Chapter_03

Electrochemistry

- 1. Cells are the devices in which interconversion of electrical energy and chemical energy takes place. *It is of two basic types:*
 - (i) Electrochemical cell
 - (ii) Electrolytic cell
- **2.** An **electrochemical cell** is a device in which chemical energy of the redox reaction is converted into electrical energy. e.g. Daniell cell
- **3.** While **writing a cell**, the anode is written on the left and the cathode on the right. A vertical line separates the metal from the metal ion (electrolyte solution) and a double vertical line indicates a salt-bridge which is written between the two half-cells (two electrolytes). The Daniell cell is represented as :

 $Zn(s) | Zn^{2+}(aq) | | Cu^{2+}(aq) | Cu(s)$

- 4. The electrode potential under the conditions of unit concentration at 25°C of all the species in the half-cell is called the **standard electrode potential** and the electrodes of known potential is known as **reference electrode**, e.g. standard hydrogen electrode (potential of which is arbitraily taken as zero) and calomel electrode.
- 5. The potential difference between the electrode potentials of the cathode and anode is called the **cell potential**. Electromotive force (emf) is the potential given as $E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ}$
- 6. The arrangement of various standard half-cells in order of their decreasing values of standard reduction potentials is called electrochemical series. If the standard electrode potential of an electrode is greater than zero (positive value) then its reduced form is more stable as compared to hydrogen gas. Similarly, in case of standard electrode potential being less than zero (negative value), hydrogen gas is more stable than the reduced form of the species.
- **7. Nernst equation** is the equation which gives the relation between electrode potential and concentration of metal ions at given temperature Nernst equation for the electrode reaction (half cell reaction) is as follows :

$$M^{n+} (aq) + ne^{-} \longrightarrow M(s) \text{ is:}$$

$$E_{(M^{n+}/M)} = E_{(M^{n+}/M)}^{\circ} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

For a general electrochemical reaction of the type

 $aA + bB \xrightarrow{ne^-} cC + dD$ The Nernst equation can be written as

$$\frac{E_{\text{(cell)}} = E_{\text{(cell)}}^{\odot} - \frac{RT}{nF} \ln Q}{E_{\text{(cell)}} = E_{\text{(cell)}}^{\odot} - \frac{RT}{nF} \ln \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$$

In general, at equilibrium,

$$E_{\text{cell}} = 0$$

$$E_{\text{(cell)}}^{\circ} = \frac{2.303 \, RT}{nF} \log K_C$$

8. Gibb's energy of the reaction The emf of a cell is related to the Gibb's free energy $\Delta_r G^{\circ}$ as

$$\Delta_r G = - n F E_{cell}$$

If the concentration of all the reacting species is unity, then $E_{cell} = E_{cell}^{\circ}$ and we have

$$\Delta_r G^\circ = - nFE^\circ_{cell}$$

Relation between Gibb's energy and equilibrium constant (\mathcal{K})

 $\Delta_r G^\circ = -RT \ln K$

9. Resistance (*R*) of any object is directly proportional to its length (*l*) and inversely proportional to its area of cross-section (*A*).

Its unit is ohm (Ω). $R = \frac{\rho}{A}$

The constant of proportionality, ρ is called resistivity (specific resistance). Its units are Ωm or Ω cm.

10. Conductance (*G*) of electrolytic solutions is the inverse of resistance (*R*). Its unit is Ω^{-1} .

$$G = \frac{1}{R} = \frac{A}{\rho/}$$

11. The inverse of resistivity is called the **conductivity** or **specific conductance** (κ).

Its units are
$$\Omega^{-1}$$
 m⁻¹ or S m⁻¹.

$$\kappa = \frac{\text{Cell constant } (G^*)}{R} \qquad \left[\text{where, } G^* = \frac{l}{a} \right]$$

12. Molar conductivity (Λ_m) of a solution is the conductance of the volume of solution containing one mole of electrolyte, kept between two electrodes having unit length between them and sufficient cross-sectional area to contain the electrolyte. The unit of Λ_m will be $\Omega^{-1}m^2mol^{-1}$ or Sm² mol⁻¹.

$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{M}$$

- 13. Variation of conductivity and molar conductivity with concentration The conductivity of an electrolyte increases with the decrease in concentration, i.e. increase in dilution. Although, at infinite dilution, the conductivity of weak as well as strong electrolyte are nearly same, i.e. equal to one (as weak electrolyte is assumed to be completely ionised at infinite dilution) but their variation is not same with the increase in dilution. Upon dilution, equivalent and molar conductivities increases, while specific conductivity decreases. It is because concentration of ions per cubic centimetre decreases upon dilution.
- 14. Kohlrausch's law of independent migration of ions states that limiting molar conductivity of strong electrolyte is the sum of the individual contributions of the cation and the anion of the strong electrolyte. In general, if an electrolyte produces ν_+ cations and ν_- anions, then its limiting molar conductivity is given by

$$\Lambda_{\rm m}^{\rm o} = \nu_+ \lambda_+^{\rm o} + \nu_- \lambda_-^{\rm o}$$

15. Electrolytic cells are those cells in which electrical energy is used to carry out non-spontaneous chemical reactions and the reaction takes place in an electrolytic cell is called electrolysis.

16. Faraday's Laws of Electrolysis

· Faraday's first law states that, the amount of substance deposited at an electrode by passing current is proportional to the quantity of electricity passed through the electrolyte (in solution or in molten state).

$$W = Zit$$

where, Z = electrochemical equivalent $Z = \frac{\text{equivalent weight of substances}}{2}$ 96500

• Faraday's second law states that, when the same quantity of electricity is passed through different electrolytes, the amount of different substances deposited at respective electrodes are proportional to their chemical equivalent weights.

$$\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3} = \dots$$

where, W is the mass of substance and E is its equivalent weight.

17. A battery contains one or more than one electrochemical cells connected in series. It may be a primary battery (non-chargeable battery, like dry cell or a Leclanche cell) or secondary battery (rechargeable), like lead storage battery.

· Reactions involved in dry cell

At anode

$$Zn(s) \longrightarrow Zn^{2+} + 2e^{-}$$

At cathode

 $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

 Reactions involved in mercury cell At anode

 $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

At cathode

 $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

• When the lead storage battery is in use (discharging), the cell reactions are:

At anode Pb (s) + SO₄²⁻ (aq) \longrightarrow

 $PbSO_4(s) + 2e^-$ At cathode

 $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow$ Lead dioxide $PbSO_4(s) + 2H_2O(l)$ Lead sulphate

The overall reaction of the cell is written as :

$$Pb(s) + PbO_2(s) + 2H_2SO_4 (aq) \longrightarrow$$

Sulphuric acid
 $2PbSO_4(s) + 2H_2O(l)$

On charging the battery, the reaction is reversed. Actually, it forces the electrons to flow in opposite direction resulting $PbSO_{4}(s)$ on the anode as Pb and PbO₂ on the cathode. In this case, batteries behave, like electrochemical batteries.

18. A fuel cell is a galvanic cell in which chemical energy is converted into electrical energy by combustion of fuels. One of the most successful fuel cell is H2-O2 fuel cell. It was used for providing electrical power in Apollo space programme.

The electrode reactions are :

At cathode $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

At anode $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

The overall reaction of the cell is written as

$$2\mathsf{H}_2(g) + \mathsf{O}_2(g) \longrightarrow 2\mathsf{H}_2\mathsf{O}\ (l)$$

Fuel cells are pollution free, produce electricity with an efficiency of about 70% and never become dead due to continuous supply of fuel.

- 19. Corrosion is an electrochemical process in which a metal oxide or other salt of the metal forms a coating over the metal surface. e.g. the rusting of iron, tarnishing of silver surface, turning of surface of copper and bronze into green colour.
 - The anodic and cathodic reactions occurring in the process of rusting are :

At anode $2Fe(s) \longrightarrow 2Fe^{2+} + 4e^{-}$; $E_{(\text{Fe}^{2+}/\text{Fe})}^{\ominus} = -0.44 \text{ V}$ (Oxidation)

At cathode $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow$

$$2H_2O(l);$$

 $E_{H^+|O_2|H_2O}^{\ominus} = 1.23 V$

(Reduction)

• The overall reaction of the cell is written as: $2Fe(s) + O_2(g) + 4H^+(aq)$ —

$$2\text{Fe}^{2+}$$
 (aq) + $2\text{H}_2\text{O}(l)$;
 $E_{(\text{cell})}^{\odot} = 1.67 \text{ V}$

· Ferrous ions produced are further oxidised by atmospheric oxygen.

$$2\operatorname{Fe}^{2+}(aq) + 2\operatorname{H}_{2}O(l) + \frac{1}{2}O_{2}(g) \longrightarrow$$

$$\operatorname{Fe}_{2}O_{3}(s) + 4\operatorname{H}^{+}(aq)$$

$$\bigvee_{\substack{X\operatorname{H}_{2}O\\ \operatorname{Fe}_{2}O_{3} \cdot X\operatorname{H}_{2}O\\ \operatorname{Rust}}} x\operatorname{H}_{2}O$$

Hydrated ferric oxided (Fe₂O₃ \cdot xH₂O) is called rust.

• The methods used for prevention of corrosion are covering the surface with paint or by some chemical (bisphenol) to provide a sacrificial electrode of another metal (Mg, Zn, etc).