Chapter 2

ELECTROCHEMISTRY

Question and answers

2MARKS

1. Arrange the following metals in the order in which they displace each other from their salts.

Al, Cu, Fe, Mg and Zn Sol: Mg, Al, Zn, Fe, Cu.

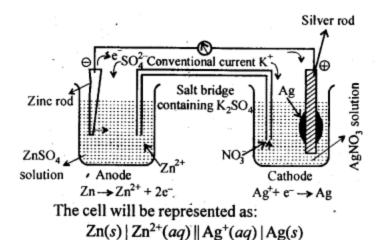
2. Given the standard electrode potentials, $K^+/K=-2$. 93 V, $Ag^+/Ag = 0.80$ V, $Hg^{2+}/Hg = 0.79$ V, $Mg^{2+}/Mg=-2.37$ V, $Cr^{3+}/Cr=0.74$ V.

Arrange these metals in their increasing order of reducing power.

Sol: Higher the oxidation potential more easily it is oxidized and hence greater is the reducing power. Thus, increasing order of reducing power will be Ag<Hg<Cr<Mg<K.

- 3. Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^{+}(aq) \longrightarrow 7M^{2+}(aq) + 2Ag(s)$ takes place. Further show:
- (i) Which of the electrode is negatively charged?
- (ii) The carriers of the current in the cell.
- (iii) Individual reaction at each electrode.

Sol. The set-up will be similar to as shown below,



- (i) Anode, i. e, zinc electrode will be negatively charged.
- (ii) The current will flow from silver to copper in the external circuit.

4. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm⁻¹. Calculate its molar conductivity.

Sol:

$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{0.0248 \, \text{cm}^{-1} \times 1000 \, \text{cm}^{3} L^{-1}}{0.20 \, \text{mol} \, L^{-1}}$$
$$= 124 \, \text{S cm}^{2} \, \text{mol}^{-1}$$

5. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146 x 10⁻³ S cm⁻¹?

Sol:

Cell constant =
$$\frac{\text{Conductivity}}{\text{Conductance}}$$

= Conductivity × Resistance
= $0.146 \times 10^{-3} \text{ S cm}^{-1} \times 1500 \Omega$
= 0.219 cm^{-1} .

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- 6. How much charge is required for the following reductions:
- (i) 1 mol of Al³⁺ to Al?
- (ii) 1 mol of Cu²⁺ to Cu?
- (iii) 1 mol of Mn04- to Mn²⁺?

Sol: (i) The electrode reaction is Al³⁺ + 3e ----> Al

- ∴ Quantity of charge required for reduction of 1 mol of Al³⁺=3F=3 x 96500C=289500C.
- (ii) The electrode reaction is Cu²⁺ + 2e⁻ -----> Cu
- ∴ Quantity of charge required for reduction of 1 mol of Cu²⁺=2F=2 x 96500=193000 C.
- (iii) The electrode reaction is Mn04- ——--> Mn²⁺.
- i.e., $Mn^{7+} + 5e^{-} \rightarrow Mn^{2+}$.
- ∴ Quantity of charge required = 5F
- =5 x 96500 C=4825000.

5MARKS

- 1. Write the Nernst equation and emf of the following cells at 298 K:
- (i) $Mg(s) \mid Mg^{2+}(0.001 M) \parallel Cu^{2+}(0.0001 M) \parallel Cu^{2+}(0.000$ M) | Cu(s)
- (ii) $Fe(s) | Fe^{2+} (0.001 \text{ M}) | H^{+} (1\text{ M}) | H_{2}(g)$ (1 bar) | Pt(s)
- (iii) $Sn(s) [Sn^{2+} (0.050 M) || H^{+} (0.020 M) ||$ $H_2(g)$ (1 bar) | Pt(s)
- (i) Cell reaction: $Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu (n=2)$ Nernst equation: $E_{\text{ceil}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$ $\therefore E_{\text{cell}} = 0.34 - (-2.37) - \frac{0.0591}{2} \log \frac{10^{-3}}{10^{-4}}$ =2.71-0.02955=2.68 V. (ii) Cell reaction:
- $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2 (n=2)$ Nernst equation:

$$\begin{split} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{\left[\text{Fe}^{2+}\right]}{\left[\text{H}^{+}\right]^{2}} \\ &\therefore E_{\text{cell}} = 0 - (-0.44) - \frac{0.0591}{2} \log \frac{10^{-3}}{(1)^{2}} \\ &= 0.44 - \frac{0.0591}{2} \times (-3) \\ &= 0.44 + 0.0887 = 0.5287 \text{ V.} \end{split}$$

(iii) Cell reaction:

$$\operatorname{Sn} + 2\operatorname{H}^+ \longrightarrow \operatorname{Sn}^{2+} + \operatorname{H}_2(n=2)$$

Nernst equation

Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\text{o}} - \frac{0.0591}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^{+}]^{2}}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\text{o}} - \frac{0.0591}{2} \log \frac{0.05}{(0.02)^{2}}$$

$$= 0 - (-0.14) - \frac{0.0591}{2} \log \frac{0.05}{(0.02)^{2}}$$

$$= 0.14 - \frac{0.0591}{2} \log 125$$

$$= 0.14 - \frac{0.0591}{2} (2.0969) = 0.078 \text{ V}.$$

(iv) Cell reaction: $2Br^-+2H^+\longrightarrow Br_2+H_2 (n=2)$

(iv)
$$Pt(s) | Br_2(l) | Br^-(0.010 \text{ M}) | H^+(0.030 \text{ M}) | H_2(g) (1 \text{ bar}) | Pt (s)$$

Given $E_{Mg^{2+},Mg}^{\circ} = -2.37 \text{V}$,
 $E_{Cu^{2+},Cu}^{\circ} = +0.34 \text{ V}$, $E_{Fe^{2+},Fe}^{\circ} = -0.44 \text{ V}$.
 $E_{Sn^{2+}/Sn}^{\circ} = -0.14 \text{V}$
 $E_{1/2Br_2/Br^-}^{\circ} = +1.08 \text{V}$

Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{1}{[\text{Br}^{-}]^{2} [\text{H}^{+}]^{2}}$$

$$= (0 - 1.08) - \frac{0.0591}{2} \log \frac{1}{(0.01)^{2} (0.03)^{2}}$$

$$= -1.08 - \frac{0.0591}{2} \log (1.111 \times 10^{7})$$

$$= -1.08 - \frac{0.0591}{2} (7.0457)$$

$$= -1.08 - 0.208 = -1.288 \text{ V}.$$

Thus, oxidation will occur at the hydrogen electrode and reduction will occur on Br₂ electrode.

2. Conductivity of 0.00241 M acetic acid is 7.896 x 10^{-5} S cm⁻¹. Calculate its molar conductivity. If Λ_{m0} , for acetic acid is 390.5 S cm² mol⁻¹, what is its dissociation constant?

$$\Lambda_{\rm m}^{\rm c} = \frac{\kappa \times 1000}{\text{Molarity}}$$

$$= \frac{(7.896 \times 10^{-5} \, \text{S cm}^{-1}) \times 1000 \, \text{cm}^3 \, \text{L}^{-1}}{0.00241 \, \text{mol L}^{-1}}$$

$$= 32.76 \, \text{S cm}^2 \, \text{mol}^{-1}$$

$$\alpha = \frac{\Lambda_{\rm m}^{\rm c}}{\Lambda_{\rm m}^{\circ}} = \frac{32.76}{390.5} = 8.4 \times 10^{-2}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.0024 \times (8.4 \times 10^{-2})^2}{1-0.084} = 1.86 \times 10^{-5}.$$

- 3. How much electricity in terms of Faraday is required to produce :
- (i) 20-0 g of Ca from molten CaCl₂
- (ii) 40-0 g of Al from molten Al₂O₃ ?

Sol:

(i)
$$\operatorname{Ca}^{2+}(aq) + 2e^{-} \longrightarrow \operatorname{Ca}(s)$$

2F 40 g

To produce 40 g of $CaCl_2$, charge needed = 2F

To produce 20 g of CaCl2, charge needed = 1F

(ii)
$$Al_2O_3 + 6e^- \longrightarrow 2Al + 3O^{2-}$$

$$6F \qquad (2 \times 27) g$$

To produce 54 g of Al, charge needed = 6F

To produce 40 g of Al, charge needed =
$$\frac{(40 \text{ g})}{(54 \text{ g})} \times (6 \text{ F}) = 4.44 \text{ F}$$
.

- 4. How much electricity is required in coulomb for the oxidation of (i) 1 mol of H_2O to O_2 (ii) 1 mol of FeO to Fe_2O_3 Sol:
- (i) The electrode reaction for 1 mol of H₂O is

$$H_2O \longrightarrow H_2 + \frac{1}{2}O_2$$

i.e.,
$$O^{2-} \longrightarrow \frac{1}{2}O_2 + 2e^{-}$$

.. Quantity of electricity required = $2F = 2 \times 96500 C = 193000 C$

(ii) The electrode reaction for 1 mol of FeO is

$$FeO + \frac{1}{2}O_2 \longrightarrow \frac{1}{2} Fe_2O_3$$

i.e.,
$$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$$

- .. Quantity of electricity required = 1F = 96500 C
- 5. A solution of $Ni(N0_3)_2$ is electrolyzed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Quantity of electricity passed

$$=(5A)\times(20\times60\text{ sec.})=6000C$$

$$Ni^{2+} + 2e^{-} \longrightarrow Ni$$

Thus, 2F, i.e., 2 × 96500C of charge deposit

.. 6000 C of charge will deposite

$$= \frac{58.7 \times 6000}{2 \times 96500} = 1.825 \,\mathrm{g} \,\mathrm{of} \,\mathrm{Ni}.$$

6. Three electrolytic cells A, B, C containing solutions of ZnS0₄, AgNO₃ and CuS0₄, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 45 g of silver deposited at the cathode of call B. How long did the current flow? What mass of copper and zinc were deposited?

Sol:

Given:
$$I = 1.5 \text{ A}$$
, $W = 1.45 \text{ g}$ of Ag, $t = ?$, $E = 108$, $n = 1$

Using Faraday's 1st law of electrolysis W = ZIt

or,
$$W = \frac{E}{nF} It$$

or,
$$t = \frac{1.45 \times 96500}{1.5 \times 108} = 863.73$$
 seconds.

Now for Cu,
$$W_1 = 1.45$$
 g of Ag, $E_1 = 108$, $W_2 = ?$, $E_2 = 31.75$

From Faraday's 2nd law of electrolysis $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

$$\frac{1.45}{W_2} = \frac{108}{31.75} \therefore W_2 = \frac{1.45 \times 31.75}{108}$$

$$= 0.426 g of Cu.$$

Similarly, for Zn, $W_1 = 1.45 \text{ g of Ag}$, $E_1 = 108$, $W_2 = ?$, $E_2 = 32.65$

Using formula,
$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

$$\frac{1.45}{W_2} = \frac{108}{32.65}$$

$$\therefore W_2 = \frac{1.45 \times 32.65}{108} = 0.438 \text{ of } Zn.$$

- 7. Using the standard electrode potentials given in the table, predict if the reaction between the following is feasible.
- (a) Fe^{3+} (aq) and I^{-} (aq)
- (b) Ag⁺(aq) and Cu(s)
- (c) Fe³⁺(aq) and Br⁻(aq)
- (d) Ag(s) and $Fe^{3+}(aq)$
- (e) $Br_2(aq)$ and $Fe^{2+}(aq)$.

Sol:

A particular reaction can be feasible if e.m.f. of the cell based on the E° values is positive. Keeping this in mind, let us predict the feasibility of the reactions.

(a)
$$I^{-}(aq) + Fe^{3+}(aq) \longrightarrow Fe^{2+}(aq) + 1/2 I_{2}(g)$$

 $E_{cell}^{\circ} = 0.77 - 0.54 = 0.23 V$ (feasible)
(b) $Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$
 $E_{cell}^{\circ} = (0.80 - 0.34) = 0.46 V$ (feasible)
(c) $Br^{-}(aq) + Fe^{3+}(aq) \longrightarrow Fe^{2+}(aq) + 1/2 Br_{2}(g)$
 $E_{cell}^{\circ} = 0.77 - (1.08) = -0.31 V$ (not feasible)
(d) $3Ag(s) + Fe^{3+}(aq) \longrightarrow 3Ag^{+}(aq) + Fe(s)$
 $E_{cell}^{\circ} = (0.77 - 0.80) = -0.03 V$ (not feasible)
(e) $2Fe^{2+}(aq) + Br_{2}(g) \longrightarrow 2Fe^{3+}(aq) + 2 Br^{-}(aq)$
 $E_{cell}^{\circ} = 1.08 - 0.77 = 0.31 V$ (feasible)

7MARKS

1. Calculate the standard cell potentials of the galvanic cells in which the following reactions take place.

(a)
$$2\text{Cr }(s) + 3\text{Cd}^{2+}(aq) \longrightarrow 2\text{Cr}^{3+}(aq) + 3\text{Cd }(s)$$

Given $E^{\circ}_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$; $E^{\circ}_{\text{Cd}^{2+}/\text{Cd}} = -0.40 \text{ V}$
(b) $\text{Fe}^{2+}(aq) + \text{Ag}^{+}(aq) \longrightarrow \text{Fe}^{3+}(aq) + \text{Ag }(s)$
Given $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = 0.80 \text{ V}$; $E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$

Also calculate ΔG° and equilibrium constant for the reaction. (C.B.S.E. Outside Delhi 2008)

 $\Delta G^{\circ} = -2.303 \text{ RT log } K_{\circ}$

(a) Calculation of E°_{cell} .

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = -0.40 - (-0.74) = + 0.34 \text{ V}$$
Calculation of ΔG° ,
$$\Delta G^{\circ} = -nF E^{\circ}_{cell} = -(6 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.34 \text{ V})$$

$$= -196860 \text{ CV} = -196860 \text{ J} = -196.86 \text{ kJ}$$

Calculation of Equilibrium Constant (Kc)

$$\log K_c = \frac{(-) \Delta G^{\circ}}{2 \cdot 303 \text{ RT}} = (-) \frac{(-) 196860}{2 \cdot 303 \times 8 \cdot 314 \times 298} = 34.501$$

$$K_c = \text{Antilog } (34.501) = 3.17 \times 10^{34}$$

(b) Calculation of E°cell,

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = (0.80 - 0.77) = 0.03 \text{ V}$$

Calculation of ΔG° ,

$$\Delta G^{\circ} = -nF E^{\circ}_{cell} = -(1 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.03 \text{ V})$$

= -2895 CV = -2895 J = -2.895 kJ

Calculation of Equilibrium Constant (Kc)

$$\Delta G^{\circ} = -2.303 \text{ RT log } K_c$$

$$\log K_c = (-)\frac{(-\Delta G^{\circ})}{2.303 \text{ RT}} = (-)\frac{(-)2895}{2.303 \times 8.314 \times 298} = 0.5074$$

$$K_c = \text{Antilog } (0.5074) = 3.22$$

2. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration. Sol: The reciprocal of resistivity is known as specific conductance or simply conductivity. It is denoted by K (kappa). Thus, if K is the specific conductance and G is the conductance of the solution, then

$$R = \frac{1}{G}$$
 and $\rho = \frac{1}{\kappa}$ $\therefore \frac{1}{G} = \frac{1}{\kappa} \times \frac{l}{A}$ $\kappa = G \times \frac{l}{A}$

Now, if I = 1 cm and A = 1 sq.cm, then K = G.

Hence, conductivity of a solution is defined as the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section. Alternatively, it may be defined as conductance of one centimetre cube of the solution of the electrolyte.

Molar conductivity of a solution at a dilution V is the conductance of all the ions produced from 1 mole of the electrolyte dissolved in V cm³ of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole of the solution is contained between them. It is represented by Δ_m .

$$\Lambda_m = \frac{\kappa A}{l}$$

Since l = 1 cm and A = V (volume containing 1 mole of electrolyte)

$$\Lambda_m = \kappa V$$

Variation of conductivity and molar conductivity with concentration: Conductivity always decreases with decrease in concentration, for both weak and strong electrolytes. This is because the number of ions per unit volume that carry the current in a solution decreases on dilution.

Molar conductivity increases with decrease in concentration. This is because that total volume, V, of solution containing one mole of electrolyte also increases. It has been found that decrease in K on

dilution of a solution is more than compensated by increase in its volume.

3. The conductivity of NaCl at 298 K has been determined at different concentrations and the results are given below:

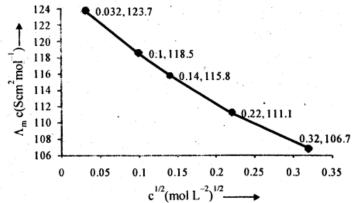
Concentration/M	0.001	0.010	0.020	0.050	0-100
10 ² × k/S m ⁻¹	1.237	11-85	23.15	55-53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value of Λ_m^0 .

Sol:

$$\frac{1 \text{S cm}^{-1}}{100 \text{S m}^{-1}} = 1 \text{ (unit conversion factor)}$$

Concentration (M)	κ (S m ⁻¹)	к (S cm ⁻¹)	$\Lambda_{\rm m} = \frac{1000 \times \kappa}{\text{Molarity}} (\text{Scm}^2 \text{mol}^{-1})$	c ^{1/2} (M ^{1/2})
10 ⁻³	1·237 × 10 ⁻²	1·237 × 10 ⁻⁴	$\frac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = 123.7$	0-0316
10-2	11-85 × 10 ⁻²	11·85 × 10 ⁻⁴	$\frac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = 118.5$	0-100
2 × 10 ⁻²	23·15 × 10 ⁻²	23-15 × 10 ⁻⁴	$\frac{1000 \times 23 \cdot 15 \times 10^{-4}}{2 \times 10^{-2}} = 115 \cdot 8$	0-141
5 × 10 ⁻²	55-53 × 10 ⁻²	55-53 × 10 ⁻⁴	$\frac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = 111.1$	0.224
10-1	106-74 × 10 ⁻²	106·74 × 10 ⁻⁴	$\frac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = 106.7$	0-316



 Λ° = Intercept on Λ_{m} axis = 124.0 S cm² mol⁻¹, which is obtained by extrapolation to zero concentration.

- 4. Predict the products of electrolysis in each of the following.
- (i) An aqueous solution of AgNO₃ with silver electrodes.
- (ii) An aqueous solution of AgNO₃ with platinum electrodes.
- (iii) A dilute solution of H₂SO₄ with platinum electrodes.
- (iv) An aqueous solution of CuCl₂ with platinum electrodes. Sol:

(i)
$$AgNO_3(s) + aq \longrightarrow Ag^+(aq) + NO_3^-(aq)$$

 $H_2O \rightleftharpoons H^+ + OH^-$

At cathode: Ag⁺ ions have lower discharge potential than H⁺ ions. Hence, Ag⁺ ions will be deposited as Ag in preference to H⁺ ions.

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

At anode: As Ag anode is attacked by NO₃⁻ ions, Ag of the anode will dissolve to form Ag⁺ ions in the solution.

$$Ag(s) \longrightarrow Ag^+(aq) + e^-$$

(ii) At cathode: Ag⁺ ions have lower discharge potential than H⁺ ions. Hence, Ag⁺ ions will be deposited as Ag in preference to H⁺ ions.

At anode: As anode is not attackable, out of OH⁻ and NO₃⁻ ions, OH⁻ ions have lower discharge potential. Hence, OH⁻ ions will be discharged in preference to NO₃⁻ ions, which then decompose to give out O₂.

$$OH^{-}(aq) \longrightarrow OH + e^{-}$$

 $4OH \longrightarrow 2H_{2}O(\ell) + O_{2}(g)$

(iii)
$$H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$$

 $H_2O \Longrightarrow H^+ + OH^-$

At cathode:
$$H^+ + e^- \longrightarrow H$$
,

At Anode:
$$H+H \longrightarrow H_2(g)$$

 $OH^- \longrightarrow OH+e^-$

$$4OH \longrightarrow 2H_2O + O_2(g)$$

Thus, H₂ gas is liberated at the cathode and O₂ gas at the anode.

(iv)
$$\operatorname{CuCl}_2(s) + aq \longrightarrow \operatorname{Cu}^{2+}(aq) + 2\operatorname{Cl}^-(aq)$$

 $\operatorname{H}_2\operatorname{O} \Longrightarrow \operatorname{H}^+ + \operatorname{OH}^-$

At cathode: Cu²⁺ ions will be reduced in preference to H⁺ ions and copper will be deposited at cathode.

$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

At anode: Cl⁻ ions will be discharged in preference to OH⁻ ions which remains in solution.

$$Cl^- \longrightarrow Cl + e^-$$

 $Cl + Cl \longrightarrow Cl_2(g)$

Thus, Cu will be deposited on the cathode and Cl, gas will be liberated at the anode.

SUMMARY

- **1. Electrochemistry** is the branch of chemistry which deals with the relationship between electrical energy and chemical energy and inter-conversion of one form into another.
- 2. An electrochemical cell consists of two metallic electrodes dipped in electrolytic solutions. The cells are of two types:
- (a) Electrolytic cells (b) Galvanic cells
- **3. A galvanic cell** consists of two half cells. Each half cell contains an electrolytic solution and a metallic electrode. The electrode at which-oxidation takes place is called an anode and the electrode at which reduction takes place is called the cathode. The half-cells are separated from each other by means of a porous pot or a salt bridge.
- **4. The passage of current from one electrode** to the other indicates the existence of potential difference between them. This difference of potential which causes current to flow from the electrode of higher negative potential is called the electromotive force (emf).
- **5. Electrical energy** = Emf (volts) x Quantity of electricity (coulombs)
- **6. The potential of SHE** is assigned an arbitrary value of zero. E° = 0 V. It is used as a reference electrode for measuring the standard electrode potentials. .
- **7. When the elements** are arranged in order of their standard electrode potentials, a series known as electrochemical series is obtained.
- 8. Standard emf of a cell,

$$\mathsf{E}^0_{\; cell} \!=\! \! \mathsf{E}^0_{\; cathode} \, - \; \mathsf{E}^0_{\; node} \! = \mathsf{E}^0_{\; Riglit} - \mathsf{E}^0_{\; Left}$$