

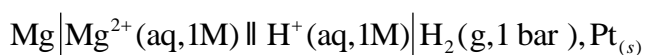
Chapter: ELECTROCHEMISTRY

INTEXT QUESTIONS

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

Ans: The standard electrode potential of $\text{Mg}^{2+} | \text{Mg}$ can be measured with respect to the standard hydrogen electrode, represented by $\text{Pt}_{(s)}, \text{H}_{2(g)} (1\text{atm}) | \text{H}_{(aq)}^+ (1\text{M})$.

$\text{Mg} | \text{MgSO}_4(\text{aq}, 1\text{M})$ consists of as the anode and SHE as the cathode, is set up.



Now, the emf of the cell is measured and the measured emf is the standard electrode potential of the magnesium electrode.

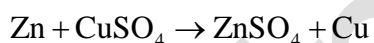
$$E^\ominus = E_R^\ominus - E_L^\ominus$$

$$E^\ominus = 0 - E_L^\ominus$$

$$E^0 = -E_L^0$$

3.2. Can you store copper sulphate solutions in a zinc pot?

Ans: Copper is more reactive than zinc. As a result, zinc has the ability to remove copper from its salt solution.



Zinc will displace copper from a copper sulphate solution if it is held in a zinc pot. Hence, copper sulphate solution cannot be stored in a zinc pot.

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

Ans: Ferrous ions can be oxidised by substances that are stronger oxidising agents than ferrous ions.

$$= 0.77 \text{ volts}$$

This means that compounds with higher reduction potentials than $+0.77 \text{ V}$ can be used.

Ferrous ions are oxidised to ferric ions. $\text{F}_2, \text{Cl}_2, \text{O}_2$ are three chemicals that can do so.

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

Ans: For hydrogen electrode $H^+ + e^- \rightarrow \frac{1}{2}H_2$

$$pH = 10$$

$$[H^+] = 10^{-10} M$$

Applying the Nernst equation, we get

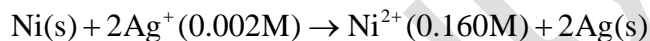
$$E_{\left(H^+, \frac{1}{2}H_2\right)} = E_{\left(H^+, \frac{1}{2}H_2\right)}^{\ominus} - \frac{RT}{nF} \ln \frac{1}{[H^+]}$$

$$E_{\left(H^+, \frac{1}{2}H_2\right)}^{\left(\frac{0.0591}{1} \log \frac{1}{[H^+]}\right)} = 0 - \frac{0.0591}{1} \log \frac{1}{[10^{-10}]}$$

$$E_{\left(H^+, \frac{1}{2}H_2\right)}^{\left(\frac{0.0591}{1} \log \frac{1}{[H^+]}\right)} = -0.0591 \log 10^{10}$$

$$E_{\left(H^+, \frac{1}{2}H_2\right)}^{\left(\frac{0.0591}{1} \log \frac{1}{[H^+]}\right)} = -0.591 V$$

3.5 Calculate the emf of the cell in which the following reaction takes place:



Give that $E_{cell}^0 = 1.05V$

Ans: $Ni_{(s)} + 2Ag^+(0.002M) \rightarrow Ni^{2+}(0.160M) + 2Ag_{(s)}$

$$E_{(cell)} = E_{(cell)}^{\ominus} - \frac{0.0591}{n} \log \frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$= 1.05 - \frac{0.0591}{2} \log \frac{(0.160)}{(0.002)^2}$$

$$= 1.05 - 0.02955 \log \frac{0.16}{0.000004}$$

$$= 1.05 - 0.02955 \log 4 \times 10^4$$

$$= 1.05 - 0.02955(\log 10000 + \log 4)$$

$$= 1.05 - 0.02955(4 + 0.6021)$$

$$= 0.914 \text{ V}$$

3.6 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 $E_{\text{cell}}^0 = 0.236 \text{ V}$ at 298 K . Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Ans: Here, $n = 2$, $E_{\text{cell}}^{\ominus} = 0.236 \text{ V}$, $T = 298 \text{ K}$

$$\Delta_r G^{\ominus} = -nFE_{\text{cell}}^{\ominus}$$

$$= -2 \times 96487 \times 0.236$$

$$= -45541.864 \text{ J mol}^{-1}$$

$$= -45.54 \text{ kJ mol}^{-1}$$

Again, $\Delta_r G^{\ominus} = -2.303RT \log K_c$

$$\Rightarrow \log K_c = -\frac{\Delta_r G^{\ominus}}{2.303RT}$$

$$= 7.981$$

$$\therefore K_c = -\frac{-45.54 \times 10^3}{2.303 \times 8.314 \times 298}$$

$$= 9.57 \times 10^7$$

3.7 Why does the conductivity of a solution decrease with dilution?

Ans: A solution's conductivity is defined as the conductance of ions in a unit volume of the solution. When a solution is diluted, the quantity of ions (which are responsible for carrying current) falls. As a result, as a solution is diluted, its conductivity drops.

3.8 Suggest a way to determine the Λ_m value of water.

Ans: Applying Kohlrausch's law of independent migration of ions, the Λ_m^0 value of water can be determined as follows:

$$\Lambda_{m_m}^0(\text{H}_2\text{O}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{OH}^-}^0$$

$$= (\lambda_{\text{H}^+}^0 + \lambda_{\text{Cr}^-}^0) + (\lambda_{\text{Na}^+}^0 + \lambda_{\text{OH}^-}^0) - (\lambda_{\text{Na}^+}^0 + \lambda_{\text{Cr}^-}^0)$$

$$\Lambda_{m(\text{HCl})}^0 + \Lambda_{m(\text{NaOH})}^0 - \Lambda_{m(\text{NaCl})}^0$$

Λ_m^0 Hence, by knowing the values of HCl, NaOH, and NaCl, the Λ_m^0 value of water can be determined

3.9 The molar conductivity of 0.025 mol L^{-1} methanoic acid is $46.1 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate its degree of dissociation and dissociation constant. Given $\lambda^0(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda^0(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$.

Ans: Given $C = 0.025 \text{ mol L}^{-1}$

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

$$\lambda^0(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda^0(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^0(\text{HCOOH}) = \lambda^0(\text{H}^+) + \lambda^0(\text{HCOO}^-)$$

$$= 349.6 + 54.6$$

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

Now, degree of dissociation:

$$\alpha = \frac{\Lambda_m(\text{HCOOH})}{\Lambda_m^0(\text{HCOOH})}$$

$$= \frac{46.1}{404.2}$$

$$= 0.114 \text{ (approx.)}$$

Thus, dissociation constant

$$K = \frac{c \alpha^2}{(1 - \alpha)}$$

$$= \frac{(0.025 \text{ mol L}^{-1})(0.114)^2}{(1 - 0.114)}$$

$$= 3.67 \times 10^{-4} \text{ mol L}^{-1}$$

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

Ans: Here $I = 0.5A$

$$t = 2 \text{ hours} = 2 \times 60 \times 60 \text{ s} = 7200 \text{ s}$$

We know that $96487C = 6.023 \times 10^{23}$ number of electrons.

$$\text{Then, } 3600C = \frac{6.023 \times 10^{23} \times 3600}{96487}$$

$$= 2.25 \times 10^{22} \text{ number of electrons}$$

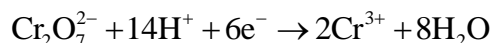
Hence the 2.25×10^{22} number of electrons will flow through the wire

3.11 Suggest a list of metals that are extracted electrolytically.

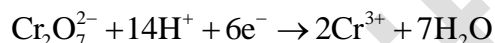
Ans: Metals that are on the top of the reactivity series such as sodium, potassium, calcium, lithium, magnesium, aluminium are extracted electrolytically

3.12 What is the quantity of electricity in coulombs needed to reduce 1 mol of $\text{Cr}_2\text{O}_7^{2-}$?

Consider the reaction:



Ans: The reaction is as follows;



Therefore, to reduce 1 mole of $\text{Cr}_2\text{O}_7^{2-} = 6F$

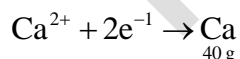
$$= 6 \times 96487C$$

$$= 578922C$$

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

(i) 20.0 g of Ca from molten CaCl_2 .

(ii) The reaction is as follows;



Electricity required to produce 40 g of calcium = $2F$

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

$$= 1F$$

(ii) $\text{Al}^{3+} + 3\text{e}^- \rightarrow \underset{27 \text{ g}}{\text{Al}}$

Electricity required to produce 27 g of Al = 3F

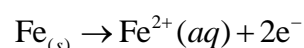
$$\begin{aligned} \text{Therefore, electricity required to produce 40 g of Al} &= \frac{3 \times 40}{27} F \\ &= 4.44F \end{aligned}$$

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

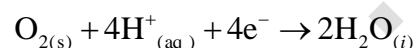
Ans: Methane and methanol can be used as fuels in fuel cells.

3.15 Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

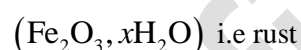
Ans: In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by,



Electrons released at the anodic spot move through the metallic object and go to another spot of the object. There, in the presence of H^{+} ions, the electrons reduce oxygen. This spot behaves as the cathode. These H^{+} ions come either from H_2CO_3 , which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides from the atmosphere in water. The reaction corresponding at the cathode is given by,



Also, ferrous ions are further oxidized by atmospheric oxygen to ferric ions. These ferric ions combine with moisture, present in the surroundings, to form hydrated ferric oxide



Hence, the rusting of iron is envisaged as the setting up of an electrochemical cell.

EXERCISE QUESTIONS

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: The displacement of metals is based on the reactivity series so the order is Mg, Al, Zn, Fe, Cu

3.2 Given the standard electrode potentials

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

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

$$\text{Mg}^{2+} / \text{Mg} = -2.37 \text{ V}, \text{Cr}^{3+} / \text{Cr} = -0.74 \text{ V}$$

Arrange these metals in their increasing order of reducing power.

Ans: The reducing power depends on the reduction potential inversely so the increasing order of reducing power is $\text{Ag} < \text{Hg} < \text{Cr} < \text{Mg} < \text{K}$

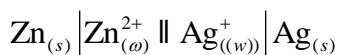
3.3 Depict the galvanic cell in which the reaction $\text{Zn}(\text{s}) + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag}(\text{s})$ takes place. Further show

(i) Which of the electrode is negatively charged?

(ii) The carriers of the current in the cell.

(iii) Individual reaction at each electrode.

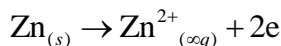
Ans: The reaction occurring in the galvanic cell is as follows;



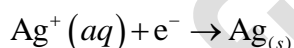
(i) Anode is negatively charged so zinc electrode is negatively charged.

(ii) The ions present are the carriers of current in the cell and external circuit and will flow from silver to zinc.

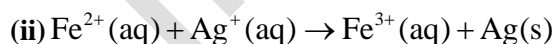
(iii) The reaction at anode is as follows;



Reaction at cathode is as follows;



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



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

Ans:

(i) $E^\ominus_{\text{Cr}^{3+}/\text{Cr}} = 0.74 \text{ V}$

$$E^\ominus_{\text{Cd}^{2+}/\text{Cd}} = -0.40 \text{ V}$$

Now standard cell potential is

$$\begin{aligned}
 E_{\text{cell}}^{\ominus} &= E_{\text{R}}^{\ominus} - E_{\text{L}}^{\ominus} \\
 &= -0.40 - (-0.74) \\
 &= +0.34 \text{ V}
 \end{aligned}$$

$$\Delta_{\text{r}}G^{\ominus} = -nFE_{\text{cell}}^{\ominus}$$

$$n = 6$$

$$E_{\text{cell}}^{\ominus} = +0.34 \text{ V}$$

$$\text{Then, } \Delta_{\text{r}}G^{\ominus} = -6 \times 96487 \text{ C mol}^{-1} \times 0.34 \text{ V}$$

$$= -196833.48 \text{ C V mol}^{-1}$$

$$= -196833.48 \text{ J mol}^{-1}$$

$$= -196.83 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{r}}G^{\ominus} = -RT \ln K$$

$$\Rightarrow \Delta_{\text{r}}G^{\ominus} = -2.303RT \ln K$$

$$\Rightarrow \log K = -\frac{\Delta_{\text{r}}G^{\ominus}}{2.303RT}$$

$$= \frac{-196.83 \times 10^3}{2.303 \times 8.314 \times 298}$$

$$= 34.496$$

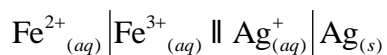
$$\therefore K = \text{antilog}(34.496) =$$

$$3.13 \times 10^{34}$$

$$\text{(ii) } E^{\ominus} \text{Fe}^{3+} / \text{Fe}^{2+} = 0.77 \text{ V}$$

$$E^{\ominus} \text{Ag}^* / \text{Ag} = 0.80 \text{ V}$$

The cell reaction is as follows;



Now the standard potential is as follows;

$$E_{\text{cell}}^{\ominus} = E_{\text{R}}^{\ominus} - E_{\text{L}}^{\ominus}$$

$$= 0.80 - 0.77$$

$$= 0.03 \text{ V}$$

$$n = 1$$

$$\Delta_r G^\ominus = -nFE_{\text{cell}}^\ominus$$

$$= -1 \times 96487 \text{ C mol}^{-1} \times 0.03 \text{ V}$$

$$= -2894.61 \text{ J mol}^{-1}$$

$$= -2.89 \text{ kJ mol}^{-1}$$

$$\Delta_r G^\ominus = -2.303RT \ln K$$

$$\Rightarrow \log K = -\frac{\Delta_r G^\ominus}{2.303RT}$$

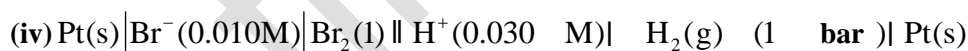
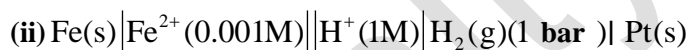
$$= \frac{-2894.61}{2.303 \times 8.314 \times 298}$$

$$= 0.5073$$

$$\therefore K = \text{antilog}(0.5073)$$

$$= 3.2$$

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



Ans:

(i) For the reaction, Nernst equation can be written as follows;

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= \{0.34 - (-2.36)\} - \frac{0.0591}{2} \log \frac{.001}{.0001}$$

$$= 2.7 - \frac{0.0591}{2} \log 10$$

$$= 2.7 - 0.02955$$

$$= 2.67V$$

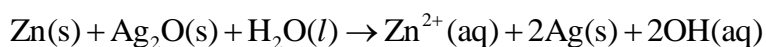
(ii) For the reaction, Nernst equation can be written as follows;

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2} \\
 &= \{0 - (-0.44)\} - \frac{0.0591}{2} \log \frac{0.001}{1^2} \\
 &= 0.44 - 0.02955(-3) \\
 &= 0.52865V \\
 &= 0.53V \text{ (approximately)}
 \end{aligned}$$

(iii) For the reaction, the Nernst equation can be written as follows;

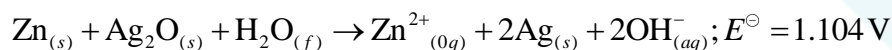
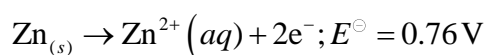
$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{1}{[\text{Br}^-]^2 [\text{H}^+]^2} \\
 &= (0 - 1.09) - \frac{0.0591}{2} \log \frac{1}{(0.010)^2 (0.030)^2} \\
 &= -1.09 - 0.02955 \times \log \frac{1}{0.0000009} \\
 &= -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}} \\
 &= -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}} \\
 &= -1.09 - 0.02955 \times \log(1.11 \times 10^7) \\
 &= -1.09 - 0.02955(0.0453 + 7) \\
 &= -1.09 - 0.208 \\
 &= -1.298V
 \end{aligned}$$

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



Determine $\Delta_r G^{\ominus}$ and E^{\ominus} for the reaction.

Ans: The reaction is as follows;



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: A solution's conductivity is defined as the conductance of a solution with a length of 1 cm and a cross-sectional area of 1 sq. cm. Conductivity, or particular conductance, is the inverse of resistivity. The symbol is used to signify it. If the variable is resistivity, we can write:

$$\kappa = \frac{1}{\rho}$$

At any given concentration, the conductivity of a solution is defined as the conductance (G) of one unit volume of solution held between two platinum electrodes with the same cross section area and separated by the same length.

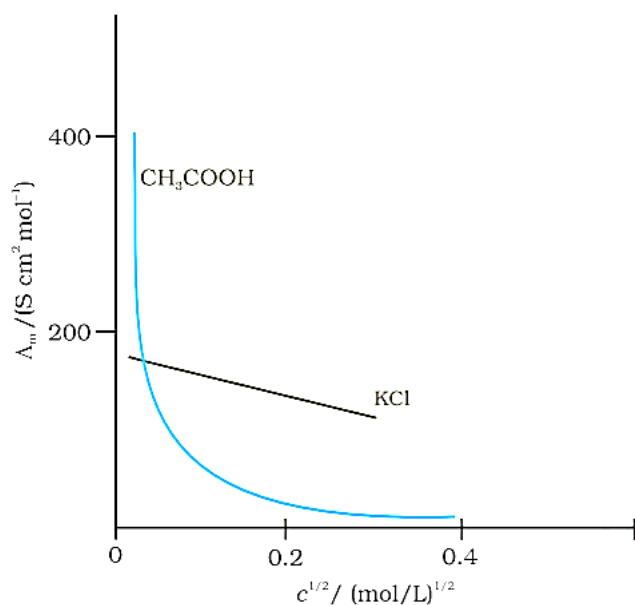
$$G = \kappa \frac{a}{l} = \kappa \cdot 1 = \kappa$$

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

Molar conductivity increases with a decrease in concentration. This is because the total volume V of the solution containing one mole of the electrolyte increases on dilution.

For both weak and strong electrolytes, conductivity diminishes as concentration decreases. This is because as the concentration of a solution declines, the number of ions per unit volume that carry the current in the solution reduces.

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



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

Ans:

Given

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

$$= 0.20\text{M}$$

∴ Molar conductivity,

$$\Lambda_m = \frac{\kappa \times 1000}{c}$$

$$= \frac{0.0248 \times 1000}{0.2}$$

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

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

Ans: Given that

$$\text{Conductivity, } k = 0.146 \times 10^{-3}\text{S cm}^{-1}$$

$$\text{Resistance, } R = 1500\Omega$$

$$\text{Resistance, } R = 1500\Omega$$

$$= 0.146 \times 10^{-3} \times 1500$$

$$= 0.219 \text{ cm}^{-1}$$

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

Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa / \text{Sm}^{-1}$	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 .

Ans: Given that

$$K = 1.237 \times 10^{-2} \text{ Sm}^{-1}, c = 0.001\text{M}$$

$$\text{Then, } k = 1.237 \times 10^{-4} \text{ Scm}^{-1}, c^{1/2} = 0.0316\text{M}^{1/2}$$

$$\therefore \Lambda_m = \frac{\kappa}{c}$$

$$= \frac{1.237 \times 10^{-4} \text{ Scm}^{-1}}{0.001 \text{ molL}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

$$= 123.7 \text{ Scm}^2 \text{ mol}^{-1} \text{ Given,}$$

$$K = 23.15 \times 10^{-2} \text{ Sm}^{-1}, c = 0.020\text{M}$$

$$\text{Then, } K = 11.85 \times 10^{-4} \text{ Scm}^{-1}, c^{1/2} = 0.1\text{M}^{1/2}$$

$$= \frac{11.85 \times 10^{-4} \text{ Scm}^{-1}}{0.010 \text{ molL}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

$$= 118.5 \text{ Scm}^2 \text{ mol}^{-1} \text{ Given,}$$

$$K = 23.15 \times 10^{-2} \text{ Sm}^{-1}, c = 0.020\text{M}$$

$$\therefore \Lambda_m = \frac{\kappa}{c}$$

$$= \frac{23.15 \times 10^{-4} \text{ Scm}^{-1}}{0.020 \text{ molL}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

$$= 115.8 \text{ Scm}^2 \text{ mol}^{-1} \text{ Given,}$$

$$K = 55.53 \times 10^{-2} \text{ Sm}^{-1}, c = 0.050\text{M}$$

$$\text{Then, } k = 55.53 \times 10^{-4} \text{ Scm}^{-1}, c^{1/2} = 0.2236\text{N}$$

$$\therefore \kappa = \frac{K}{c}$$

$$= \frac{55.53 \times 10^{-4} \text{ S cm}^{-1}}{0.050 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

$$= 111.11 \text{ s cm}^2 \text{ mol}^{-1} \text{ Given,}$$

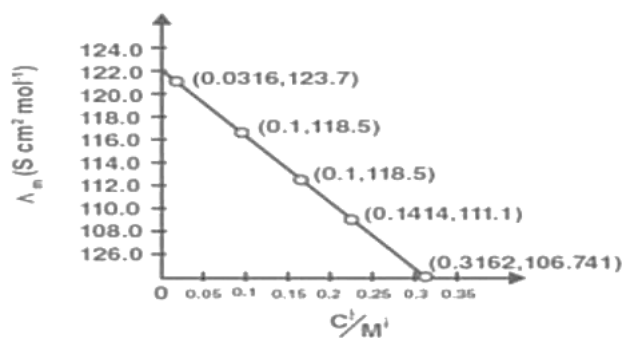
$$K = 106.74 \times 10^{-2} \text{ S m}^{-1}, c = 0.100 \text{ M}$$

$$\text{Then, } k = 106.74 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.3162 \text{ M}^{1/2}$$

$$= \frac{106.74 \times 10^{-4} \text{ S cm}^{-1}}{0.100 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

$$= 106.74 \text{ s cm}^2 \text{ mol}^{-1} \text{ Now, we}$$

$C^{1/2} / M^{1/2}$	0.0316	0.1	0.1414	0.2236	0.3162
$\Lambda_m (\text{S cm}^2 \text{ mol}^{-1})$	123.7	118.5	115.8	111.1	106.74



As the line intersects Λ_m^0 at $124.0 \text{ S cm}^2 \text{ mol}^{-1}$, $\Lambda_m^{\infty} = 124.0 \text{ S cm}^2 \text{ mol}^{-1}$

3.11 Conductivity of 0.00241M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity. If Λ_m^0 for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant?

Ans: Given, $K = 7.896 \times 10^{-5} \text{ S m}^{-1} c$

$$= 0.00241 \text{ mol L}^{-1}$$

Then, molar conductivity,

$$\Lambda_m = \frac{\kappa}{c}$$

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

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

$$\Lambda_m^0 = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{So, } \alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{32.76 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}}$$

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

$$\therefore \text{Dissociation constant, } = \frac{(0.00241 \text{ mol L}^{-1})(0.084)^2}{(1-0.084)} = 1.86 \times 10^{-5} \text{ mol L}^{-1}$$

3.12 How much charge is required for the following reductions:

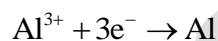
(i) 1 mol of Al^{3+} to Al

(ii) 1 mol of Cu^{2+} to Cu

(iii) 1 mol of MnO_4^- to Mn^{2+} ?

Ans:

(I) The reaction is as follows;



So, the required charge is $3F$ equal to $= 3 \times 96487\text{C}$

$$= 289461\text{C}$$

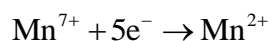
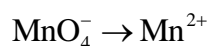
(ii) The reaction is as follows;



The required charge is $2F$ which is equal to $= 2 \times 96487\text{C}$

$$= 192974\text{C}$$

(iii) The reaction is as follows;



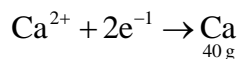
The charge required is $5F$ which is equal to $= 5 \times 96487\text{C}$

$$= 482435C$$

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

(i) 20.0g of Ca from molten CaCl_2 .

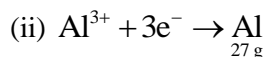
(ii) The reaction is as follows;



Electricity required to produce 40g of calcium = 2F

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

$$= 1F$$



Electricity required to produce 27g of Al = 3F

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

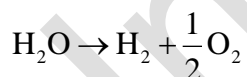
$$= 4.44F$$

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

(i) 1mol of H_2O to O_2

(ii) 1mol of FeO to Fe_2O_3

Ans: We can write as follows;



So, we can write $\text{O}^{2-} \rightarrow \frac{1}{2}\text{O}_2 + 2e^{-}$

Electricity required for the oxidation of 1mol of H_2O to $\text{O}_2 = 2F$

$$= 2 \times 96487C$$

$$= 192974C$$

(ii) We can write as follows;



Electricity required for the oxidation of 1 mol of FeO to Fe₂O₃ = 1F

$$= 96487C$$

3.15 A solution of Ni(NO₃)₂ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Ans:

Given,

$$\text{Current} = 5 \text{ A}$$

$$\text{Time} = 20 \times 60 = 1200 \text{ s}$$

$$\therefore \text{Charge} = \text{current} \times \text{time}$$

$$= 5 \times 1200$$

$$= 6000C$$

According to the question, Ni_(aq)²⁺ + 2e⁻ → Ni_(s)

$$58.7 \text{ g}$$

Nickel deposited by 2 × 96487C = 58.71 g

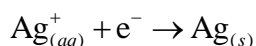
$$\text{Therefore, nickel deposited by } 6000C = \frac{58.71 \times 6000}{2 \times 96487} \text{ g}$$

$$= 1.825 \text{ g}$$

Hence, 1.825 g of nickel will be deposited at the cathode.

3.16 Three electrolytic cells A, B, C containing solutions of ZnSO₄, AgNO₃ and CuSO₄, 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: The reaction is as follows;



$$108 \text{ g}$$

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

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

$$= 1295.43\text{C}$$

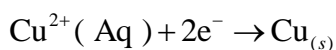
$$I = 1.5\text{A}$$

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

$$= 863.6\text{s}$$

$$= 864\text{s}$$

$$= 14.40\text{min}$$

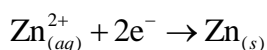


$$63.5\text{g}$$

$$2 \times 96487\text{C of charge deposit} = 63.5\text{g of Cu}$$

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

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

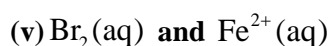
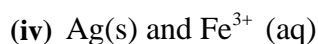
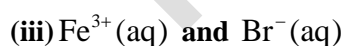
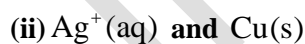
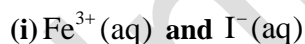


$$2 \times 96487\text{C of charge deposit} = 65.4\text{g of Zn}$$

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

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

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



Ans: The reaction is feasible when emf is positive so,

$$E_{\text{cell}}^{\circ} = E_{\text{Fe}}^{\circ} - E_{\text{I}_2}^{\circ}$$

$$= 0.77 - 0.54 = 0.23\text{V}$$

Reaction is feasible

$$(ii) E_{\text{cell}}^{\circ} = E_{\text{Ag}}^{\circ} - E_{\text{Cu}}^{\circ}$$

$$= 0.80 - 0.34 = 0.46 \text{ V}$$

Reaction is feasible

$$(iii) E_{\text{cell}}^{\circ} = E_{\text{Fe}}^{\circ} - E_{\text{Br}_2}^{\circ}$$

$$= 0.77 - 1.09 = -0.32 \text{ V}$$

Reaction is not feasible

$$(iv) E_{\text{cell}}^{\circ} = E_{\text{Fe}}^{\circ} - E_{\text{Ag}}^{\circ}$$

$$= 0.77 - 0.80 = -0.03 \text{ V}$$

Reaction is not feasible

$$(v) E_{\text{cell}}^{\circ} = E_{\text{Br}_2}^{\circ} - E_{\text{Fe}}^{\circ}$$

$$= 1.09 - 0.77 = 0.32 \text{ V}$$

Reaction is feasible

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

(i) An aqueous solution of AgNO_3 with silver electrodes.

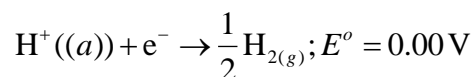
(ii) An aqueous solution of AgNO_3 with platinum electrodes.

(iii) A dilute solution of H_2SO_4 with platinum electrodes.

(iv) An aqueous solution of CuCl_2 with platinum electrodes.

Ans:

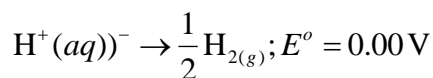
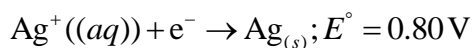
(i) The reaction at cathode is as follows;



The reaction having a more value of E° takes place at cathode so deposition of silver will take place at cathode.

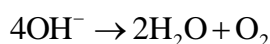
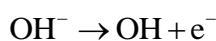
At anode, anode is attacked by nitrate ions so silver electrode at anode dissolves in solution to form Ag^+

(ii) The reactions are as follows;

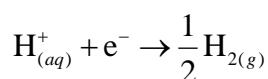


The reaction having a more value of E° takes place at cathode so deposition of silver will take place at cathode.

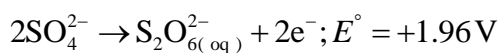
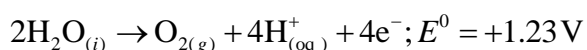
Platinum electrode is inert so anode is not attacked by nitrate ions so hydroxide or nitrate ions can be oxidised at anode but hydroxide ions having lower discharge potential decompose to liberate O_2



(iii) The reaction is as follows;

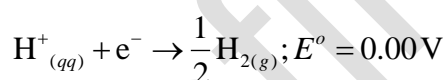
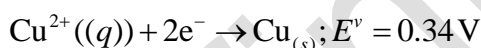


At anode,



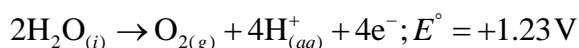
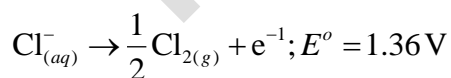
For dilute H_2SO_4 first reaction is preferred to form oxygen gas but for concentrated sulphuric acid reaction (ii) occurs.

(iv) At cathode,



The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of copper will take place at the cathode.

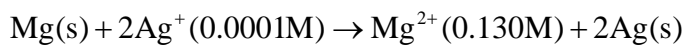
At anode,



As due to the overpotential of oxygen, Cl^- gets oxidized at the anode to produce Cl_2 gas.

SOLVED EXAMPLES

3.1 Represent the cell in which the following reaction takes place



Calculate its $E_{(\text{cell})}$ if $E_{(\text{cell})}^{\ominus} = 3.17\text{V}$

Ans: The cell can be written as $\text{Mg}|\text{Mg}^{2+}(0.130\text{M})||\text{Ag}^+(0.0001\text{M})|\text{Ag}$

$$\begin{aligned}
 E_{(\text{cell})} &= E_{(\text{cell})}^{\ominus} - \frac{RT}{2F} \ln \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2} \\
 &= 3.17\text{V} - \frac{0.059\text{V}}{2} \log \frac{0.130}{(0.0001)^2} = 3.17\text{V} - 0.21\text{V} = 2.96\text{V}
 \end{aligned}$$

3.2 Calculate the equilibrium constant of the reaction: $\text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)}$

Ans: $E_{(\text{cell})}^{\ominus} = 0.46\text{V}$

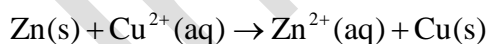
So, we can write as follows;

$$E_{(\text{cell})}^{\ominus} = \frac{0.059\text{V}}{2} \log K_C = 0.46\text{V}$$

$$\log K_C = \frac{0.46\text{V} \times 2}{0.059\text{V}} = 15.6$$

$$K_C = 3.92 \times 10^{15}$$

3.3 The standard electrode potential for Daniel cell is 1.1V . Calculate the standard Gibbs energy for the reaction:



Ans: $\Delta_r G^{\ominus} = -nFE_{(\text{cell})}^{\ominus}$

$$\text{Therefore, } \Delta_r G^{\ominus} = -2 \times 1.1\text{V} \times 96487\text{Cmol}^{-1}$$

$$= -21227\text{J mol}^{-1}$$

$$= -212.27\text{kJ mol}^{-1}$$

3.4 Resistance of a conductivity cell filled with $0.1 \text{ mol L}^{-1} \text{ KCl}$ solution is 100Ω . If the resistance of the same cell when filled with $0.02 \text{ mol L}^{-1} \text{ KCl}$ solution is 520Ω , calculate the conductivity and molar conductivity of $0.02 \text{ mol L}^{-1} \text{ KCl}$ solution. The conductivity of $0.1 \text{ mol L}^{-1} \text{ KCl}$ solution is 1.29 S m^{-1} .

Ans: The cell constant is given by the equation:

$$\text{Cell constant} = G^* = \text{conductivity} \times \text{resistance}$$

$$\text{Conductivity of } 0.02 \text{ mol L}^{-1} \text{ KCl solution} = \text{cell constant} / \text{resistance}$$

$$= \frac{G^*}{R} = \frac{129 \text{ m}^{-1}}{520 \Omega} = 0.248 \text{ S m}^{-1}$$

$$\text{Concentration is} = 0.02 \text{ mol L}^{-1}$$

$$= 1000 \times 0.02 \text{ mol m}^{-3} = 20 \text{ mol m}^{-3}$$

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c}$$

$$= \frac{248 \times 10^{-3} \text{ S m}^{-1}}{20 \text{ mol m}^{-3}} = 124 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

3.5 The electrical resistance of a column of $0.05 \text{ mol L}^{-1} \text{ NaOH}$ solution of diameter 1cm and length 50cm is $5.55 \times 10^3 \text{ ohm}$. Calculate its resistivity, conductivity and molar conductivity.

$$\text{Ans: } A = \pi r^2 = 3.14 \times 0.5^2 \text{ cm}^2 = 0.785 \text{ cm}^2 = 0.785 \times 10^{-4} \text{ m}^2$$

$$l = 50 \text{ cm} = 0.5 \text{ m}$$

$$R = \frac{\rho l}{A} \quad \text{or} \quad \rho = \frac{RA}{l} = \frac{5.55 \times 10^3 \Omega \times 0.785 \text{ cm}^2}{50 \text{ cm}} = 87.135 \Omega \text{ cm}$$

$$\text{Conductivity} = \kappa = \frac{1}{\rho} = \left(\frac{1}{87.135} \right) \text{ S cm}^{-1}$$

$$= 0.01148 \text{ S cm}^{-1}$$

$$\text{Molar conductivity, } \Lambda_m = \frac{K \times 1000}{c} \text{ cm}^3 \text{ L}^{-1}$$

$$= \frac{0.01148 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.05 \text{ mol L}^{-1}}$$

$$\rho = \frac{RA}{l}$$

$$= \frac{5.55 \times 10^3 \Omega \times 0.785 \times 10^{-4} \text{ m}^2}{0.5 \text{ m}} = 87.135 \times 10^{-2} \Omega \text{ m}$$

$$\kappa = \frac{1}{\rho} = \frac{100}{87.135} \Omega \text{ m} = 1.148 \text{ s m}^{-1}$$

$$\Lambda_m = \frac{\kappa}{c} = \frac{1.148 \text{ S m}^{-1}}{50 \text{ mol m}^{-3}} = 229.6 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1}$$

3.6 The molar conductivity of KCl solutions at different concentrations at 298 K are given below:

$c / \text{mol L}^{-1}$	$\Lambda_m / \text{scm}^2 \text{ mol}^{-1}$
0.000198	148.61
0.000309	148.29
0.000521	147.81
0.000989	147.09

Show that a plot between Λ_m and $c^{1/2}$ is a straight line. Determine the values of Λ_m° and A for KCl.

Ans: Taking the square root of concentration we obtain:

$c^{1/2} / (\text{mol L}^{-1})^{1/2}$	$\Lambda_m / \text{Scm}^2 \text{ mol}^{-1}$
0.01407	148.61
0.01758	148.29
0.02283	147.81
0.03145	147.09

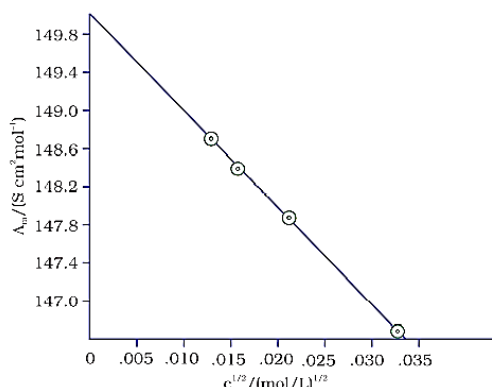
A plot of Λ_m (y-axis) and $c^{1/2}$ (x-axis) is shown in (Fig. 3.7).

It can be seen that it is nearly a straight line. From the intercept $\left(c^{1/2} = 0\right)$, we find that

A plot of Λ_m (y-axis) and $c^{1/2}$ (x-axis) is shown. It can be seen that it is nearly a straight line. From the intercept $(c^{1/2} = 0)$, we find that

$$\Lambda_m^\circ = 150.0 \text{ Scm}^2 \text{ mol}^{-1} \text{ and}$$

$$A = - \text{slope} = 87.46 \text{ Scm}^2 \text{ mol}^{-1} / (\text{mol} / \text{L}^{-1})^{1/2}$$



3.7 Calculate Λ_m^0 for CaCl_2 and MgSO_4 from the data given in Table 3.4

Ans: We know from Kohlrausch law that

$$\Lambda_m^0(\text{CaCl}_2) = \lambda_{\text{Ca}^{2+}}^0 + 2\lambda_{\text{Cl}^-}^0 = 119.0 \text{ s cm}^2 \text{ mol}^{-1} + 2(76.3) \text{ s cm}^2 \text{ mol}^{-1}$$

$$= (119.0 + 152.6) \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 271.6 \text{ s cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^0(\text{MgSO}_4) = \lambda_{\text{Mg}^{2+}}^0 + \lambda_{\text{SO}_4^{2-}}^0 = 106.0 \text{ S cm}^2 \text{ mol}^{-1} + 160.0 \text{ s cm}^2 \text{ mol}^{-1}$$

$$= 266 \text{ S cm}^2 \text{ mol}^{-1}$$

3.8 Λ_m^0 for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm² mol⁻¹ respectively.

Calculate Λ^0 for HAc.

$$\text{Ans: } \Lambda_m^0(\text{HAc}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{Ac}^-}^0 = \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0 + \lambda_{\text{Ac}^-}^0 + \lambda_{\text{Na}^+}^0 - \lambda_{\text{Cl}^-}^0 - \lambda_{\text{Na}^+}^0$$

$$= \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{NaAc}) - \Lambda_m^0(\text{NaCl})$$

$$= (425.9 + 91.0 - 126.4) \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 390.5 \text{ s cm}^2 \text{ mol}^{-1}$$

3.9 The conductivity of 0.001028 mol L⁻¹ acetic acid is $4.95 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its dissociation constant if Λ_m^0 for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$

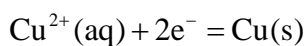
$$\text{Ans: } A_m = \frac{\kappa}{c} = \frac{4.95 \times 10^{-5} \text{ S cm}^{-1}}{0.001028 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} = 48.15 \text{ s cm}^3 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^o} = \frac{48.15 \text{Scm}^2 \text{mol}^{-1}}{390.5 \text{Scm}^2 \text{mol}^{-1}} = 0.1233$$

$$k = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028 \text{molL}^{-1} \times (0.1233)^2}{1-0.1233} = 1.78 \times 10^{-5} \text{molL}^{-1}$$

3.10 A solution of CuSO_4 is electrolysed for 10 minutes with a current of 1.5 amperes. What is the mass of copper deposited at the cathode?

Ans: $t = 600\text{s}$ charge = current \times time = $1.5 \text{A} \times 600\text{s} = 900\text{C}$



We require 2F or $2 \times 96487\text{C}$ to deposit 1mol or 63g of Cu .

For 900C , the mass of Cu deposited

$$= \left(63 \text{g mol}^{-1} \times 900\text{C}\right) / \left(2 \times 96487 \text{C mol}^{-1}\right) = 0.2938\text{g}$$

The mass of copper deposited at cathode is 0.2938g