

CHAPTER 2 ELECTROCHEMISTRY

INTEXT QUESTIONS

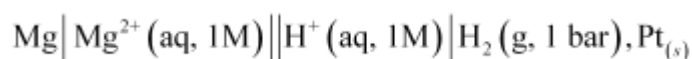
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Question 1. How would you determine the standard electrode potential of the system $\text{Mg}^{2+}|\text{Mg}$?

Solution :

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

A cell, consisting of $\text{Mg} | \text{MgSO}_4 (\text{aq } 1 \text{ M})$ as the anode and the standard hydrogen electrode as the cathode, is set up.



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

$$E^\ominus = E^\ominus_R - E^\ominus_L$$

Here, E^\ominus_R for the standard hydrogen electrode is zero.

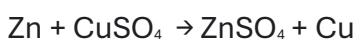
$$\therefore E^\ominus = 0 - E^\ominus_L$$

$$= - E^\ominus_L$$

Question 2. Can you store copper sulphate solutions in a zinc pot?

Solution :

Zinc is more reactive than copper. Therefore, zinc can displace copper from its salt solution. If copper sulphate solution is stored in a zinc pot, then zinc will displace copper from the copper sulphate solution.

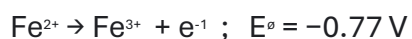


Hence, copper sulphate solution cannot be stored in a zinc pot.

Question 3. Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.

Solution :

Substances that are stronger oxidising agents than ferrous ions can oxidise ferrous ions.



This implies that the substances having higher reduction potentials than +0.77 V can oxidise ferrous ions to ferric ions. Three substances that can do so are F_2 , Cl_2 , and O_2 .

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Question 4. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Solution :

For hydrogen electrode, $\text{H}^{+} + \text{e}^{-} \longrightarrow \frac{1}{2} \text{H}_2$, it is given that pH = 10

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

Now, using Nernst equation:

$$\begin{aligned} E_{\left(\text{H}^{+}/\frac{1}{2}\text{H}_2\right)} &= E_{\left(\text{H}^{+}/\frac{1}{2}\text{H}_2\right)}^{\ominus} - \frac{RT}{nF} \ln \frac{1}{[\text{H}^{+}]} \\ &= E_{\left(\text{H}^{+}/\frac{1}{2}\text{H}_2\right)}^{\ominus} - \frac{0.0591}{1} \log \frac{1}{[\text{H}^{+}]} \\ &= 0 - \frac{0.0591}{1} \log \frac{1}{[10^{-10}]} \end{aligned}$$

$$= -0.0591 \log 10^{10}$$

$$= -0.591 \text{ V}$$

Question 5. Calculate the emf of the cell in which the following reaction takes place:



Given that $E^{\ominus}_{\text{cell}} = 1.05 \text{ V}$

Solution

:

Applying Nernst equation we have:

$$\begin{aligned} E_{(\text{cell})} &= E_{(\text{cell})}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2} \\ &= 1.05 - \frac{0.0591}{2} \log \frac{(0.160)}{(0.002)^2} \\ &= 1.05 - 0.02955 \log \frac{0.16}{0.000004} \end{aligned}$$

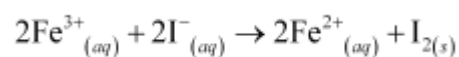
$$= 1.05 - 0.02955 \log 4 \times 10^4$$

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

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

$$= 0.914 \text{ V}$$

Question 6. The cell in which the following reactions occurs:



has $E^{\ominus}_{\text{cell}} = 0.236 \text{ V}$ at 298 K.

Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

Solution

:

Here, $n = 2$, $E^{\ominus}_{\text{cell}} = 0.236 \text{ V}$, $T = 298 \text{ K}$

We know that:

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

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

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

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

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

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

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

$$= 7.981$$

$$\therefore K_c = \text{Antilog}(7.981)$$

$$= 9.57 \times 10^7$$

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Question 7. Why does the conductivity of a solution decrease with dilution?

Solution :

The conductivity of a solution is the conductance of ions present in a unit volume of the solution. The number of ions (responsible for carrying current) decreases when the solution is diluted. As a result, the conductivity of a solution decreases with dilution.

Question 8. Suggest a way to determine the $\Lambda^\circ m$ value of water.

Solution :

Applying Kohlrausch's law of independent migration of ions, the $\Lambda^\circ m$ value of water can be determined as follows:

$$\Lambda^\circ m(\text{H}_2\text{O}) = \Lambda^\circ m(\text{HCl}) + \Lambda^\circ m(\text{NaOH}) - \Lambda^\circ m(\text{NaCl})$$

Hence, by knowing the $\Lambda^\circ m$ values of HCl, NaOH, and NaCl, the $\Lambda^\circ m$ value of water can be determined.

Question 9. The molar conductivity of 0.025 mol L^{-1} methanoic acid is

46.1 S cm² mol⁻¹.

Calculate its degree of dissociation and dissociation constant. Given $\lambda^{\circ}(\text{H}^+)$

$= 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda^{\circ}(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$

Solution

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

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

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

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

$$\begin{aligned}\Lambda_m^{\circ}(\text{HCOOH}) &= \lambda^{\circ}(\text{H}^+) + \lambda^{\circ}(\text{HCOO}^-) \\ &= 349.6 + 54.6 \\ &= 404.2 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Now, degree of dissociation:

$$\begin{aligned}\alpha &= \frac{\Lambda_m(\text{HCOOH})}{\Lambda_m^{\circ}(\text{HCOOH})} \\ &= \frac{46.1}{404.2} \\ &= 0.114 \text{ (approximately)}\end{aligned}$$

Thus, dissociation constant:

$$\begin{aligned}K &= \frac{c \alpha^2}{(1 - \alpha)} \\ &= \frac{(0.025 \text{ mol L}^{-1})(0.114)^2}{(1 - 0.114)} \\ &= 3.67 \times 10^{-4} \text{ mol L}^{-1}\end{aligned}$$

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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 :

$$I = 0.5 \text{ A}$$

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

$$\text{Thus, } Q = It$$

$$= 0.5 \text{ A} \times 7200 \text{ s}$$

$$= 3600 \text{ C}$$

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

Then,

$$\begin{aligned} 3600 \text{ C} &= \frac{6.023 \times 10^{23} \times 3600}{96487} \text{ number of electrons} \\ &= 2.25 \times 10^{22} \text{ number of electrons} \end{aligned}$$

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

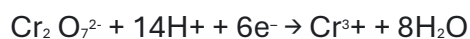
Question 11. Suggest a list of metals that are extracted electrolytically.

Solution :

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

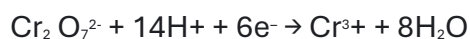
Question 12. What is the quantity of electricity in coulombs needed to reduce 1 mol of

$\text{Cr}_2\text{O}_7^{2-}$? Consider the reaction:



Solution :

The given reaction is as follows:



Therefore, to reduce 1 mole of $\text{Cr}_2\text{O}_7^{2-}$, the required quantity of electricity will be:

$$=6 F$$

$$= 6 \times 96487 C$$

$$= 578922 C$$

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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 :

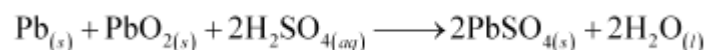
A lead storage battery consists of a lead anode, a grid of lead packed with lead oxide (PbO_2) as the cathode, and a 38% solution of sulphuric acid (H_2SO_4) as an electrolyte.

When the battery is in use, the following cell reactions take place:

At anode: $\text{Pb}_{(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$

At cathode: $\text{PbO}_{2(s)} + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{PbSO}_{4(s)} + 2\text{H}_2\text{O}_{(l)}$

The overall cell reaction is given by,



When a battery is charged, the reverse of all these reactions takes place.

Hence, on charging, present at the anode and cathode is converted into and respectively.

Question 14. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

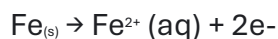
Solution :

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

Question 15. Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

Solution

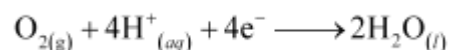
In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by,



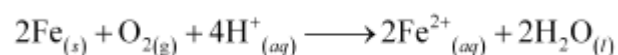
Electrons released at the anodic spot move through the metallic object and go to another spot of the object.

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,



The overall reaction is:



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 $(\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O})$, i.e., rust.

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

EXERCISES

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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 :

The following is the order in which the given metals displace each other from the solution of their salts.

Mg, Al, Zn, Fe, Cu

Question 2. Given the standard electrode potentials,

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

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

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

Arrange these metals in their increasing order of reducing power.

Solution :

The lower the reduction potential, the higher is the reducing power. The given standard electrode potentials increase in the order of $K^{+/K} < Mg^{2+}/Mg < Cr^{3+}/Cr < Hg^{2+}/Hg < Ag^+/Ag$.

Hence, the reducing power of the given metals increases in the following order:

$Ag < Hg < Cr < Mg < K$

Question 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.

Solution :

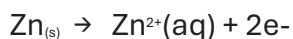
The galvanic cell in which the given reaction takes place is depicted as:



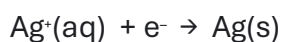
(i) Zn electrode (anode) is negatively charged.

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

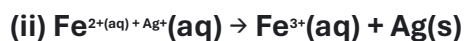
(iii) The reaction taking place at the anode is given by,



The reaction taking place at the cathode is given by,



Question 4. Calculate the standard cell potentials of galvanic cells in which the following reactions take place:



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

Solution

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

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

The galvanic cell of the given reaction is depicted as:



Now, the standard cell potential is

$$E^\ominus = E^\ominus_{\text{R}} - E^\ominus_{\text{L}}$$

$$= -0.40 - (-0.74)$$

$$= +0.34 \text{ V}$$

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

In the given equation,

$$n = 6$$

$$F = 96487 \text{ C mol}^{-1}$$

$$E^\circ_{\text{cell}} = +0.34 \text{ V}$$

$$\text{Then, } \Delta_r G^\circ = -6 \times 96487 \text{ C mol}^{-1} \times 0.34 \text{ V}$$

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

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

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

Again,

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

$$\Rightarrow \Delta_r G^\circ = -2.303 RT \log K$$

$$\begin{aligned} \Rightarrow \log K &= -\frac{\Delta_r G^\circ}{2.303 RT} \\ &= \frac{-196.83 \times 10^3}{2.303 \times 8.314 \times 298} \end{aligned}$$

$$= 34.496$$

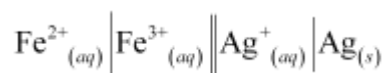
$$\Rightarrow K = \text{antilog}(34.496)$$

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

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

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

The galvanic cell of the given reaction is depicted as:



Now, the standard cell potential is

$$E^\ominus = E^\ominus_R - E^\ominus_L$$

$$= 0.80 - 0.77$$

$$= 0.03 \text{ V}$$

Here, $n = 1$.

$$\text{Then, } \Delta_r G^\ominus = -nFE^\ominus$$

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

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

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

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

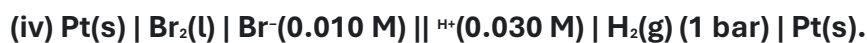
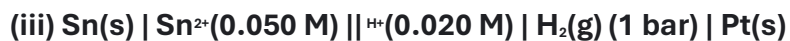
$$\begin{aligned} \Rightarrow \log K &= -\frac{\Delta_r G^\ominus}{2.303 RT} \\ &= \frac{-2894.61}{2.303 \times 8.314 \times 298} \end{aligned}$$

$$= 0.5073$$

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

$$= 3.2 \text{ (approximately)}$$

Question 5. Write the Nernst equation and emf of the following cells at 298 K:



Solution

:

(i) For the given reaction, the Nernst equation can be given as:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} \\ &= \{0.34 - (-2.36)\} - \frac{0.0591}{2} \log \frac{.001}{.0001} \\ &= 2.7 - \frac{0.0591}{2} \log 10 \end{aligned}$$

$$= 2.7 - 0.02955$$

$$= 2.67 \text{ V (approximately)}$$

(ii) For the given reaction, the Nernst equation can be given as:

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

$$= 0.52865 \text{ V}$$

$$= 0.53 \text{ V (approximately)}$$

(iii) For the given reaction, the Nernst equation can be given as:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2} \\ &= \{0 - (-0.14)\} - \frac{0.0591}{2} \log \frac{0.050}{(0.020)^2} \end{aligned}$$

$$= 0.14 - 0.0295 \times \log 125$$

$$= 0.14 - 0.062$$

$$= 0.078 \text{ V}$$

= 0.08 V (approximately)

(iv) For the given reaction, the Nernst equation can be given as:

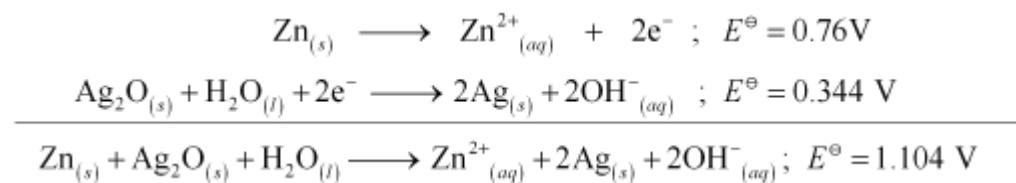
$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{cell}}^{\ominus} - \frac{0.0591}{n} \log \frac{1}{[\text{Br}^-]^2 [\text{H}^+]^2} \\
 &= (0 - 1.09) - \frac{0.0591}{2} \log \frac{1}{(0.010)^2 (0.030)^2} \\
 &= -1.09 - 0.02955 \times \log \frac{1}{0.00000009} \\
 &= -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}} \\
 &= -1.09 - 0.02955 \times \log (1.11 \times 10^7) \\
 &= -1.09 - 0.02955 (0.0453 + 7) \\
 &= -1.09 - 0.208 \\
 &= -1.298 \text{ V}
 \end{aligned}$$

Question 6. In the button cells widely used in watches and other devices the following reaction takes place:



Determine $\Delta_r G^\ominus$ for the reaction.

Solution



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

We know that,

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

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

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

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

Question 7. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Solution :

Conductivity of a solution is defined as the conductance of a solution of 1 cm in length and area of cross-section 1 sq. cm. The inverse of resistivity is called conductivity or specific conductance. It is represented by the symbol κ . If ρ is resistivity, then we can write:

$$\kappa = 1 / \rho$$

The conductivity of a solution at any given concentration is the conductance (G) of one unit volume of solution kept between two platinum electrodes with the unit area of cross-section and at a distance of unit length.

$$\text{i.e., } G = \kappa \frac{a}{l} = \kappa \cdot 1 = \kappa$$

(Since $a = 1$, $l = 1$)

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

Molar conductivity:

Molar conductivity of a solution at a given concentration is 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.

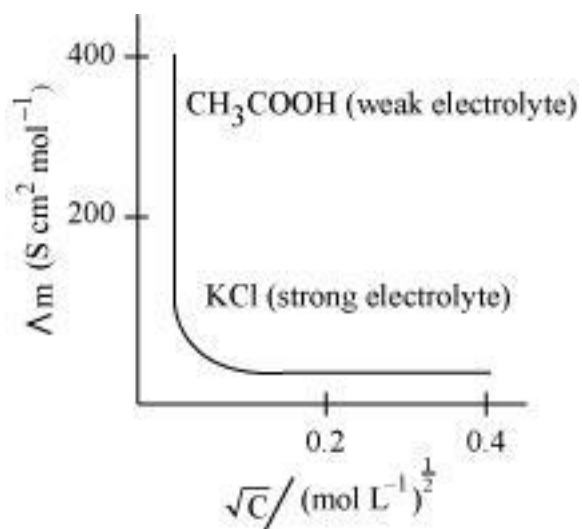
$$\Lambda_m = \kappa \frac{A}{l}$$

Now, $l = 1$ and $A = V$ (volume containing 1 mole of the electrolyte).

$$\Lambda_m = \kappa V$$

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.

The variation of Λ_m with \sqrt{c} for strong and weak electrolytes is shown in the following plot:



Question 8. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 Scm^{-1} . Calculate its molar conductivity.

Solution :

Given,

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

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

$$\Rightarrow \text{Molar conductivity, } \Lambda_m = (\kappa \times 1000) / c$$

$$= 0.0248 \times 1000 / 0.20$$

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

Question 9. The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500Ω . What is the cell constant if conductivity of 0.001M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$.

Solution :

Given,

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

Resistance, $R = 1500 \Omega$

\Rightarrow Cell constant = $\kappa \times R$

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

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

Question 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

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

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

Solution

Given,

$$\kappa = 1.237 \times 10^{-2} \text{ S m}^{-1}, c = 0.001 \text{ M}$$

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

$$\begin{aligned} \therefore \Lambda_m &= \frac{\kappa}{c} \\ &= \frac{1.237 \times 10^{-4} \text{ S cm}^{-1}}{0.001 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \end{aligned}$$

$$= 123.7 \text{ S cm}^2 \text{ mol}^{-1}$$

Given,

$$\kappa = 11.85 \times 10^{-2} \text{ S m}^{-1}, c = 0.010 \text{ M}$$

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

$$\begin{aligned} \therefore \Lambda_m &= \frac{k}{c} \\ &= \frac{11.85 \times 10^{-4} \text{ S cm}^{-1}}{0.010 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{L} \end{aligned}$$

$$= 118.5 \text{ S cm}^2 \text{ mol}^{-1}$$

Given,

$$\kappa = 23.15 \times 10^{-2} \text{ S m}^{-1}, c = 0.020 \text{ M}$$

$$\text{Then, } \kappa = 23.15 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.1414 \text{ M}^{1/2}$$

$$\begin{aligned} \therefore \Lambda_m &= \frac{k}{c} \\ &= \frac{23.15 \times 10^{-4} \text{ S cm}^{-1}}{0.020 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{L} \end{aligned}$$

$$= 115.8 \text{ S cm}^2 \text{ mol}^{-1}$$

Given,

$$\kappa = 55.53 \times 10^{-2} \text{ S m}^{-1}, c = 0.050 \text{ M}$$

$$\text{Then, } \kappa = 55.53 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.2236 \text{ M}^{1/2}$$

$$\begin{aligned} \therefore k &= \frac{k}{c} \\ &= \frac{55.53 \times 10^{-4} \text{ S cm}^{-1}}{0.050 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{L} \end{aligned}$$

$$= 111.1 \text{ S cm}^2 \text{ mol}^{-1}$$

Given,

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

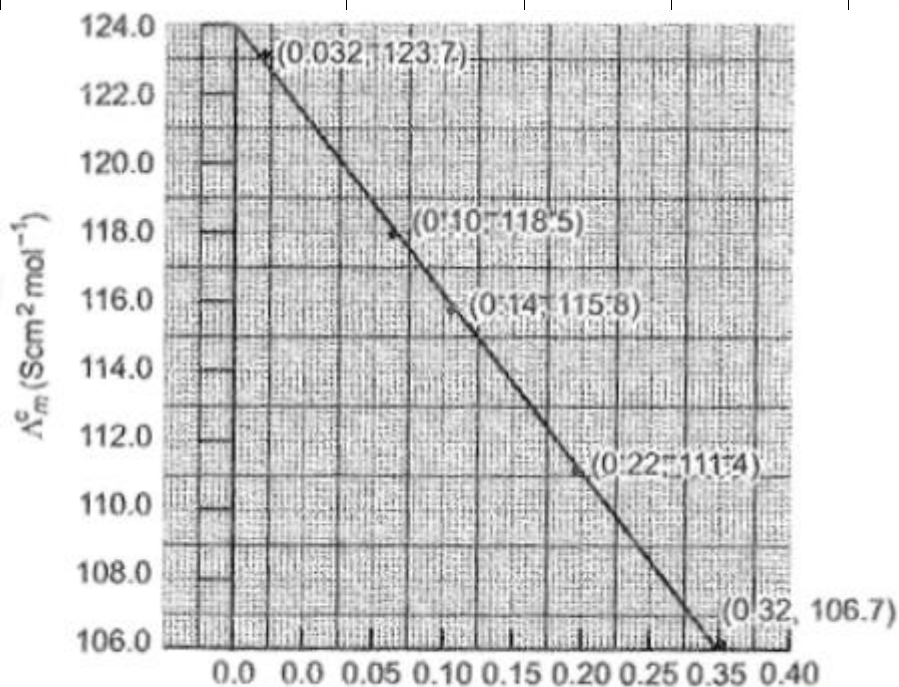
$$\text{Then, } \kappa = 106.74 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.3162 \text{ M}^{1/2}$$

$$\begin{aligned} \therefore \Lambda_m &= \frac{\kappa}{c} \\ &= \frac{106.74 \times 10^{-4} \text{ S cm}^{-1}}{0.100 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} \end{aligned}$$

$$= 106.74 \text{ S cm}^2 \text{ mol}^{-1}$$

Now, we have the following data:

$C^{1/2} / \text{M}^{1/2}$	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



$$\lambda_m^0 = \text{Intercept on the } \lambda_m^c \text{ axis} = 124.05 \text{ S cm}^2 \text{ mol}^{-1}$$

Since the line intercepts λ_m at $124.0 \text{ S cm}^2 \text{ mol}^{-1}$, $\lambda_m^0 = 124.0 \text{ S cm}^2 \text{ mol}^{-1}$.

Question 11. Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and if Λ_m° for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant?

Solution

Given, $\kappa = 7.896 \times 10^{-5} \text{ S m}^{-1}$

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

Then, molar conductivity, $\Lambda_m = \kappa / c$

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

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

Again, $\Lambda_m^\circ = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$

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

$$= 0.084$$

$$\Rightarrow \text{Dissociation constant, } K_a = \frac{c\alpha^2}{(1-\alpha)}$$

$$\Rightarrow (0.00241 \text{ mol L}^{-1})(0.084)^2 / (1-0.084)$$

$$= 1.86 \times 10^{-5} \text{ mol L}^{-1}$$

Question 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+} .

Solution

:

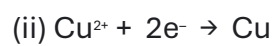
(i)



⇒ Required charge = 3 F

$$= 3 \times 96487 \text{ C}$$

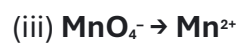
$$= 289461 \text{ C}$$



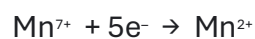
⇒ Required charge = 2 F

$$= 2 \times 96487 \text{ C}$$

$$= 192974 \text{ C}$$



i.e.,



⇒ Required charge = 5 F

$$= 5 \times 96487 \text{ C}$$

$$= 482435 \text{ C}$$

Question 13. How much electricity in terms of Faraday is required to produce

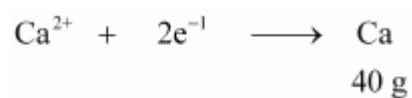
(i) 20.0 g of Ca from molten CaCl_2 .

(ii) 40.0 g of Al from molten Al_2O_3 .

Solution

:

(i) According to the question,

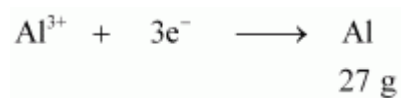


Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium $(2 \times 20) / 40$

= 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 = 3F

= 4.44 F

Question 14. How much electricity is required in coulomb for the oxidation of

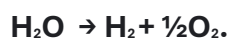
(i) 1 mol of H₂O to O₂.

(ii) 1 mol of FeO to Fe₂O₃.

Solution

:

(i) According to the question,



Now, we can write:



Electricity required for the oxidation of 1 mol of H₂O to O₂ = 2 F

$$= 2 \times 96487 \text{ C}$$

$$= 192974 \text{ C}$$

(ii) According to the question,



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

$$= 96487 \text{ C}$$

Question 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?

Solution

Given,

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

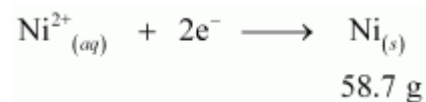
$$\text{Time} = 20 \times 60 = 1200 \text{ s}$$

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

$$= 5 \times 1200$$

$$= 6000 \text{ C}$$

According to the reaction,



$$\text{Nickel deposited by } 2 \times 96487 \text{ C} = 58.71 \text{ g}$$

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

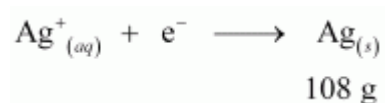
$$= 1.825 \text{ g}$$

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

Question 16. Three electrolytic cells A,B,C containing solutions of ZnSO_4 , AgNO_3 and CuSO_4 , 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?

Solution

According to the reaction:



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

Therefore, 1.45 g of Ag is deposited by = $96487 \times 1.45 / 108$ C

= 1295.43 C

Given,

Current = 1.5 A

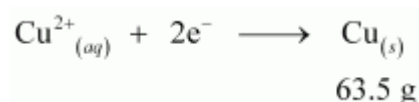
\Rightarrow Time = $1295.43 / 1.5$ s

= 863.6 s

= 864 s

= 14.40 min

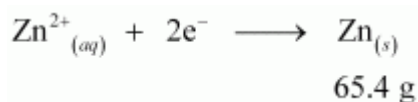
Again,



i.e., 2×96487 C of charge deposit = 63.5 g of Cu

Therefore, 1295.43 C of charge will deposit = $(63.5 \times 1295.43) / (2 \times 96487)$ g

= 0.426 g of Cu



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

Therefore, 1295.43 C of charge will deposit

$$= (65.4 \times 1295.43) / (2 \times 96487) \text{ g}$$

= 0.439 g of Zn

Question 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 $\text{I}^{-}(\text{aq})$

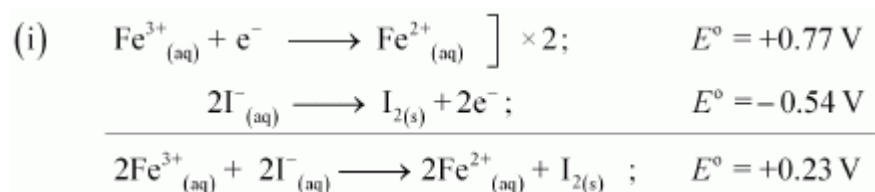
(ii) $\text{Ag}^{+}(\text{aq})$ and $\text{Cu}(\text{s})$

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

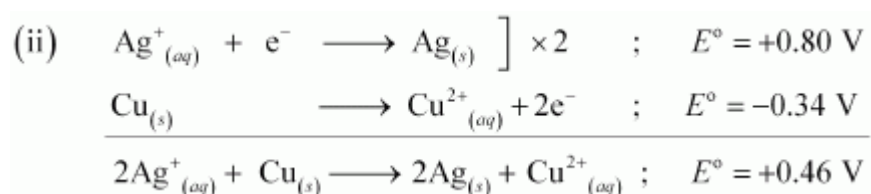
(iv) $\text{Ag}(\text{s})$ and $\text{Fe}^{3+}(\text{aq})$

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

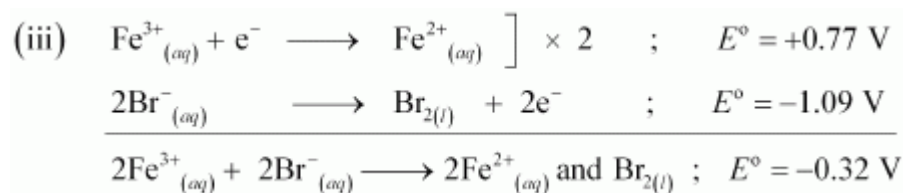
Solution



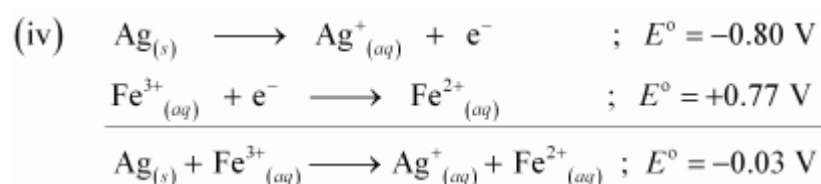
Since E° for the overall reaction is positive, the reaction between $\text{Fe}^{3+}(\text{aq})$ and $\text{I}^{-}(\text{aq})$ is feasible.



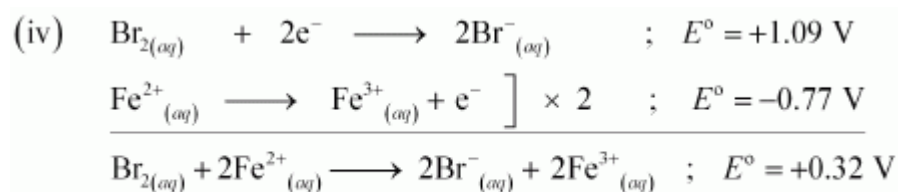
Since E° for the overall reaction is positive, the reaction between $\text{Ag}^+_{(aq)}$ and $\text{Cu}_{(s)}$ is feasible.



Since E° for the overall reaction is negative, the reaction between $\text{Fe}^{3+}_{(aq)}$ and $\text{Br}^-_{(aq)}$ is not feasible.



Since E° for the overall reaction is negative, the reaction between $\text{Ag}_{(s)}$ and $\text{Fe}^{3+}_{(aq)}$ is not feasible.



Since E° for the overall reaction is positive, the reaction between $\text{Br}_{2(aq)}$ and $\text{Fe}^{2+}_{(aq)}$ is feasible.

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.

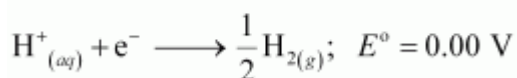
(iv) An aqueous solution of CuCl_2 with platinum electrodes.

Solution

(i) At cathode:

:

The following reduction reactions compete to take place at the cathode.



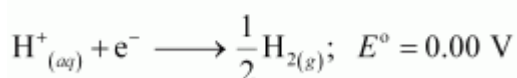
The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

At anode:

The Ag anode is attacked by NO_3^- ions. Therefore, the silver electrode at the anode dissolves in the solution to form Ag^+ .

(ii) At cathode:

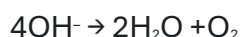
The following reduction reactions compete to take place at the cathode.



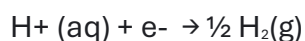
The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

At anode:

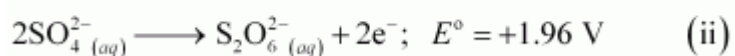
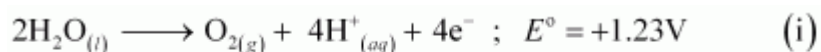
Since Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH^- or NO_3^- ions can be oxidized at the anode. But OH^- ions having a lower discharge potential and get preference and decompose to liberate O_2 .



(iii) At the cathode, the following reduction reaction occurs to produce H_2 gas.



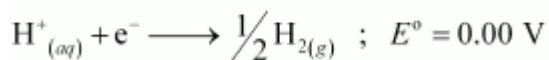
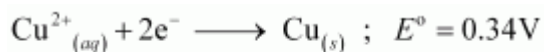
At the anode, the following processes are possible.



For dilute sulphuric acid, reaction (i) is preferred to produce O_2 gas. But for concentrated sulphuric acid, reaction (ii) occurs.

(iv) At cathode:

The following reduction reactions compete to take place at the cathode.

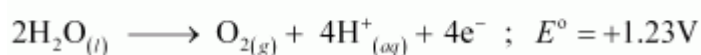
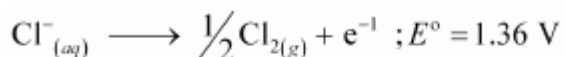


The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of copper will take place at the cathode.

At

anode:

The following oxidation reactions are possible at the anode.



At the anode, the reaction with a lower value of E° is preferred. But due to the over-potential of oxygen, Cl^- gets oxidized at the anode to produce Cl_2 gas.