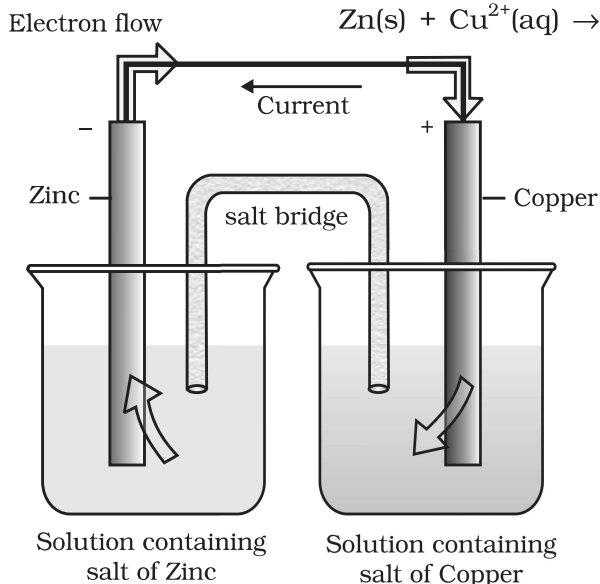
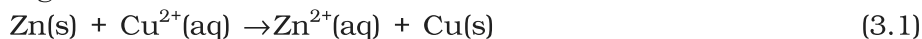


### 3.1 Electrochemical Cells

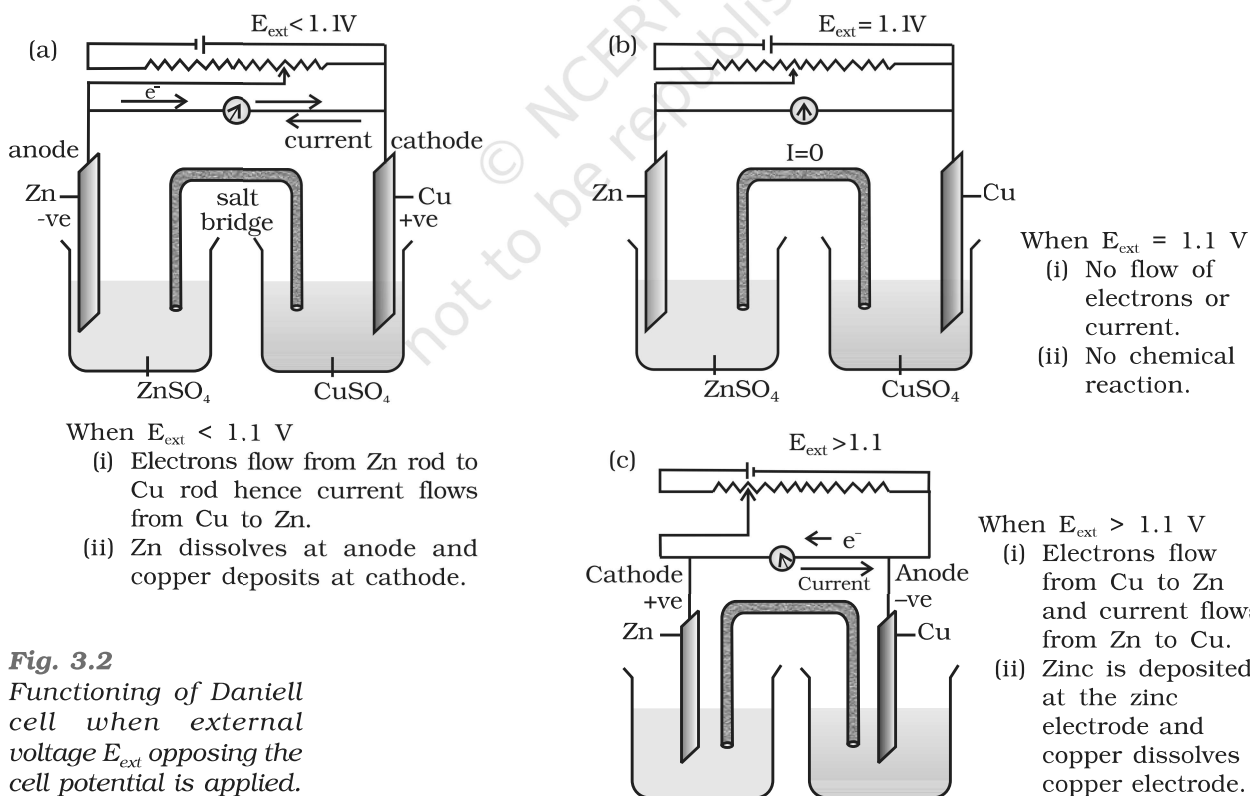
In Class XI, Unit 8, we had studied the construction and functioning of **Daniell cell** (Fig. 3.1). This cell converts the chemical energy liberated during the redox reaction



**Fig. 3.1:** Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

to electrical energy and has an electrical potential equal to 1.1 V when concentration of  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  ions is unity ( $1 \text{ mol dm}^{-3}$ )\*. Such a device is called a **galvanic** or a **voltic cell**.

If an external opposite potential is applied in the galvanic cell [Fig. 3.2(a)] and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V [Fig. 3.2(b)] when, the reaction stops altogether and no current flows through the cell. Any further increase in the external potential again starts the reaction but in the opposite direction [Fig. 3.2(c)]. It now functions as an **electrolytic cell**, a device for using electrical energy to carry non-spontaneous chemical reactions. Both types of cells are quite important and we shall study some of their salient features in the following pages.

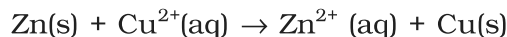


**Fig. 3.2**  
Functioning of Daniell cell when external voltage  $E_{\text{ext}}$  opposing the cell potential is applied.

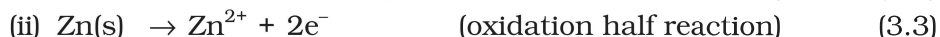
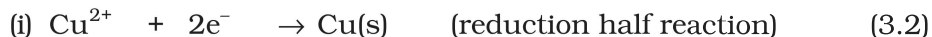
\*Strictly speaking activity should be used instead of concentration. It is directly proportional to concentration. In dilute solutions, it is equal to concentration. You will study more about it in higher classes.

As mentioned earlier (Class XI, Unit 8) a galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the **Gibbs energy** of the spontaneous redox reaction is converted into electrical work which may be used for running a motor or other electrical gadgets like heater, fan, geyser, etc.

Daniell cell discussed earlier is one such cell in which the following redox reaction occurs.



This reaction is a combination of two half reactions whose addition gives the overall cell reaction:



These reactions occur in two different portions of the Daniell cell. The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called **half-cells** or **redox couples**. The copper electrode may be called the reduction half cell and the zinc electrode, the oxidation half-cell.

We can construct innumerable number of galvanic cells on the pattern of Daniell cell by taking combinations of different half-cells. Each half-cell consists of a metallic electrode dipped into an electrolyte. The two half-cells are connected by a metallic wire through a voltmeter and a switch externally. The electrolytes of the two half-cells are connected internally through a salt bridge as shown in Fig. 3.1. Sometimes, both the electrodes dip in the same electrolyte solution and in such cases we do not require a salt bridge.

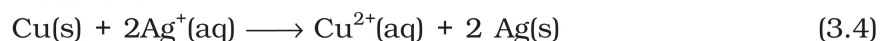
At each electrode-electrolyte interface there is a tendency of metal ions from the solution to deposit on the metal electrode trying to make it positively charged. At the same time, metal atoms of the electrode have a tendency to go into the solution as ions and leave behind the electrons at the electrode trying to make it negatively charged. At equilibrium, there is a separation of charges and depending on the tendencies of the two opposing reactions, the electrode may be positively or negatively charged with respect to the solution. A potential difference develops between the electrode and the electrolyte which is called **electrode potential**. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**. According to IUPAC convention, standard reduction potentials are now called standard electrode potentials. In a galvanic cell, the half-cell in which oxidation takes place is called **anode** and it has a negative potential with respect to the solution. The other half-cell in which reduction takes place is called **cathode** and it has a positive potential with respect to the solution. Thus, there exists a potential difference between the two electrodes and as soon as the switch is in the *on* position the electrons flow from negative electrode to positive electrode. The direction of current flow is opposite to that of electron flow.

The potential difference between the two electrodes of a galvanic cell is called the *cell potential* and is measured in volts. The **cell potential** is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the **cell electromotive force (emf)** of the cell when no current is drawn through the cell. It is now an accepted convention that we keep the anode on the left and the cathode on the right while representing the galvanic cell. A galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge. Under this convention the emf of the cell is positive and is given by the potential of the half-cell on the right hand side minus the potential of the half-cell on the left hand side i.e.,

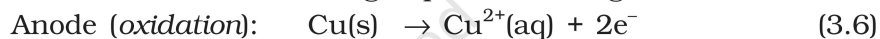
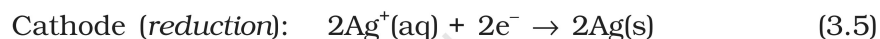
$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

This is illustrated by the following example:

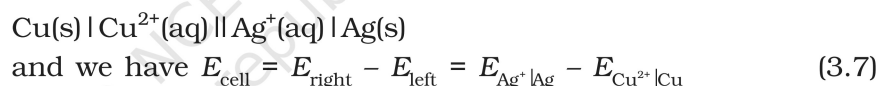
Cell reaction:



Half-cell reactions:



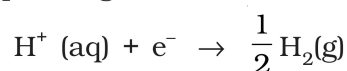
It can be seen that the sum of (3.5) and (3.6) leads to overall reaction (3.4) in the cell and that silver electrode acts as a cathode and copper electrode acts as an anode. The cell can be represented as:



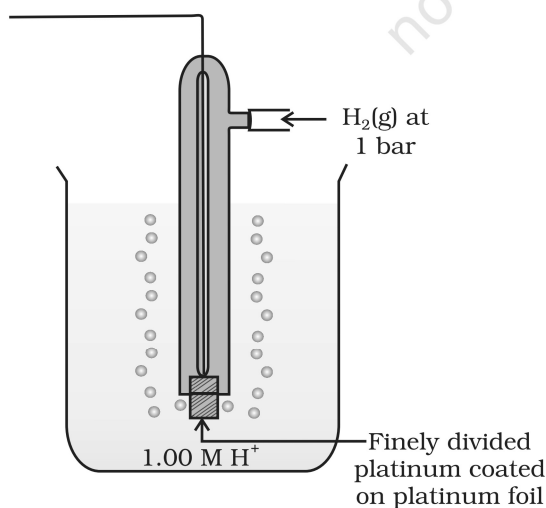
### 3.2.1 Measurement of Electrode Potential

The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. If we arbitrarily choose the potential of one electrode (half-cell) then that of the other can be determined with respect

to this. According to convention, a half-cell called standard hydrogen electrode (Fig.3.3) represented by  $\text{Pt(s)} | \text{H}_2(\text{g}) | \text{H}^+(\text{aq})$ , is assigned a zero potential at all temperatures corresponding to the reaction



The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity (Fig. 3.3). This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar.



**Fig. 3.3:** Standard Hydrogen Electrode (SHE).

At 298 K the emf of the cell, standard hydrogen electrode || second half-cell constructed by taking standard hydrogen electrode as anode (reference half-cell) and the other half-cell as cathode, gives the reduction potential of the other half-cell. If the concentrations of the oxidised and the reduced forms of the species in the right hand half-cell are unity, then the cell potential is equal to standard electrode potential,  $E^{\ominus}_R$  of the given half-cell.

$$E^{\ominus} = E^{\ominus}_R - E^{\ominus}_L$$

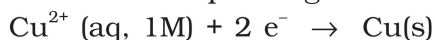
As  $E^{\ominus}_L$  for standard hydrogen electrode is zero.

$$E^{\ominus} = E^{\ominus}_R - 0 = E^{\ominus}_R$$

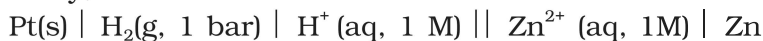
The measured emf of the cell:



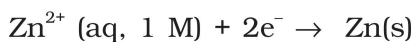
is 0.34 V and it is also the value for the standard electrode potential of the half-cell corresponding to the reaction:



Similarly, the measured emf of the cell:

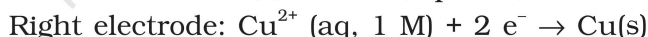
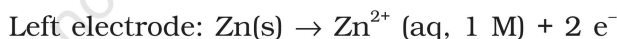


is -0.76 V corresponding to the standard electrode potential of the half-cell reaction:

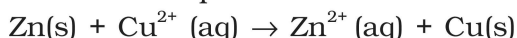


The positive value of the standard electrode potential in the first case indicates that  $\text{Cu}^{2+}$  ions get reduced more easily than  $\text{H}^+$  ions. The reverse process cannot occur, that is, hydrogen ions cannot oxidise Cu (or alternatively we can say that hydrogen gas can reduce copper ion) under the standard conditions described above. Thus, Cu does not dissolve in HCl. In nitric acid it is oxidised by nitrate ion and not by hydrogen ion. The negative value of the standard electrode potential in the second case indicates that hydrogen ions can oxidise zinc (or zinc can reduce hydrogen ions).

In view of this convention, the half reaction for the Daniell cell in Fig. 3.1 can be written as:



The overall reaction of the cell is the sum of above two reactions and we obtain the equation:



$$\begin{aligned} \text{emf of the cell} &= E^{\ominus}_{\text{cell}} = E^{\ominus}_R - E^{\ominus}_L \\ &= 0.34\text{V} - (-0.76)\text{V} = 1.10 \text{ V} \end{aligned}$$

Sometimes metals like platinum or gold are used as inert electrodes. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for the conduction of electrons. For example, Pt is used in the following half-cells:

