

Chapter 2: Electrochemistry

NCERT · Class 12 · Chemistry

Questions

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.

Solution

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

Question 3.2

Given the standard electrode potentials.

$$\text{K}^+/\text{K} = -2.93\text{V}$$

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

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

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

$$\text{Cr}^{3+}/\text{Cr} = -0.74\text{V}$$

Arrange these metals in their increasing order of reducing power.

Solution

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

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

Question 3.3

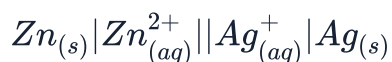
Depict the galvanic cell in which the reaction

$\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$ takes place. Further show:

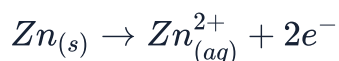
- (i) Which of the electrode is negatively charged?
- (ii) The carriers of the current in the cell.
- (iii) Individual reaction at each electrode.

Solution

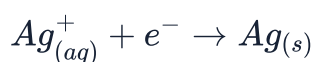
The galvanic cell in which the given reaction takes place is depicted as



- (i) 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



Reaction at the anode is given by



Question 3.4

Calculate the standard cell potentials of the galvanic cell in which the following reactions take place.



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

Solution

(i)

$$E_{\text{Cr}^{3+}/\text{Cr}}^\ominus$$

$$E_{\text{Cd}^{2+}/\text{Cd}}^\ominus$$

The galvanic cell of the given reaction is depicted as



Now, the standard cell potential is

$$E_{cell}^{\ominus} = E_g^{\ominus} - E_L^{\ominus}$$

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

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

In the given equation, $n = 6$

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

$$E_{cell}^{\ominus}$$

Then,

$$\Delta_r G^{\ominus}$$

$$-1$$

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

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

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

Again,

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

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

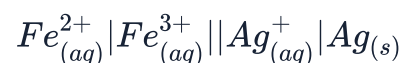
$$\log k = \frac{\Delta_r G}{2.303RT}$$

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

$$= 34.496$$

$$K = \text{antilog}(34.496) = 3.13 \times 10^{34}$$

The galvanic cell of the given reaction is depicted as



Now, the standard cell potential is

$$E_{cell}^{\ominus} = E_g^{\ominus} - E_L^{\ominus}$$

Here, $n = 1$

Then,

$$\Delta_t G^0 = -nFE_{cell}^0$$

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

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

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

Again,

$$\Delta_t G^0 = -2.303RT \ln K$$

$$\ln K = \frac{\Delta_t G}{2.303RT}$$

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

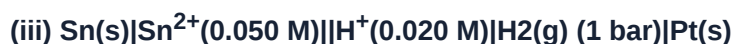
$$= 0.5073$$

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

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

Question 3.5

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



Solution

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

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= 0.34 - (-2.36) - \frac{0.0591}{2} \log \frac{0.001}{0.0001}$$

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

$$= 2.7 - 0.02955$$

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

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

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

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

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

$$= 0.52865 \text{ V}$$

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

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

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

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

$$\frac{0.591}{2} \log \frac{0.050}{(0.020)^2}$$

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

$$= 0.14 - 0.062$$

$$= 0.078 \text{ V}$$

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

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

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

$$= 0 - 1.09 -$$

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

$$= -1.09 - 0.02955 \times$$

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

$$= -1.09 - 0.02955 \times$$

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

$$= -1.09 - 0.02955 \times$$

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

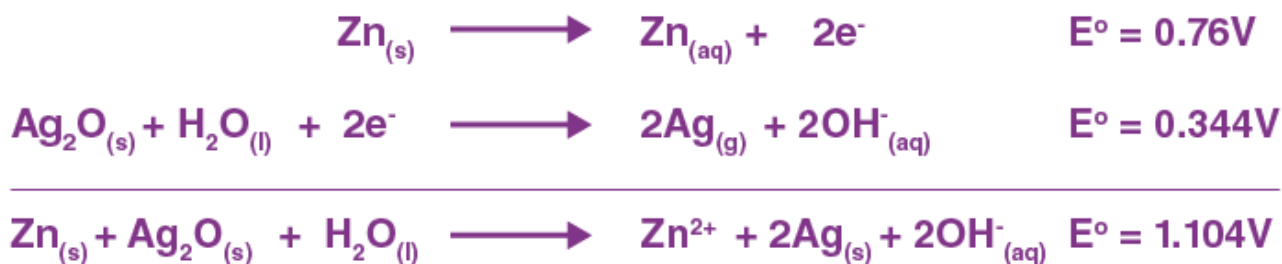
$$= -1.09 - 0.02955 \times (0.0453 + 7)$$

$$= -1.09 - 0.208$$

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

Question 3.6

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



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

Solution

$$E^\ominus$$

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.

Solution

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

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

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.

$$G = k \frac{a}{l} = k \times 1 = k$$

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.

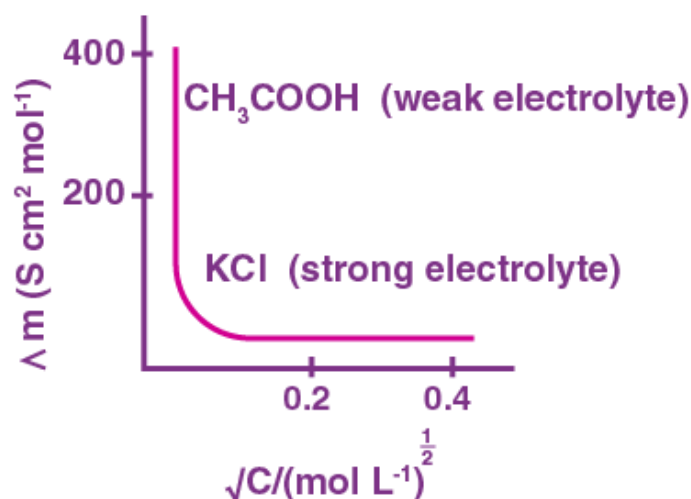
$$\Lambda_m = k \frac{A}{l}$$

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

$$\frac{\Lambda_m}{\sqrt{c}}$$



Question 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.

Solution

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

$c = 0.20 \text{ M}$

Molar conductivity,

$$\begin{aligned}\Lambda_m &= \frac{\kappa \times 1000}{c} \\ &= \frac{0.0248 \times 1000}{0.2} \\ &= 124 \text{ Scm}^2\text{mol}^{-1}\end{aligned}$$

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 the conductivity of 0.001M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$

Solution

Given,

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

Resistance, $R = 1500 \Omega$

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

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

Solution

Given,

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

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

$$\begin{aligned}\Lambda_m &= \frac{\kappa}{c} \\ &= \frac{1.237 \times 10^{-4} \text{ S cm}^{-1}}{0.001 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{\text{L}} \\ &= 123.7 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Given,

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

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

$$\begin{aligned}\Lambda_m &= \frac{\kappa}{c} \\ &= \frac{11.85 \times 10^{-4} \text{ S cm}^{-1}}{0.010 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{\text{L}} \\ &= 118.5 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Given,

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

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

$$\begin{aligned}\Lambda_m &= \frac{\kappa}{c} \\ &= \frac{23.15 \times 10^{-4} \text{ S cm}^{-1}}{0.020 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{\text{L}} \\ &= 115.8 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Given,

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

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

$$\begin{aligned}\Lambda_m &= \frac{\kappa}{c} \\ &= \frac{55.53 \times 10^{-4} \text{ S cm}^{-1}}{0.050 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{\text{L}} \\ &= 111.1 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Given,

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

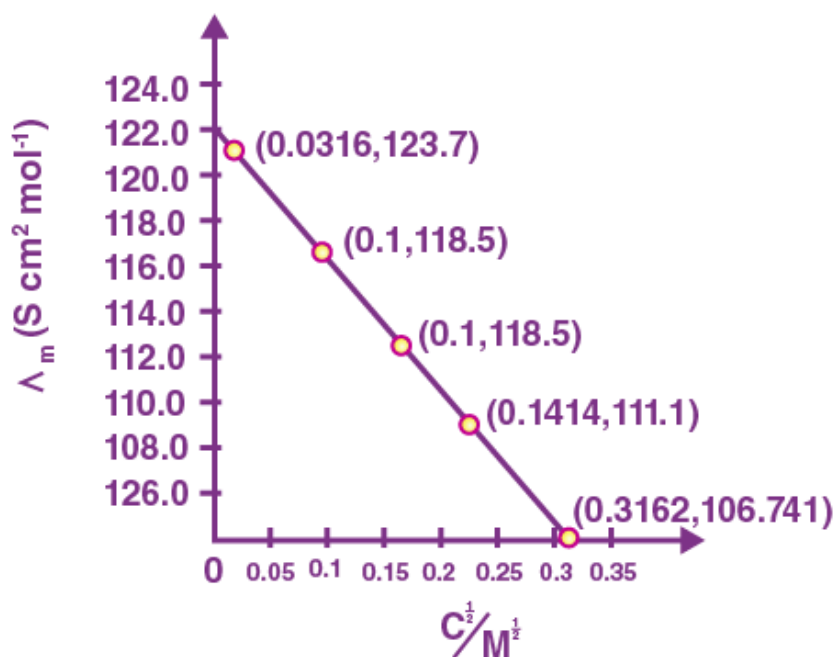
$$\text{Then, } \kappa = 106.74 \times 10^{-4} \text{ S cm}^{-1}, c^{1/2} = 0.3162 \text{ M}^{1/2}$$

$$\begin{aligned} \Lambda_m &= \frac{\kappa}{c} \\ &= \frac{106.74 \times 10^{-4} \text{ S cm}^{-1}}{0.100 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^{-1}}{\text{L}} \\ &= 106.74 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

Now, we have the following data:



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

$$\Lambda_m$$

2-1

$$\Lambda_m^0$$

2-1

Question 3.11

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

Solution

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

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

Then, molar conductivity,

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

=

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

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

$$\Lambda_m^0 =$$

2-1

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,

$$= 0.084$$

Dissociation constant,

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

=

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

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

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+}

Solution

(i)



Required charge = 3 F

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

$$= 289461 \text{ C}$$

(ii)

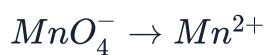


Required charge = 2 F

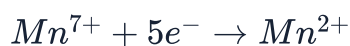
$$= 2 \times 96487 \text{ C}$$

$$= 192974 \text{ C}$$

(iii)



i.e



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 ?

Solution

(i) From the given data,



Electricity required to produce 40 g of calcium = 2 F

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

$$= 1 \text{ F}$$

(ii) From the given data,



Electricity required to produce 27 g of Al = 3 F

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

$$= 4.44 \text{ F}$$

Question 3.14

How much electricity is required in coulomb for the oxidation of

(i) 1 mol of H_2O to O_2 ?

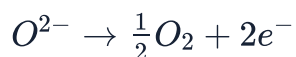
(ii) 1 mol of FeO to Fe_2O_3 ?

Solution

(i) From the given data,



We can say that



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

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

$$= 192974 \text{ C}$$

(ii) From the given data,



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

$$= 96487 \text{ C}$$

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?

Solution

Given,

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

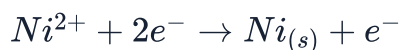
$$\text{Time} = 20 \times 60 = 1200 \text{ s}$$

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

$$= 5 \times 1200$$

$$= 6000 \text{ C}$$

According to the reaction,



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

Therefore, nickel deposited by 6000 C =

$$\frac{58.71 \times 6000}{2 \times 96487} \text{ g}$$

$$= 1.825 \text{ g}$$

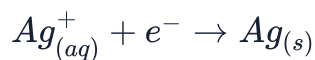
Hence, 1.825 g of nickel will be deposited at the cathode.

Question 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?

Solution

According to the reaction,



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

Therefore, 1.45 g of Ag is deposited by =

$$\frac{96487 \times 1.45}{108} C$$
$$= 1295.43 C$$

Given,

Current = 1.5 A

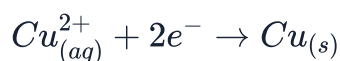
Time = 1295.43 / 1.5 s

$$= 863.6 s$$

$$= 864 s$$

$$= 14.40 \text{ min}$$

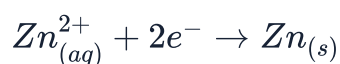
Again,



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

Therefore, 1295.43 C of charge will deposit

$$\frac{63.5 \times 1295.43}{2 \times 96487}$$
$$= 0.426 \text{ g of Cu}$$



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

Therefore, 1295.43 C of charge will deposit

$$\frac{65.4 \times 1295.43}{2 \times 96487}$$
$$= 0.439 \text{ g of Zn}$$

Question 3.17

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

(i) $Fe^{3+}(aq)$ 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)**Solution**

(i)



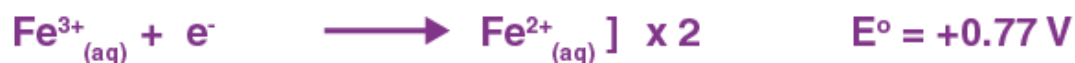
E° is positive, hence reaction is feasible

(ii)



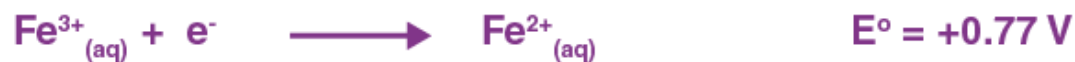
E° is positive; hence, the reaction is feasible.

(iii)



E° is negative; hence, the reaction is not feasible.

(iv)



E° is negative; hence, the reaction is not feasible.

(v)



E° is positive; hence, the reaction is feasible.

Question 3.18

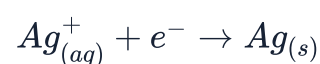
Predict the products of electrolysis in each of the following.

- (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

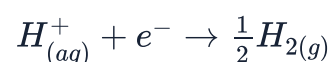
Solution

(i) At the cathode,

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



0



0

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

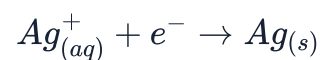
At the anode,

The Ag anode is attacked by

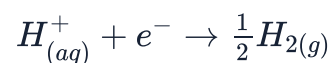


(ii) At the cathode,

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



0



0

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,

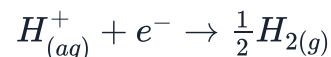
Since Pt electrodes are inert, the anode is not attacked by



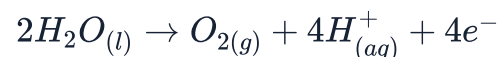
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 $^{-}_2$ 

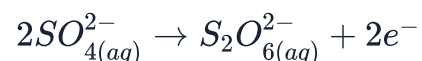
(iii) At the cathode, the following reduction reaction occurs to produce H_2 gas.



At the anode, the following processes are possible.



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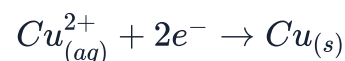


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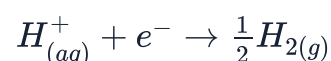
For dilute sulphuric acid, reaction (i) is preferred to produce O_2 gas. But for concentrated sulphuric acid, reaction (ii) occurs.

(iv) At the cathode,

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



0

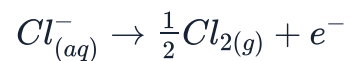


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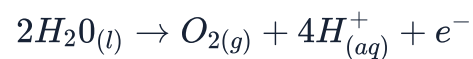
The reaction with a higher value takes place at the cathode. Therefore, the deposition of copper will take place at the cathode.

At the anode,

The following oxidation reactions are possible at the anode.



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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.