= −196833.48 CV mol^{-1}

= −196833.48 J mol^{-1}

= −196.83 kJ mol^{-1}

Again,

$\Delta_r G^\ominus$ = −RT ln K

$$\Rightarrow \Delta_r G^\ominus = -2.303\ \text{R}T \ln K$$

$$\Rightarrow \log K = -\frac{\Delta_r G}{2.303\ \text{R}T}$$

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

= 34.496

∴ K = antilog (34.496)

= 3.13 × 10^{34}

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

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

The galvanic cell of the given reaction is depicted as:

$$\text{Fe}^{2+}{}_{(aq)}\Big|\text{Fe}^{3+}{}_{(aq)}\Big\|\text{Ag}^{+}{}_{(aq)}\Big|\text{Ag}_{(s)}$$

Now, the standard cell potential is

$$\begin{aligned} E^\ominus_{\text{cell}} &= E^\ominus_{\text{R}} - E^\ominus_{\text{L}} \\ &= 0.80 - 0.77 \\ &= 0.03\ \text{V} \end{aligned}$$

Here, n = 1.

Then, $\Delta_r G^\ominus = -n\text{F}E^\ominus_{\text{cell}}$

= −1 × 96487 C mol^{-1} × 0.03 V

= −2894.61 J mol^{-1}

= −2.89 kJ mol^{-1}

Again, $\Delta_r G^\ominus = -2.303\ \text{R}T \ln K$

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

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

= 0.5073

∴ K = antilog (0.5073)

= 3.2 (approximately)

Question 3.5:

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

(i) Mg(s) | Mg^{2+}(0.001M) || Cu^{2+}(0.0001 M) | Cu(s)

(ii) Fe(s) | Fe^{2+}(0.001M) || H^+(1M)|H_2(g)(1bar) | Pt(s)

(iii) Sn(s) | Sn^{2+}(0.050 M) || H^+(0.020 M) | H_2(g) (1 bar) | Pt(s)

(iv) Pt(s) | Br_2(*l*) | Br^-(0.010 M) || H^+(0.030 M) | H_2(g) (1 bar) | Pt(s).

Answer

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

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

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

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

= 2.7 − 0.02955

= 2.67 V (approximately)

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

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0591}{n} \log \frac{\left[\text{Fe}^{2+}\right]}{\left[\text{H}^{+}\right]^2}$$

$$= \left\{0 - (-0.44)\right\} - \frac{0.0591}{2} \log \frac{0.001}{1^2}$$

$$= 0.44 - 0.02955(-3)$$

= 0.52865 V

= 0.53 V (approximately)

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

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0591}{n}\log\frac{\left[\text{Sn}^{2+}\right]}{\left[\text{H}^{+}\right]^{2}}$$

$$= \left\{0-\left(-0.14\right)\right\} - \frac{0.0591}{2}\log\frac{0.050}{\left(0.020\right)^{2}}$$

= 0.14 − 0.0295 × log125

= 0.14 − 0.062

= 0.078 V

= 0.08 V (approximately)

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

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{0.0591}{n}\log\frac{1}{\left[\text{Br}^{-}\right]^{2}\left[\text{H}^{+}\right]^{2}}$$

$$= \left(0-1.09\right) - \frac{0.0591}{2}\log\frac{1}{\left(0.010\right)^{2}\left(0.030\right)^{2}}$$

$$= -1.09 - 0.02955\times\log\frac{1}{0.00000009}$$

$$= -1.09 - 0.02955\times\log\frac{1}{9\times10^{-8}}$$

$$= -1.09 - 0.02955\times\log\left(1.11\times10^{7}\right)$$

$$= -1.09 - 0.02955\left(0.0453+7\right)$$

$$= -1.09 - 0.208$$

$$= -1.298\ \text{V}$$

Question 3.6:

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

$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^{-}(aq)$

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

Answer

$$\begin{array}{l} Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^- \ ; \ E^\ominus = 0.76V \\ Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \longrightarrow 2Ag_{(s)} + 2OH^-_{(aq)} \ ; \ E^\ominus = 0.344 \text{ V} \\ \hline Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)} ; \ E^\ominus = 1.104 \text{ V} \end{array}$$

$\therefore E^\ominus$ = 1.104 V

We know that,

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

= −2 × 96487 × 1.04

= −213043.296 J

= −213.04 kJ

Question 3.7:

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

Answer

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 symbolκ. If ρ is resistivity, then we can write:

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

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.

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.

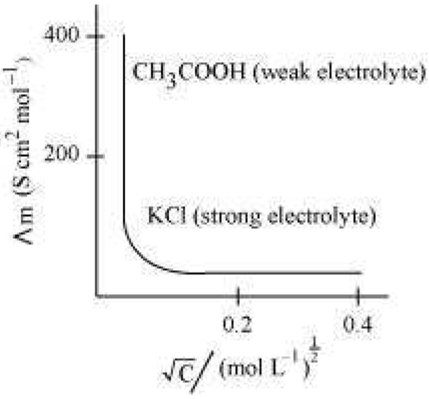
$$\Lambda_m = \kappa \frac{A}{l}$$

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

$$\therefore \Lambda_m = \kappa V$$

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 3.8:

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

Answer

Given,

κ = 0.0248 S cm^{-1}

c = 0.20 M

$\therefore$ Molar conductivity, $\Lambda_m = \frac{\kappa \times 1000}{c}$

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

= 124 Scm^2mol^{-1}

Question 3.9:

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

Answer

Given,

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

Resistance, $R = 1500\ \Omega$

∴ Cell constant = $\kappa \times R$

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

$= 0.219\ cm^{-1}$

Question 3.10:

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

Concentration/M 0.001 0.010 0.020 0.050 0.100

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

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

Answer

Given,

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

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

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

$$= \frac{1.237 \times 10^{-4}\ S\ cm^{-1}}{0.001\ mol\ L^{-1}} \times \frac{1000\ cm^3}{L}$$

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

Given,

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

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

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

$$= \frac{11.85\times10^{-4}\ \text{S cm}^{-1}}{0.010\ \text{mol L}^{-1}} \times \frac{1000\ \text{cm}^3}{\text{L}}$$

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

Given,

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

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

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

$$= \frac{23.15\times10^{-4}\ \text{S cm}^{-1}}{0.020\ \text{mol L}^{-1}} \times \frac{1000\ \text{cm}^3}{\text{L}}$$

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

Given,

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

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

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

$$= \frac{55.53\times10^{-4}\ \text{S cm}^{-1}}{0.050\ \text{mol L}^{-1}} \times \frac{1000\ \text{cm}^3}{\text{L}}$$

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

Given,

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

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

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

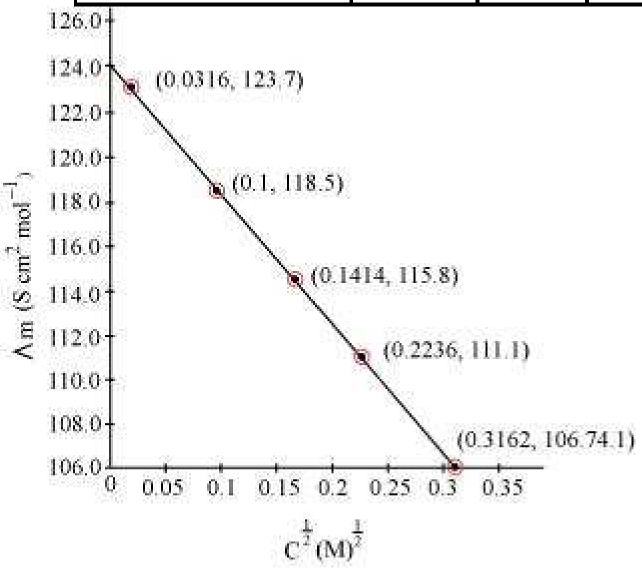
$$= \frac{106.74\times10^{-4}\ \text{S cm}^{-1}}{0.100\ \text{mol L}^{-1}} \times \frac{1000\ \text{cm}^3}{\text{L}}$$

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

Now, we have the following data:

$C^{1/2}/M^{1/2}$	0.0316	0.1	0.1414	0.2236	0.3162

$\Lambda_m \left(\text{S cm}^2 \text{ mol}^{-1}\right)$	123.7	118.5	115.8	111.1	106.74



Since the line interrupts Λ_m at 124.0 S cm^2 mol^{-1}, Λ_m^0 = 124.0 S cm^2 mol^{-1}.

Question 3.11:

Conductivity of 0.00241 M acetic acid is 7.896 × 10^{-5} S cm^{-1}. Calculate its molar conductivity and if Λ_m^0 for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

Answer

Given, κ = 7.896 × 10^{-5} S m^{-1}

c = 0.00241 mol L^{-1}

Then, molar conductivity, $\Lambda_m = \frac{\kappa}{c}$

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

= 32.76S cm^2 mol^{-1}

Again, Λ_m^0 = 390.5 S cm^2 mol^{-1}

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

= 0.084

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

$= \frac{(0.00241 \text{ mol L}^{-1})(0.084)^2}{(1-0.084)}$

= 1.86 × 10^{-5} mol L^{-1}

Question 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+}.

Answer

(i) $Al^{3+} + 3e^- \longrightarrow Al$

∴ Required charge = 3 F

= 3 × 96487 C

= 289461 C

(ii) $Cu^{2+} + 2e^- \longrightarrow Cu$

∴ Required charge = 2 F

= 2 × 96487 C

= 192974 C

(iii) $MnO_4^- \longrightarrow Mn^{2+}$

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

∴ Required charge = 5 F

= 5 × 96487 C

= 482435 C

Question 3.13:

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.

Answer

(i) According to the question,

$$\underset{}{Ca^{2+}} + 2e^{-1} \longrightarrow \underset{40\text{ g}}{Ca}$$

Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium $= \frac{2\times20}{40}$ F

= 1 F

(ii) According to the question,

$$Al^{3+} + 3e^{-} \longrightarrow \underset{27\text{ g}}{Al}$$

Electricity required to produce 27 g of Al = 3 F

Therefore, electricity required to produce 40 g of Al $= \frac{3\times40}{27}$ F

= 4.44 F

Question 3.14:

How much electricity is required in coulomb for the oxidation of

(i) 1 mol of H_2O to O_2.

(ii) 1 mol of FeO to Fe_2O_3.

Answer

(i) According to the question,

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

Now, we can write:

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

Electricity required for the oxidation of 1 mol of H_2O to O_2 = 2 F

= 2 × 96487 C

= 192974 C

(ii) According to the question,

$Fe^{2+} \longrightarrow Fe^{3+} + e^{-1}$

Electricity required for the oxidation of 1 mol of FeO to Fe_2O_3 = 1 F

= 96487 C

Question 3.15:

A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Answer

Given,

Current = 5A

Time = 20 × 60 = 1200 s

∴ Charge = current × time

= 5 × 1200

= 6000 C

According to the reaction,

$$\underset{}{Ni^{2+}_{(aq)}} + 2e^- \longrightarrow \underset{58.7\ g}{Ni_{(s)}}$$

Nickel deposited by 2 × 96487 C = 58.71 g

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

= 1.825 g

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

Question 3.16:

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?

Answer

According to the reaction:

$$Ag^{+}_{(aq)} + e^{-} \longrightarrow \underset{108\ g}{Ag_{(s)}}$$

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

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

= 1295.43 C

Given,

Current = 1.5 A

∴ Time $= \frac{1295.43}{1.5} s$

= 863.6 s

= 864 s

= 14.40 min

Again,

$$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow \underset{63.5\ g}{Cu_{(s)}}$$

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

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

= 0.426 g of Cu

$$Zn^{2+}_{(aq)} + 2e^{-} \longrightarrow \underset{65.4\ g}{Zn_{(s)}}$$

i.e., 2 × 96487 C of charge deposit = 65.4 g of Zn

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

= 0.439 g of Zn

Question 3.17:

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

(i) Fe^{3+}(aq) and I^{-}(aq)

(ii) Ag^+ (aq) and Cu(s)

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

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

(v) Br_2 (aq) and Fe^{2+} (aq).

Answer

(i)

$$\begin{array}{ll}
\left.Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}\right] \times 2; & E^\circ = +0.77\text{ V} \\
2I^-_{(aq)} \longrightarrow I_{2(s)} + 2e^-; & E^\circ = -0.54\text{ V} \\
\hline
2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(s)} \; ; & E^\circ = +0.23\text{ V}
\end{array}$$

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

(ii)

$$\begin{array}{ll}
\left.Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}\right] \times 2 \; ; & E^\circ = +0.80\text{ V} \\
Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^- \; ; & E^\circ = -0.34\text{ V} \\
\hline
2Ag^+_{(aq)} + Cu_{(s)} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)} \; ; & E^\circ = +0.46\text{ V}
\end{array}$$

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

(iii)

$$\begin{array}{ll}
\left.Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}\right] \times 2 \; ; & E^\circ = +0.77\text{ V} \\
2Br^-_{(aq)} \longrightarrow Br_{2(l)} + 2e^- \; ; & E^\circ = -1.09\text{ V} \\
\hline
2Fe^{3+}_{(aq)} + 2Br^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} \text{ and } Br_{2(l)} \; ; & E^\circ = -0.32\text{ V}
\end{array}$$

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

(iv)

$$\begin{array}{ll}
Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e^- \; ; & E^\circ = -0.80\text{ V} \\
Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)} \; ; & E^\circ = +0.77\text{ V} \\
\hline
Ag_{(s)} + Fe^{3+}_{(aq)} \longrightarrow Ag^+_{(aq)} + Fe^{2+}_{(aq)} \; ; & E^\circ = -0.03\text{ V}
\end{array}$$

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

(iv)

$$
\begin{array}{lr}
Br_{2(aq)} + 2e^- \longrightarrow 2Br^-_{(aq)} & ;\ E^\circ = +1.09\ V \\
\left. Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^- \right] \times 2 & ;\ E^\circ = -0.77\ V \\
\hline
Br_{2(aq)} + 2Fe^{2+}_{(aq)} \longrightarrow 2Br^-_{(aq)} + 2Fe^{3+}_{(aq)} & ;\ E^\circ = +0.32\ V
\end{array}
$$

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

Question 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.

Answer

(i) At cathode:

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

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}\ ;\ E^\circ = 0.80V$$

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)};\ E^\circ = 0.00\ V$$

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.

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}\ ;\ E^\circ = 0.80V$$

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)};\ E^\circ = 0.00\ V$$

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.

$$OH^- \longrightarrow OH + e^-$$
$$4OH^- \longrightarrow 2H_2O + O_2$$

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

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}$$

At the anode, the following processes are possible.

$$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \;;\; E^{\circ} = +1.23V \qquad (i)$$
$$2SO_4^{2-}{}_{(aq)} \longrightarrow S_2O_6^{2-}{}_{(aq)} + 2e^-;\; E^{\circ} = +1.96\ V \qquad (ii)$$

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.

$$Cu^{2+}{}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \;;\; E^{\circ} = 0.34V$$
$$H^+_{(aq)} + e^- \longrightarrow {}^1\!/_2 H_{2(g)} \;;\; E^{\circ} = 0.00\ V$$

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.

$$Cl^-_{(aq)} \longrightarrow {}^1\!/_2 Cl_{2(g)} + e^{-1} \;; E^{\circ} = 1.36\ V$$
$$2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \;;\; E^{\circ} = +1.23V$$

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.

Text solution

Question 3.1:

How would you determine the standard electrode potential of the systemMg^{2+} | Mg?

Answer

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

A cell, consisting of Mg | $MgSO_4$ (*aq* 1 M) as the anode and the standard hydrogen electrode as the cathode, is set up.

$$\mathrm{Mg}\left|\mathrm{Mg}^{2+}(\mathrm{aq},1\mathrm{M})\right|\left|\mathrm{H}^{+}(\mathrm{aq},1\mathrm{M})\right|\mathrm{H}_2(\mathrm{g},1\ \mathrm{bar}),\mathrm{Pt}_{(s)}$$

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

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

Here, $E_R^{\ominus}$ for the standard hydrogen electrode is zero.

$\therefore E^{\ominus} = 0 - E_L^{\ominus}$

$= -E_L^{\ominus}$

Question 3.2:

Can you store copper sulphate solutions in a zinc pot?

Answer

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.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

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

Question 3.3:

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

Answer

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

$Fe^{2+} \longrightarrow Fe^{3+} + e^{-1}$; $E^{\ominus} = -0.77$ V

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.

Question 3.4:

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

Answer

For hydrogen electrode, $H^+ + e^- \longrightarrow \frac{1}{2} H_2$, it is given that pH = 10

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

Now, using Nernst equation:

$$H_{\left(H^+/\frac{1}{2}H_2\right)} = E^{\ominus}_{\left(H^+/\frac{1}{2}H_2\right)} - \frac{RT}{nF} \ln \frac{1}{\left[H^+\right]}$$

$$= E^{\ominus}_{\left(H^+/\frac{1}{2}H_2\right)} - \frac{0.0591}{1}\log\frac{1}{\left[H^+\right]}$$

$$= 0 - \frac{0.0591}{1}\log\frac{1}{\left[10^{-10}\right]}$$

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

$= -0.591$ V

Question 3.5:

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

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

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

Answer

Applying Nernst equation we have:

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

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

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

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

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

$= 1.05 - 0.02955 (4 + 0.6021)$

$= 0.914$ V

Question 3.6:

The cell in which the following reactions occurs:

$$2Fe^{3+}{}_{(aq)} + 2I^{-}{}_{(aq)} \rightarrow 2Fe^{2+}{}_{(aq)} + I_{2(s)}$$

has E^0_{cell} = 0.236 V at 298 K.

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

Answer

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

We know that:

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

$= -2 \times 96487 \times 0.236$

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

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

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

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

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

$= 7.981$

$\therefore K_c$ = Antilog (7.981)

$= 9.57 \times 10^7$

Question 3.7:

Why does the conductivity of a solution decrease with dilution?

Answer

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 3.8:

Suggest a way to determine the Λ^0_m value of water.

Answer

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

$$\Lambda^0_{m(H_2O)} = \lambda^0_{H^+} + \lambda^0_{OH^-}$$
$$= \left(\lambda^0_{H^+} + \lambda^0_{Cl^-}\right) + \left(\lambda^0_{Na^+} + \lambda^0_{OH^-}\right) - \left(\lambda^0_{Na^+} + \lambda^0_{Cl^-}\right)$$
$$\Lambda^0_{m(HCl)} + \Lambda^0_{m(NaOH)} - \Lambda^0_{m(NaCl)}$$

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

Question 3.9:

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 λ $^{\circ}$(H$^+$)
= 349.6 S cm^2 mol^{-1} and λ $^{\circ}$(HCOO−) = 54.6 S cm^2 mol

Answer

C = 0.025 mol L^{-1}

$$\Lambda_m = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$$
$$\lambda^0\left(H^+\right) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$$
$$\lambda^0\left(HCOO^-\right) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$$
$$\Lambda^0_m\left(HCOOH\right) = \lambda^0\left(H^+\right) + \lambda^0\left(HCOO^-\right)$$
$$= 349.6 + 54.6$$
$$= 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$

Now, degree of dissociation:

$$\alpha = \frac{\Lambda_m\left(HCOOH\right)}{\Lambda^0_m\left(HCOOH\right)}$$
$$= \frac{46.1}{404.2}$$
$$= 0.114\left(\text{approximately}\right)$$

Thus, dissociation constant:

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

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

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

Question 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?

Answer

I = 0.5 A

t = 2 hours = 2 × 60 × 60 s = 7200 s

Thus, $Q = It$

= 0.5 A × 7200 s

= 3600 C

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

Then,

$$3600\ \text{C} = \frac{6.023 \times 10^{23} \times 3600}{96487}\text{number of electrons}$$

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

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

Question 3.11:

Suggest a list of metals that are extracted electrolytically.

Answer

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

Question 3.12:

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

$Cr_2O_7^{2-}$? Consider the reaction:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 8H_2O$

Answer

The given reaction is as follows:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Therefore, to reduce 1 mole of $Cr_2O_7^{2-}$, the required quantity of electricity will be:

=6 F

= 6 × 96487 C

= 578922 C

Question 3.14:

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

Answer

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

Question 3.15:

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

Answer

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,

$Fe_{(s)} \longrightarrow Fe^{2+}{}_{(aq)} + 2e^-$

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,

$O_{2(g)} + 4H^+{}_{(aq)} + 4e^- \longrightarrow 2H_2O_{(l)}$

The overall reaction is:

$$2\mathrm{Fe}_{(s)} + \mathrm{O}_{2(g)} + 4\mathrm{H}^{+}{}_{(aq)} \longrightarrow 2\mathrm{Fe}^{2+}{}_{(aq)} + 2\mathrm{H}_2\mathrm{O}_{(l)}$$

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 $\left(\mathrm{Fe_2O_3}, x\,\mathrm{H_2O}\right)$ i.e., rust.

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

Question 4.1:

For the reaction R → P, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

Answer

Average rate of reaction $= -\frac{\Delta[\mathrm{R}]}{\Delta t}$

$$= -\frac{[\mathrm{R}]_2 - [\mathrm{R}]_1}{t_2 - t_1}$$

$$= -\frac{0.02 - 0.03}{25}\ \mathrm{M\ min^{-1}}$$

$$= -\frac{-0.01}{25}\mathrm{M\ min^{-1}}$$

$$= 4 \times 10^{-4}\ \mathrm{M\ min^{-1}}$$

$$= \frac{4 \times 10^{-4}}{60}\ \mathrm{M\ s^{-1}}$$

$= 6.67 \times 10^{-6}\ \mathrm{M\ s^{-1}}$

Question 4.2:

In a reaction, 2A → Products, the concentration of A decreases from 0.5 mol $\mathrm{L^{-1}}$ to 0.4 mol $\mathrm{L^{-1}}$ in 10 minutes. Calculate the rate during this interval?

Answer

Average rate $= -\frac{1}{2}\frac{\Delta[\mathrm{A}]}{\Delta t}$

$$= -\frac{1}{2}\frac{[A]_2 - [A]_1}{t_2 - t_1}$$

$$= -\frac{1}{2}\frac{0.4 - 0.5}{10}$$

$$= -\frac{1}{2}\frac{-0.1}{10}$$

= 0.005 mol L^{-1} min^{-1}

= 5 × 10^{-3} M min^{-1}

Question 4.3:

For a reaction, A + B → Product; the rate law is given by, $r = k[A]^{1/2}[B]^2$. What is the order of the reaction?

Answer

The order of the reaction $= \frac{1}{2} + 2$

$= 2\frac{1}{2}$

= 2.5

Question 4.4:

The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y?

Answer

The reaction X → Y follows second order kinetics.

Therefore, the rate equation for this reaction will be:

Rate = $k[X]^2$ (1)

Let [X] = a mol L^{-1}, then equation (1) can be written as:

$\text{Rate}_1 = k\,.(a)^2$

$= ka^2$

If the concentration of X is increased to three times, then [X] = $3a$ mol L^{-1}

Now, the rate equation will be:

Rate = $k\ (3a)^2$

= $9(ka^2)$

Hence, the rate of formation will increase by 9 times.

Question 4.5:

A first order reaction has a rate constant 1.15 $10^{-3}\ s^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?

Answer

From the question, we can write down the following information:

Initial amount = 5 g

Final concentration = 3 g

Rate constant = 1.15 $10^{-3}\ s^{-1}$

We know that for a 1st order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$= \frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3}$$

$$= \frac{2.303}{1.15 \times 10^{-3}} \times 0.2219$$

= 444.38 s

= 444 s (approx)

Question 4.6:

Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Answer

We know that for a 1st order reaction,

$$t_{1/2} = \frac{0.693}{k}$$

It is given that $t_{1/2}$ = 60 min

$$\therefore k = \frac{0.693}{t_{1/2}}$$

$$= \frac{0.693}{60}$$

$$= 0.01155 \text{ min}^{-1}$$
$$= 1.155 \text{ min}^{-1}$$

$$\text{Or } k = 1.925 \times 10^{-4} \text{ s}^{-1}$$

Question 4.7:

What will be the effect of temperature on rate constant?

Answer

The rate constant of a reaction is nearly doubled with a 10° rise in temperature. However, the exact dependence of the rate of a chemical reaction on temperature is given by Arrhenius equation,

$$k = \text{A}e^{-Ea/RT}$$

Where,

A is the Arrhenius factor or the frequency factor

T is the temperature

R is the gas constant

E_a is the activation energy

Question 4.8:

The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E_a.

Answer

It is given that T_1 = 298 K

$\therefore T_2$ = (298 + 10) K

= 308 K

We also know that the rate of the reaction doubles when temperature is increased by 10°.

Therefore, let us take the value of $k_1 = k$ and that of $k_2 = 2k$

Also, $R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$

Now, substituting these values in the equation:

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

We get:

$$\log\frac{2k}{k} = \frac{E_a}{2.303 \times 8.314}\left[\frac{10}{298 \times 308}\right]$$

$$\Rightarrow \log 2 = \frac{E_a}{2.303 \times 8.314}\left[\frac{10}{298 \times 308}\right]$$

$$\Rightarrow E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10}$$

$= 52897.78\ \text{J mol}^{-1}$

$= 52.9\ \text{kJ mol}^{-1}$

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Question 4.9:

The activation energy for the reaction

$2HI_{(g)} \rightarrow H_2 + I_{2(g)}$

is 209.5 kJ mol^{-1} at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Answer

In the given case:

$E_a = 209.5\ \text{kJ mol}^{-1} = 209500\ \text{J mol}^{-1}$

$T = 581$ K

$R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$

Now, the fraction of molecules of reactants having energy equal to or greater than activation energy is given as:

$$x = e^{-Ea/RT}$$

$$\Rightarrow \ln x = -E_a / RT$$

$$\Rightarrow \log x = -\frac{E_a}{2.303\ RT}$$

$$\Rightarrow \log x = \frac{209500\ \text{J mol}^{-1}}{2.303 \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 581} = 18.8323$$

$$\begin{aligned} \text{Now, } x &= \text{Anti log}\,(18.8323) \\ &= \text{Anti log}\,\overline{19}.1677 \\ &= 1.471 \times 10^{-19} \end{aligned}$$

Question 4.1:

From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

(i) 3 NO(g) → N_2O (g) Rate = $k[NO]^2$

(ii) H_2O_2 (aq) + 3 I^- (aq) + 2 H^+ → 2 H_2O (l) + I_3^- Rate = $k[H_2O_2][I^-]$

(iii) $CH_3CHO(g)$ → $CH_4(g)$ + CO(g) Rate = $k\ [CH_3CHO]^{3/2}$

(iv) $C_2H_5Cl(g)$ → $C_2H_4(g)$ + HCl(g) Rate = $k\ [C_2H_5Cl]$