NCERT Solution for Class 12 Chemistry Chapter 3 Electrochemistry

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, Cu.

Mg: Al: Zn: Fe: Cu

Q 3.2:

Given the standard electrode potentials,
K+/K = −2.93V,

Ag+/Ag = 0.80V,
Hg2+/Hg = 0.79V
Mg2+/Mg = −2.37 V, Cr3+/Cr = − 0.74V
Arrange these metals in their increasing order of reducing power.

Ans:

The reducing power increases with the lowering of 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
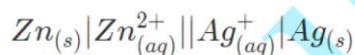**Zn(s)+2Ag+(aq) →Zn2+(aq)+2Ag(s) takes place. Further show:**
(i) Which of the electrode is negatively charged?
(ii) The carriers of the current in the cell.
**(iii) Individual reaction at each electrode.**

Ans :

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

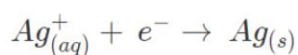$$Zn_{(s)}|Zn^{2+}_{(aq)}||Ag^+_{(aq)}|Ag_{(s)}$$

(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 :

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

Reaction at the anode is given by :

$$Ag^+_{(aq)} + e^- \to Ag_{(s)}$$
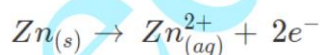
Q 3.4:

Calculate the standard cell potentials of galvanic cell in which the following
reactions take place:
(i) 2Cr(s) + 3Cd2+(aq) → 2Cr3+(aq) + 3Cd
(ii) Fe2+(aq) + Ag+(aq) → Fe3+(aq) + Ag(s)
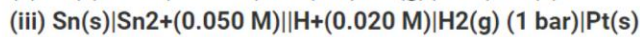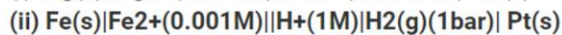**Calculate the ∆rGJ and equilibrium constant of the reactions.**

Ans :

= 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)|Mg2+(0.001M)||Cu2+(0.0001 M)|Cu(s)
(ii) Fe(s)|Fe2+(0.001M)||H+(1M)|H2(g)(1bar)| Pt(s)
(iii) Sn(s)|Sn2+(0.050 M)||H+(0.020 M)|H2(g) (1 bar)|Pt(s)
(iv) Pt(s)|Br−(0.010 M)|Br2(l)||H+(0.030 M)| H2(g) (1 bar)|Pt(s).

Answer

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

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

= 2.7 − 0.02955

= 2.67 V (approximately)

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

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

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

= 0.52865 V

= 0.53 V (approximately)

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

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

$$= 0 - (-0.14) - \frac{0.591}{2} log \frac{0.050}{(0.020)^2}$$

= 0.14 − 0.0295 × log125

= 0.14 − 0.062

= 0.078 V

= 0.08 V (approximately)

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

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

$$= 0 - 1.09 - \frac{0.591}{2} log \frac{1}{(0.010)^2(0.030)^2}$$

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

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

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

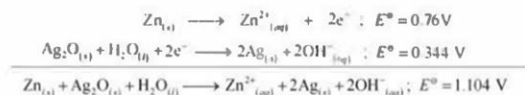= -1.09 − 0.02955 x (0.0453 + 7)

= -1.09 − 0.208

= -1.298 V

Q 3.6:

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

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

Determine ∆r GJ and EJ for the reaction.

Ans:

E^0 = 1.104 V

We know that,

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

= −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 cross-section at a distance of unit length.

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

When concentration decreases there will a decrease in Conductivity. It is applicable for both weak and strong electrolyte. This is because the number of ions per unit volume that carry the current in a solution decreases with a decrease in concentration.
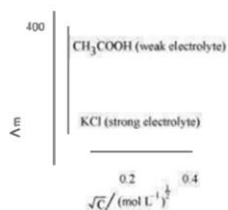
Molar conductivity −

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.

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

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

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 0.20 M solution of KCl at 298 K is 0.0248 S cm−1. Calculate its molar conductivity

Ans :

Given, κ = 0.0248 S cm^{-1} c

= 0.20 M

Molar conductivity, $\Lambda_m = \dfrac{k \times 1000}{c}$ $\qquad \dfrac{0.0248 \times 1000}{0.2}$

= 124 Scm^{2}mol^{-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 conductivity of 0.001M KCl solutionat 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 × 10^{-3} × 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$^{1/2}$

$\Lambda_m = \dfrac{k}{c} = \dfrac{1.237 \times 10^{-4} \, S \, cm^{-1}}{0.001 \, mol \, L^{-1}} \times \dfrac{1000 \, cm^{-1}}{L}$

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

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

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

$$\Lambda_m = \frac{k}{c} = \frac{11.85 \times 10^{-4} S\ cm^{-1}}{0.010\ mol\ L^{-1}} \times \frac{1000\ cm^{-1}}{L}$$

= 118.5 S cm^2 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$^{1/2}$

$$\Lambda_m = \frac{k}{c} = \frac{23.15 \times 10^{-4} S\ cm^{-1}}{0.020\ mol\ L^{-1}} \times \frac{1000\ cm^{-1}}{L}$$

= 115.8 S cm^2 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$^{1/2}$

$$\Lambda_m = \frac{k}{c} = \frac{106.74 \times 10^{-4} S\ cm^{-1}}{0.050\ mol\ L^{-1}} \times \frac{1000\ cm^{-1}}{L}$$

= 111.1 1 S cm^2 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$^{1/2}$

$$\Lambda_m = \frac{k}{c} = \frac{106.74 \times 10^{-4} S\ cm^{-1}}{0.100\ mol\ L^{-1}} \times \frac{1000\ cm^{-1}}{L}$$

= 106.74 S cm^2 mol^{-1}

Now, we have the following data :

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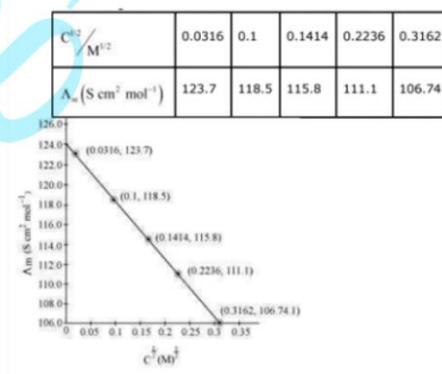
Since the line interrupts Λ_m at 124.0 S cm^2 mol^{-1}, Λ_m^0 = 124.0 S cm^2 mol^{-1}

Q 3.11:

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 cm2 mol−1, what is its dissociation constant?

Ans:

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

= 0.00241 mol L^{-1}

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

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

$\Lambda_m^0 = 390.5$ 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, $K_a = \frac{c\alpha^2}{(1-\alpha)}$

$$= \frac{(0.00241 \ mol \ L^{-1})(0.084)^2}{(1-0.084)}$$
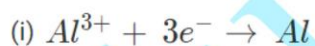
= 1.86 × 10^{-5} mol L^{-1}

Q 3.12:

How much charge is required for the following reductions:
(i) 1 mol of Al3+ to Al?
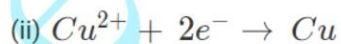**(ii) 1 mol of Cu2+ to Cu?**
(iii) 1 mol of MnO4− to Mn2+?

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

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

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

$\Lambda_m^0 = 390.5$ 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, $K_a = \frac{c\alpha^2}{(1-\alpha)}$

$$= \frac{(0.00241 \, mol \, L^{-1})(0.084)^2}{(1-0.084)}$$
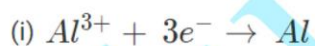
= 1.86 × 10^{-5} mol L^{-1}

Q 3.12:

How much charge is required for the following reductions:
(i) 1 mol of Al3+ to Al?
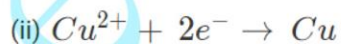**(ii) 1 mol of Cu2+ to Cu?**
(iii) 1 mol of MnO4− to Mn2+?

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

= 5 × 96487 C

= 482435 C

Q 3.13:

How much electricity in terms of Faraday is required to produce
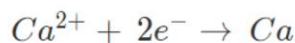**(i) 20.0 g of Ca from molten CaCl2?**
(ii) 40.0 g of Al from molten Al2O3?'

Ans:

(i) From given data,

$$Ca^{2+} + 2e^- \rightarrow Ca$$
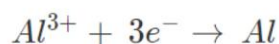
Electricity required to produce 40 g of calcium = 2 F

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

= 1 F

(ii) From 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
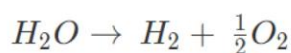
= 4.44 F

Q 3.14:

How much electricity is required in coulomb for the oxidation of
(i) 1 mol of H2O to O2?
(ii) 1 mol of FeO to Fe2O3?

Ans :

(i) From given data,

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

We can say that :

$$O^{2-} \rightarrow \tfrac{1}{2}O_2 + 2e^-$$
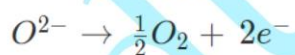
Electricity required for the oxidation of 1 mol of H_2O to O_2 = 2 F

= 2 × 96487 C

= 192974 C

(ii) From given data,

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$
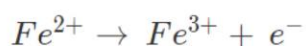
Electricity required for the oxidation of 1 mol of FeO to Fe_2O_3 = 1 F

= 96487 C

Q 3.15:

A solution of Ni(NO3)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 :

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

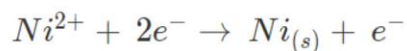Therefore, nickel deposited by 6000 C = $\frac{58.71 \times 6000}{2 \times 96487} g$

= 1.825 g

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

Q 3.16:

Three electrolytic cells A,B,C containing solutions of ZnSO4, AgNO3 and CuSO4, 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:

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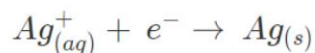
i.e., 108 g of Ag is deposited by 96487 C.

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,

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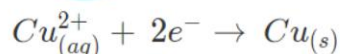
i.e., 2 × 96487 C of charge deposit = 63.5 g of Cu

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

= 0.426 g of Cu

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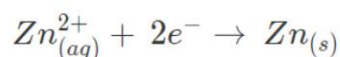
i.e., 2 × 96487 C of charge deposit = 65.4 g of Zn

Therefore, 1295.43 C of charge will deposit $\frac{65.4 \times 1295.43}{2 \times 96487}$
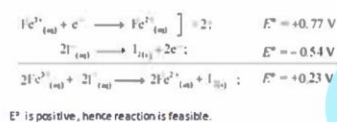
= 0.439 g of Zn

Q 3.17:

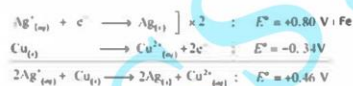**Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:**
(i) Fe3+(aq) and I−(aq)
(ii) Ag+ (aq) and Cu(s)
(iii) Fe3+ (aq) and Br− (aq)
(iv) Ag(s) and Fe 3+ (aq)
(v) Br2 (aq) and Fe2+ (aq).

Ans :

(i)
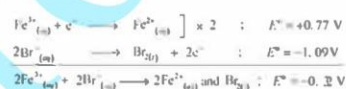
$$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)} \Big] \times 2; \qquad E^\circ = +0.77\ V$$
$$2I^-_{(aq)} \longrightarrow I_{2(s)} + 2e^-; \qquad E^\circ = -0.54\ V$$
$$2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(s)} : \qquad E^\circ = +0.23\ V$$

E° is positive, hence reaction is feasible.

(ii)

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)} \Big] \times 2 \ : \qquad E^\circ = +0.80\ V$$
$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^- : \qquad E^\circ = -0.34\ V$$
$$2Ag^+_{(aq)} + Cu_{(s)} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)} : \qquad E^\circ = +0.46\ V$$

E^0 is positive, hence reaction is feasible.

(iii)

$$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)} \Big] \times 2 \ : \qquad E^\circ = +0.77\ V$$
$$2Br^-_{(aq)} \longrightarrow Br_{2(l)} + 2e^- : \qquad E^\circ = -1.09\ V$$
$$2Fe^{3+}_{(aq)} + 2Br^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} \text{ and } Br_{2(l)} : \qquad E^\circ = -0.32\ V$$

E^0 is negative, hence reaction is not feasible.

(iv)

$$Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e^- \ : \qquad E^\circ = -0.80\ V$$
$$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)} \ : \qquad E^\circ = +0.77\ V$$
$$Ag_{(s)} + Fe^{3+}_{(aq)} \longrightarrow Ag^+ + Fe^{2+} : \qquad E^\circ = -0.03\ V$$

E^0 is negative, hence reaction is not feasible.

(v)

$$Br_{2(aq)} + 2e^- \longrightarrow 2Br^-_{(aq)} \ : \qquad E^\circ = +1.09\ V$$
$$Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^- \Big] \times 2 \ : \qquad E^\circ = -0.77\ V$$
$$Br_{2(aq)} + 2Fe^{2+}_{(aq)} \longrightarrow 2Br^-_{(aq)} + 2Fe^{3+}_{(aq)} \ : \qquad E^\circ = +0.32\ V$$
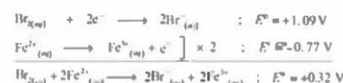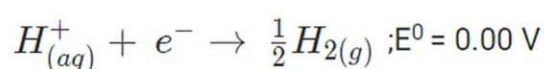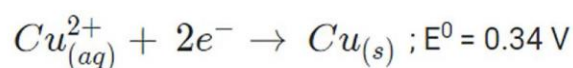
E^0 is positive, hence reaction is feasible.

Q 3.18:

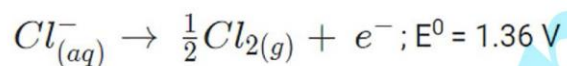**Predict the products of electrolysis in each of the following:**
(i) An aqueous solution of AgNO3 with silver electrodes.
(ii) An aqueous solution of AgNO3 with platinum electrodes.
(iii)   A dilute solution of H2SO4 with platinum electrodes.
(iv)   An aqueous solution of CuCl2 with platinum electrodes.

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \; ; E^0 = 0.34 \text{ V}$$

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

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.

$$Cl^-_{(aq)} \rightarrow \tfrac{1}{2}Cl_{2(g)} + e^- \; ; E^0 = 1.36 \text{ V}$$

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + e^- \; ; E^0 = +1.23 \text{ V}$$

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