CBSE Class 12 physics
Important Questions
Chapter 3
Electrochemistry

5 Marks Questions

1. Explain construction and working of standard Hydrogen electrode?

Ans. Construction :

SHE consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure Hydrogen gas is bubbled through it. The concentration of both the reduced and oxidized. Forms of Hydrogen is maintained at unity i.e) pressure of H_2 gas is 1 bar and concentration of Hydrogen ions in the solution is 1 molar.

Working – The reaction taking place in SHE is $H^+\left(aq\right)+e^-\rightarrow à H_2\left(g\right)$ At 298 K , the emf of the cell constructed by taking SHE as anode and other half cell as cathode, gives the reduction potential of the other half cell where as for a cell constructed by taking SHE as anode gives the oxidation potential of other half cell as conventionally the electrode potential of SHE is zero.
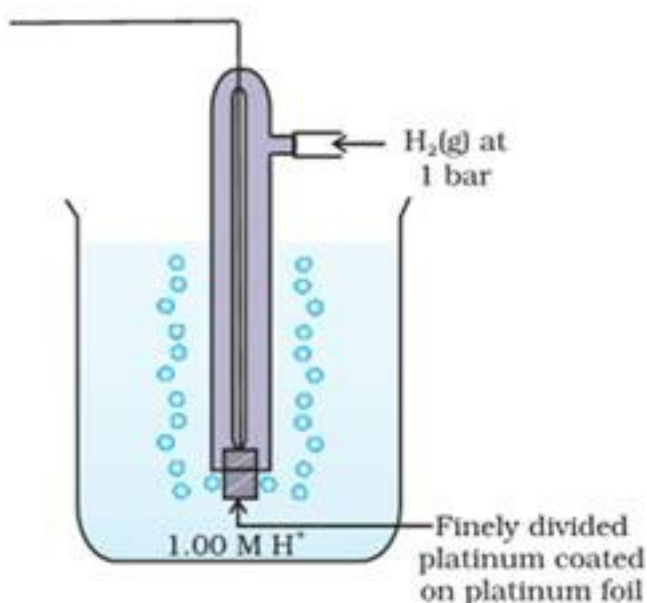
2. **The molar conductivity of 0.025 mol L-1 methanoic acid is 46.1 S** $cm^2\,mol^{-1}$.

Calculate its degree of dissociation and dissociation constant. Given $\lambda^{\circ}H^{+}$ **= 349.6 S** $cm^2\,mol^{-1}$ **and** $\lambda^{\circ}(HCOO-)=54.6\,S\,cm^2\,mol$

Ans. C = 0.025 $mol\,L^{-1}$

$$A_m = 46.1\,S\,cm^2\,mol^{-1}$$

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

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

$$A_m^{\circ}\left(HCOOH\right)=\lambda^{\circ}\left(H^+\right)+\lambda^{\circ}\left(HCOO^-\right)$$

= 349.6 + 54.6 = $404.2\,S\,cm^2\,mol^{-1}$

Now, degree of dissociation:

$$\alpha = \frac{A_m\left(HCOOH\right)}{A_m^0\left(HCOOH\right)}$$

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

= 0.114 (approximately)

Thus, dissociation constant:

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

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

$$=3.67\times10^{-4}\,mol\,L^{-1}$$

3. 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, $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$

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.
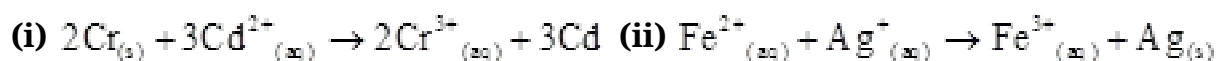
The reaction corresponding at the cathode is given by, $O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(1)}$

The overall reaction is: $2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(1)}$

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 $\left(Fe_2O_3 \cdot xH_2O\right)$ i.e., rust.

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

4. Calculate the standard cell potentials of galvanic cells 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 $\Delta_r G^\circ$, and equilibrium constant of the reactions

Ans. (i) $E^\circ_{Cr^{3+}/Cr} = 0.74\,V$

$E^\circ_{Cd^{2+}/Cd} = 0.40V$

The galvanic cell of the given reaction is depicted as: $Cr_{(s)} \mid Cr^{3+}_{(aq)} \parallel Cd^{2+}_{(aq)} \mid Cd_{(s)}$

Now, the standard cell potential is $E^\circ_{cell} = E^\circ_R - E^\circ_L$

= 0.40 – (–0.74)

= +0.34 V

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

In the given equation,

n = 6

F = 96487 C mol - 1

$E^{\ominus}_{cell}$ = +0.34 V

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

= –196833.48 CV mol^{-1}

= –196833.48 J mol^{-1}

= –196.83 kJ v

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

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

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

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

= 34.496

Therefore, K = antilog (34.496)

$= 3.13 \times 1034$

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

$E^{\circ}_{Ag^+/Ag} = 0.80\,V$

The galvanic cell of the given reaction is depicted as: $Fe^{2+}_{(aq)} \mid Fe^{3+}_{(aq)} \parallel Ag^+_{(aq)} \mid Ag_{(s)}$

Now, the standard cell potential is $E^{\circ}_{cell} = E^{\circ}_R - E^{\circ}_L$

= 0.80 – 0.77

= 0.03 V

Here, n = 1.

Then, $\Delta_r G^{\circ} = -nFE^{\circ}_{cell}$

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

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

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

Again, $\Delta_r G^{\circ} = 2.303\,RT\,\ln K$

$\log K = -\dfrac{\Delta_r G}{2.303\,RT}$
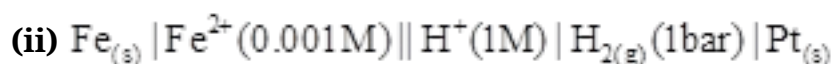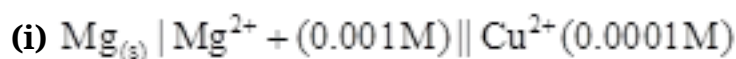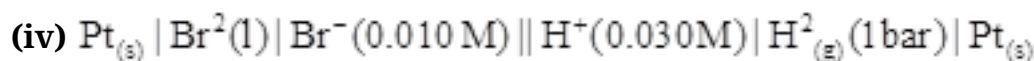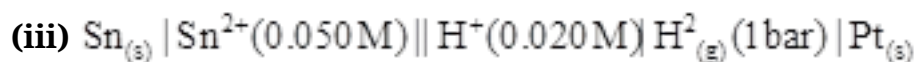
$= \dfrac{-2894.61}{2.303 \times 8.314 \times 298}$

= 0.5073

Therefore, K = antilog (0.5073)

= 3.2 (approximately)

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

(i) $Mg_{(s)} \mid Mg^{2+} + (0.001\,M) \parallel Cu^{2+}(0.0001\,M)$

(ii) $Fe_{(s)} \mid Fe^{2+}(0.001\,M) \parallel H^+(1M) \mid H_{2(g)}(1bar) \mid Pt_{(s)}$

(iii) $Sn_{(s)} | Sn^{2+}(0.050\,M) \| H^+(0.020\,M) | H^2_{(g)}(1\,bar) | Pt_{(s)}$

(iv) $Pt_{(s)} | Br^2(l) | Br^-(0.010\,M) \| H^+(0.030\,M) | H^2_{(g)}(1\,bar) | Pt_{(s)}$

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

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

$$= \{0.34 - (-236)\} - \frac{0.0591}{2} \log \frac{.001}{.0001}$$

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

= 2.7 – 0.02955

= 2.67 V (approximately)

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

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

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

= 0.44–0.02955(–3)

= 0.52865 V

= 0.53 V (approximately)

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

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

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

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

$$= 0.14 - 0.062$$

$$= 0.078 \text{ V}$$

= 0.08 V (approximately)

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

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

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

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

$$= -1.09 - 0.02955 \times \log \frac{1}{9 \times 10^{-8}}$$

$$= -1.09 - 0.02955 \times \log \left(1.11 \times 10^7\right)$$

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

$$= -1.09 - 0.208$$

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

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

Ans. 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 K. If ρ is resistivity, then we can write: $K = \dfrac{1}{\rho}$

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., $G = K\dfrac{a}{1} = k.1 = k$

(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.
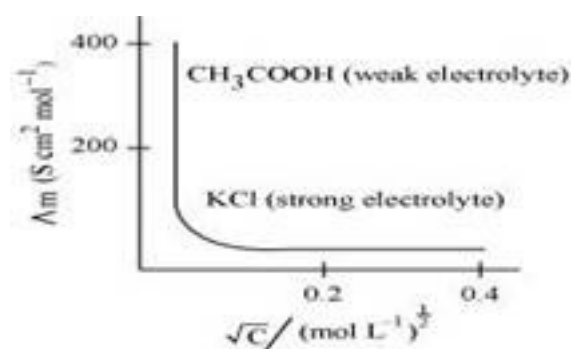
Molar conductivity:

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. $A_m = K\dfrac{A}{1}$

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

Therefore, $A_m = KV$

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 A_m with $\sqrt{c}$ for strong and weak electrolytes is shown in the following plot:

7. **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** $10^2 \times \kappa / Sm^{-1}$ 1.237 11.85 23.15 55.53 106.74

Calculate A_m **for all concentrations and draw a plot between** A_m **and** $c^{\frac{1}{2}}$. **Find the value of** A_m^0.

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

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

Therefore, $A_m = \dfrac{K}{c}$

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

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

Given,

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

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

Therefore, $A_m = \dfrac{K}{c}$

$$= \frac{11.85 \times 10^{-4} \, S \, cm^{-1}}{0.010 \, mol \, L^{-1}} \times \frac{1000 \, cm^3}{L}$$

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

Given,

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

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

Therefore, $A_m = \dfrac{K}{c}$

$$= \dfrac{23.15 \times 10^{-4}\, S\, cm^{-1}}{0.020\, mol\, L^{-1}} \times \dfrac{1000\, cm^3}{L}$$

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

Given,

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

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

Therefore, $K = \dfrac{K}{c}$

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

$= 111.11$ S cm^{2}mol^{-1}

Given,

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

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

Therefore, $A_m = \dfrac{K}{c}$

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

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

Now, we have the following data:

$\dfrac{C^{\frac{1}{2}}}{M^{\frac{1}{2}}}$	0.0316	0.1	0.1414	0.2236	0.3162
$A_m (\text{S cm}^2 \text{ mol}^{-1})$	123.7	118.5	115.8	111.1	106.74
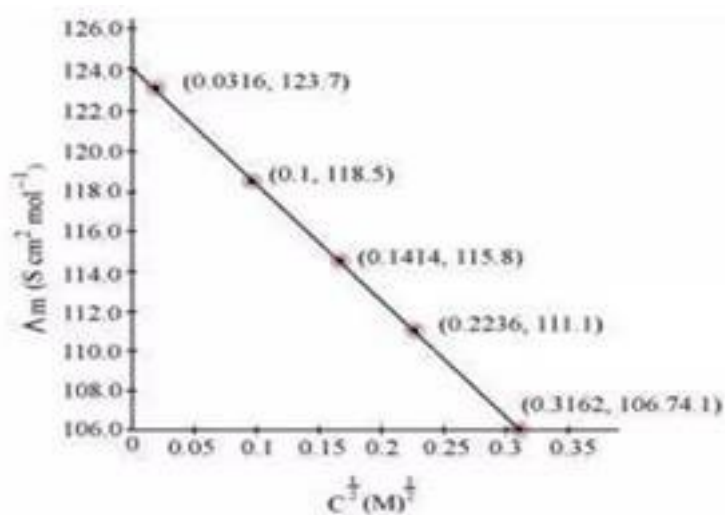
Since the line interrupts A_m at $124.0 \text{ S cm}^2 \text{ mol}^{-1}$, $A_m^0 = 124.0 \text{ S cm}^2\text{mol}^{-1}$

8. Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and if A_m^0 for acetic acid is $390.5 \text{ cm}^2 \text{ mol}^{-1}$, 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, $A_m = \dfrac{K}{c}$

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

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

Again, $A_m^0 = 390.5 \text{ S cm}^2\text{mol}^{-1}$

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

= 0.084

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

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

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

9. 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?

Ans. According to the reaction:

$$\underset{108g}{Ag^{+}}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$$
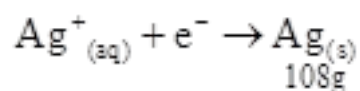
i.e., 108 g of Ag is deposited by 96487 C.

Therefore, 1.45 g of Ag is deposited by = $\dfrac{96487 \times 1.45}{108} C$
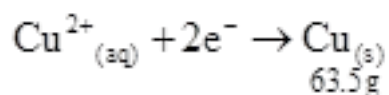
= 1295.43 C

Given,

Current = 1.5 A

Therefore, Time $= \dfrac{1295.43}{1.5} s$

= 863.6 s

= 864 s

= 14.40 min

Again,

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow \underset{63.5g}{Cu_{(s)}}$$
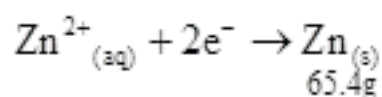
i.e., 2×96487 C of charge deposit = 63.5 g of Cu

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

= 0.426 g of Cu

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

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

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

= 0.439 g of Zn

10. Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:
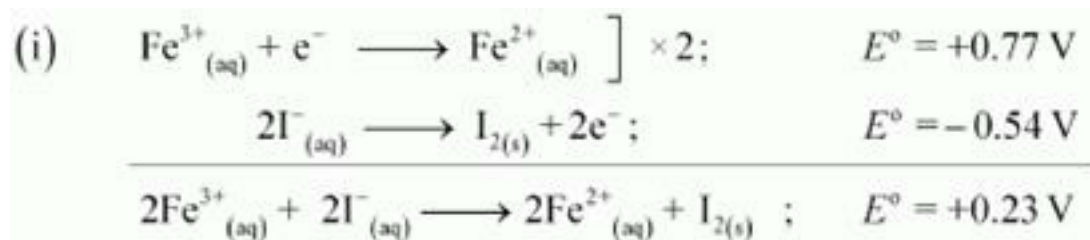
(i) $Fe^{3+}(aq)$ and $I^-(aq)$

(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)

$$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)} \Big] \times 2; \qquad E° = +0.77\ V$$

$$2I^-_{(aq)} \longrightarrow I_{2(s)} + 2e^-; \qquad E° = -0.54\ V$$

$$\overline{2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}}; \qquad E° = +0.23\ V$$

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

(ii)

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)} \Big] \times 2 \qquad ; \qquad E° = +0.80\ V$$

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^- \qquad ; \qquad E° = -0.34\ V$$

$$\overline{2Ag^+_{(aq)} + Cu_{(s)} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)}} \qquad ; \qquad E° = +0.46\ V$$
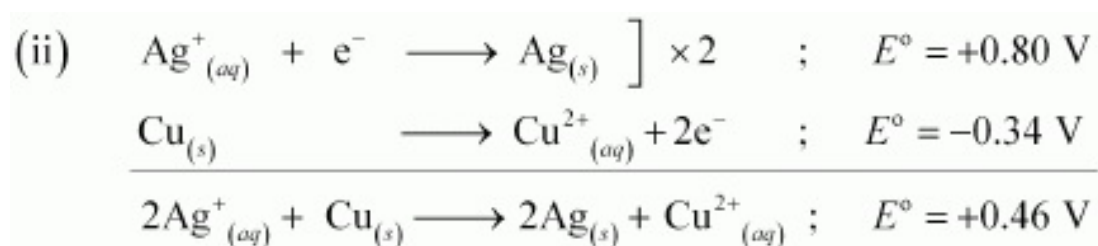
Since $E°$ for the overall reaction is positive, the reaction between $Ag^+(aq)$ and Cu(s) is feasible.

(iii)

$$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)} \Big] \times 2 \qquad ; \qquad E° = +0.77\ V$$

$$2Br^-_{(aq)} \longrightarrow Br_{2(l)} + 2e^- \qquad ; \qquad E° = -1.09\ V$$

$$\overline{2Fe^{3+}_{(aq)} + 2Br^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} \text{ and } Br_{2(l)}} \qquad ; \qquad E° = -0.32\ V$$
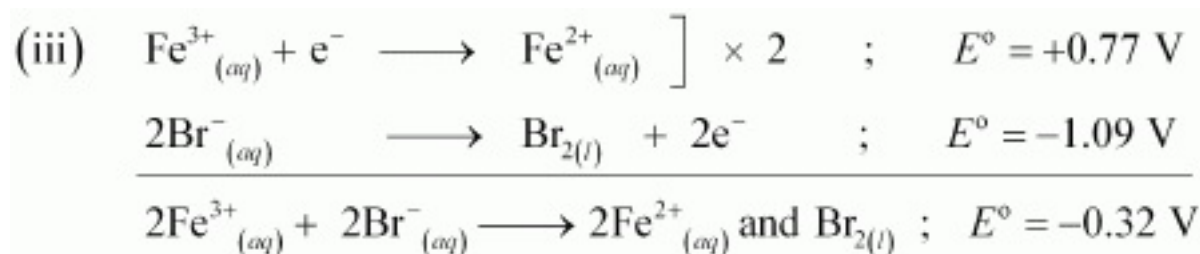
Since $E°$ for the overall reaction is negative, the reaction between $Fe^{3+}(aq)$ and $Br^-(aq)$ is not feasible.

(iv)

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

$$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)} \qquad ; \qquad E° = +0.77\ V$$

$$\overline{Ag_{(s)} + Fe^{3+}_{(aq)} \longrightarrow Ag^+_{(aq)} + Fe^{2+}_{(aq)}} \qquad ; \qquad E° = -0.03\ V$$
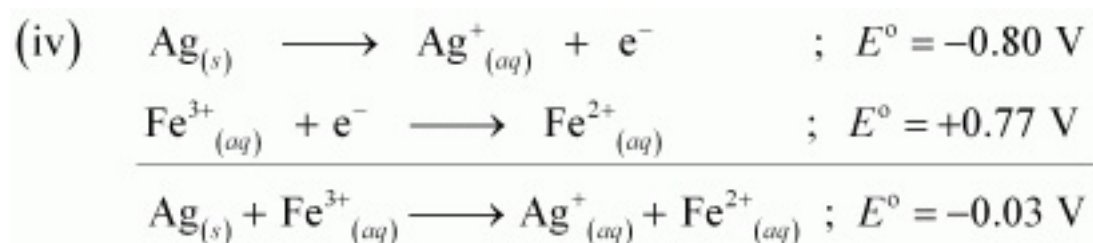
Since $E°E$ for the overall reaction is negative, the reaction between Ag(s) and $Fe^{3+}(aq)$ is not feasible.

(iv) $Br_{2(aq)} + 2e^- \longrightarrow 2Br^-_{(aq)}$; $E° = +1.09\ V$

$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^-\ ] \times 2$; $E° = -0.77\ V$

$Br_{2(aq)} + 2Fe^{2+}_{(aq)} \longrightarrow 2Br^-_{(aq)} + 2Fe^{3+}_{(aq)}$; $E° = +0.32\ V$
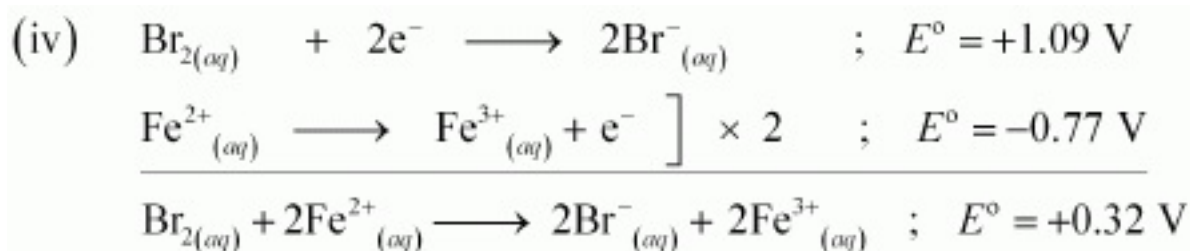
Since $E°$ for the overall reaction is positive, the reaction between $Br^2(aq)$ and $Fe^{2+}(aq)$s is feasible.

11. 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 cathode:

The following reduction reactions compete to take place at the cathode.
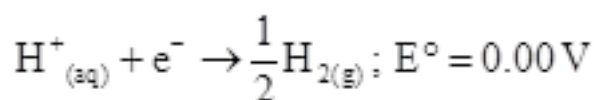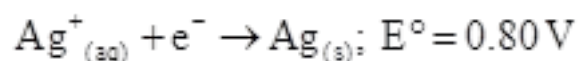
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$: $E° = 0.80\ V$

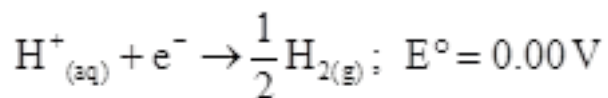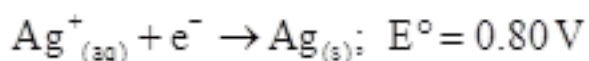$H^+_{(aq)} + e^- \rightarrow \dfrac{1}{2}H_{2(g)}$: $E° = 0.00\ V$

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^+.
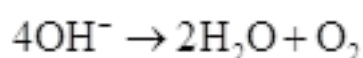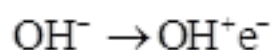
(ii) At cathode:

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

$$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}; \quad E° = 0.80\,V$$

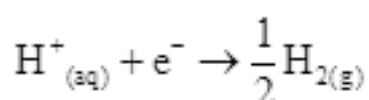$$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}; \quad E° = 0.00\,V$$

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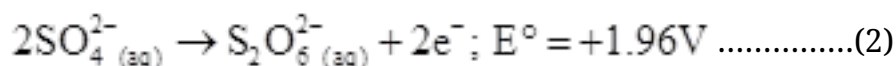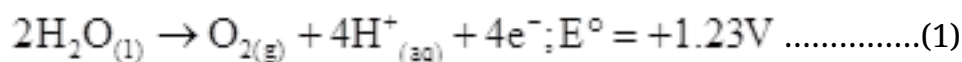
At anode:

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.

$$OH^- \rightarrow OH^+ e^-$$

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

(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.

$$2H_2O_{(1)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-; E° = +1.23V \quad \ldots\ldots\ldots\ldots(1)$$
$$2SO_4^{2-}{}_{(aq)} \rightarrow S_2O_6^{2-}{}_{(aq)} + 2e^-; E° = +1.96V \quad \ldots\ldots\ldots(2)$$
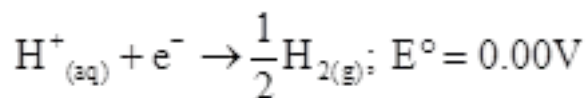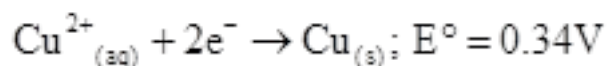
For dilute sulphuric acid, reaction (i) is preferred to produce O_2 gas. But for concentrated sulphuric acid, reaction (ii) occurs.

(iv) At cathode:

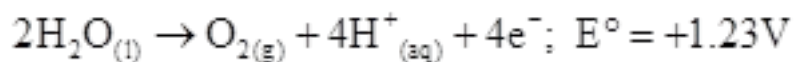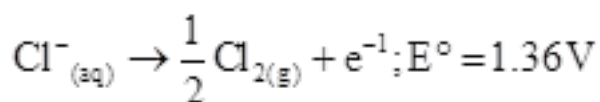The following reduction reactions compete to take place at the cathode.

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}; \; E° = 0.34V$$

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

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

Atanode:

The following oxidation reactions are possible at the anode.

$$Cl^-_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^{-1}; E° = 1.36V$$

$$2H_2O_{(1)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-; \; E° = +1.23V$$

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.