

## Chapter 3

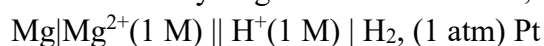
### Electrochemistry

#### Question 1:

How would you determine the standard electrode potential of the system  $\text{Mg}^{2+}/\text{Mg}$ ?

#### Solution 1:

A cell will be set up consisting of  $\text{Mg}/\text{MgSO}_4$  (1 M) as one electrode and standard hydrogen electrode  $\text{Pt}, \text{H}_2$  (1 atm)  $|\text{H}^+$  (1 M) as second electrode, measure the emf of the cell and also note the direction of deflection in the voltmeter. The direction of deflection shows that  $e^-$ 's flow from Mg electrode to hydrogen electrode, i.e., oxidation takes place on magnesium electrode and reduction on hydrogen electrode. Hence, the cell may be represented as follows:



$$E_{\text{cell}}^{\circ} = E_{\text{H}^+/\frac{1}{2}\text{H}_2}^{\circ} - E_{\text{Mg}^{2+}/\text{Mg}}^{\circ}$$

$$\text{Put } E_{\text{H}^+/\frac{1}{2}\text{H}_2}^{\circ} = 0$$

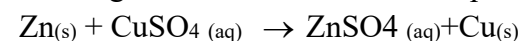
$$\therefore E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} = -E_{\text{cell}}^{\circ}$$

#### Question 2:

Can you store copper sulphate solutions in a zinc pot?

#### Solution 2:

Zn being more reactive than Cu, displaces Cu from  $\text{CuSO}_4$  solution as follows:



In terms of emf, we have



$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

$$= 0.34\text{ V} - (-0.76\text{ V}) = 1.10\text{ V}$$

As  $E_{\text{cell}}^{\circ}$  is positive, reaction takes place, i.e., Zn reacts with copper and hence, we cannot store  $\text{CuSO}_4$  Solution in zinc pot.

#### Question 3:

Consult the table of standard electrode potentials and suggest three substances that can oxidize ferrous ions under suitable conditions.

#### Solution 3:

Oxidation of  $\text{Fe}^{2+}$  converts it to  $\text{Fe}^{3+}$ , i.e.,  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$ ;  $E^\circ_{\text{OX}} = -0.77 \text{ V}$  Only those substances can oxidise  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  which are stronger oxidizing agents and have positive reduction potentials greater than  $0.77 \text{ V}$ , so that emf of the cell reaction is positive. This is so for elements lying below  $\text{Fe}^{3+}/\text{Fe}^{2+}$  in the series ex:  $\text{Br}_2$ ,  $\text{Cl}_2$  and  $\text{F}_2$

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#### Question 4:

Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

#### Solution 4:

For hydrogen electrode,  $\text{H}^+ + e^- \rightarrow 1/2 \text{H}_2$

Applying Nernst equation,

$$E_{\text{H}^+/\frac{1}{2}\text{H}_2} = E^\circ_{\text{H}^+/\frac{1}{2}\text{H}_2} - \frac{0.0591}{n} \log \frac{1}{[\text{H}^+]}$$

$$0 - \frac{0.0591}{1} \log \frac{1}{10^{-10}}$$

$$\left\{ \begin{array}{l} \text{pH} = 10 \\ \Rightarrow [\text{H}^+] = 10^{-10} \text{ M} \end{array} \right\} = -0.0591 \times 10$$

$$= 0.591 \text{ V}$$


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#### Question 5:

Calculate the emf of the cell in which the following reaction takes place:  $\text{Ni}_{(\text{s})} + 2\text{Ag}^+(0.002 \text{ M}) \rightarrow \text{Ni}^{2+}(0.160 \text{ M}) + 2\text{Ag}_{(\text{s})}$  Given that  $E^\circ_{\text{cell}} = 1.05 \text{ V}$ .

#### Solution 5:

Applying Nernst equation

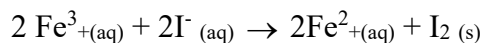
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

$$\begin{aligned}
 &= 1.05V - \frac{0.0519}{2} \log \frac{0.160}{(0.002)^2} \\
 &= 1.05 - \frac{0.0591}{2} \log (4 \times 10^4) \\
 &= 1.05 - \frac{0.0591}{2} (4.6021) \\
 &= 1.05 - 0.14 \text{ V} = 0.91 \text{ V}
 \end{aligned}$$


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**Question 6:**

The cell in which the following reaction occurs:  $2\text{Fe}^{3+}_{(\text{aq})} + 2\text{I}^{-}_{(\text{aq})} \rightarrow 2\text{Fe}^{2+}_{(\text{aq})} + \text{I}_{2(\text{s})}$  has  $E^{\circ}_{\text{cell}} = 0.236 \text{ V}$  at 298 K. calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

**Solution 6:**

For the given cell,  $n = 2$

$$\Delta_r G^{\circ} = -nF E^{\circ}_{\text{cell}}$$

$$= -2 \times 96500 \times 0.236$$

$$= -45.55 \text{ kJ mol}^{-1}$$

Also,  $\Delta_r G^{\circ} = -2.303 RT \log K_C$

$$\Rightarrow \log K_C = \frac{\Delta_r G^{\circ}}{2.303RT} = \frac{-45.55}{2.303 \times 8.314 \times 10^{-3} \times 298} = 7.983$$

$$\Rightarrow K_C = \text{antilog}(7.983)$$

$$= 9.616 \times 10^7$$


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**Question 7:**

Why does the conductivity of solution decrease with dilution?

**Solution 7:**

Conductivity of a solution is the conductance of ions present in a unit volume of the solutions. On dilution, number of ions per unit volume decreases. Hence, the conductivity decreases.

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**Question 8:**

Suggest a way to determine the value  $\Lambda^{\circ}_m$  of water.

**Solution 8:**

By using Kohlrausch's law,  $\Lambda_m^\circ$  for  $\text{H}_2\text{O}$  can be calculated, we can write,

$$\Lambda_m^\circ = \Lambda_m^\circ(\text{HCl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl})$$

Being strong electrolytes,  $\Lambda_m^\circ$  values of HCl, NaOH and NaCl are known.

By substituting their values, we can obtain  $\Lambda_m^\circ$  for  $\text{H}_2\text{O}$ .

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#### Question 9:

The molar conductivity of  $0.025 \text{ mol L}^{-1}$  methanoic acid is  $46.1 \text{ S cm}^2 \text{ mol}^{-1}$ . Calculate its degree of dissociation and dissociation constant Given  $\lambda^\circ(\text{H}^+) = 349.6 \text{ cm}^2$  and  $\lambda^\circ(\text{HCOO}^-) = 54.6 \text{ cm}^2 \text{ mol}^{-1}$

#### Solution 9:

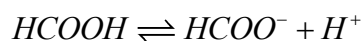
$$\Lambda_m^\circ(\text{HCOOH}) = \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{HCOO}^-)$$

$$= 349.6 + 54.6$$

$$= 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^c = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\therefore \alpha \therefore \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{46.1}{404.2} = 0.114$$



|               |   |   |   |
|---------------|---|---|---|
| Initial conc. | c | 0 | 0 |
|---------------|---|---|---|

|          |               |           |           |
|----------|---------------|-----------|-----------|
| at equi, | $c(1-\alpha)$ | $c\alpha$ | $c\alpha$ |
|----------|---------------|-----------|-----------|

$$\therefore K_a = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$= \frac{0.025 \times (0.114)^2}{1-0.114} = 3.67 \times 10^{-4}$$


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#### Question 10:

If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

#### Solution 10:

We know  $Q = It$

$$= 0.5 \times (2 \times 60 \times 60) = 3600 \text{ C}$$

$$1\text{F} \Rightarrow 96500\text{C} \Rightarrow 1 \text{ mole of } e^{-1} \text{ s}$$

$$\therefore 6.02 \times 10^{23} e^{-1} \text{ s}$$

$$\therefore 3600 \text{ C is equivalent to the flow of } e^{-1} \text{ s}$$

$$= \frac{6.02 \times 10^{23}}{96500} \times 3600 = 2.246 \times 10^{22} e^{-1} s$$


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**Question 11:**

Suggest a list of metals that are extracted electrolytically.

**Solution 11:**

Na, Ca, Mg, and Al

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**Question 12:**

Consider the reaction:  $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ . What is the quantity of electricity in coulombs needed to reduce 1 mol of  $\text{Cr}_2\text{O}_7^{2-}$

**Solution 12:**

From the reaction 1 mol of  $\text{Cr}_2\text{O}_7^{2-}$  require 6F  
 $= 6 \times 96500 = 579000 \text{ C}$

$\therefore$  579000 C of electricity are required for reduction of  $\text{Cr}_2\text{O}_7^{2-}$  to  $\text{Cr}^{3+}$

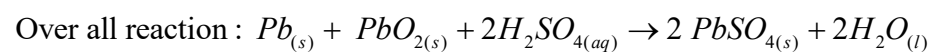
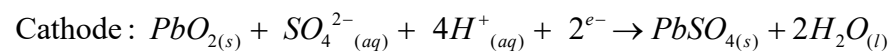
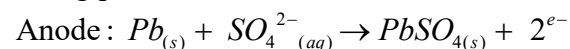
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**Question 13:**

Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

**Solution 13:**

A lead storage battery consists of anode of lead, cathode of a grid of lead packed with lead dioxide ( $\text{PbO}_2$ ) and 38%  $\text{H}_2\text{SO}_4$  solution as electrolyte. When the battery is in use, the reaction taking place are:



On charging the battery, the reverse reaction takes place, i.e.,  $\text{PbSO}_4$  deposited on electrodes is converted back to Pb and  $\text{PbO}_2$  and  $\text{H}_2\text{SO}_4$  is regenerated.

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**Question 14:**

Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

**Solution 14:**

Methane and Methanol.

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**Question 15:**

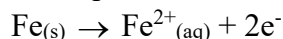
Explain how rusting of iron is envisaged as setting up of an electro chemical cell

**Solution 15:**

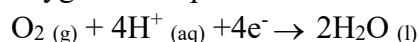
The Water present on the surface of iron dissolves acidic oxides of air like CO<sub>2</sub>, SO<sub>2</sub> etc, to form acids which dissociate to give H<sup>+</sup> ions:



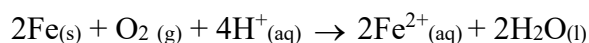
In the presence of H<sup>+</sup>, iron loses e<sup>-</sup> to form Fe<sup>3+</sup>. Hence, this spot acts as anode:



The e<sup>-</sup> released move through the metal to reach another spot, where H<sup>+</sup> ions and dissolved oxygen take up these e<sup>-</sup>s and reduction occurs. This spot, thus acts as cathode:



The overall reaction is:



Thus, an electro chemical cell is set up on the surface.

Ferrous ions are further oxidized by atmospheric oxygen to ferric ions which combine with water to form hydrated ferric oxide, Fe<sub>2</sub>O<sub>3</sub>.XH<sub>2</sub>O which is rust.

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**NCERT EXERCISES****Question 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.

**Solution 1:**

Mg, Al, Zn, Fe, Cu, Ag

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**Question 2:**

Given the standard electrode potentials,

$$\text{K}^+/\text{K} = 2.93 \text{ V}, \text{Ag}^+/\text{Ag} = 0.80 \text{ V},$$

$$\text{Hg}^{2+}/\text{Hg} = 0.79 \text{ V}$$

$$\text{Mg}^{2+}/\text{Mg} = -2.73 \text{ V}, \text{Cl}^3+/\text{Cr} = 0.74 \text{ V}$$

Arrange these metals in their increasing order of reducing power.

**Solution 2:**

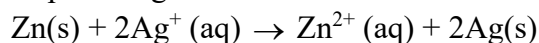
Higher the oxidation potential more easily it is oxidized and hence greater is the reducing power.

Thus, increasing order of reducing power will be Ag < Hg < Cl < Mg < K.

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**Question 3:**

Depict the galvanic cell in which the reaction,

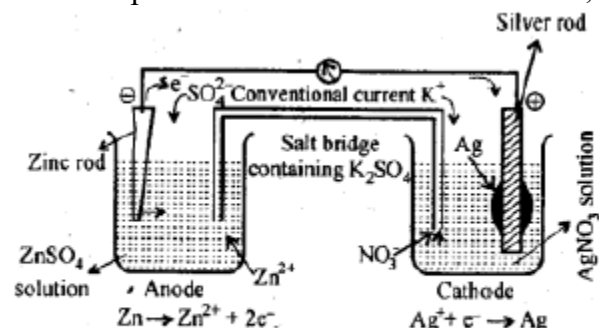


takes place. Further show:

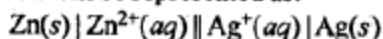
- (i) Which of the electrode is negatively charged?
- (ii) The carriers of the current in the cell.
- (iii) Individual reaction at each electrode.

#### Solution 3:

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



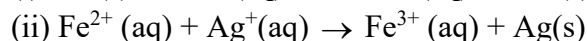
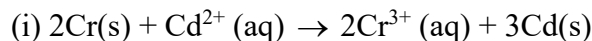
The cell will be represented as:



- (i) Anode, i.e., zinc electrode will be negatively charged
- (ii) The current will flow from silver to copper in the external circuit
- (iii) At anode:  $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2e^-$   
At cathode:  $2\text{Ag}^+(\text{aq}) + 2e^- \rightarrow 2\text{Ag(s)}$

#### Question 4:

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



Calculate the  $\Delta_r G^\circ$  and equilibrium constant of the reactions

Given

$$E^\circ_{\text{Cr}^{3+}, \text{Cr}} = -0.74 \text{ V},$$

$$E^\circ_{\text{Cd}^{2+}, \text{Cd}} = -0.40 \text{ V},$$

$$E^\circ_{\text{Ag}^+ \text{Ag}} = 0.80 \text{ V},$$

$$E^\circ_{\text{Fe}^{3+} \text{Fe}^{2+}} = 0.77 \text{ V}.$$

#### Solution 4:

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

$$\begin{aligned} \Delta_r G^\circ &= nFE^\circ_{\text{cell}} \\ &= -6 \times 96500 \text{ C mol}^{-1} \times 0.34 \text{ V} \\ &= 196860 \text{ C V mol}^{-1} \\ &= 196860 \text{ J mol}^{-1} \\ &= -196.86 \text{ kJ mol}^{-1} \\ -\Delta_r G^\circ &= 2.303 \times 8.314 \times 298 \log K \\ 196860 &= 2.303 \times 8.314 \times 298 \log K \\ \text{or } \log K &= 34.5014 \\ K &= \text{Antilog } 34.5014 = 3.172 \times 10^{34} \\ \text{(ii) } E^\circ_{\text{cell}} &= +0.80 \text{ V} - 0.77 \text{ V} = +0.03 \text{ V} \\ \Delta_r G^\circ &= nFE^\circ_{\text{Cell}} \\ &= -1 \times (96500 \text{ C V mol}^{-1}) \times (0.03 \text{ V}) \\ &= -2.895 \text{ C V mol}^{-1} = -2.895 \text{ J mol}^{-1} \\ &= 2.895 \text{ kJ mol}^{-1} \\ \Delta_r G^\circ &= 2.303 RT \log K \\ -2895 &= -2.303 \times 8.314 \times 298 \times \log K \\ \text{or } \log K &= 0.5074 \\ \text{or } K &= \text{Antilog } (0.5074) = 3.22 \end{aligned}$$


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### Question 5:

Write the Nernst equation and emf of the following cells at 298 K.

- (i)  $\text{Mg}_{(s)} \mid \text{Mg}^{2+}(0.001 \text{ M}) \parallel \text{Cu}^{2+}(0.0001 \text{ M}) \mid \text{Cu}_{(s)}$   
 (ii)  $\text{Fe}_{(s)} \mid \text{Fe}^{2+}(0.001 \text{ M}) \parallel \text{H}^+(1 \text{ M}) \mid \text{H}_2(\text{g}) (1 \text{ bar}) \mid \text{Pt}_{(s)}$   
 (iii)  $\text{Sn}_{(s)} \mid \text{Sn}^{2+}(0.050 \text{ M}) \parallel \text{H}^+(0.020 \text{ M}) \mid \text{H}_2(\text{g}) (1 \text{ bar}) \mid \text{Pt}_{(s)}$   
 (iv)  $\text{Pt}_{(s)} \mid \text{Br}_2(\text{l}) \mid \text{Br}^-(0.010 \text{ M}) \parallel \text{H}^+(0.030 \text{ M}) \mid \text{H}_2(\text{g}) (1 \text{ bar}) \mid \text{Pt}_{(s)}$

Given  $E^\circ_{\text{Cell}} \text{Mg}^{2+}, \text{Mg} = -2.37 \text{ V}$ ,

$E^\circ_{\text{Cu}^{2+}, \text{Cu}} = +0.34 \text{ V}$ ,  $E^\circ_{\text{Fe}^{2+}, \text{Fe}} = -0.44 \text{ V}$ .

$E^\circ_{\text{Sn}^{2+}, \text{Sn}} = -0.14 \text{ V}$

$E^\circ_{1/2 \text{ Br}_2/\text{Br}^-} = +1.08 \text{ V}$

### Solution 5:

#### (i) Cell reaction:



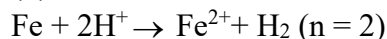
Nernst equation:

$$E_{\text{cell}} = E^\circ_{\text{Cell}} - \frac{0.0591}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\therefore E_{\text{cell}} = 0.34 - (-2.37) - \frac{0.0591}{2} \log \frac{10^{-3}}{10^{-4}}$$



$$= 2.71 - 0.02955 = 2.68 \text{ V}$$

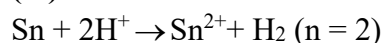
**(ii) Cell reaction:**

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

$$\therefore E_{\text{cell}} = 0 - (-0.44) - \frac{0.0591}{2} \log \frac{10^{-3}}{(1)^2}$$

$$= 0.44 - \frac{0.0591}{2} \times (-3)$$

$$= 0.44 + 0.0887 = 0.5287 \text{ V.}$$

**(iii) Cell reaction:**

Nernst equation:

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

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

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

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

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

**(iv) Cell reaction:**

Nernst equation:

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

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

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

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

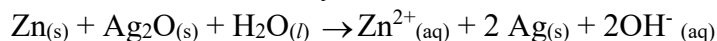
$$= -1.08 - 0.208 = -1.288 \text{ V.}$$

Thus, oxidation will occur at the hydrogen electrode, and reduction will occur on Br<sub>2</sub> electrode.

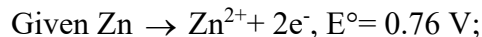
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**Question 6:**

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



Determine  $\Delta_r G^\circ$  and  $E^\circ$  for the reaction.

**Solution 6:**

Zn is oxidized and  $\text{Ag}_2\text{O}$  is reduced.

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{Ag}_2\text{O, Ag}(\text{reduction})} - E^\circ_{\text{Zn/Zn}^{2+}(\text{oxidation})} \\ &= 0.344 + 0.76 = 1.104 \text{ V} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ &= nFE^\circ_{\text{cell}} = -2 \times 96500 \times 1.104 \text{ J} \\ &= -2.13 \times 10^5 \text{ J}. \end{aligned}$$


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**Question 7:**

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

**Solution 7:**

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.

Molar conductivity of a solution at a dilution (V) is the conductance of all the ions produced from one mole of the electrolyte dissolved in  $V \text{ cm}^3$  of the solution when the electrodes are one cm apart and the area of cross-section of the electrodes is so large that the whole of the solution is contained between them. It is usually represented by  $\Lambda_m$ .

The conductivity of a solution (both for strong and weak electrolytes) decreases with decrease in concentration of the electrolyte, i.e., on dilution. This is due to the decrease in the number of ions per unit volume of the solution on dilution. The molar conductivity of a solution increases with decrease in concentration of the electrolyte, i.e., on dilution. This is due to the decrease in the number of ions per unit volume of the solution on dilution. The molar conductivity of a solution increases with decrease in concentration of the electrolyte. This is because both number of ions as well as mobility of ions increases with dilution. When concentration approaches zero, the molar conductivity is known as limiting molar conductivity.

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**Question 8:**

The conductivity of 0.20 M solution of KCl at 298 K is  $0.0248 \text{ S cm}^{-1}$ . Calculate its molar conductivity.

**Solution 8:**

$$\Lambda_m = \frac{k \times 1000}{\text{Molarity}} = \frac{0.0248 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.20 \text{ mol L}^{-1}}$$

$$= 124 \text{ S cm}^2 \text{ mol}^{-1}$$

**Question 9:**

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

**Solution 9:**

$$\begin{aligned} \text{Cell constant} &= \frac{\text{Conductivity}}{\text{Conductance}} \\ &= \text{Conductivity} \times \text{Resistance} \\ &= 0.146 \times 10^{-3} \text{ S cm}^{-1} \times 1500 \Omega \\ &= 0.218 \text{ cm}^{-1} \end{aligned}$$

**Question 10:**

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  |
| $10^2 \times \text{K/S m}^{-1}$ | 1.237 | 11.85 | 23.15 | 55.53 | 106.74 |

Calculate  $\Lambda_m$  for all concentrations and draw a plot between  $\Lambda_m$  and  $C^{1/2}$ .

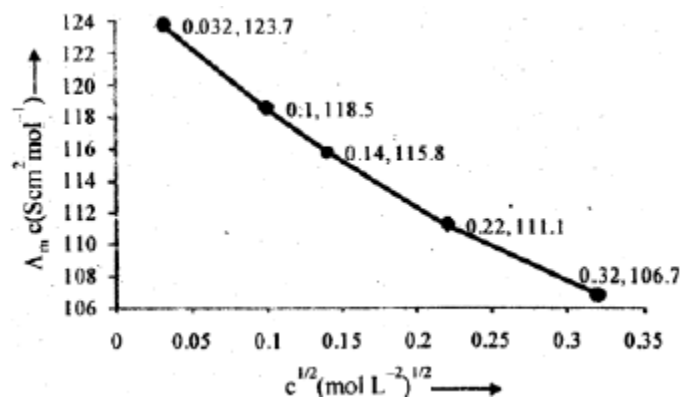
Find the value of  $\Lambda_m^\circ$

**Solution 10:**

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

| Concentration (M)  | K(S m <sup>-1</sup> )  | K (S cm <sup>-1</sup> ) | $\Lambda_m = \frac{1000 \times k}{\text{Molarity}} (\text{S cm}^2 \text{ mol}^{-1})$ | $C^{1/2} (\text{M}^{1/2})$ |
|--------------------|------------------------|-------------------------|--|----------------------------|
| $10^{-3}$          | $1.237 \times 10^{-2}$ | $1.237 \times 10^{-4}$  | $\frac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = 123.7$                           | 0.0316                     |
| $10^{-2}$          | $11.85 \times 10^{-2}$ | $11.85 \times 10^{-4}$  | $\frac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = 1118.5$                          | 0.100                      |
| $2 \times 10^{-2}$ | $23.15 \times 10^{-2}$ | $23.15 \times 10^{-4}$  | $\frac{1000 \times 23.15 \times 10^{-4}}{2 \times 10^{-2}} = 115.8$                  | 0.141                      |
| $5 \times 10^{-2}$ | $55.53 \times 10^{-2}$ | $55.53 \times 10^{-4}$  | $\frac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = 111.1$                  | 0.224                      |

|           |                         |                         |   |       |
|-----------|-------------------------|-------------------------|---|-------|
| $10^{-1}$ | $106.74 \times 10^{-2}$ | $106.74 \times 10^{-4}$ | $\frac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = 106.7$ | 0.316 |
|-----------|-------------------------|-------------------------|---|-------|



$\Lambda_m^\circ$  cm = Intercept of  $\Lambda_m$  axis =  $124.0 \text{ S cm}^2 \text{ mol}^{-1}$ , which is obtained by extrapolation to zero concentration.

#### Question 11:

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

#### Solution 11:

$$\begin{aligned} \Lambda_m^c &= \frac{\kappa \times 1000}{\text{Molarity}} \\ &= \frac{(7.896 \times 10^{-5} \text{ S cm}^{-1}) \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.00241 \text{ mol L}^{-1}} \\ &= 32.76 \text{ S cm}^2 \text{ mol}^{-1} \\ \alpha &= \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{32.76}{390.5} = 8.4 \times 10^{-2} \\ k_a &= \frac{C\alpha^2}{1-\alpha} = \frac{0.0024 \times (8.4 \times 10^{-2})^2}{1-0.084} = 1.86 \times 10^{-5} \end{aligned}$$

#### Question 12:

How much charge is required for the following reductions:

- (i) 1 mol of  $\text{Al}^{3+}$  to  $\text{Al}$ ?
- (ii) 1 mol of  $\text{Cu}^{2+}$  to  $\text{Cu}$ ?
- (iii) 1 mol of  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$ ?

#### Solution 12:

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

$\therefore$  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  $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$

$\therefore$  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  $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$  i.e.,  $\text{Mn}^{7+} + 5e^- \rightarrow \text{Mn}^{2+}$

$\therefore$  Quantity of charge required =  $5F = 5 \times 96500 \text{ C} = 4825000 \text{ C}$ .

---

#### Question 13:

How much electricity in terms of Faraday is required to produce.

(i) 20.0 g of Ca from molten  $\text{CaCl}_2$ ?

(ii) 40.0 g of Al from molten  $\text{Al}_2\text{O}_3$ ?

#### Solution 13:

(i)  $\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$

Thus, 1 mol of Ca, i.e., 40g of Ca require = 2F electricity

$\therefore$  20 g of Ca require = 1 F of electricity

(ii)  $\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$

Thus, 1 mole of Al, i.e., 27g of Al require = 3 F electricity

$\therefore$  40g of Al will require electricity

$$= \frac{3}{27} \times 40 = 4.44F \text{ of electricity.}$$


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#### Question 14:

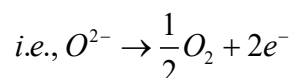
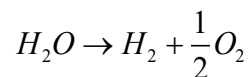
How much electricity is required in coulomb for the oxidation of

(i) 1 mol of  $\text{H}_2\text{O}$  to  $\text{O}_2$

(ii) 1 mol of  $\text{FeO}$  to  $\text{Fe}_2\text{O}_3$

#### Solution 14:

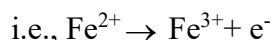
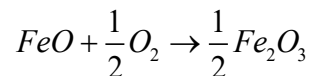
(i) The electrode reaction for 1 mol of  $\text{H}_2\text{O}$  is



$\therefore$  Quantity of electricity required

$$= 2F = 2 \times 96500 \text{ C} = 193000 \text{ C}$$

(ii) The electrode reaction for 1 mol of  $\text{FeO}$  is



∴ Quantity of electricity required = 1 F = 96500 C

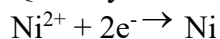
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#### Question 15:

A solution of  $\text{Ni}(\text{NO}_3)_2$  is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

#### Solution 15:

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



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

∴ 6000 C of charge will deposit

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


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#### Question 16:

Three electrolytic cells, A, B, C containing solutions of  $\text{ZnSO}_4$ ,  $\text{AgNO}_3$  and  $\text{CuSO}_4$ , 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 cell B. How long did the current flow? What mass of copper and zinc were deposited?

#### Solution 16:

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

Using Faraday's 1st law of electrolysis  $W = ZIt$  or  $W = \frac{E}{nF} It$

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

Now for Cu,  $W_1 = 1.45 \text{ g of Ag}$   $E_1 = 108$ ,  $W_2 = ?$

$$E_2 = 31.75$$

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

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

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

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

$$W_2 = ? \quad E_2 = 32.65$$

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

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

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


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### Question 17:

Predict if the reaction between the following is feasible:

- (i)  $\text{Fe}^{3+}_{(aq)}$  and  $\text{I}^{-}_{(aq)}$
- (ii)  $\text{Ag}^{+}_{(aq)}$  and  $\text{Cu}_{(s)}$
- (iii)  $\text{Fe}^{3+}_{(aq)}$  and  $\text{Br}^{-}_{(aq)}$
- (iv)  $\text{Ag}_{(s)}$  and  $\text{Fe}^{3+}_{(aq)}$
- (v)  $\text{Br}_2_{(aq)}$  and  $\text{Fe}^{2+}_{(aq)}$ .

Given standard electrode potentials:

$$E^{\circ}_{1/2, \text{I}_2, \text{I}^{-}} = +0.541 \text{ V},$$

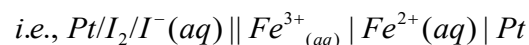
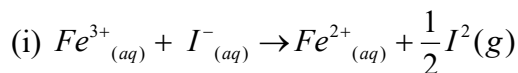
$$E^{\circ}_{\text{Cu}^{2+}, \text{Cu}} = +0.34 \text{ V},$$

$$E^{\circ}_{1/2 \text{Br}_2, \text{Br}^{-}} = +1.09 \text{ V},$$

$$E^{\circ}_{\text{Ag}^{+}, \text{Ag}} = +0.80 \text{ V}, E^{\circ}_{\text{Fe}^{3+}, \text{Fe}^{2+}} = +0.77 \text{ V}.$$

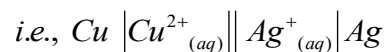
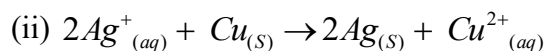
### Solution 17:

The reaction is feasible if the emf of the cell reaction is positive.



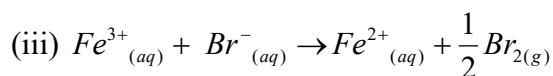
$$\therefore E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Fe}^{3+}, \text{Fe}^{2+}} - E^{\circ}_{1/2 \text{I}_2, \text{I}^{-}}$$

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

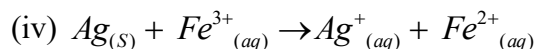


$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{Ag}^{+}, \text{Ag}} - E^{\circ}_{\text{Cu}^{2+}, \text{Cu}}$$

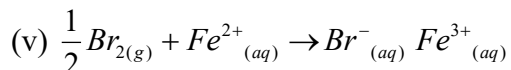
$$= 0.80 - 0.34 = 0.46 \text{ V (Feasible)}.$$



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



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



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

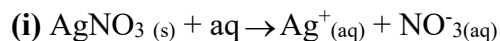

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### Question 18:

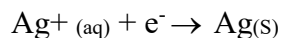
Predict the products of electrolysis in each of the following .

- (i) An aqueous solution of  $AgNO_3$  with silver electrodes.
- (ii) An aqueous solution of  $AgNO_3$  With platinum electrodes.
- (iii) A dilute solution of  $H_2SO_4$  with platinum electrodes.
- (iv) An aqueous solution of  $CuCl_2$  with platinum electrodes.

### Solution 18:



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

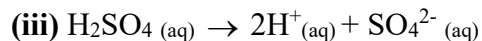
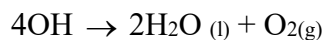
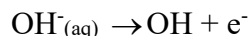


**At anode:** As  $Ag$  anode is attacked by  $NO_3^{-}$  ions,  $Ag$  of the anode will dissolve to form  $Ag^{+}$  ions in the solution.

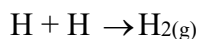


**(ii) At cathode:**  $Ag^{+}$  ions have lower discharge potential than  $H^{+}$  ions. Hence,  $Ag^{+}$  ions will be deposited as  $Ag$  in preference to  $H^{+}$  ions.

**At anode:** As anode is not attackable, out of  $OH^{-}$  and  $NO_3^{-}$  ions,  $OH^{-}$  ions have lower discharge potential. Hence  $OH^{-}$  will be discharged in preference to  $NO_3^{-}$  ions, which then decompose to give out  $O_2$ .



**At cathode:**  $H^{+} + e^{-} \rightarrow H,$



**At anode:**  $OH^{-} \rightarrow OH + e^{-}$

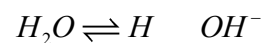
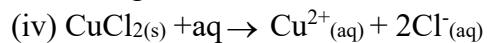




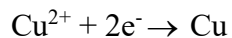
### Chapter 3

## Electrochemistry

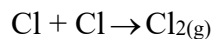
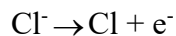
Thus H<sub>2</sub> gas is liberated at the cathode and O<sub>2</sub> gas at the anode.



**At cathode:** Cu<sup>2+</sup> ions will be reduced in preference to H<sup>+</sup> ions and copper will be deposited at cathode.



**At anode:** Cl<sup>-</sup> ions will be discharged in preference to OH<sup>-</sup> ions which remains in solution.



Thus, Cu will be deposited on the cathode and Cl<sub>2</sub> gas will be liberated at the anode.

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