$$\begin{array}{rcl} \text{Cu} & \longrightarrow & \text{Cu}^{2+} + 2e^- \\ \text{Zn}^{2+} + 2e^- & \longrightarrow & \text{Zn} \\ \hline \text{Cu} + \text{Zn}^{2+} & \longrightarrow & \text{Cu}^{2+} + \text{Zn} \end{array}$$

With the help of a potentiometer (Fig. 29.6), the cell emf is exactly balanced by the external emf. At the balance point, no current will flow through the circuit. Now let the external emf increase and then decrease by an infinitesimal amount. A minute current will flow first to the left and then to the right. This reversal of the cell current is accompanied by a corresponding change in the direction of the cell reaction. This type of reversible behaviour is a feature of the reversible cells. **A reversible cell** may be defined as : **a cell that operates by reversal of the cell current and direction of cell reaction by infinitesimal change of emf on either side of the balance point.**

All voltaic cells are reversible cells.

RELATION BETWEEN EMF AND FREE ENERGY

When a cell produces a current, the current can be used to do work–to run a motor, for instance. 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.

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

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 to the cell.

According to thermodynamics, the maximum work that can be derived from a chemical reaction is equal to the free energy (ΔG) for the reaction.

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

Therefore from (1) and (2), we can write

$$\Delta G = -nFE \qquad ...(3)$$

According to Gibbs-Helmholtz equation, the decrease in free energy of a system at constant pressure is given by the expression

$$-\Delta G = -\Delta H - T\left(\frac{\partial(\Delta G)}{\partial T}\right)_p$$

where – ΔH is the decrease in heat content of the system or heat of the reaction at constant pressure.

Substituting the value of ΔG from (3)

$$nFE = -\Delta H - T\left(\frac{\partial(-nFE)}{\partial T}\right)_p$$

$$nFE = -\Delta H + nFT\left(\frac{\partial E}{\partial T}\right)_p$$

$$E = \frac{-\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)_p$$

The temperature coefficient of the emf of the cell ($\partial E/\partial T$), at constant pressure, therefore, determines whether the electrical energy would be equal to, more or less than the heat of reaction. Accordingly, three cases may arise:

Case 1. When the temperature coefficient is zero *i.e.*,

$$(\partial E/\partial T)_p = 0, \text{ then}$$
$$nFE = -\Delta H$$

Case 2. When the temperature coefficient is +ve *i.e.*,

$$(\partial E/\partial T)_p > 0, \text{ then}$$
$$nFE > -\Delta H$$

The additional energy will come either from the surroundings or the temperature of the cell would fall.

Case 3. When the temperature coefficient is negative *i.e.*,

$$(\partial E/\partial T)_p < 0, \text{ then}$$
$$nFE < -\Delta H$$

The excess energy will be given either to the surroundings or the temperature of the cell would rise.

If the heat of the reaction (or free energy change) and the temperature coefficient of a cell are known, we can calculate the emf, E, of the cell. For example, in case of a Daniel cell $(\partial E/\partial T)_p$ is nearly zero, $n = 2$ and $\Delta H = -50{,}100$ Cals.

Since 1 Cal = 4.185 Volt-Coulomb,

$$E = \frac{-\Delta H}{nF} = \frac{-4.185 \times (-50{,}100)}{2 \times 96{,}500}$$
$$= 1.09 \text{ V}$$

Thus the emf of Daniel cell is 1.09 volts. Conversely, if the emf of a reversible cell and its temperature coefficient $(\partial E/\partial T)_p$ are known, ΔH (or ΔG) can be calculated. The heats of reaction calculated from emf measurements are nearly the same as derived from thermal measurements.

Single electrode potential

An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the **Single electrode potential.** Thus in a Daniel cell in which the electrodes are not connected externally, the anode Zn/Zn^{2+} develops a negative charge and the cathode Cu/Cu^{2+}, a positive charge. The amount of the charge produced on individual electrode determines its single electrode potential.

The single electrode potential of a half-cell depends on : (*a*) concentration of ions in solution; (*b*) tendency to form ions; and (*c*) temperature

Standard emf of a cell

The emf generated by an electrochemical cell is given by the symbol E. It can be measured with the help of a potentiometer. The value of emf varies with the concentration of the reactants and products in the cell solutions and the temperature of the cell. When the emf of a cell is determined under standard conditions, it is called **the standard emf.** The standard conditions are (*a*) 1 M solutions of reactants and products; and (*b*) temperature of 25°C. Thus standard emf may be defined as : **the emf of a cell with 1 M solutions of reactants and products in solution measured at 25°C.**

Standard emf of a cell is represented by the symbol **E°.** With gases 1 atm pressure is a standard condition instead of concentration.

For a simple Zn-Cu voltaic cell, the standard emf, E°, 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. That is,

$$Zn \mid Zn^{2+} (aq, 1\underline{M}) \parallel Cu^{2+} (aq, 1\underline{M}) \mid Cu \qquad E^{o} = +1.1 \text{ V}$$

Determination of emf of a half-cell

By a single electrode potential, we also mean the emf of an isolated half-cell or its half-reaction. The emf of a cell that is made of two half-cells can be determined by connecting them to a voltmeter. However, there is no way of measuring the emf of a single half-cell directly. A convenient procedure to do so is to combine the given half-cell with another standard half-cell. The emf of the newly constructed cell, E, is determined with a voltmeter. The emf of the unknown half-cell, $E°_?$, can then be calculated from the expression

$$E_{measured} = E_R - E_L$$

If the standard half-cell acts as anode, the equation becomes.

$$E_R = E_{measured} \qquad (\because E_L = 0)$$

On the other hand, if standard half-cell is cathode, the equation takes the form

$$E_L = -E_{measured} \qquad (\because E_R = 0)$$

The standard hydrogen half-cell or **Standard Hydrogen Electrode (SHE),** is selected for coupling with the unknown half-cell. It consists of a platinum electrode immersed in a 1 M solution of H^+ ions maintained at 25°C. Hydrogen gas at one atmosphere enters the glass hood and bubbles over the platinum electrode. The hydrogen gas at the platinum electrode passes into solution, forming H^+ ions and electrons.

$$H_2 \longrightarrow 2H^+ + 2e^-$$

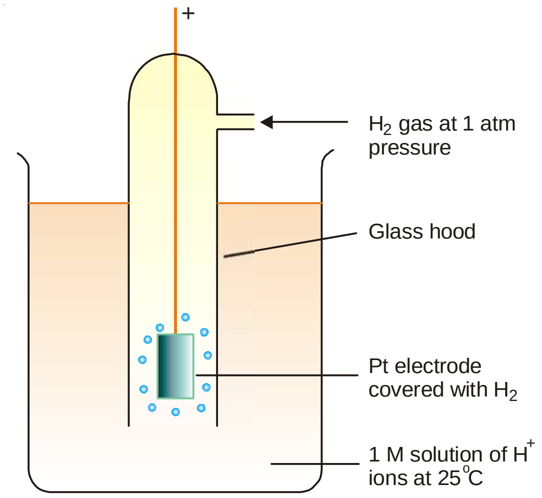

Figure 29.9
The standard hydrogen electrode.

The emf of the standard hydrogen electrode is arbitrarily assigned the value of zero volts. So, SHE can be used as a standard for other electrodes.

The half-cell whose potential is desired, is combined with the hydrogen electrode and the emf of the complete cell determined with a voltmeter. The emf of the cell is the emf of the half-cell.

$$\begin{aligned} E^\circ_{cell} &= E^\circ_R - E^\circ_L \\ &= 0 - 0.76 = -0.76 \text{ V} \end{aligned}$$

For example, it is desired to determine the emf of the zinc electrode, $Zn \mid Zn^{2+}$. It is connected with the SHE as shown in Fig. 29.10. The complete electrochemical cell may be represented as :

$$Zn \mid Zn^{2+} \parallel H^+ \mid H_2 \text{ (1 atm), Pt}$$

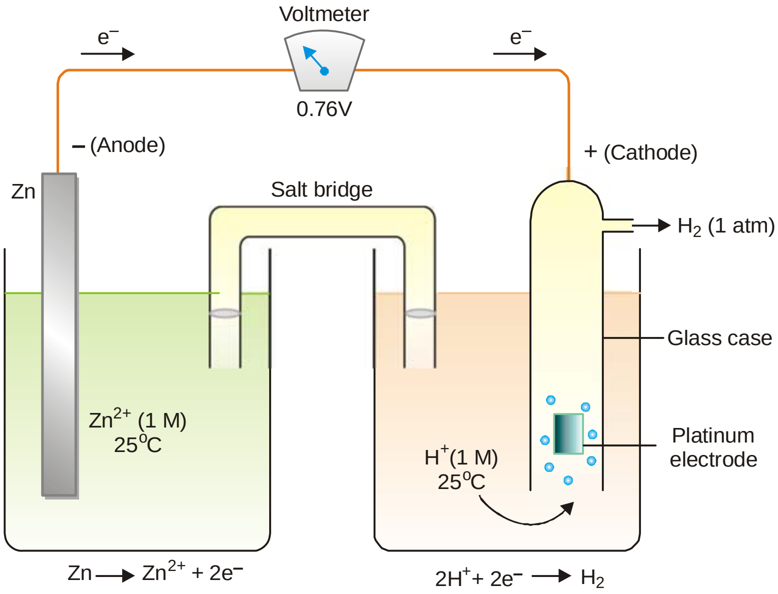

Figure 29.10

The zinc electrode (Zn, Zn^{2+}) coupled with hydrogen electrode.

The emf of the cell has been found to be – 0.76V which is the emf of the zinc half-cell. Similarly, the emf of the copper electrode, Cu^{2+} | Cu can be determined by pairing it with the SHE when the electrochemical cell can be represented as :

$$\text{Pt}, H_2 \text{ (1 atm)} \mid H^+ \parallel Cu^{2+} \mid Cu$$

The emf of this cell has been determined to be 0.34 V which is the emf of the copper half-cell.

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{Cu/Cu^{2+}} - E^\circ_{SHE} \\ &= 0.34 - \text{Zero} \\ &= 0.34\text{ V} \end{aligned}$$

The two situations are shown in Fig. 29.11.

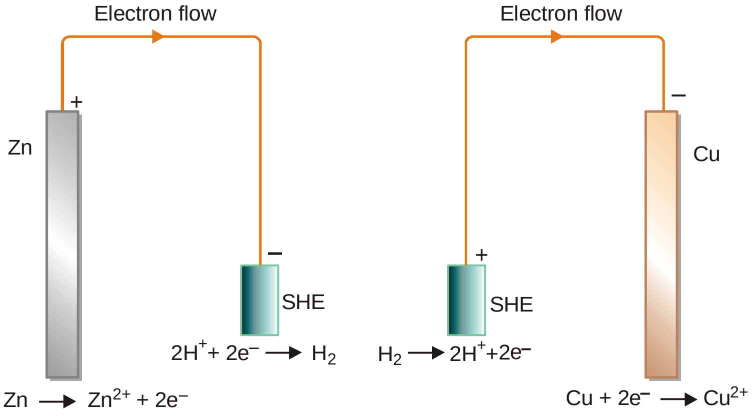

Figure 29.11

SHE can act both as cathode and anode when joined with another half-cell.

When it is placed on the right-hand side of the Zinc electrode, the hydrogen electrode reaction is

$$2H^+ + 2e^- \longrightarrow H_2$$

The electrons flow to the SHE and it acts as the cathode.

When the SHE is placed on the left hand side, the electrode reaction is

$$H_2 \longrightarrow 2H^+ + 2e^-$$

The electrons flow to the copper electrode and the hydrogen electrode as the anode. Evidently, **the SHE can act both as anode and cathode** and, therefore can be used to determine the emf of any other half-cell electrode (or single electrode).

IUPAC convention places the SHE on the left-hand side

In the procedure for determining the emf of a given half-cell, the standard hydrogen electrode can be placed on the left-hand or the right-hand. In the convention adopted by the IUPAC (International Union of Pure and Applied Chemistry), the SHE is always placed on the left-hand side of the half-cell under study. The electrons flow from left-to-right and the given half-cell electrode gains electrons (reduction). The observed emf of the combined electrochemical cell is then the emf of the half-cell on the right-hand. Such emf values of half-cells, or half reactions, are known as the **Standard reduction potentials or Standard potentials.** However, if the SHE be placed on the right-hand side of the given half-cell, the potential so obtained is called as the **Standard oxidation potential.** The latter potentials are the standard potentials with the sign reversed, the only difference being that cells have been turned around.

According to IUPAC convention, the standard reduction potentials alone are the standard potentials. The values of the standard potentials at 25°C (298 K) for some common Reduction Half-reactions are listed in Table **29.1.**

TABLE 29.1. STANDARD REDUCTION POTENTIALS AT 25°C (298 K)

Reduction Half-reaction	$E°$ (V)
$F_2 + 2e^- \longrightarrow 2F^-$	2.87
$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$	1.78
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$	1.69
$Au^{3+} + 3e^- \longrightarrow Au$	1.50
$Cl_2 + 2e^- \longrightarrow 2Cl^-$	1.36
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.23
$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$	1.21
$Br_2 + 2e^- \longrightarrow 2Br^-$	1.09
$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	0.77
$MnO_4^- + e^- \longrightarrow MnO_4^{2-}$	0.56
$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34
$2H^+ + 2e^- \longrightarrow H_2$	**0.00**
$Sn^{2+} + 2e^- \longrightarrow Sn$	–0.14
$Cd^{2+} + 2e^- \longrightarrow Cd$	–0.40
$Zn^{2+} + 2e^- \longrightarrow Zn$	–0.76
$H_2 + 2e^- \longrightarrow 2H^-$	–2.23
$Mg^{2+} + 2e^- \longrightarrow Mg$	–2.37
$Na^+ + e^- \longrightarrow Na$	–2.71
$Li^+ + e^- \longrightarrow Li$	–3.05