

(Chapter 3)(Electrochemistry)

XII

Question 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

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 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.

Answer

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: $Ag < Hg < Cr < Mg < K$

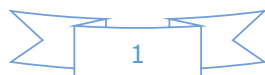
Question 3.3:

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.

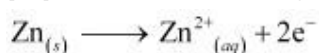
Answer

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

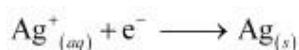




- (i) Zn electrode (anode) is negatively charged.
- (ii) Ions are carriers of current in the cell and in the external circuit, current will flow from silver to zinc.
- (iii) The reaction taking place at the anode is given by,

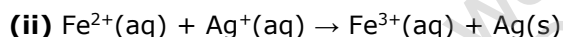
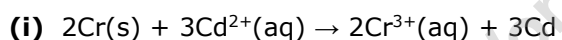


The reaction taking place at the cathode is given by,



Question 3.4:

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.

Answer

(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

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

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

In the given equation, n

$= 6$

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

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

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

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

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

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

Again,

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

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

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

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

$$= 34.496$$

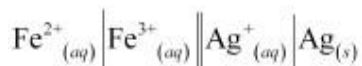
$$\therefore K = \text{antilog} (34.496) =$$

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

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

$$E_{\text{Ag}^+/\text{Ag}}^{\ominus} = 0.80 \text{ V}$$

The galvanic cell of the given reaction is depicted as:



Now, the standard cell potential is

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

$$= 0.80 - 0.77$$

$$= 0.03 \text{ V}$$

Here, $n = 1$.

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

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

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

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

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

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

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

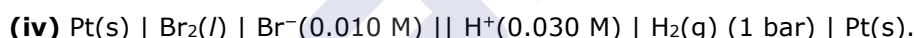
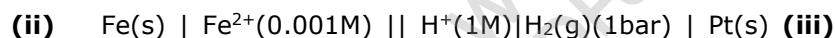
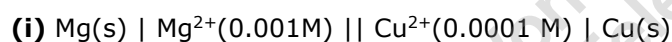
$$= 0.5073$$

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

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

Question 3.5:

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



Answer

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

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

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

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

$$= 2.7 - 0.02955$$

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

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

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

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

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

$$= 0.52865 \text{ V}$$

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

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

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

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

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

$$= 0.14 - 0.062$$

$$= 0.078 \text{ V}$$

$$= 0.08 \text{ V (approximately)}$$

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

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

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

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

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

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

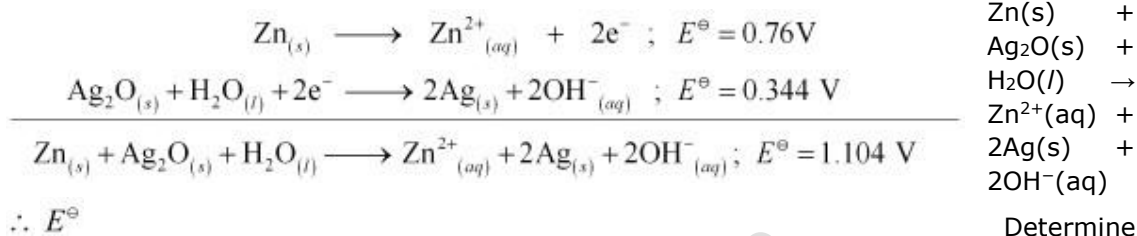
$$= -1.09 - 0.02955(0.0453 + 7)$$

$$= -1.09 - 0.208$$

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

Question 3.6:

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



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

Answer

$$= 1.104\text{ V}$$

We know that,

$$\begin{aligned} \Delta_r G^{\ominus} &= -nFE^{\ominus} \\ &= -2 \times 96487 \times 1.04 \\ &= -213043.296\text{ J} \\ &= -213.04\text{ kJ} \end{aligned}$$

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 symbol κ . 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.

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

i.e.,

(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.

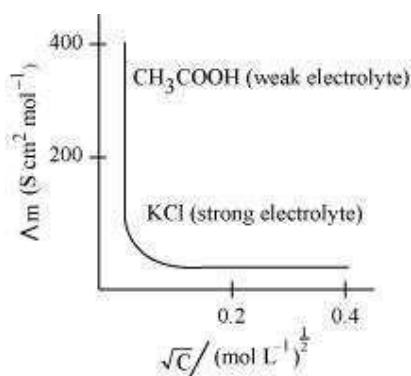
$$\Lambda_m = \kappa \frac{A}{l}$$

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 S cm^{-1} . Calculate its molar conductivity.

Answer Given, κ
 $= 0.0248 \text{ S cm}^{-1}$
 $= 0.20 \text{ M}$

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

∴ Molar conductivity,

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

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

Question 3.9:

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 $0.146 \times 10^{-3} \text{ S cm}^{-1}$.

Answer

Given,

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

Resistance, $R = 1500 \Omega$

∴ Cell constant $= \kappa \times R$

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

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

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

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

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

Calculate Λ_m° of

$$\Lambda_m^\circ$$

Answer Given,

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

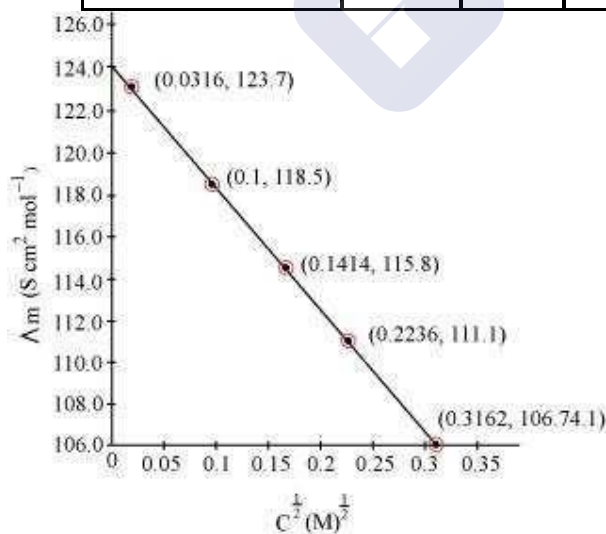
$$\text{Then, } \kappa = 106.74 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.3162 \text{ M}^{1/2}$$

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

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

$$= 106.74 \text{ S cm}^2 \text{ mol}^{-1} \text{ Now, we have the following data:}$$

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



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 3.11:

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^0 for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant?

Answer

Given, $\kappa = 7.896 \times 10^{-5} \text{ S m}^{-1} \text{ c}$
 $= 0.00241 \text{ mol L}^{-1}$

Then, molar conductivity,

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

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

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

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

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

Now,

$= 0.084$

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

\therefore Dissociation constant,

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

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

Question 3.12:

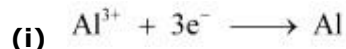
How much charge is required for the following reductions:

(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+} .

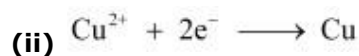
Answer



\therefore Required charge = 3 F

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

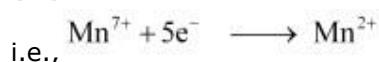
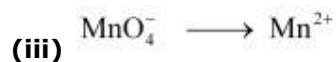
$$= 289461 \text{ C}$$



\therefore Required charge = 2 F

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

$$= 192974 \text{ C}$$



\therefore

Required charge = 5 F

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

$$= 482435 \text{ C}$$

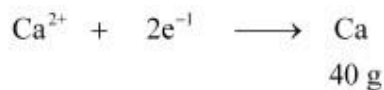
Question 3.13:

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

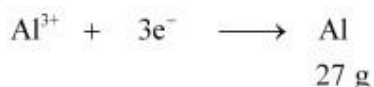
(i) According to the question,



Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium $= \frac{2 \times 20}{40} \text{ F}$
 $= 1 \text{ F}$

(ii) According to the question,



Electricity required to produce 27 g of Al = 3 F

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

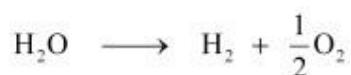
Question 3.14:

How much electricity is required in coulomb for the oxidation of (i)
1 mol of H_2O to O_2 .

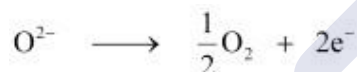
(ii) 1 mol of FeO to Fe_2O_3 .

Answer

(i) According to the question,



Now, we can write:

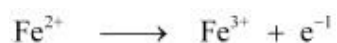


Electricity required for the oxidation of 1 mol of H_2O to O_2 = 2 F

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

= 192974 C

(ii) According to the question,



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

= 96487 C

Question 3.15:

A solution of $\text{Ni}(\text{NO}_3)_2$ 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

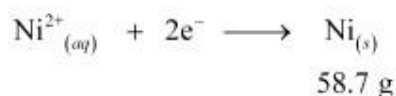
Time = $20 \times 60 = 1200$ s

∴ Charge = current \times time

= 5×1200

= 6000 C

According to the reaction,



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

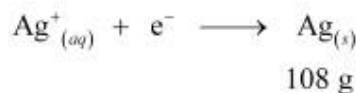
Hence, 1.825 g of nickel will be deposited at the cathode.

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:



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

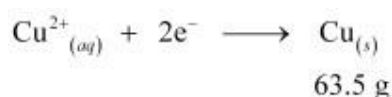
$$\therefore \text{Time} = \frac{1295.43}{1.5} \text{ s}$$

$$= 863.6 \text{ s}$$

$$= 864 \text{ s}$$

$$= 14.40 \text{ min}$$

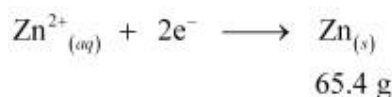
Again,



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

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

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



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

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

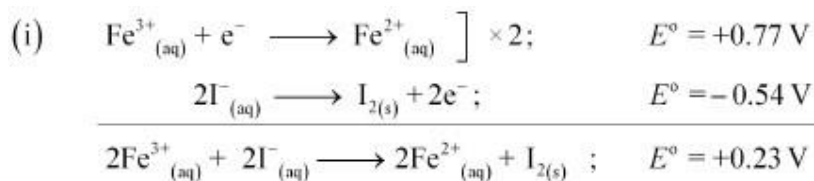
$$= 0.439 \text{ g of Zn}$$

Question 3.17:

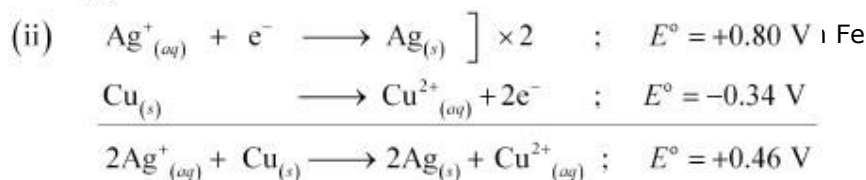
Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:

- (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 $\text{Fe}^{2+}(\text{aq})$.

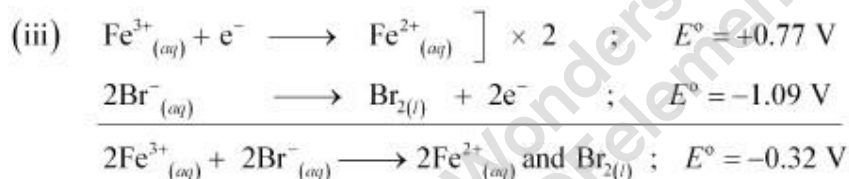
Answer



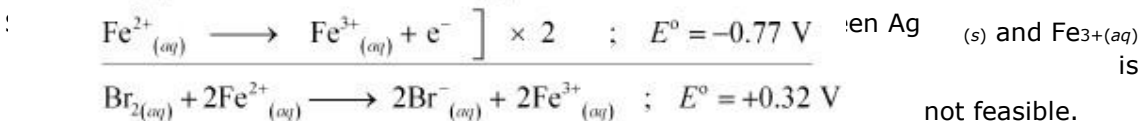
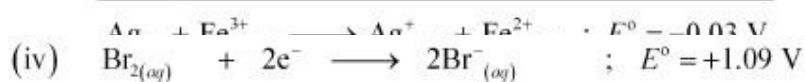
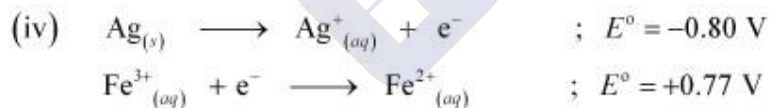
Since $\text{I}^{-}_{(aq)}$ and $\text{Fe}^{3+}_{(aq)}$ is feasible.



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

Question 3.18:

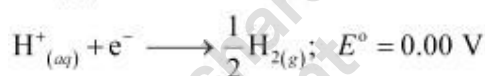
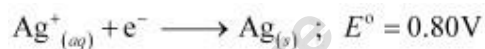
Predict the products of electrolysis in each of the following:

- (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.



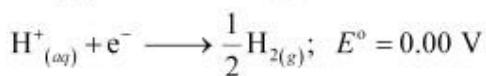
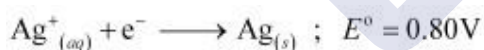
The reaction with a higher value of E^0 takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

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:

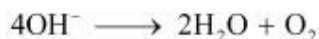
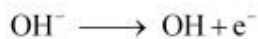
The following reduction reactions compete to take place at the cathode.



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

At anode:

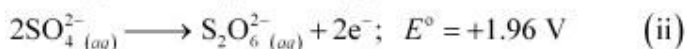
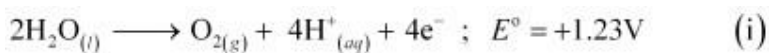
Since Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH^- or NO_3^- ions can be oxidized at the anode. But OH^- ions having a lower discharge potential and get preference and decompose to liberate O_2 .



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



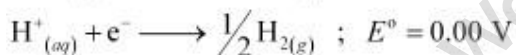
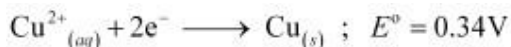
At the anode, the following processes are possible.



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.



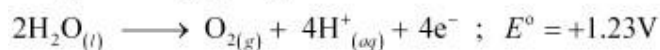
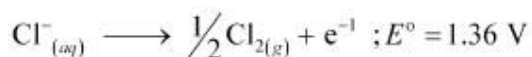
E° The reaction with a higher value of takes place at the cathode. Therefore, deposition of copper will take place at the cathode.

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