CHAPTER 2

Electrochemistry

CLASS 12TH

NCERT EXERCISE AND SOLUTIONS - CHEMISTRY

Q. 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:-

Mg > Al > Zn > Fe > Cu

This means that any metal on the left side can replace the one immediately to its right in a salt solution.

Q. 2. Given the standard electrode potentials, K^+/K = –2.93V, Ag^+/Ag = 0.80V, Hg^{2+}/Hg = 0.79V, Mg^{2+}/Mg = –2.37V, Cr^{3+}/Cr = 0.74V.

Arrange these metals in their increasing order of reducing power.

ANSWER:-

$$\text{Reducing power } \alpha \frac{1}{\text{Reduction potential}}$$

As the reduction potential decreases, the reducing power increases. Therefore, the metals will have the following increasing order of reducing power:

Ag < Hg < Cr < Mg < K.

Q. 3. Depict the galvanic cell in which the reaction

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$$

takes place. Further show:

$Zn(s) + 2Ag^+(aq)\ Zn^{2+}(aq) + 2Ag(s)$ 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 set-up will be similar to as shown below.

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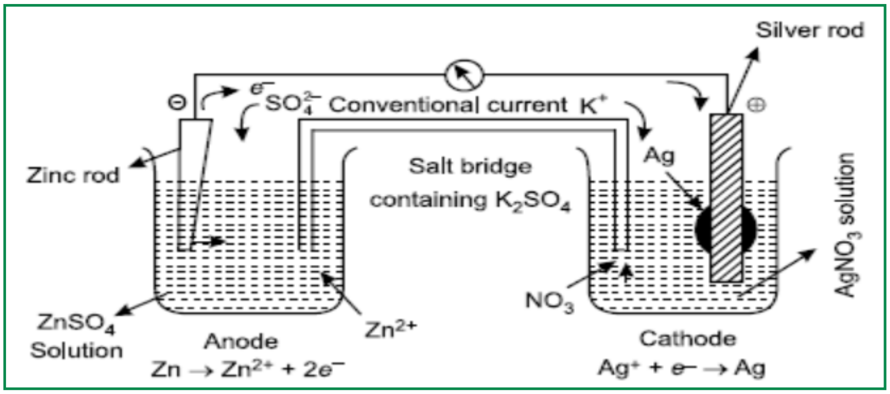


The cell will be represented as:

$Zn(s)|\ Zn^{2+}(aq)\ ||\ Ag^{+}(aq)|Ag(s)$

(i) Anode, i.e., zinc electrode will be negatively charged.

(ii) The carriers of the current in cell is electrons and ions.

(iii) At anode: $An(s) \rightarrow Zn^{2+}\ (aq) + 2e^{-}$ (Reduction)

At cathode: $2Ag^{+}\ (aq) + 2e^{-} \rightarrow 2Ag(s)$ (Oxidation)

Q. 4. Calculate the standard cell potentials of the galvanic cells in which the following reactions take place.

(i) $\mathbf{2Cr(s) + 3Cd^{2+}\ (aq) \rightarrow 2Cr^{3+}\ (aq) + 3Cd(s)}$

Given: $E^{O}_{Cr^{3+}/Cr} = -0.74V;\ E^{O}_{Cd^{2+}/Cd} = -0.40V$

(ii) $\mathbf{Fe^{2+}(aq) + Ag^{+}(aq) \rightarrow Fe^{3+}(aq) + Ag(s)}$

Given: $E^{\circ}_{Ag+/Ag} = 0.80V;\ E^{O}_{Fe^{3+}/Fe^{2+}} = 0.77V$

Calculate $\Delta_r G^{\circ}$ and equilibrium constant for the reaction.

ANSWER:-

(i) Calculation of E°_{cell},

$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = -0.40 - (-0.74) = +0.34V$

Calculation of $\Delta_r G^{\circ}$

$\Delta_r G^{\circ} = nF\ E^{\circ}_{cell} = -(6\ mol) \times (96500\ C\ mol^{-1}) \times (0.34\ V)$

$= -\ 196860\ CV = -\ 196860\ J = -\ 196.86\ kJ$

Calculation of Equilibrium Constant (K_c)

$\Delta_r G^{\circ} = -2.303\ RT\ \log K_c$

$$\log K_c = \frac{(-)\Delta_r G^{\circ}}{2.303RT} = (-)\frac{(-)196860}{2.303 \times 8.314 \times 298} = 34.501$$

$K_c = \text{Antilog}\ (34.501) = 3.17 \times 10^{34}$

(ii) Calculation of E°_{cell},

$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = (0.80 - 0.77) = 0.03V$

Calculation of ΔG°,

$\Delta_r G^{\circ} = -nF\ E^{\circ}_{cell} = -(1\ mol) \times (96500\ C\ mol^{-1}) \times (0.03\ V)$

$= -2895$ CV $= -2895$ J $= -2.895$ kJ

Calculation of Equilibrium Constant (K_c)

$\Delta_r G° = -2.303\ RT \log K_c$

$$\log K_c = (-)\frac{(-\Delta_r G^\circ)}{2.303RT} = (-)\frac{(-)2895}{2.303 \times 8.314 \times 298} = 0.5074$$

K_c = Antilog (0.5074) = 3.22

Q. 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) $\mid Cu(s)$

(ii) $Fe(s) \mid Fe^{2+}$ (0.001 M) $\parallel H^+$ (1M) $\mid H_2(g)$ (1 bar) $\mid Pt(s)$

(iii) $Sn(s) \mid Sn^{2+}$ (0.050 M) $\parallel H^+$ (0.020 M) $\mid H_2(g)$ (1 bar) $\mid Pt(s)$

(iv) $Pt(s) \mid Br^-$ (0.010 M) $\mid Br_2(1) \parallel H^+$ (0.030 M) $H_2(g)$ (1 bar) $\mid Pt(s)$

ANSWER:-

(i) Cell reaction

$$Mg + Cu^{2+} \quad Mg^{2+} + Cu (n = 2)$$

Nernst equation:

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$\therefore E_{cell} = 0.34 - (-2.37) - \frac{0.0591}{2}\log\frac{10^{-3}}{10^{-4}}$$

$= 2.71 - 0.02955 = 2.68V$

(ii) Cell reaction

$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$ (n=2)

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

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

$= 0.44 - 0.02955(-3)$

$= 0.52865$ V

$= 0.53$ V (approximately)

(iii) Cell reaction

$Sn + 2H^+ \longrightarrow Sn^{2+} + H_2$ (n = 2)

Nernst equation:

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Sn^{2+}]}{[H^+]^2}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2}\log\frac{0.05}{(0.02)^2}$$

$$= 0 - (-0.14) - \frac{0.0591}{2}\log\frac{0.05}{(0.02)^2}$$

$$= 0.14 - \frac{0.0591}{2}\log 125$$

$$= 0.14 - \frac{0.0591}{2}(2.0969) = 0.078\text{V}$$

(iv) Cell reaction

$2Br^- + 2H^+ \rightarrow Br_2 + H_2 (n = 2)$

Nernst equation:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2}\log\frac{1}{[Br^-]^2[H^+]^2}$$

$$= (0 - 1.08) - \frac{0.0591}{2}\log\frac{1}{(0.01)^2(0.03)^2}$$

$$= -1.08 - \frac{0.0591}{2}\log(1.111 \times 107)$$

$$= -1.08 - \frac{0.0591}{2}(7.0457)$$

$= 1.08 - 0.208 = -1.288\text{V}$

Hence, oxidation will occur at the hydrogen electrode and reduction will occur on Br_2 electrode.

Q. 6. In the button cells widely used in watches and other devices the following reaction takes place:

$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

Determine $\Delta_r G^0$ and E^0 for the reaction

Given: $Zn \rightarrow Zn^{2+} + 2e^-, E^{\circ} = 0.76V;$

$Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^-, E^{\circ} = 0.344V.$

Ans Zn is oxidised and Ag_2O is reduced.

$E^{\circ}_{cell} = E^{O}_{Ag_2O/Ag}$ (reduction) – $E^{O}_{Zn/Zn^{2+}}$ (oxidation)

$= 0.344 - (-0.76) = 1.104$ V

$\Delta G^{\circ} = -nFE_{cell} = -2 \times 96500 \times 1.104$ J

$= -2.13 \times 10^5$ J.

Q. 7. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

ANSWER:-

Conductivity is the inverse of resistivity, also known as specific conductance, and is represented by κ (kappa). Therefore, if κ is the specific conductance and G is the conductance of the solution, then

$$R = \frac{1}{G} \text{ and } \rho = \frac{1}{k}$$

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

$$k = G \times \frac{l}{A}$$

Now, if l = 1 cm and A = 1 sq.cm, then k = G.

The conductivity of a solution is defined as the conductance of a solution with a length of 1 cm and a cross-sectional area of 1 square cm. Alternatively, it can be described as the conductance of one cubic centimeter of the electrolyte solution.

Molar conductivity: The molar conductivity of a solution at a given dilution V is the conductance of all the ions produced from 1 mole of the electrolyte dissolved in V cm^3 of the solution. This occurs when the electrodes are placed 1 cm apart and the area of the electrodes is sufficiently large to contain the entire solution between them. It is denoted by Λm.

$$\Lambda_m = \frac{kA}{l}$$

Since, l = 1cm and A = V (volume containing 1 mole of electrolyte)

$$\Lambda_m = \kappa V$$

Variation of conductivity and molar conductivity with concentration: Conductivity decreases as the concentration decreases, for both weak and strong electrolytes. This occurs because the number of ions per unit volume that carry the current decreases upon dilution.

Molar conductivity, on the other hand, increases as concentration decreases. This is because the total volume, V, of the solution containing one mole of electrolyte also increases. It has been observed that the reduction in conductivity (k) due to dilution is more than offset by the increase in volume.

Q. 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, Molar Conductivity = ?, k = 0.0248 S cm^{-1}, Molarity = 0.20M

Molar conductivity $\Lambda_m = \frac{k \times 1000}{\text{Molarity}} = \frac{0.0248\text{ S cm}^{-1} \times 1000\text{ cm}^3\text{ L}^{-1}}{0.20\text{ mol L}^{-1}} = 124\text{S cm}^2\text{ mol}^{-1}$

Q. 9. **The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}.**

ANSWER:-

Given, Cell constant =?, R = 1500 Ω ,K= 0.146×10^{-3} S cm^{-1}

Cell constant = Conductivity × Resistance

= 0.146×10^{-3} S cm^{-1} × 1500 W

= 0.219 cm^{-1}.

Q. 10. **The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:**

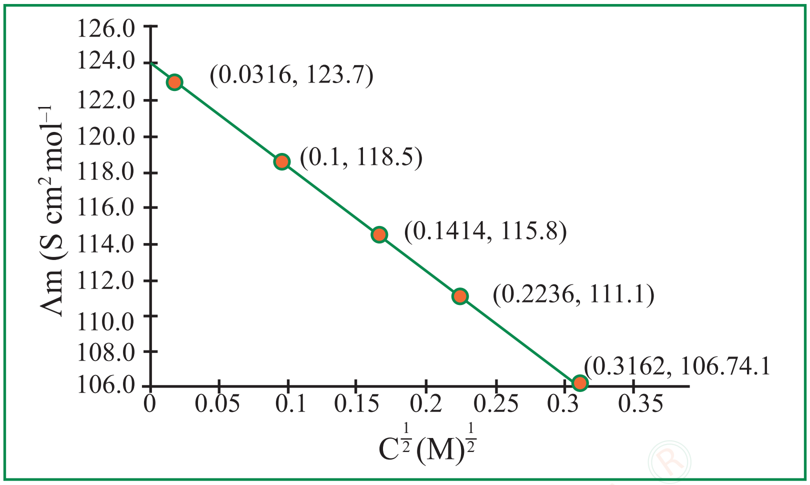
Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^2 \times k/Sm^{-1}$	1.237	11.85	23.15	55.53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value of $\Lambda°_m$

ANSWER:-

Concentration(M)	k(S m^{-1})	k(Scm^{-1})	$\Lambda_m = \frac{100 \times k}{\text{Molarity}} (Scm^2mol^{-1})$	$c^{1/2}(M^{1/2})$
10^{-3}	1.237×10^{-2}	1.237×10^{-4}	$\frac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = 123.7$	0.031
10^{-2}	11.85×10^{-2}	11.85×10^{-4}	$\frac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = 118.5$	0.100
2×10^{-2}	23.15×10^{-2}	23.15×10^{-4}	$\frac{1000 \times 23.15 \times 10^{-4}}{10^{-3}} = 115.8$	0.141
5×10^{-2}	55.53×10^{-2}	55.53×10^{-4}	$\frac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = 111.1$	0.224
10^{-1}	106.74×10^{-2}	106.74×10^{-4}	$\frac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = 106.7$	0.316

$\Lambda°$ = Intercept on Λ_m axis = 124.0 S cm^2 mol^{-1}, which is obtained by extrapolation to zero concentration.



Q. 11. **Conductivity of 0.00241 M acetic acid is 7.896 × 10^{-5} S cm^{-1}. Calculate its molar conductivity. If Λ_m^o for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?**

ANSWER:-

Given, k = 7.896 × 10^{-5} S cm^{-1}. Concentration= 0.00241 M

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

Then, molar conductivity,

$$= \frac{7.896\times10^{-5}\ \text{S cm}^{-1}}{0.00241\ \text{mol L}^{-1}}\times\frac{1000\ \text{cm}^3}{\text{L}}$$

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

$\Lambda_m^o = 390.5\text{S cm}^2\ \text{mol}^{-1}$

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

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

Dissociation constant,

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

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

Q. 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:-

(i) 1 mol of Al^{3+} to Al

Electrode reaction : $\underset{1mol}{Al^{3+}(aq)} + 3e^- \rightarrow \underset{3mol}{Al(s)}$

Quantity of charge required to reduce 1 mol of Al^{3+} = 3 faraday = 3 × 96500 C = 289500 C = 2.89 × 10^5 C

(ii) 1 mol Cu^{2+} to Cu

Electrode reaction: $\underset{1mol}{Cu^{2+}}(aq) + 2e^- \rightarrow \underset{2mol}{Cu(s)}$

Quantity of charge required to reduce 1 mol of Cu^{2+} = 2 faraday = 2 × 96500 C = 1.93 × 10^5 C

(iii) 1 mol of MnO^-_4 to Mn^{2+}

Electrode reaction: $\underset{1mol}{MnO_4^-} + 5e^- \rightarrow \underset{5mol}{Mn^{2+}}$

Quantity of change require to reduce 1 mol MnO_4^- = 5 faraday = 5 × 96500 C = 4.83 × 10^5 C

Q. 13. **How much electricity in terms of Faraday is required to produce:**

(i) 20.0g of Ca from molten $CaCl_2$?
(ii) 40.0g of Al from molten Al_2O_3?

ANSWER:-

(i) Electrode reaction : $\underset{1mol}{Ca^{2+}}(aq) + 2e^- \rightarrow \underset{2mol}{Ca(s)}$

To produce 1 mol or 40gm of Ca from molten $CaCl_2$, electricity required = 2 F

To produce 20gm of Ca from molten $CaCl_2$, electricity required = $\frac{2 \times 20}{40}$ =1 F

(ii) Electrode reaction : $\underset{6mol}{Al_2O_3(l) + e^-} \rightarrow 2Al + 3O^{2-}$

To produce 54g Al from molten Al_2O_3,electricity required = 6F

To produce 40g Al from molten A_2O_3,electricity required = 6 × $\frac{40}{54}$ = 4.44F

Q. 14. **How much electricity is required in coulomb for the oxidation of:**

(i) 1 mol of H_2O to O_2?
(ii) 1 mol of FeO to Fe_2O_3?

ANS

(i) According to the question,

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

Now, we can write:

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

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

= 2 × 96487C

= 192974C

(ii) According to the question,

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-1}$$

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

Q. 15. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes used a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

ANSWER:-

Charge = Current × time = 5 × 1200s = 6000C

Chemical equation:

$Ni(NO_3)_2(aq) + 2H^+ + 2e^- \rightarrow Ni + 2HNO_3$

Charge required to deposite 1 mol nickel =2 F

= 2 × 96500 = 1.93×10^5 C

So, 1 mol or 58.7 g nickel produce charge of 1.93×10^5 C

Therefore, 6000 C change produced by $= \frac{58.7 \times 6000}{1.93 \times 10^5} = 1.825$ g nickel.

Hence, the mass of Ni deposited at the cathode is 1.825 g .

Q. 16. Three electrolytic cells A,B,C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, respectively are connected in series. A current of 1.5 amperes was passed through them unit 1.45g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

ANSWER:-

$Ag^+ (aq)+e^- \rightarrow Ag(s)$

108 g silver deposited by electricity = 1F = 96500 C

1.45 g silver deposited by electricity $= \frac{96500}{108} \times 1.45$

=1295.6C

$Q = i \times t$

$$t = \frac{Q}{i} = \frac{1295.6}{1.5} = 14 \text{ min } 39\text{s}$$

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

On passing electricity of 2×96500C,Cu deposited = 63.5 g

On passing electricity of 1295.6C, Cu deposited $= \frac{63.5 \times 1295.6}{2 \times 96500} = 0.426$g

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

On passing electricity of 2 ×96500C,Zn deposited = 65.3g

On passing electricity of 1295.6 C, Zn deposited $= 65.3 \times \frac{1295.6}{2} \times 96500$

$= 0.438g$

Q. 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 B^- (aq)

(iv) Ag(s) and Fe^{3+} (aq)

(v) Br_2 (aq) and Fe^{2+} (aq)

ANSWER:-

The reaction is feasible, its E°cell value is positive.

(i) $Fe^{3+}(aq) + I^-(aq) \rightarrow Fe^{2+}(aq) + \frac{1}{2}I_2(g)$

$$E^\circ \text{ cell} = E^\circ_{(Fe^{3+}/Fe^{2+})} - E^\circ_{\left(\frac{1}{2}I_2/I^-\right)} = 0.77 - 0.54 = 0.23V$$

This reaction is feasible.

(ii) $Cu(s) + 2Ag^+ (aq) \rightarrow 2Ag(s) + Cu^{2+} (aq)$

$$E^\circ_{cell} = E^\circ_{(Ag^+/Ag)} - E^\circ_{(Cu^{2+}/Cu)} = 0.80 - 0.34 = 0.46V$$

This reaction is feasible

(iii) $Fe^{3+}(aq) + Br^-(aq) \rightarrow Fe^{2+}(aq) + \frac{1}{2}Br_2(aq)$

$$E^\circ_{cell} = E^\circ_{(Fe^{3+}/Fe^{2+})} - E^\circ_{\left(\frac{1}{2}Br_2/Br^-\right)} = 0.77 - 1.09 = -0.32V$$

This reaction is not feasible

(iv) $Ag(s) + Fe^{3+}(aq) \rightarrow Ag^+(aq) + Fe^{2+}(aq)$

$$E^0_{cell} = E^0_{(Fe^{3+}/Fe^{2+})} - E^0_{(Ag^+/Ag)} = 0.77 - 0.80 = -0.03V$$

This reaction is not feasible

(v) $\frac{1}{2}Br_2(aq) + Fe^{2+}(aq) \rightarrow Br^-(aq) + Fe^{3+}(aq)$

$$E^\circ_{cell} = E^\circ_{\left(\frac{1}{2}Br_2/Br^-\right)} - E^\circ_{(Fe^{3+}/Fe^{2+})} = 1.09 - 0.77 = 0.32V$$

This reaction is feasible

Q. 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 o $AgNO_3$ 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

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

$$H^{+}(aq) + e^{-} \rightarrow \frac{1}{2}H_2$$

The reaction with a higher E° value occurs at the cathode. As a result, silver will be deposited at the cathode.

At the anode:

The Ag anode is oxidized by NO_3^- ions. Consequently, the silver electrode at the anode dissolves into the solution, forming Ag^+.

(ii) At Cathode:

The following reduction reactions compete to take place

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

$$H^{+}(aq) + e^{-} \rightarrow \frac{1}{2}H_2$$

The reaction with a higher E° value occurs at the cathode, so silver will be deposited there.

At the anode:

Since platinum electrodes are inert, the anode is not affected by NO_3^- ions. As a result, either OH^- or NO_3^- ions can be oxidized at the anode. However, OH^- ions, which have a lower discharge potential, are preferentially oxidized, leading to the release of O_2.

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

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

At Cathode: The following reduction reaction occurs to produce H_2 gas

$$H^{+}(aq) + e^{-} \rightarrow \frac{1}{2}H_2(g)$$

(iii) At Anode:

$$2H_2O(l) \rightarrow O_2(g) + 4H^{+}(aq) + 4e^{-} \ldots(i)$$

$$2SO_4^{2-} \rightarrow S_2O_6^{2-} + 2e^{-} ..(ii)$$

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

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

$$\mathbf{H}^+(aq) + e^- \rightarrow \frac{1}{2}\mathbf{H}_2(g)$$

The reaction with the higher E° value occurs at the cathode, so copper will be deposited there.

At the anode:

The following oxidation reactions can take place at the anode.

$$Cl^-(aq) \rightarrow \frac{1}{2}Cl_2(g) + e^-$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

At the anode, the reaction with the lower E° value is preferred. However, due to the overpotential of O_2, Cl^- ions are oxidized at the anode to produce Cl_2.