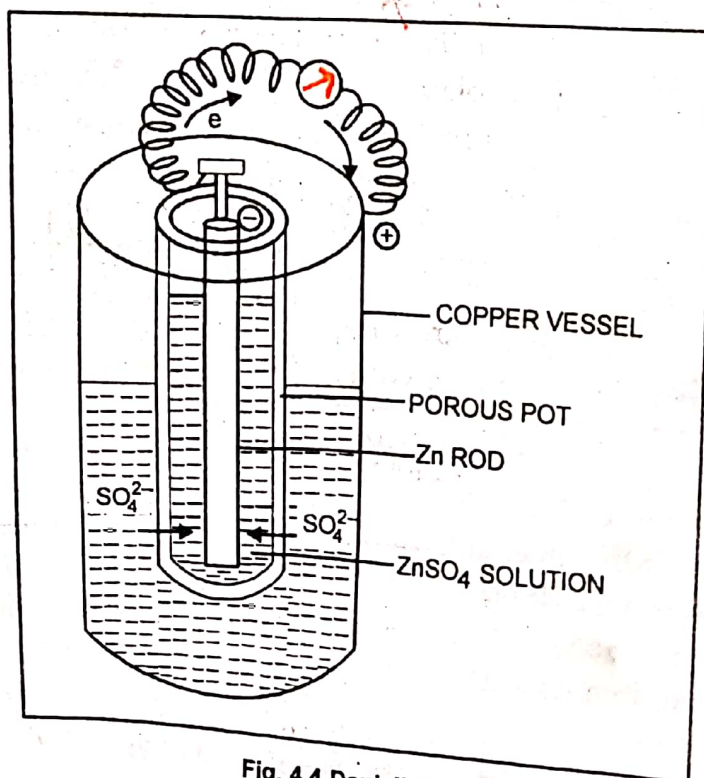
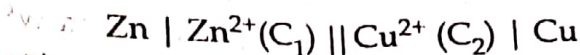


Fig. 4.4 Daniell Cell

4.3.5 Representation of an Electrochemical Cell

For the Daniel cell, the representation is



The electrode on which oxidation takes place is written on the left hand side while on which reduction takes place is written on the right hand side. The electrode on the left hand side is written, the symbol of metal first and then the metal ion formed from it with conc. in the bracket. The metal and metal ion are separated by a line. Similarly, the electrode on the right hand side is written with the symbol of metal ion formed with its conc. in the brackets and the metal both of which are separated by a single line. The single vertical line represents the interface between the two phases.

A double line appears at the centre, representing the salt bridge and showing the separation between the two electrodes.

4.3.6 Differences between Electrochemical and Electrolytic Cell

Electrochemical Cell	Electrolytic Cell
1. Chemical energy is converted into electric energy.	Electric energy is converted into the chemical energy.
2. Redox reaction is spontaneous.	Redox reaction is non-spontaneous. It takes place only when electrical energy is supplied to it.
3. The electrode on which oxidation takes place is called anode and is represented as '-' (negative) pole. On the other electrode reduction takes place and is called Cathode. This is represented as '+' (positive) pole.	The electrode which is attached to the negative terminal of the battery is called cathode, and other electrode attached to the positive terminal of the battery is called Anode. Oxidation always takes place at anode and reduction always takes place at Cathode irrespective of the type of cell.
4. Salt bridge is used.	No salt bridge is used.
5. The two different electrodes are set up in the two different electrolytic solutions usually. (This statement will be different for concentration cells)	Two different electrodes are set up in the same electrolytic solution.

4.4 SOME DEFINITIONS

4.4.1 Electrode Potential

The tendency of the electrode to lose or gain electrons which it is in contact with its own ions in the electrolytic solution is called electrode potential.

If the electrode acts as cathode (i.e., shows reduction) it is represented as :
 $\text{H}^+/\text{Q}/\text{QH}_2; \text{Pt}$

4.7 MEASUREMENT OF ELECTRODE POTENTIAL

Absolute value of electrode potential of an electrode can't be measured. It can be measured only by using another electrode as reference electrode. The reference electrode used can be standard hydrogen electrode (SHE) or Calomel electrode.

To determine the electrode potential of an electrode (test electrode), an electrochemical cell is set up. In this cell, a reference electrode is used along with test electrode. Let us explain one example by selecting SHE as reference electrode.

Example 1. Determination of standard electrode potential of Zn/Zn^{2+} electrode using SHE as reference electrode.

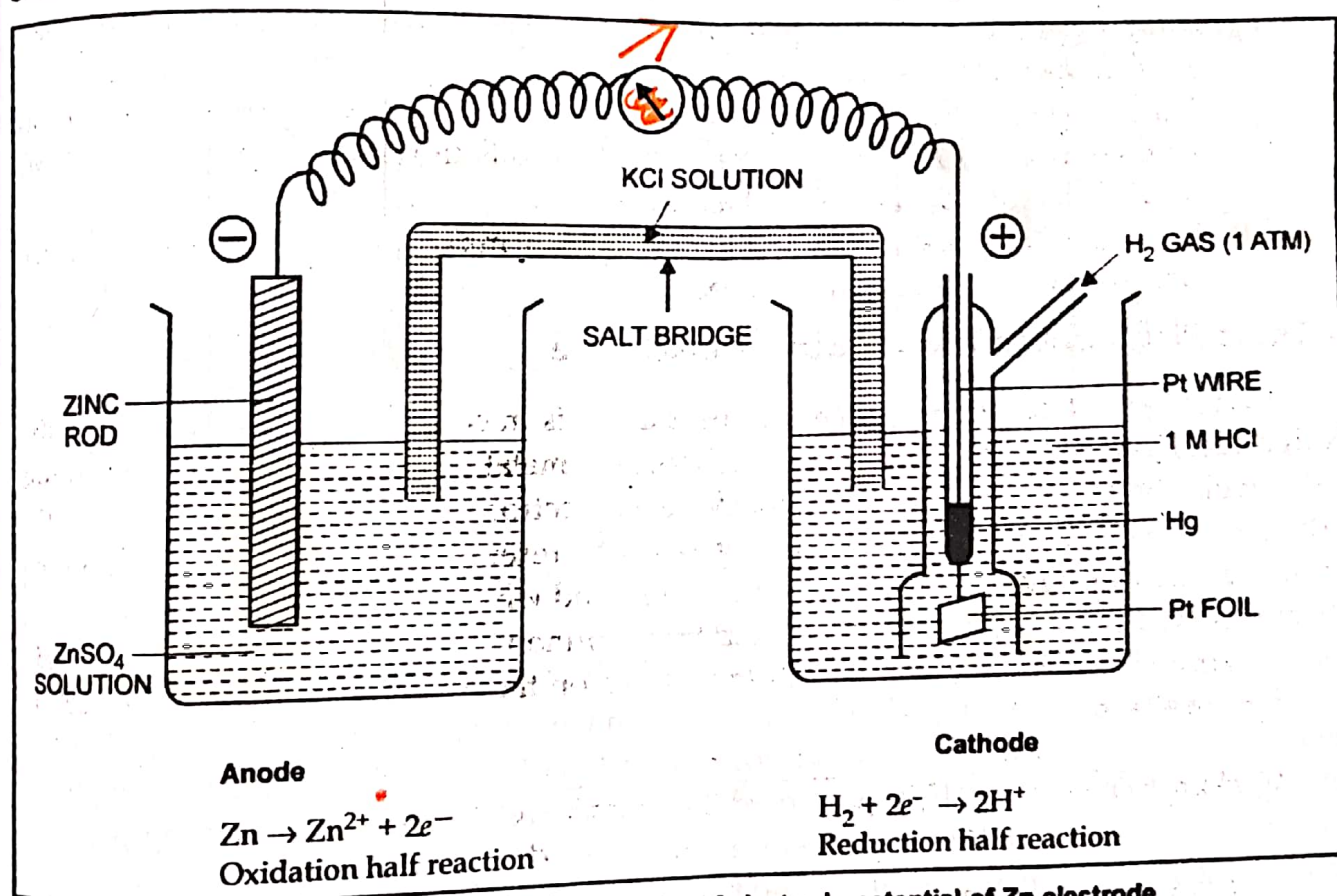


Fig. 4.7 Arrangement for measurement of electrode potential of Zn electrode

This is a cell comprising Zn rod immersed in ZnSO_4 (1 M) solution and a standard hydrogen electrode. The two half cells are connected to each other. It has been observed that current flows from RHS to LHS. It indicates that electrons are flowing from LHS to RHS (Because direction of flow of current is opposite to the direction of flow of electrons). Hence it has been observed that oxidation takes place at LHS i.e. test electrode. So it will act as an anode. Now EMF of this cell is measured and comes out to be 0.76 Volt.

Now we know that EMF of the cell = oxidation potential of oxidation half reaction
 + reduction potential of reduction half reaction.

Electrode potential of SHE is equal to zero.

$$0.76 = \text{Oxidation potential of oxidation half reaction} + 0$$

Hence oxidation potential of the oxidation half reaction

$$= \text{Oxidation potential of anode}$$

$$= \text{Electrode potential of the test electrode} = 0.76 \text{ V}$$

Standard electrode potential/standard oxidation potential of Zn/Zn^{2+} electrode = 0.76V.

Example 2. Determination of standard electrode potential of Cu/Cu^{2+} electrode using SHE reference electrode.

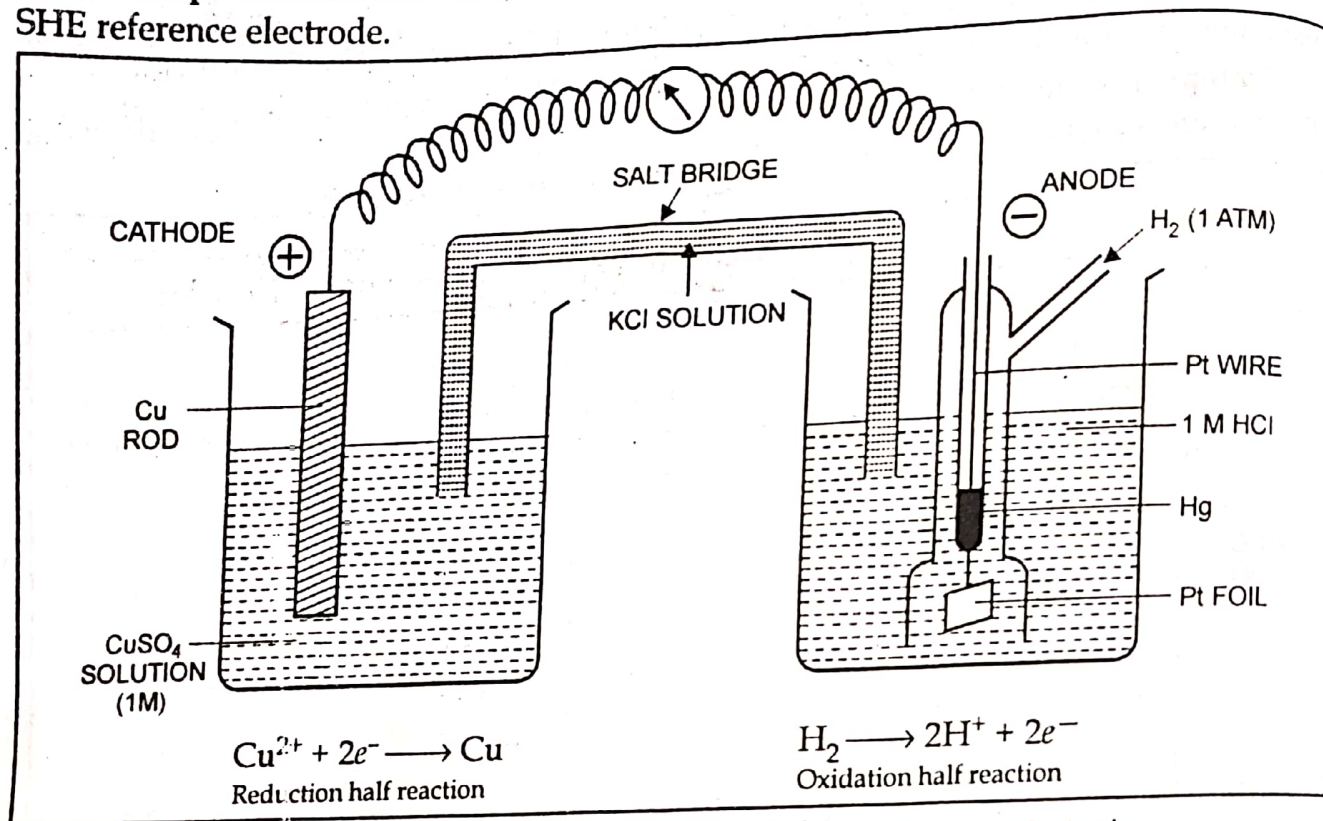


Fig. 4.8 Arrangement for measurement of electrode potential of Cu electrode

This is a cell comprising Cu rod immersed in CuSO_4 (1 M) solution and SHE. It has been seen that direction of flow of current is from LHS to RHS. Hence electrons might be flowing from RHS to LHS. If so then oxidation i.e. release of electrons is taking place on RHS i.e. SHE. And reduction i.e. gain of electrons is taking place at LHS i.e. at Cu/Cu^{2+} electrode. It means SHE acts as anode and Cu electrode is behaving as Cathode, EMF of the cell comes out to be 0.34 Volt

$$\text{Standard EMF of cell} = \left(\begin{array}{l} \text{Standard Oxidation} \\ \text{Potential of Oxidation} \\ \text{half reaction} \end{array} + \begin{array}{l} \text{Standard Reduction} \\ \text{Potential of Reduction} \\ \text{half reaction} \end{array} \right)$$

$$0.34 = \left(\begin{array}{l} \text{Standard Oxidation} \\ \text{Potential of SHE} \end{array} \right) + \left(\begin{array}{l} \text{Standard Reduction} \\ \text{Potential of Cu electrode} \end{array} \right)$$

$$0.34 = 0 + \text{Standard Reduction Potential of Cu electrode}$$

So, standard electrode potential/standard reduction potential of Cu electrode = 0.34 V.

4.8 ELECTROCHEMICAL SERIES

The standard electrode potentials of large number of electrodes have been determined using standard hydrogen electrode as reference electrode. (Electrode potential for SHE is arbitrarily fixed as zero). Electrode potential is expressed as reduction potential conventionally. The various electrodes have thus been arranged in order of their increasing values of standard reduction potential as shown in Table 4.1. This arrangement is called Electrochemical series.

If at an electrode reduction takes place w.r.t. SHE, its standard reduction potential is given positive sign. If at an electrode, oxidation takes place w.r.t. SHE, its standard reduction potential is given negative sign.

Table 4.1 Electrochemical series standard reduction potential at 25°C.

Reduction half-reaction	Standard Reduction Potential E° (in volts)
$\text{Li}^+ + e^- \longrightarrow \text{Li}$	-3.05
$\text{K}^+ + e^- \longrightarrow \text{K}$	-2.93
$\text{Ba}^{2+} + 2e^- \longrightarrow \text{Ba}$	-2.90
$\text{Ca}^{2+} + 2e^- \longrightarrow \text{Ca}$	-2.87
$\text{Na}^+ + e^- \longrightarrow \text{Na}$	-2.71
$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}$	-2.37
$\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$	-1.66
$\text{Mn}^{2+} + 2e^- \longrightarrow \text{Mn}$	-1.18
$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	-0.76
$\text{Cr}^{3+} + 3e^- \longrightarrow \text{Cr}$	-0.74
$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$	-0.44
$\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd}$	-0.40
$\text{PbSO}_4 + 2e^- \longrightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.31
$\text{Co}^{2+} + 2e^- \longrightarrow \text{Co}$	-0.28
$\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}$	-0.25
$\text{Sn}^{2+} + 2e^- \longrightarrow \text{Sn}$	-0.14
$\text{Pb}^{2+} + 2e^- \longrightarrow \text{Pb}$	-0.13
$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	0.00
$\text{Sn}^{4+} + 2e^- \longrightarrow \text{Sn}^{2+}$	0.13
$\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+$	0.15
$\text{AgCl} + e^- \longrightarrow \text{Ag} + \text{Cl}^-$	0.22
$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	0.34
$\text{I}_2 + 2e^- \longrightarrow 2\text{I}^-$	0.53
$\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$	0.77
	0.80