

## EXERCISE QUESTIONS

### CHAPTER – 3 ELECTROCHEMISTRY

**3.1 Arrange the following metals in the order in which they displace each other from the solution of their salts. Al, Cu, Fe, Mg and Zn.**

**Ans -** Mg, Al, Zn, Fe, Cu, Ag.

**3.2 Given the standard electrode potentials,  $K^+ / K = -2.93V$ ,  $Ag^+ / Ag = 0.80V$ ,  $Hg^{2+} / Hg = 0.79V$ ,  $Mg^{2+} / Mg = -2.37 V$ ,  $Cr^{3+} / Cr = - 0.74V$  Arrange these metals in their increasing order of reducing power.**

**Ans -** Greater reducing power results from easier oxidation and higher oxidation potential. As a result, A will be the diminishing power in ascending order.

$Ag < Hg < Cr < Mg < K$ .

**3.3 Depict the galvanic cell in which the reaction  $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$  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.**

**Ans -**  $Zn(s) | Zn^{2+}(aq) || Ag^+(aq) | Ag(s)$

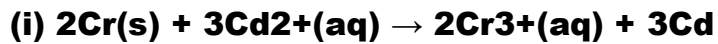
(i) Zn electrode (anode) is negatively charged

(ii) Ions are carriers of current in the cell and in the external circuit, current from silver to Zinc.

(iii) The reaction taking place at the anode is given by,

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

**3.4 Calculate the standard cell potentials of galvanic cell in which the following reactions take place:**



**(ii)  $\text{Fe}^{2+}(\text{aq}) + \text{Ag}^+(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{Ag(s)}$  Calculate the  $\Delta_r G^\circ$  and equilibrium constant of the reactions.**

**Ans -**

(a) Calculation of  $E^\circ_{\text{cell}}$ ,

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.40 - (-0.74) = +0.34 \text{ V}$$

Calculation of  $\Delta G^\circ$ ,

$$\begin{aligned} \Delta G^\circ &= -nF E^\circ_{\text{cell}} = -(6 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.34 \text{ V}) \\ &= -196860 \text{ CV} = -196860 \text{ J} = -196.86 \text{ kJ} \end{aligned}$$

Calculation of Equilibrium Constant ( $K_c$ )

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

$$\log K_c = \frac{(-)\Delta G^\circ}{2.303 RT} = (-) \frac{(-)196860}{2.303 \times 8.314 \times 298} = 34.501$$

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

(b) Calculation of  $E^\circ_{\text{cell}}$ ,

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

Calculation of  $\Delta G^\circ$ ,

$$\begin{aligned} \Delta G^\circ &= -nF E^\circ_{\text{cell}} = -(1 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.03 \text{ V}) \\ &= -2895 \text{ CV} = -2895 \text{ J} = -2.895 \text{ kJ} \end{aligned}$$

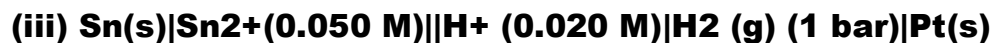
Calculation of Equilibrium Constant ( $K_c$ )

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

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

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

**3.5 Write the Nernst equation and emf of the following cells at 298 K:**



**Ans -**

(i) Cell reaction :  $\text{Mg}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{Cu}(s)$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} = [0.34 - (-2.37)] - \frac{0.0591}{2} \log \frac{10^{-3}}{10^{-4}} \\ &= 2.71 - 0.02955 = \mathbf{2.68 \text{ V}} \end{aligned}$$

(ii) Cell reaction :  $\text{Fe}(s) + 2\text{H}^{+}(aq) \longrightarrow \text{Fe}^{2+}(aq) + \text{H}_2(g)$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^{+}]^2} = [0 - (-0.44)] - \frac{0.0591}{2} \log \frac{10^{-3}}{(1)^2} \\ &= 0.44 - \frac{0.0591}{2} \times (-3) = 0 = 0.44 + 0.0887 = \mathbf{0.523 \text{ V}} \end{aligned}$$

(iii) Cell reaction :  $\text{Sn}(s) + 2\text{H}^{+}(aq) \longrightarrow \text{Sn}^{2+}(aq) + \text{H}_2(g)$

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^{+}]^2} = [0 - (-0.14)] - \frac{0.0591}{2} \log \frac{0.05}{(0.02)^2} \\ &= 0.14 - \frac{0.0591}{2} \times (2.097) = 0.14 - 0.0620 = \mathbf{0.08 \text{ V}} \end{aligned}$$

(iv) Cell reaction :  $2\text{Br}^{-} + 2\text{H}^{+} \longrightarrow \text{Br}_2 + \text{H}_2$

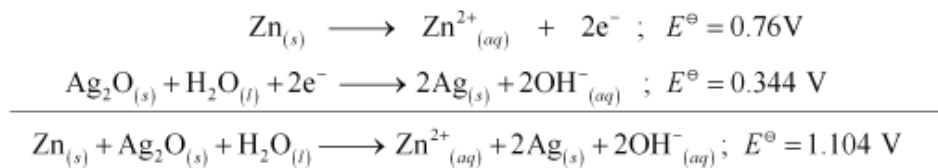
$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{1}{[\text{Br}^{-}]^2 [\text{H}^{+}]^2} \\ &= (0 - 1.08) - \frac{0.0591}{2} \log \frac{1}{(0.01)^2 \times (0.03)^2} = -1.08 - \frac{0.0591}{2} \log(1.111 \times 10^7) \\ &= -1.08 - \frac{0.0591}{2} (7.0457) = -1.08 - 0.208 = \mathbf{-1.288 \text{ V}} \end{aligned}$$

**3.6 In the button cells widely used in watches and other devices the following reaction takes place:**



**Determine  $\Delta_r G$  J and E J for the reaction.**

**Ans -**



$$\therefore E^{\ominus} = 1.104\text{ V}$$

We know that,

$$\Delta_r G^{\ominus} = -nFE^{\ominus}$$

$$= -2 \times 96487 \times 1.04$$

$$= -213043.296\text{ J}$$

$$= -213.04\text{ kJ}$$

### 3.7 Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

**Ans** - The area of the cross-section and the conductance of a solution with a length of 1 cm are used to determine a solution's conductivity. K is a symbol for  $\kappa$ .

For both weak and strong electrolytes, conductivity always drops as concentration rises. This is due to the fact that when concentration lowers, fewer ions per unit volume are required to carry the current in a solution.

The conductance of a volume V of a solution containing 1 mole of the electrolyte kept between two electrodes with an area of cross-section A and a distance of unit length is the molar conductivity of a solution at a particular concentration.

A reduction in concentration causes an increase in molar conductivity. This is so because one mole's worth of the solution's entire volume

**3.8 The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm<sup>-1</sup>. Calculate its molar conductivity.**

**Ans -**

Given,

$$\kappa = 0.0248 \text{ S cm}^{-1}$$

$$c = 0.20 \text{ M}$$

$$\begin{aligned} \therefore \text{Molar conductivity, } \Lambda_m &= \frac{\kappa \times 1000}{c} \\ &= \frac{0.0248 \times 1000}{0.2} \\ &= 124 \text{ Scm}^2\text{mol}^{-1} \end{aligned}$$

**3.9 The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500  $\Omega$ . What is the cell constant if conductivity of 0.001M KCl solution at 298 K is  $0.146 \times 10^{-3} \text{ S cm}^{-1}$ .**

**Ans -** Cell constant =  $K \times R = 0.146 \times 10^{-3} \times 1500 = 0.219 \text{ cm}^{-1}$

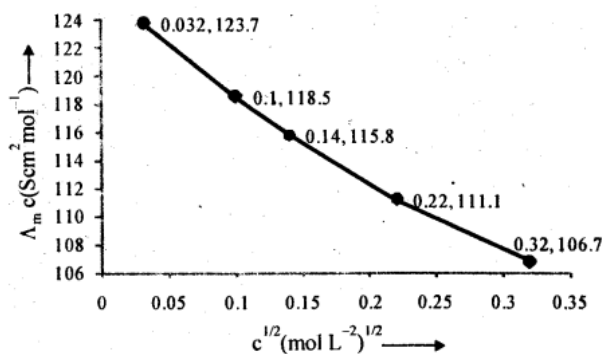
**3.10 The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:**

Concentration/M	0.001	0.010	0.020	0.050	0.100	0.200
$\kappa/\text{S m}^{-1}$	1.237	11.85	23.15	55.53	106.74	167.0

**Calculate  $\Lambda_m$  for all concentrations and draw a plot between  $\Lambda_m$  and  $c^{1/2}$ . Find the value of  $\Lambda_m^\circ$ .**

**Ans -**

Concentration (M)	$\kappa$ (S m <sup>-1</sup> )	$\kappa$ (S cm <sup>-1</sup> )	$\Lambda_m = \frac{1000 \times \kappa}{\text{Molarity}}$ (S cm <sup>2</sup> mol <sup>-1</sup> )	$c^{1/2}$ (M <sup>1/2</sup> )
10 <sup>-3</sup>	1.237 × 10 <sup>-2</sup>	1.237 × 10 <sup>-4</sup>	$\frac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = 123.7$	0.0316
10 <sup>-2</sup>	11.85 × 10 <sup>-2</sup>	11.85 × 10 <sup>-4</sup>	$\frac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = 118.5$	0.100
2 × 10 <sup>-2</sup>	23.15 × 10 <sup>-2</sup>	23.15 × 10 <sup>-4</sup>	$\frac{1000 \times 23.15 \times 10^{-4}}{2 \times 10^{-2}} = 115.8$	0.141
5 × 10 <sup>-2</sup>	55.53 × 10 <sup>-2</sup>	55.53 × 10 <sup>-4</sup>	$\frac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = 111.1$	0.224
10 <sup>-1</sup>	106.74 × 10 <sup>-2</sup>	106.74 × 10 <sup>-4</sup>	$\frac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = 106.7$	0.316



$\Lambda^{\circ}$  = Intercept on  $\Lambda_m$  axis = 124.0 S cm<sup>2</sup> mol<sup>-1</sup>, which is obtained by extrapolation to zero concentration.

**3.11 Conductivity of 0.00241 M acetic acid is  $7.896 \times 10^{-5}$  S cm<sup>-1</sup>. Calculate its molar conductivity. If  $\Lambda_m^{\circ}$  for acetic acid is 390.5 S cm<sup>2</sup> mol<sup>-1</sup>, what is its dissociation constant?**

**Ans -**

Step I. Calculation of molar conductance ( $\Lambda_m^c$ )

$$\kappa = 7.896 \times 10^{-5} \text{ S cm}^{-1}; C = 0.00241 \text{ mol L}^{-1} = \frac{0.00241 \text{ mol}}{10^3 \text{ cm}^3} = 241 \times 10^{-8} \text{ mol cm}^{-3}$$

$$\Lambda_m^c = \frac{\kappa}{C} = \frac{(7.896 \times 10^{-5} \text{ S cm}^{-1})}{(241 \times 10^{-8} \text{ mol cm}^{-3})} = 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

Step II. Calculation of degree of dissociation of acetic acid.

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^{\circ}} = \frac{(32.76 \text{ S cm}^2 \text{ mol}^{-1})}{(390.5 \text{ S cm}^2 \text{ mol}^{-1})} = 0.084 = 8.4 \times 10^{-2}$$

Step III. Calculation of dissociation constant  $K_c$

$$K_c = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$$= \frac{(0.00241 \text{ mol L}^{-1}) \times (0.084)^2}{1 - 0.084} = 0.0000185 \text{ mol L}^{-1} = 1.85 \times 10^{-5} \text{ mol L}^{-1}$$

**3.12 How much charge is required for the following reductions:**

**(i) 1 mol of Al<sup>3+</sup> to Al?**

**(ii) 1 mol of Cu<sup>2+</sup> to Cu?**

**(iii) 1 mol of MnO<sub>4</sub><sup>-</sup> to Mn<sup>2+</sup> ?**

**Ans -**

(i) The electrode reaction is  $\text{Al}^{3+} + 3\text{e}^{-} \longrightarrow \text{Al}$

∴ Quantity of charge required for reduction of 1 mol of  $\text{Al}^{3+} = 3F = 3 \times 96500\text{C} = 289500\text{C}$ .

(ii) The electrode reaction is  $\text{Cu}^{2+} + 2\text{e}^{-} \longrightarrow \text{Cu}$

∴ Quantity of charge required for reduction of 1 mol of  $\text{Cu}^{2+} = 2F = 2 \times 96500 = 193000\text{C}$ .

(iii) The electrode reaction is  $\text{MnO}_4^{-} \longrightarrow \text{Mn}^{2+}$ .

i.e.,  $\text{Mn}^{7+} + 5\text{e}^{-} \longrightarrow \text{Mn}^{2+}$ .

∴ Quantity of charge required =  $5F$   
 $= 5 \times 96500\text{C} = 482500\text{C}$ .

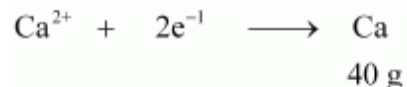
**3.13 How much electricity in terms of Faraday is required to produce**

**(i) 20.0 g of Ca from molten CaCl<sub>2</sub> ?**

**(ii) 40.0 g of Al from molten Al<sub>2</sub>O<sub>3</sub> ?**

**Ans -**

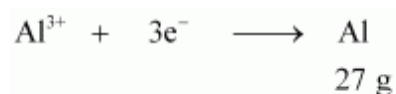
(i) According to the question,



Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium  $= \frac{2 \times 20}{40} \text{ F}$   
= 1 F

(ii) According to the question,



Electricity required to produce 27 g of Al = 3 F

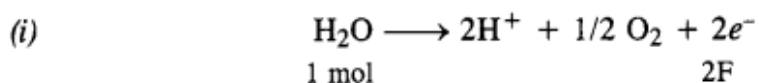
Therefore, electricity required to produce 40 g of Al  $= \frac{3 \times 40}{27} \text{ F}$   
= 4.44 F

### 3.14 How much electricity is required in coulomb for the oxidation of

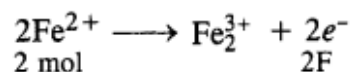
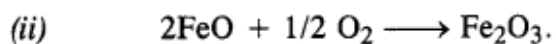
(i) 1 mol of H<sub>2</sub>O to O<sub>2</sub> ?

(ii) 1 mol of FeO to Fe<sub>2</sub>O<sub>3</sub> ?

**Ans -**



Electricity (charge) required = 2F = 2 × 96500 C = **1.93 × 10<sup>5</sup> C**

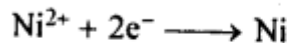




**3.15 A solution of Ni(NO<sub>3</sub>)<sub>2</sub> is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?**

**Ans -**

$$\begin{aligned} \text{Quantity of electricity passed} \\ &= (5\text{A}) \times (20 \times 60 \text{ sec.}) = 6000\text{C} \end{aligned}$$



$$\begin{aligned} \text{Thus, } 2\text{F, i.e., } 2 \times 96500\text{C of charge deposit} \\ &= 1 \text{ mole of Ni} = 58.7 \text{ g} \end{aligned}$$

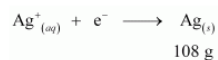
$\therefore$  6000 C of charge will deposit

$$\begin{aligned} &= \frac{58.7 \times 6000}{2 \times 96500} = 1.825 \text{ g of Ni.} \end{aligned}$$

**3.16 Three electrolytic cells A,B,C containing solutions of ZnSO<sub>4</sub>, AgNO<sub>3</sub> and CuSO<sub>4</sub>, respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?**

**Ans -**

According to the reaction:



i.e., 108 g of Ag is deposited by 96487 C.

$$\text{Therefore, 1.45 g of Ag is deposited by} = \frac{96487 \times 1.45}{108} \text{ C}$$

$$= 1295.43 \text{ C}$$

Given,

$$\text{Current} = 1.5 \text{ A}$$

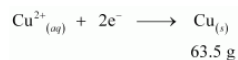
$$\therefore \text{Time} = \frac{1295.43}{1.5} \text{ s}$$

$$= 863.6 \text{ s}$$

$$= 864 \text{ s}$$

$$= 14.40 \text{ min}$$

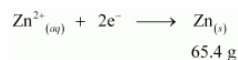
Again,



i.e.,  $2 \times 96487$  C of charge deposit = 63.5 g of Cu

$$\text{Therefore, 1295.43 C of charge will deposit} = \frac{63.5 \times 1295.43}{2 \times 96487} \text{ g}$$

$$= 0.426 \text{ g of Cu}$$



i.e.,  $2 \times 96487$  C of charge deposit = 65.4 g of Zn

$$\text{Therefore, 1295.43 C of charge will deposit} = \frac{65.4 \times 1295.43}{2 \times 96487} \text{ g}$$

$$= 0.439 \text{ g of Zn}$$

**3.17 Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:**

**(i)  $\text{Fe}^{3+}(\text{aq})$  and  $\text{I}^- (\text{aq})$**

**(ii)  $\text{Ag}^+ (\text{aq})$  and  $\text{Cu}(\text{s})$**

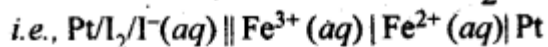
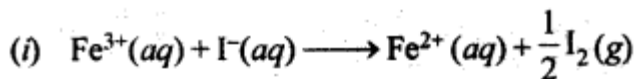
**(iii)  $\text{Fe}^{3+} (\text{aq})$  and  $\text{Br}^- (\text{aq})$**

**(iv)  $\text{Ag}(\text{s})$  and  $\text{Fe}^{3+} (\text{aq})$**

**(v)  $\text{Br}_2 (\text{aq})$  and  $\text{Fe}^{2+} (\text{aq})$ .**

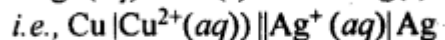
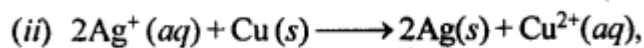
**Ans -**

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



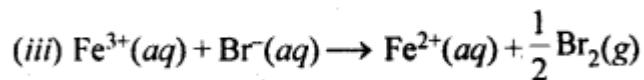
$$\therefore E_{\text{cell}}^\circ = E_{\text{Fe}^{3+}, \text{Fe}^{2+}}^\circ - E_{1/2\text{I}_2, \text{I}^{-}}^\circ$$

$$= 0.77 - 0.54 = 0.23 \text{ V (Feasible).}$$



$$E_{\text{cell}}^\circ = E_{\text{Ag}^{+}, \text{Ag}}^\circ - E_{\text{Cu}^{2+}, \text{Cu}}^\circ$$

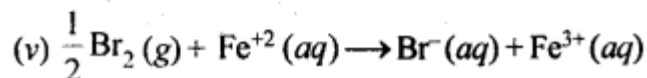
$$= 0.80 - 0.34 = 0.46 \text{ V (Feasible).}$$



$$E_{\text{cell}}^\circ = 0.77 - 1.09 = -0.32 \text{ V (Not feasible).}$$



$$E_{\text{cell}}^\circ = 0.77 - 0.80 = -0.03 \text{ V (Not feasible).}$$



$$E_{\text{cell}}^\circ = 1.09 - 0.77 = 0.32 \text{ V (Feasible).}$$

**3.18 Predict the products of electrolysis in each of the following:**

**(i) An aqueous solution of  $\text{AgNO}_3$  with silver electrodes.**

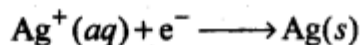
**(ii) An aqueous solution of  $\text{AgNO}_3$  with platinum electrodes.**

**(iii) A dilute solution of  $\text{H}_2\text{SO}_4$  with platinum electrodes.**

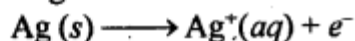
**(iv) An aqueous solution of  $\text{CuCl}_2$  with platinum electrodes.**

**Ans -**

**At cathode:**  $\text{Ag}^+$  ions have lower discharge potential than  $\text{H}^+$  ions. Hence,  $\text{Ag}^+$  ions will be deposited as Ag in preference to  $\text{H}^+$  ions:



**At anode:** As Ag anode is attacked by  $\text{NO}_3^-$  ions, Ag of the anode will dissolve to form  $\text{Ag}^+$  ions in the solution.



(ii) **At cathode:**  $\text{Ag}^+$  ions have lower discharge potential than  $\text{H}^+$  ions. Hence,  $\text{Ag}^+$  ions will be deposited as Ag in preference to  $\text{H}^+$  ions.

**At anode:** As anode is not attackable, out of  $\text{OH}^-$  and  $\text{NO}_3^-$  ions,  $\text{OH}^-$  ions have lower discharge potential. Hence,  $\text{OH}^-$  ions will be discharged in preference to  $\text{NO}_3^-$  ions, which then decompose to give out  $\text{O}_2$ .

