Q 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.

Answer:

According to their reactivity, the given metals replace the others from their salt solutions in the said order: Mg, Al, Zn, Fe, and Cu.

Mg: Al: Zn: Fe: Cu

Q 3.2:

Given the standard electrode potentials.
$K^+/K = -2.93V$

$Ag^+/Ag = 0.80V$

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

$Mg^{2+}/Mg = -2.37\ V$

$Cr^{3+}/Cr = -\ 0.74V$
Arrange these metals in their increasing order of reducing power.

Ans:

The reducing power increases with the lowering of the reduction potential. In order of given standard electrode potential (increasing order): $K^+/K < Mg^{2+}/Mg < Cr^{3+}/Cr < Hg^{2+}/Hg < Ag^+/Ag$

Thus, in the order of reducing power, we can arrange the given metals as Ag< Hg < Cr < Mg < K

Q 3.3 :

Depict the galvanic cell in which the reaction
$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. Further show:
(i) Which of the electrode is negatively charged?
(ii) The carriers of the current in the cell.
(iii) Individual reaction at each electrode.

Ans :

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

$$Zn_{(s)}|Zn^{2+}_{(aq)}||Ag^{+}_{(aq)}|Ag_{(s)}$$

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

(ii) The current carriers in the cell are ions. Current flows to zinc from silver in the external circuit.

(iii) Reaction at the anode is given by

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

Reaction at the anode is given by

$$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$$

Q 3.4:

Calculate the standard cell potentials of the galvanic cell in which the following reactions take place.
(i) $2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd$
(ii) $Fe^{2+}(aq) + Ag^{+}(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$
Calculate the ∆rGJ and equilibrium constant of the reactions.

Ans :

(i)

$E^{\Theta}_{Cr^{3+}/Cr}$
= 0.74 V

$E^{\Theta}_{Cd^{2+}/Cd}$
= -0.40 V

The galvanic cell of the given reaction is depicted as

$$Cr_{(s)}|Cr^{3+}_{(aq)}||Cd^{2+}_{aq}|Cd_{(s)}$$

Now, the standard cell potential is

$$E^{\Theta}_{cell} = E^{\Theta}_{g} - E^{\Theta}_{L}$$

= – 0.40 – (-0.74)

= + 0.34 V

In the given equation, n = 6

F = 96487 C mol^{-1}

E^{Θ}_{cell} = + 0.34 V

Then,

$\Delta_r G^{\Theta}$ = −6 × 96487 C mol^{-1} × 0.34 V

= −196833.48 CV mol−1

= −196833.48 J mol−1

= −196.83 kJ mol−1

Again,

$$\begin{aligned}
&\Delta_r G^{\Theta} = -RTlnK \\
&\Delta_r G^{\Theta} = -2.303RTlnK \\
&logk = \frac{\Delta_r G}{2.303RT} \\
&= \frac{-196.83 \times 10^3}{2.303 \times 8.314 \times 298}
\end{aligned}$$

= 34.496

K = antilog (34.496) = 3.13 × 10^{34}

The galvanic cell of the given reaction is depicted as

$$Fe^{2+}_{(aq)}|Fe^{3+}_{(aq)}||Ag^{+}_{(aq)}|Ag_{(s)}$$

Now, the standard cell potential is

$$E^{\Theta}_{cell} = E^{\Theta}_{g} - E^{\Theta}_{L}$$

Here, n = 1

Then,

$$\Delta_t G^0 = -nFE^0_{cell}$$

= −1 × 96487 C mol^{-1} × 0.03 V

= −2894.61 J mol^{-1}

= −2.89 kJ mol^{-1}

Again,

$$\Delta_t G^0 = -2.303RT\, lnK$$
$$lnK = \frac{\Delta_t G}{2.303RT}$$
$$= \frac{-2894.61}{2.303\times 8.314\times 298}$$

= 0.5073

K = antilog (0.5073)

= 3.2 (approximately)

Q 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)|H2(g)(1bar)| Pt(s)
(iii) Sn(s)|Sn^{2+}(0.050 M)||H^+(0.020 M)|H2(g) (1 bar)|Pt(s)
(iv) Pt(s)|Br–(0.010 M)|Br_2(l)||H^+(0.030 M)| H_2(g) (1 bar)|Pt(s)

Answer

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

$$E_{cell} = E^0_{cell} - \frac{0.591}{n} log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$
$$= 0.34 - (-2.36) - \frac{0.0591}{2} log \frac{0.001}{0.0001}$$
$$2.7 - \frac{0.0591}{2} log 10$$

= 2.7 − 0.02955

= 2.67 V (approximately)

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

$$E_{cell} = E^0_{cell} - \frac{0.591}{n} log \frac{[Fe^{2+}]}{[H^+]^2}$$
$$= 0 - (-0.14) -$$
$$\frac{0.0591}{n} log \frac{0.050}{(0.020)^2}$$

= 0.52865 V

= 0.53 V (approximately)

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

$$E_{cell} = E^0_{cell} - \frac{0.591}{n} log \frac{[Fe^{2+}]}{[H^+]^2}$$

$$= 0 - (- 0.14) -$$

$$\frac{0.0591}{n} log \frac{0.050}{(0.020)^2}$$

= 0.14 − 0.062

= 0.078 V

= 0.08 V (approximately)

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

$$E_{cell} = E^0_{cell} - \frac{0.591}{n} log \frac{1}{[Br^-]^2[H^+]^2}$$

$$= 0 - 1.09 -$$

$$\frac{0.591}{2} log \frac{1}{(0.010)^2(0.030)^2}$$

$$= -1.09 - 0.02955 \times$$

$$log \frac{1}{0.00000009}$$

$$= -1.09 - 0.02955 \times$$

$$log \frac{1}{9 \times 10^{-8}}$$

$$= -1.09 - 0.02955 \times$$

$$log(1.11 \times 10^7)$$

$$= -1.09 - 0.02955 \times (0.0453 + 7)$$

$$= -1.09 - 0.208$$

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

Q 3.6:

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

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

Determine Δ_r GJ and EJ for the reaction.

Ans:

E^0 = 1.104 V

We know that,

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

= −2 × 96487 × 1.04

= −213043.296 J

= −213.04 kJ

Q 3.7:

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

Answer

The 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. Specific conductance is the inverse of resistivity, and it is represented by the symbol κ. If ρ is resistivity, then we can write $k = \frac{1}{\rho}$. At any given concentration, the conductivity of a solution is defined as the unit volume of solution kept between two platinum electrodes with the unit area of the cross-section at a distance of unit length.

$$G = k\frac{a}{l} = k \times 1 = k$$ [Since a = 1 , l = 1]

When concentration decreases, there will be a decrease in Conductivity. It is applicable for both 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 –

The 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.

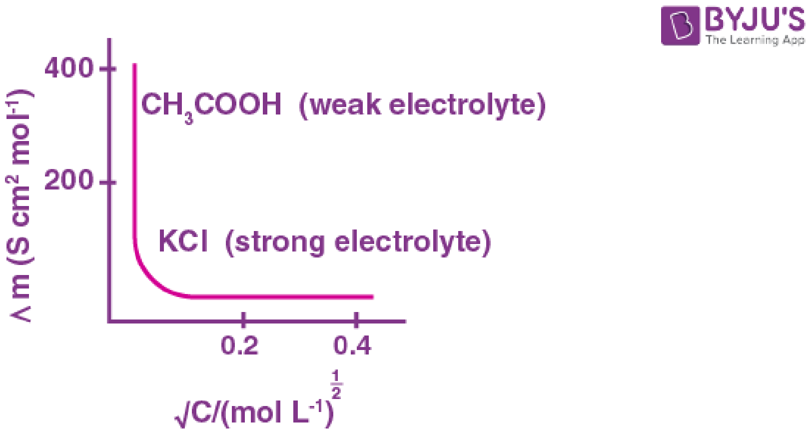
$$\Lambda_m = k\frac{A}{l}$$

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

$$\Lambda_m = kV$$

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 :



Q 3.8:

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

Ans :

Given, $\kappa = 0.0248$ S cm^{-1} c

c = 0.20 M

Molar conductivity,

$$\Lambda_m = \frac{k \times 1000}{c}$$
$$= \frac{0.0248 \times 1000}{0.2}$$

= 124 Scm^2mol^{-1}

Q 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 the conductivity of 0.001M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}

Answer

Given,

Conductivity, k = 0.146×10^{-3} S cm−1

Resistance, R = 1500 Ω

Cell constant = k × R

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

= 0.219 cm^{-1}

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

Calculate Λm for all concentrations and draw a plot between Λm and c½. Find the value of 0 Λ m.

Ans:

Given,

κ = 1.237×10^{-2} S m−1, c = 0.001 M

Then, κ = 1.237×10^{-4} S cm^{-1}, $c^{1/2}$ = 0.0316 $M^{1/2}$

$$\Lambda_m = \frac{k}{c}$$
$$= \frac{1.237 \times 10^{-4} S\ cm^{-1}}{0.001\ mol\ \ L^{-1}} \times \frac{1000\ cm^{-1}}{L}$$
$$= 123.7\ \mathrm{S\ cm^2\ mol^{-1}}$$

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$^{1/2}$

$$\Lambda_m = \frac{k}{c}$$
$$= \frac{11.85\times10^{-4} S\ cm^{-1}}{0.010\ mol\ \ L^{-1}} \times \frac{1000\ cm^{-1}}{L}$$
$$= 118.5 \text{ S cm}^2 \text{ mol}^{-1}$$

Given,

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

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

$$\Lambda_m = \frac{k}{c}$$
$$= \frac{23.15\times10^{-4} S\ cm^{-1}}{0.020\ mol\ \ L^{-1}} \times \frac{1000\ cm^{-1}}{L}$$
$$= 115.8 \text{ S cm}^2 \text{ mol}^{-1}$$

Given,

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

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

$$\Lambda_m = \frac{k}{c}$$
$$= \frac{106.74\times10^{-4} S\ cm^{-1}}{0.050\ mol\ \ L^{-1}} \times \frac{1000\ cm^{-1}}{L}$$
$$= 111.1\ 1 \text{ S cm}^2 \text{ mol}^{-1}$$

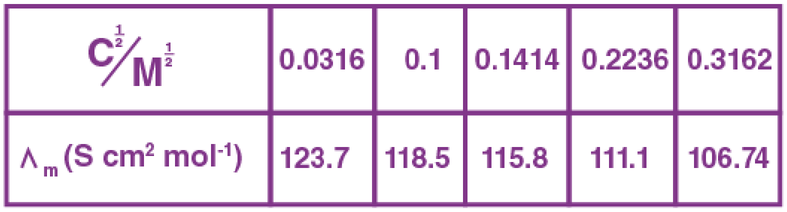
Given,

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

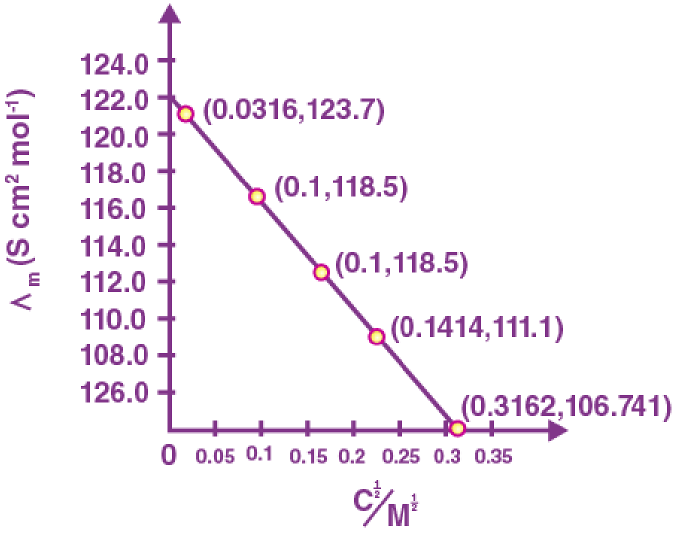
Then, $\kappa = 106.74 \times 10^{-4}$ S cm^{-1}, $c^{1/2} = 0.3162$ M$^{1/2}$

$$\Lambda_m = \frac{k}{c}$$
$$= \frac{106.74\times10^{-4} S\ cm^{-1}}{0.050\ mol\ \ L^{-1}} \times \frac{1000\ cm^{-1}}{L}$$
$$= 111.1\ 1 \text{ S cm}^2 \text{ mol}^{-1}$$

Now, we have the following data:



$C^{\frac{1}{2}}/M^{\frac{1}{2}}$	0.0316	0.1	0.1414	0.2236	0.3162
Λ_m (S cm² mol⁻¹)	123.7	118.5	115.8	111.1	106.74



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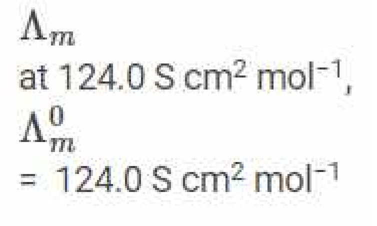

Λ_m
at 124.0 S cm^2 mol^{-1},
Λ_m^0
= 124.0 S cm^2 mol^{-1}

Q 3.11:

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

Ans:

Given, κ = 7.896 × 10^{-5} S m^{-1} c

= 0.00241 mol L^{-1}

Then, molar conductivity,

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

=

$$\frac{7.896\times10^{-5}\,Scm^{-1}}{0.00241\ mol\ L^{-1}} \times \frac{1000cm^3}{L}$$

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

Λ_m^0 =390.5 S cm^2 mol^{-1}

Again,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0}$$

=

$$= \frac{32.76\ S\ cm^2\ mol^{-1}}{390.5\ S\ cm^2\ mol^{-1}}$$

Now,

= 0.084

Dissociation constant,

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

=

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

= 1.86 × 10^{-5} mol L^{-1}

Q 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)

$$Al^{3+} + 3e^- \rightarrow Al$$

Required charge = 3 F

= 3 × 96487 C

= 289461 C

(ii)

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

Required charge = 2 F

= 2 × 96487 C

= 192974 C

(iii)

$$MnO_4^- \rightarrow Mn^{2+}$$

i.e

$$Mn^{7+} + 5e^- \rightarrow Mn^{2+}$$

Required charge = 5 F

= 5 × 96487 C

= 482435 C

Q 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?

Ans:

(i) From the given data,

$$Ca^{2+} + 2e^- \rightarrow Ca$$

Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium = (2 x 20)/ 40 F

= 1 F

(ii) From the given data,

$$Al^{3+} + 3e^- \rightarrow Al$$

Electricity required to produce 27 g of Al = 3 F

Therefore, electricity required to produce 40 g of Al = (3 x 40)/27 F

= 4.44 F

Q 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?

Ans :

(i) From the given data,

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

We can say that

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

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

= 2 × 96487 C

= 192974 C

(ii) From the given data,

��2+→��3++�−
Electricity required for the oxidation of 1 mol of FeO to Fe_2O_3 = 1 F

= 96487 C

Q 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?

Ans :

Given,

Current = 5A

Time = 20 × 60 = 1200 s

Charge = current × time

= 5 × 1200

= 6000 C

According to the reaction,

$$Ni^{2+} + 2e^- \rightarrow Ni_{(s)} + e^-$$

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.

Q 3.16:

Three electrolytic cells, A, B, and 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 was deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

Ans :

According to the reaction,

$$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$$

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

Therefore, 1.45 g of Ag is deposited by =

$$\frac{96487 \times 1.45}{107} C$$

= 1295.43 C

Given,

Current = 1.5 A

Time = 1295.43/ 1.5 s

= 863.6 s

= 864 s

= 14.40 min

Again,

$$Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)}$$

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

Therefore, 1295.43 C of charge will deposit

$$\frac{63.5 \times 1295.43}{2 \times 96487}$$

= 0.426 g of Cu

$Zn^{2+}_{(aq)} + 2e^{-} \rightarrow Zn_{(s)}$ i.e., 2 × 96487 C of charge deposit = 65.4 g of Zn

Therefore, 1295.43 C of charge will deposit

$$\frac{65.4 \times 1295.43}{2 \times 96487}$$

= 0.439 g of Zn

Q 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 $Fe^{2+}(aq)$

Ans :

(i)

$$
\begin{array}{llll}
Fe^{3+}_{(aq)} + e^- & \longrightarrow & Fe^{2+}_{(aq)}]\ \times 2 & E^\circ = 0.76\ V \\
2I^-_{(aq)} & \longrightarrow & I_{2(aq)} + e^- & E^\circ = 0.54\ V \\
Fe^{3+}_{(aq)} + 2I^-_{(aq)} & \longrightarrow & 2Fe^{2+}_{(aq)} + I_{2(s)} & E^\circ = 0.23\ V
\end{array}
$$

E^o is positive, hence reaction is feasible

(ii)

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

E^0 is positive; hence, the reaction is feasible.

(iii)

$$\begin{array}{lll}
Fe^{3+}_{(aq)} + e^{-} \longrightarrow Fe^{2+}_{(aq)}\ ]\ \times 2 & & E^{o} = +0.77\ V \\
2Br^{-}_{(aq)} \longrightarrow Br_{2(l)} + 2e^{-} & & E^{o} = -1.09\ V \\
 & & \\
2Fe^{3+}_{(aq)} + 2Br^{-}_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)}\ \text{and}\ Br_{2(l)} & & E^{o} = -0.32\ V
\end{array}$$

E^{0} is negative; hence, the reaction is not feasible.

(iv)

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

E^{0} is negative; hence, the reaction is not feasible.

(v)

$$\begin{array}{llll}
Br_{2(aq)} + 2e^- & \longrightarrow & 2Br^-_{(aq)} & E^o = +1.09V \\
Fe^{2+}_{(aq)} & \longrightarrow & Fe^{3+}_{(aq)} + e^-] \times 2 & E^o = -0.77\,V \\
\hline
Br_{2(aq)} + 2Fe^{2+}_{(aq)} & \longrightarrow & 2Br^-_{(aq)} + 2Fe^{3+}_{(aq)} & E^o = +0.32\,V
\end{array}$$

E^0 is positive; hence, the reaction is feasible.

Q 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) At the cathode,

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

$$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$$
$$; E^0 = 0.80\ V$$
$$H^+_{(aq)} + e^- \rightarrow \tfrac{1}{2} H_{2(g)}$$
$$; E^0 = 0.00\ V$$

The reaction with a higher value of E^0 takes place at the cathode. Therefore, the deposition of silver will take place at the cathode.

At the 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 the cathode,

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

$$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$$
$; E^0 = 0.80$ V
$$H^+_{(aq)} + e^- \rightarrow \frac{1}{2} H_{2(g)}$$
$;E^0 = 0.00$ V

The reaction with a higher value of E^0 takes place at the cathode. Therefore, the deposition of silver will take place at the cathode.

At the anode,

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

$$OH^- \rightarrow OH + E^-$$
$$4OH^- \rightarrow 2H_2O + O_2$$

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

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

At the anode, the following processes are possible.

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$$
$; E^0 = +1.23$ V ——(i)
$$2SO^{2-}_{4(aq)} \rightarrow S_2O^{2-}_{6(aq)} + 2e^-$$
$; E^0 = +1.96$ V ——(ii)

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

(iv) At the cathode,

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

$Cu^{2+}_{(aq)} + 2e^{-} \rightarrow Cu_{(s)}$

; $E^0 = 0.34$ V

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

;$E^0 = 0.00$ V

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

At the anode,

The following oxidation reactions are possible at the anode.

$Cl^{-}_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^{-}$

; $E^0 = 1.36$ V

$2H_{2}0_{(l)} \rightarrow O_{2(g)} + 4H^{+}_{(aq)} + e^{-}$

; $E^0 = +1.23$ V

At the anode, the reaction with a lower value of E^0 is preferred. But due to the overpotential of oxygen, Cl^- gets oxidised at the anode to produce Cl_2 gas.