6.2 REDOX REACTION

Various chemical reactions occur through redistribution of electrons among the reacting substances. 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, a substance can lose electrons only if there is present 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 are called redox reactions.

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{aq} + Cu_{(s)}$$

In this $Zn_{(s)}$ loses two electrons whereas Cu^{2+} gains two electrons, and hence this is a redox reaction. The redox reactions are of two types:

(*a*) **Direct Redox Reactions:** The redox reactions in which oxidation and reduction take place in the same vessel are called direct redox reactions. Example, displacement of copper from $CuSO_4$ solution when a zinc rod is dipped in it.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu_{(s)} \quad \text{or} \quad Zn_{(s)} + Cu^{2+} \longrightarrow Zn^{2+} + Cu_{(s)}$$

The above reaction can be split into two halves,

$$Zn \longrightarrow Zn^{2+} + 2e^- \text{ (oxidation half reaction)}$$
$$Cu^{2+} + 2e^- \longrightarrow Cu \text{ (reduction half reaction)}$$

(*b*) **Indirect Redox Reaction:** If redox reaction is allowed to take place in such a way that oxidation reaction takes place in one beaker and the reduction half reaction in another beaker, the electrons given out by former will be taken by latter and a current will flow. These indirect redox reactions form the basis of electro-chemical cells.

6.4 ELECTROCHEMICAL CELL

Electrochemical cell or the galvanic cell is a device which converts free energy of a physical or chemical process into electrical energy. Electrochemical cell usually consists of two electrodes immersed in one or more suitable electrolytes. When the electrodes are connected externally, a chemical reaction occurs in the cell resulting into oxidation at one electrode and reduction at the other electrode. The electrode at which oxidation occurs is called *cathode* and the electrode at which reduction occurs is called anode.

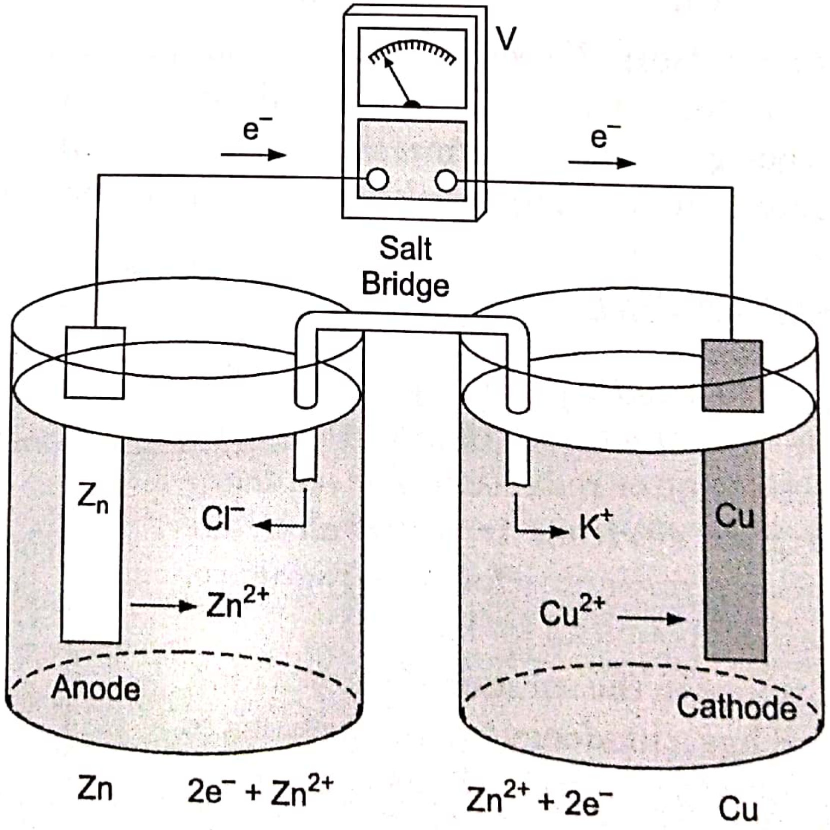

Fig. 6.1(b) Daniell cell

A typical example of galvanic cell is that of Daniell cell (Fig. 6.1(b)). It consists of a zinc rod dipping in $ZnSO_4$ solution, where oxidation takes place and a copper rod dipped in $CuSO_4$ solution, where reduction takes place. In other words, each electrode may be regarded as a half cell.

The metallic rods in the two beakers are connected to an ammeter by means of an insulated wire. The solutions in two beakers are connected by an inverted U-tube known as salt bridge. The tube is filled with a solution of electrolyte such as KNO_3, KCl, NH_4NO_3 or solidified solution of an electrolyte agar-agar and gelatine. The ends of the U-tube are plugged with glass wool or cotton wool. The salt in the bridge is such that it does not chemically react with either of the two solutions connected by it.

As soon as the circuit is closed, i.e. the two electrodes are connected, a current starts flowing which is shown by the deflection in the ammeter. The electric current flows due to the passage of electrons from zinc to copper rod. The electrode reactions involved as:

At anode	$Zn \longrightarrow Zn^{2+} + 2e^-$	(Oxidation)
At cathode	$Cu^{2+} + 2e^- \longrightarrow Cu$	(reduction)
	$Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$	

Since electrons, i.e., negative electricity flows from zinc to the copper rod, the conventional current, i.e., positive electricity flows from copper to zinc rod. Thus zinc rod serves as negative electrode and copper rod serves as positive electrode.

As shown in the figure, in an electrochemical cell the two half reactions take place in two different compartments. The electrode where oxidation takes place (the anode) is assigned the *negative charge* because oxidation is accompanied by liberation of negatively charged electrons. Each time an ion leaves the electrode surface, two electrons are left on the electrode surface making it negatively charged. Similarly, the electrode where reduction takes place (the cathode) is assigned the *positive charge* because the metal cations from the solution tend to withdraw electrons from electrode surface and get deposited as metal atoms on electrode. This process decreases the availability of electrons on the electrode surface and thus leaves the electrode surface positively charged.

Note: However, in an *electrolytic cell*, the situation will be just opposite. The anode would acquire positive charge and cathode would acquire negative charge.

Function of Salt Bridge

(*i*) It maintains the electrical neutrality of the two electrolyte solutions. In the Daniell cell, which consists of $Zn/ZnSO_4$ and $Cu/CuSO_4$ electrodes, the Zn metal undergoes oxidation to release electrons to the external circuit and Zn^{2+} ions are added to $ZnSO_4$ solution. To maintain the electrical neutrality the negative ions (Cl^- or SO_4^{2-}) from the salt bridge migrate to $ZnSO_4$ solution and neutralize the excess positive charge in the oxidation half cell. Similarly in reduction half cell, Cu^{2+} ions from $CuSO_4$ solution are reduced. This leads to an excess of SO_4^{2-} ions in $CuSO_4$. The positive ions (K^+ or NH_4^+) from the salt bridge migrate to reduction half cell neutralizing the excess negative charge in $CuSO_4$ solution. In this way salt bridge maintains the electrical neutrality of the electrolytes.

(*ii*) It also completes the circuit.

(*iii*) It prevents the intermixing of the solutions of both the half cells.

Representation of Electrochemical Cell: The electrochemical cell is represented as

Anode	Salt bridge	Cathode
Zn/Zn^{2+}	KNO_3	Cu^{2+}/Cu

The electrode at which oxidation takes place (anode) is written on the left hand side. The electrode at which reduction takes place (cathode) is written on the right hand side of the salt bridge.

In some galvanic cells, the same electrolyte is used in two half cells. In such cases, no separation is shown between two electrolytes of two electrodes for example

$$Pt, H_2 \text{ (1 atm); HCl (0.1 M); } Cl_2, Pt$$

Here HCl is an electrolyte and provides H^+ ions to the hydrogen electrode and Cl^- ion to the chlorine electrode.