



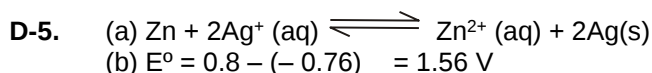
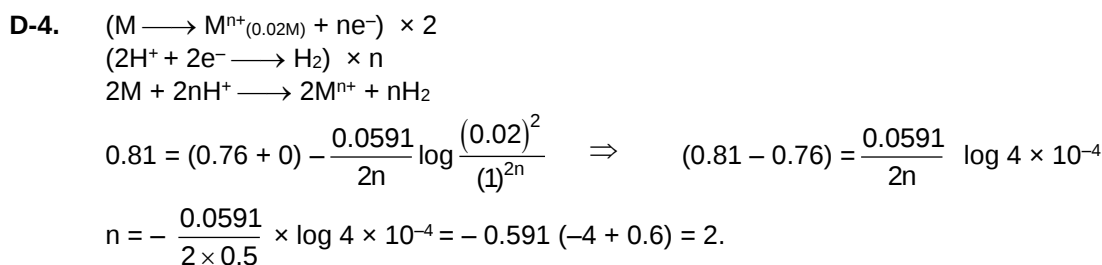
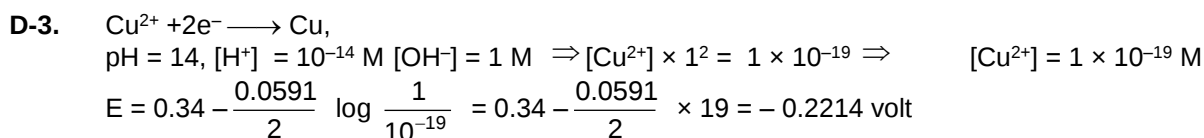
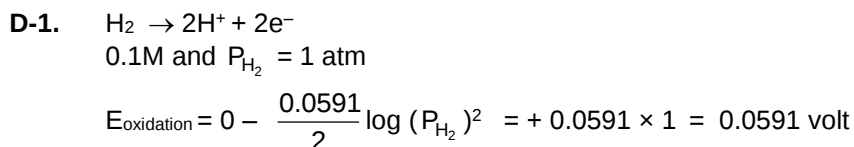
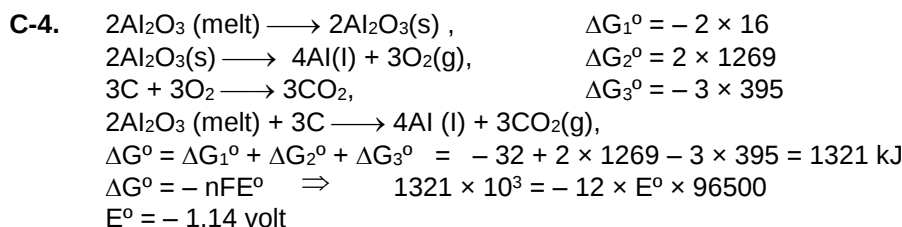
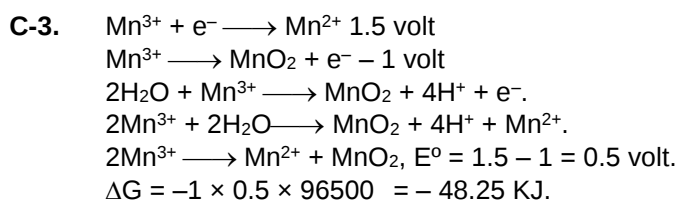
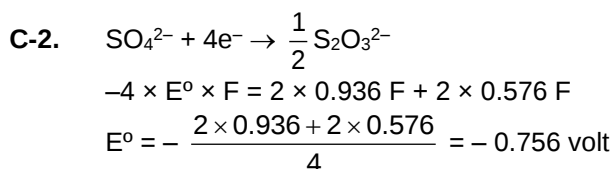
SOLUTION OF ELECTROCHEMISTRY

EXERCISE # 1

PART - I

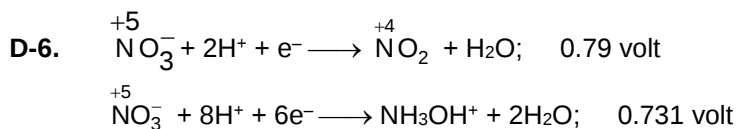
B-1. Lowest standard reduction potential highest reducing power.

B-2. Lowest standard reduction potential highest reducing power.

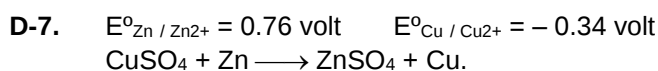




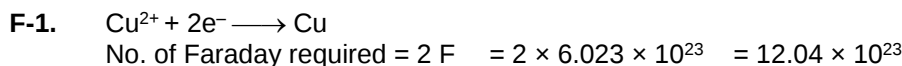
$$\begin{aligned}
 \text{(c)} \quad 1.6 &= 1.56 - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} & \text{or} \quad 1.356 &= \log \frac{[\text{Ag}^+]^2}{[\text{Zn}^{2+}]} \\
 \text{or} \quad \log \frac{[0.1]^2}{[\text{Zn}^{2+}]} &= 1.356 & \text{or} \quad \frac{0.01}{[\text{Zn}^{2+}]} &= 22.7 \\
 \text{or} \quad [\text{Zn}^{2+}] &= \frac{0.01}{22.7} = 4.4 \times 10^{-4} \text{ M}
 \end{aligned}$$



$$\begin{aligned}
 E &= 0.79 - \frac{0.0591}{1} \log \frac{1}{[\text{H}^+]^2} = 0.731 - \frac{0.0591}{6} \log \frac{1}{[\text{H}^+]^8} \\
 0.79 + 2 \times \frac{0.0591}{2} \log [\text{H}^+] &= 0.731 + \frac{0.0591}{6} \times 8 \times \log [\text{H}^+] \\
 0.059 &= 0.059 \left(2 - \frac{8}{6}\right) \text{ pH} \quad \Rightarrow \text{pH} = \frac{6}{4} = 1.5
 \end{aligned}$$



$$0 = (0.76 + 0.34) - \frac{0.0591}{2} \log \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right) \quad \Rightarrow \quad \log \left(\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \right) = 37.22$$

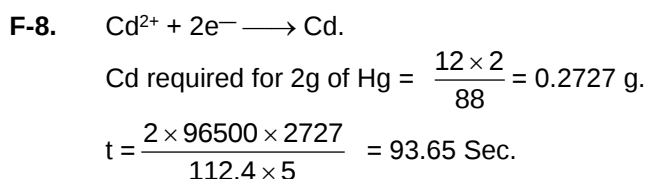
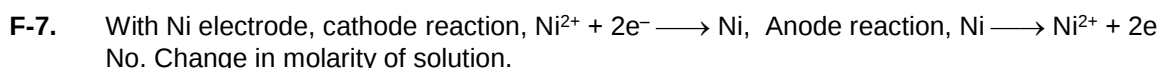
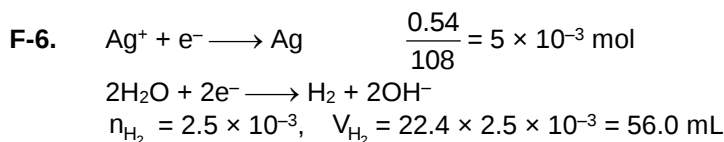


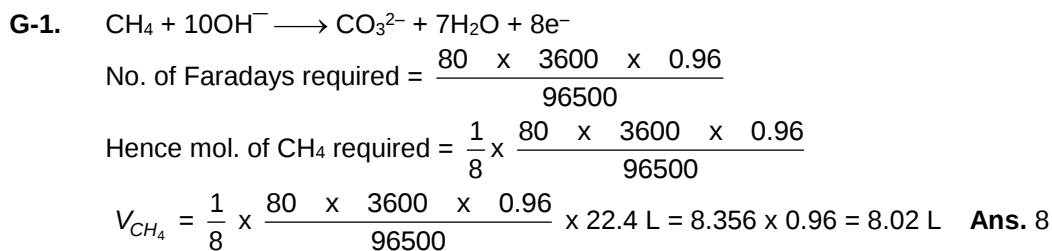
F-2. $0.108 = \frac{E}{96500} \times 0.5 \times 193 \quad E = 108 \text{ g/eq.}$

F-3. $\frac{W_{\text{Ag}}}{W_{\text{metal}}} = \frac{E_{\text{Ag}}}{E_{\text{M}}} = \frac{108}{\frac{108}{n}} = n \quad n = \frac{0.5094}{0.2653} = 1.92 \quad n = 2.$

F-4. $\frac{2.977}{106.4/n} = \frac{3 \times 1 \times 60 \times 60}{96500} \quad \Rightarrow \quad n = 4.$

F-5. $10.8 \times 80 \times 5 \times 10^{-4} = \frac{108}{1 \times 96500} \times 2 \times t \quad \Rightarrow \quad t = 193 \text{ sec}$





H-1. $K = \frac{1}{245} \times \frac{4}{7} = 2.332 \times 10^{-3} \text{ mho cm}^{-1}$.
 $\Lambda_m = \frac{2.33 \times 10^{-3} \times 1000}{0.1} = 23.32 \text{ mho cm}^2 \text{ mol}^{-1}$.

H-2. $\Lambda_{\text{eq}} = 97.1 \text{ Scm}^2 \text{ eq}^{-1}$, $C = 0.1 \text{ N}$
 $A = 1.5 \text{ cm}^2$, $l = 0.5 \text{ cm}$
 $\Lambda_{\text{eq}} = \frac{1000 \times \left(\frac{1}{R} \times \frac{l}{A}\right)}{C} \Rightarrow 97.1 = \frac{1000}{0.1} \times \frac{1}{R} \times \frac{0.5}{1.5}$
 $R = 34.33 \Omega \Rightarrow i = \frac{V}{R} = \frac{5}{34.33} = 0.1456 \text{ amp}$

H-3. $C = 0.1 \text{ N}$, $K = 1.12 \times 10^{-2} \text{ Scm}^{-1}$, $R = 65 \Omega$
 $K = \frac{1}{R} \times \frac{l}{A}$ $\frac{l}{A} = \text{cell constant} = 1.12 \times 10^{-2} \times 65 = 0.728 \text{ cm}^{-1}$

I-1. $\Lambda_m^\circ(\text{NH}_4\text{Cl}) = 150 = \Lambda_m^\circ(\text{NH}_4^+) + \Lambda_m^\circ(\text{Cl}^-)$
 $\Lambda_{\text{OH}^-}^\circ = 198$, $\Lambda_{\text{Cl}^-}^\circ = 76$, $\Lambda_m(\text{NH}_4\text{OH}) = 9.6$, $C = 0.01$
 $\Lambda_m^\circ(\text{NH}_4\text{OH}) = 150 - 76 + 198 = 272$
 $\alpha = \frac{\Lambda_m(\text{NH}_4\text{OH})}{\Lambda_m^\circ(\text{NH}_4\text{OH})} = \frac{9.6}{272} = 0.0353$

I-2. $\Lambda_m(\text{NaA}) = 83 \text{ S cm}^2 \text{ mol}^{-1}$ $\Lambda_m(\text{NaCl}) = 127 \text{ S cm}^2 \text{ mol}^{-1}$ $\Lambda_m(\text{HCl}) = 426 \text{ S cm}^2 \text{ mol}^{-1}$
 $\Lambda_m(\text{HA}) = 83 + 426 - 127 = 382 \text{ S cm}^2 \text{ mol}^{-1}$.

I-3. $\alpha = \frac{7.36}{390.7}$ $K_a = C\alpha^2 = 0.05 \times \left(\frac{7.36}{390.7}\right)^2 = 1.77 \times 10^{-5} \text{ mol/lit}$

I-4. $K_{\text{AgCl}} = 2.28 \times 10^{-6} \text{ Scm}^{-1}$, $138.3 = \frac{1000 \times 2.28 \times 10^{-6}}{S}$
 $S = 1.65 \times 10^{-5}$ and $K_{\text{sp}} = (S)^2 = 2.72 \times 10^{-10} \text{ M}^2$.

PART - II

- A-1.** In galvanic cell/electro chemical cell electrical energy is produced due to some chemical reaction.
A-2. Salt bridge complete the electrical circuit and minimises the liquid-liquid junction potential.
A-3. Agar-Agar is a gelatin, it used in salt bridge along with KCl electrolyte.



A-4. $E_{\text{cell}} = E^{\circ}_{\text{Ni} / \text{Ni}^{2+}} + E^{\circ}_{\text{Ag}^{+} / \text{Ag}}$
 $= 0.25 + 0.80 = \mathbf{1.05 \text{ Volt}}$

B-1. E° is intensive property and it does not depend on mass of F_2 taking part.

B-2. Lowest S.R.P., highest reducing power.

B-3. $E^{\circ}_{\text{Cu}^{2+} / \text{Cu}} = 0.34$ $E^{\circ}_{\text{Fe}^{2+} / \text{Fe}} = -0.44 \text{ volt}$
 So Cu can't displace Fe^{2+} .

B-4. Cu can't displace Al^{3+} ion from aluminium nitrate.

B-5. Lower S.R.P. containing ion can displace higher S.R.P. containing ion.

B-6. Lowest S.R.P., highest reducing power.

B-7. KCl can make precipitate with AgNO_3 , $\text{Pb}(\text{NO}_3)_2$ so can't be used along these electrolyte.

C-1. $\text{Fe}^{3+} + 3\text{e}^{-} \longrightarrow \text{Fe}$, -0.036 volt
 $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^{-}$ 0.44 volt
 $\text{Fe}^{3+} + \text{e}^{-} \longrightarrow \text{Fe}^{2+}$
 $+ 3 \times 0.036 - 2 \times 0.44 \times f = -1 \times E^{\circ} \times f$
 $E^{\circ} = \mathbf{0.772 \text{ Volt}}$

C-2. $\text{Cu}^{+} + \text{e}^{-} \longrightarrow \text{Cu}$, $E^{\circ} = x_1 \text{ Volt}$
 $\text{Cu}^{2+} + 2\text{e}^{-} \longrightarrow \text{Cu}$, $x_2 \text{ Volt}$
 $\text{Cu} \longrightarrow \text{Cu}^{+} + \text{e}^{-}$ $-x_1 \text{ Volt}$
 $\text{Cu}^{2+} + \text{e}^{-} \longrightarrow \text{Cu}^{+}$
 $-2 \times x_2 \times f + 1 \times x_1 \times f = -1 \times E^{\circ} \times f$
 $E^{\circ} = \mathbf{2x_2 - x_1}$

C-3. For spontaneous reaction in every condition
 $E_{\text{cell}} > 0$, $\Delta G < 0$ and Q (reaction quotient) $< K$ (equilibrium constant).

D-1. $E = 1.1 - \frac{0.0591}{2} \log \frac{0.1}{0.1} \Rightarrow \mathbf{E = 1.10 \text{ Volt}}$

D-2. $\text{H}_2(\text{Pt}) (1 \text{ atm}) | \text{H}_3\text{O}^{+} || \text{Ag}^{+}(\text{xM}) | \text{Ag}$

$$1.0 = (0 + 0.8) - \frac{0.06}{1} \log \frac{[\text{H}^{+}]}{x}$$

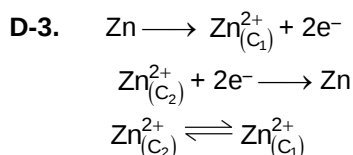
$$-\frac{0.2}{0.06} = \log \frac{[\text{H}^{+}]}{x}$$

$$\frac{10}{3} = \text{pH} + \log x$$

$$\log x = -1.7$$

$$\frac{10^{-5.5}}{x} = 1.62 \times 10^{-4}$$

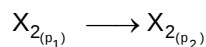
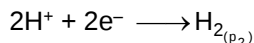
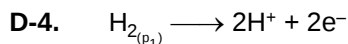
$$\mathbf{x = 2 \times 10^{-2} \text{ M}}$$





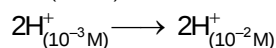
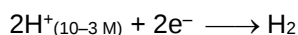
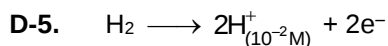
$$E = 0 - \frac{0.0591}{2} \log \frac{C_1}{C_2}$$

$E \rightarrow +ve$ When $C_1 < C_2$



$$E = 0 - \frac{0.0591}{2} \log \frac{p_2}{p_1}$$

$P_2 < P_1$ for $E \rightarrow +ve$



$$E = 0 - \frac{0.0591}{2} \log \left(\frac{10^{-1}}{10^{-2}} \right)^2$$

$E \rightarrow -ve$ (Non spontaneous).

D-6. $E = 0 - \frac{0.0591}{2} \log \frac{16}{4} = - \frac{0.0591}{2} \times 2 \log 2 = - 0.0591 \times 0.301 = - 0.0178 \text{ Volt.}$

If connected in reverse direction, $E = 0.0178 \text{ volt.}$



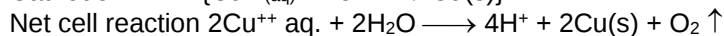
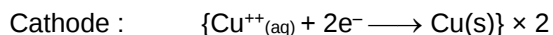
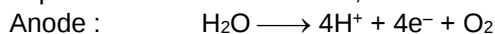
So conc. of Ag^+ will remain same.

E-2. equivalence of H_2 = equivalence of O_2

$$\frac{0.224}{22.4} \times 2 = \frac{\text{volume of } O_2}{22.4} \times 4$$

0.112 litre = volume of O_2 .

E-5. In presence of inert electrode, the cell reaction is -



Due to increases in $[H^+]$, pH decreases.

$\therefore$ (B) is answer



(1 mole)

5 mole e^- = 5 Faraday.

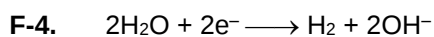
F-2. Mole of Fe deposited = $\frac{1}{2} \times 3 = 1.5 \text{ mole}$

$$W_{Fe} = 1.5 \times 56 = 84 \text{ g.}$$

F-3. $W = \frac{63.5}{2 \times 96500} \times 2 \times 60 \times 60 = 2.37 \text{ g}$

$$\% \text{ of efficiency} = \frac{3}{2.37} \times 100.$$





$$\text{No. of Faraday passed} = \frac{9.65 \times 1000}{96500} = 0.1 \text{ F}$$

$$n_{\text{OH}^-} \text{ formed} = 0.1 \text{ mol}$$

$$n\text{NaOH} = 0.1 \text{ mol} \equiv \mathbf{4 \text{ g.}}$$

F-5. According to Faraday's second law

$$\frac{\text{mass of A}}{\text{equivalent mass of A}} = \frac{\text{mass of B}}{\text{equivalent mass of B}} = \frac{\text{mass of C}}{\text{equivalent mass of C}}$$

$$\frac{4.5}{15/n_1} = \frac{2.7}{27/n_2} = \frac{9.6}{48/n_3}$$

$$0.3n_1 = 0.1n_2 = 0.2n_3 = k$$

$$n_1 = \frac{10}{3}k$$

$$n_2 = 10k$$

$$n_3 = 5k$$

$$n_1 : n_2 : n_3 = \frac{10}{3} : 10 : 5 = \frac{1}{3} : 1 : \frac{1}{2} = 2 : 6 : 3$$

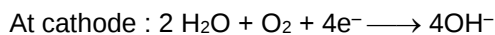
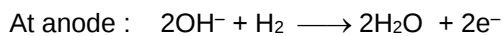
$$0.3 : 0.1 : 0.2$$

$$3 : 1 : 2$$

G-1. Discharging reaction



G-2. $\text{H}_2\text{-O}_2$ fuel cell



H-1. For strong electrolyte

$$\Lambda_M^c = \Lambda_M^\infty - b\sqrt{C}$$

H-2. Molar conductivity $\propto$ no. of ions per mole of electrolyte.

I-1. $K_a = 25 \times 10^{-6}$ $\wedge_{\text{eq}} = 19.6 \text{ Scm}^2 \text{ eq}^{-1}$, $C = 0.01$

$$K_a = 0.01 \times \alpha^2 \quad \Rightarrow \quad \alpha = \sqrt{\frac{25 \times 10^{-6}}{10^{-2}}} = 5 \times 10^{-2}$$

$$\alpha = 5 \times 10^{-2} = \frac{19.6}{\wedge_{\text{eq}}^\circ} \quad \Rightarrow \quad \wedge_{\text{eq}}^\circ = \frac{19.6}{5 \times 10^{-2}} = 392 \text{ Scm}^2 \text{ eq}^{-1}.$$

I-2. $1.53 = \frac{1000 \times 3.06 \times 10^{-6}}{\text{Normality}}$

$$\text{Normality} = 2 \times 10^{-3} \text{ M}$$

$$\text{Molarity} = \frac{2 \times 10^{-3}}{2} = 10^{-3} \text{ M}$$

$$K_{\text{sp}} = 10^{-6} \text{ M}$$

I-3. $K_a = C\alpha^2 = 0.1 \times \left(\frac{7}{380.8}\right)^2 = \mathbf{3.38 \times 10^{-5}}$





I-4. $K = 1.382 \times 10^{-6} \text{ s cm}^{-1}$

$$\Lambda_{\text{AgCl}} = 61.9 + 76.3 = 138.2 = \frac{1000 \times 1.382 \times 10^{-6}}{S} \Rightarrow S = 10^{-5} \text{ M.}$$

I-5. $\Lambda_{\text{m, BaSO}_4} = (X_1 + X_2 - 2X_3) \Rightarrow \Lambda_{\text{eq, BaSO}_4} = \frac{\Lambda_{\text{eq, BaSO}_4}}{n - \text{factor}}$

$$\Lambda_{\text{eq, BaSO}_4} = \frac{(X_1 + X_2 - 2X_3)}{2}$$

PART - III

1. (A) $E^\circ_{\text{Zn}^{2+}/\text{Zn}} > E^\circ_{\text{Mg}^{2+}/\text{Mg}}$ SO $E^\circ_{\text{cell}} = -\text{ve}$
 (B) $E^\circ_{\text{Ag}^+/\text{Ag}} > E^\circ_{\text{Zn}^{2+}/\text{Zn}}$ SO $E^\circ_{\text{cell}} = +\text{ve}$
 (C) $E^\circ_{\text{Ag}^+/\text{Ag}} > E^\circ_{\text{Zn}^{2+}/\text{Zn}}$ SO $E^\circ_{\text{cell}} = 0$ (at equilibrium)
 (D) $E^\circ_{\text{Ag}^+/\text{Ag}} > E^\circ_{\text{Fe}^{2+}/\text{Fe}}$ SO $E^\circ_{\text{cell}} = +\text{ve}$

2. (A) $E_{\text{cell}} = -\frac{0.059}{2} \log \frac{(P_{\text{H}_2})_c [\text{H}^+]_a^2}{(P_{\text{H}_2})_a [\text{H}^+]_c^2}$,
 $E_{\text{cell}}^\circ = -\frac{0.059}{2} \log \frac{0.01 \times (0.1)^2}{(0.1) \times (1)^2} = \frac{0.059}{2} \times 3 = +\text{ve}$
 (B) Cell reaction $\text{Ag}^+_c (10^{-2}) \rightarrow \text{Ag}^+_a (10^{-9})$
 $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{1} \log \frac{10^{-9}}{10^{-2}} = E_{\text{cell}}^\circ + \frac{0.059}{1} \times 7 > 0$
 $E_{\text{cell}}^\circ \neq 0$ and not conc. cell
 (C) $E_{\text{cell}} = 0 - \frac{0.059}{2} \log \frac{[\text{Cu}^{+2}]_a}{[\text{Cu}^{+2}]_c} = -\frac{0.059}{2} \log \frac{0.1}{0.01} = -\text{ve}$
 (D) $E_{\text{cell}} = -\frac{0.059}{2} \log \frac{[\text{Cl}^-]_c}{[\text{Cl}^-]_a} = \frac{0.059}{2} \log \frac{0.1}{0.1} = 0$
 And $E_{\text{cell}}^\circ = 0$.

EXERCISE # 2

PART - I

1. As $E^\circ_{\text{Cu}^{2+}} \longrightarrow \text{Cu} = 0.337 \text{ V} > E^\circ_{\text{H}^+/\text{H}_2}$
 $\therefore \text{Cu}^{2+}$ can be reduced by H_2 .
2. Lower standard reduction potential related metal ions can displace higher standard reduction potential related metal ions.
3. (C) M is more reactive than carbon and B is more reactive than A. Also both B and A are less reactive than C.
4. Only anode or cathode can't work alone so absolute value of reduction potential can't be determined.



5. $E_1 = E^0 - \frac{R}{n} \frac{T}{F} \ln 2$

$$E_2 = E^0 - \frac{R}{n} \frac{\times 2T}{F} \ln 1 = E^0$$

$$\therefore E_2 > E_1$$

6. $E_{\text{cell}} = 0.059 \log \frac{C_1}{C_2}$

For E_{cell} to be +ve and maximum

$$\frac{C_1}{C_2} < 1$$

$$\text{or } C_1 < C_2$$

$$\text{Give } C_2 = 1M.$$

$\therefore C_1$ should be the minimum conc. of H^+ .

$\therefore$ (B) is the right answer.

7. $E_{\text{cell}} = \frac{0 - 0.059}{1} \log \sqrt{\frac{10^{-5}}{10^{-3}}} = 0.059 \text{ V}$

8. $E_1 = -\frac{0.059}{1} \log [H^+]$

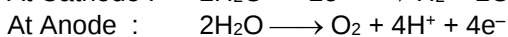
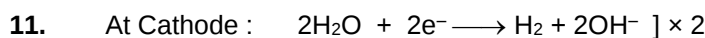
$$\text{or } pH_1 = E_1 / 0.059 = pK_a + \log \frac{x}{y}$$

$$pH_2 = E_2 / 0.059 = pK_a + \log \frac{y}{x}$$

$$\text{or } \frac{E_1 + E_2}{0.059} = 2 pK_a \quad \text{or } pK_a = \frac{E_1 + E_2}{0.118}$$

9. $E_{\text{cell}} = (0.77 - 0.0713) - \frac{0.059}{1} \log \frac{0.02}{0.1 \times 0.34} = 0.713 \text{ volt.}$

10. Impure Cu will oxidise from anode along with Zn but only Cu^{2+} will reduce on cathode in purification of Cu^{2+} .



$H_2 = 2 \text{ mole}$

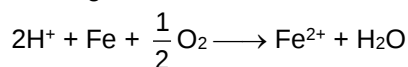
$O_2 = 1 \text{ mole}$ Total volume = $3 \times 22.4 = 67.2 \text{ L.}$

12. $\frac{1000 \times 2}{(55 + 32)} = \frac{27 \times 24 \times 3600 \times \eta}{96500} \quad \text{or } \eta = 0.951 = 95.1\%$

13. $\frac{9.72}{22.4} \times 2 = \frac{2.35}{22.4} \times 4 + \frac{W}{194} \times 2 \quad \text{or } W = 43.47 \text{ g}$

14. After removing cathode no net charge will flow but ions move randomly.

15. Rusting reaction of Fe is -





PART - II

1. (A) H_4XeO_6 has more SRP, so better oxidizing agent than F_2
 (B) O_3 has more SRP, so will oxidize Cl_2
 (C) $E^\circ_{\text{ClO}_4^-/\text{ClO}_3^-}$ is more in acidic medium than in basic medium
 (D) $E^\circ_{[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}} = 0.36 \text{ V}$
 Hence $[\text{Fe}(\text{CN})_6]^{4-}$ can be easily oxidized by ClO^- , Ce^{4+} , Br_2O^- but not by Li^+
 (E) $E^\circ_{\text{ClO}^-/\text{Cl}^-(\text{OH}^-)}$ is more than $E^\circ_{\text{BrO}^-/\text{Br}^-}$ and $E^\circ_{\text{ClO}_4^-/\text{ClO}_3^-(\text{OH}^-)}$ so true.
 (F) Ce^{4+} can't oxidize Cl_2 in acidic medium.

2. $\text{H}_2 \longrightarrow 2\text{H}^+ + 2\text{e}^-$
 1 atm 10^{-10}

$$E_{\text{H}_2/\text{H}^+} = 0 - \frac{0.059}{2} \log \frac{(10^{-10})^2}{1} \Rightarrow E_{\text{H}_2/\text{H}^+} = +0.59 \text{ V}$$

3. $\text{Cu}^{2+} + 4\text{NH}_3 \longrightarrow [\text{Cu}(\text{NH}_3)_4]^{2+}$
 $\begin{array}{ccc} 1 & a & 0 \\ 0 & 2 & 1 \end{array}$

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}] [\text{NH}_3]^4}$$

$$\text{or } 1 \times 10^{12} = \frac{1}{[\text{Cu}^{2+}] (2)^4} \text{ or } [\text{Cu}^{2+}] = 6.25 \times 10^{-14}.$$

$$\text{Now, } E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1.1 - \frac{0.059}{2} \log \frac{1}{6.25 \times 10^{-14}} = 0.71 \text{ V}.$$

4. $\lambda_m = \frac{K \times 1000}{M}$

$$200 = \frac{K \times 1000}{0.04}$$

$$K = \frac{200 \times 0.04}{1000} = 8 \times 10^{-3} \text{ S cm}^{-1}.$$

$$K = \left(\frac{\ell}{9} \right) \times \frac{1}{R}$$

$$8 \times 10^{-3} = \left[\frac{8}{4} \right] \times \frac{1}{R}$$

$$R = \frac{2}{8 \times 10^{-3}} = \frac{1}{4} \times 10^3 \Omega.$$

$$\text{Again } \Rightarrow V = IR$$

$$\text{So } I = \frac{V}{R} = \left(\frac{10}{\frac{1}{4} \times 10^3} \right) = 4 \times 10^{-2} \text{ A}.$$

5. $K_{\text{sol}} = K_{\text{Ba}^{2+}} + K_{\text{Ag}^+} + K_{\text{NO}_3^-}$

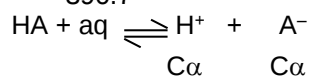
$$5.3 = \frac{\lambda_{\text{Ba}^{2+}}^0 \times [\text{Ba}^{2+}]}{10^{-3}} + \frac{\lambda_{\text{Ag}^+}^0 \times [\text{Ag}^+]}{10^{-3}} + \frac{\lambda_{\text{NO}_3^-}^0 \times [\text{NO}_3^-]}{10^{-3}}$$



$$\therefore 5.3 = \frac{13 \times 10^{-3} \times 0.1}{10^{-3}} + \frac{6 \times 10^{-3} \times 0.2}{10^{-3}} + \frac{\lambda_{(\text{NO}_3^-)}^0 \times 0.4}{10^{-3}}$$

$$\therefore \lambda_{(\text{NO}_3^-)}^0 = 7 \times 10^{-3} \times 1000 \text{ Sm}^2 \text{mol}^{-1} = 7 \text{ Sm}^2 \text{mol}^{-1}$$

$$6. \quad \alpha = \frac{3.907}{390.7} = 0.1$$



$$\text{C}\alpha - \text{C}\alpha$$

$$[\text{H}^+] = \text{C}\alpha = 0.01 \times 0.01 = 10^{-4}$$

$$\text{pH} = -\log [\text{H}^+] = 4$$

$$7. \quad \lambda^0 = \frac{1000 \times (\kappa_{\text{sol}} - \kappa_{\text{H}_2\text{O}})}{S}$$

$$138 = \frac{1000 \times (3.4 - 2.02) \times 10^{-6}}{S}$$

$$S = 1 \times 10^{-5}$$

$$8. \quad \lambda_m^0 (\text{H}_2\text{O}) = \frac{\lambda_m^0 (\text{Ba}(\text{OH})_2) + 2 \lambda_m^0 (\text{HCl}) - \lambda_m^0 (\text{BaCl}_2)}{2}$$

$$= 5.5 \times 10^{-2} \text{ S m}^2 \text{mol}^{-1}.$$

Now, in SI units,

$$\lambda_m^0 = \frac{K \times 10^{-3}}{M} \quad \therefore \lambda_m^0 (\text{H}_2\text{O}) = \frac{K \times 10^{-3}}{[\text{H}_2\text{O}]_{\text{diss}}}$$

$$5.5 \times 10^{-2} = \frac{5.5 \times 10^{-6} \times 10^{-3}}{[\text{H}_2\text{O}]_{\text{diss}}}$$

$$[\text{H}_2\text{O}]_{\text{diss}} = [\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$$

For equilibrium : $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

$$\text{Dissociation constant } K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{10^{-7} \times 10^{-7}}{\left(\frac{1000}{18}\right)}$$

$$= 1.8 \times 10^{-16}$$

Reported answer = 18

9. H_3O^+ has highest Λ_m^∞ among cations. A doubly charged cation has higher Λ_m^∞ than unipositive cation.

PART - III

- Lower S.R.P. containing ion can displace higher S.R.P. containing ion.
- $\Delta G^\circ = -nFE^\circ_{\text{cell}}$
If $E^\circ_{\text{cell}} = +\text{ve}$ then $\Delta G^\circ = -\text{ve}$ and reaction is spontaneous.
- | | |
|-----------|--|
| (A) Anode | $2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ |
| (B) Anode | $2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ |
| (C) Anode | $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{e}^-$ |
| (D) Anode | $2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ |



5. At Cathode : $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu(s)}$
 At Anode : $\text{Cu (s)} \longrightarrow \text{Cu}^{2+} + 2\text{e}^-$

$$\text{Increase in mass of cathode} = \text{decrease in mass of Anode} = \frac{2.68 \times 3600}{96500} \times \frac{63.5}{2} = 3.174 \text{ g.}$$

6.

	Ag	Cu	Au
equivalent ratio	1	1	1
Mole ratio	$\frac{1}{1}$	$\frac{1}{2}$	$\frac{1}{3}$
	6	3	2.

7. $\text{Fe}^{2+} + 2\text{e}^- \longrightarrow \text{Fe [in FeSO}_4\text{]} ; \quad \text{Fe}^{3+} + 3\text{e}^- \longrightarrow \text{Fe [in Fe}_2\text{(SO}_4\text{)}_3\text{]}$
 $\text{Fe}^{3+} + 3\text{e}^- \longrightarrow \text{Fe [in Fe (NO}_3\text{)}_3\text{]}$

$$\text{Amount of Fe deposited in FeSO}_4 = \frac{Q}{96500} \times \frac{56}{2}$$

$$\text{Amount of Fe deposited in Fe}_2\text{(SO}_4\text{)}_3 = \frac{Q}{96500} \times \frac{56}{3}$$

8. **Anode** : Pb(s)

Cathode : $\text{PbO}_2\text{(s)}$

$\text{H}_2\text{SO}_4\text{(conc.)}$ about 38% solution of H_2SO_4 is taken.

Anode : $\text{Pb(s)} \longrightarrow \text{Pb}^{2+} \text{(aq)} + 2\text{e}^-$

$\text{Pb}^{2+}\text{(aq)} + \text{SO}_4^{2-} \text{(aq)} \longrightarrow \text{PbSO}_4\text{(s)}$

$\text{Pb(s)} + \text{SO}_4^{2-} \text{(aq)} \longrightarrow \text{PbSO}_4 + 2\text{e}^-$

most of the $\text{PbSO}_4\text{(s)}$ ppt sticks to the lead rod.

Cathode : $2\text{e}^- + 4\text{H}^+ + \text{PbO}_2\text{(s)} \longrightarrow \text{Pb}^{2+}\text{(aq)} + 2\text{H}_2\text{O(l)}$

$\text{Pb}^{2+}\text{(aq)} + \text{SO}_4^{2-} \text{(aq)} + 4\text{H}^+ + 2\text{e}^- \longrightarrow \text{PbSO}_4\text{(s)} + 2\text{H}_2\text{O(l)}$

$\text{PbSO}_4\text{(s)}$ sticks to cathode rod.

Over all reaction : $\text{Pb(s)} + \text{PbO}_2 \text{(s)} + 2\text{H}_2\text{SO}_4 \text{(aq)} \longrightarrow 2\text{PbSO}_4\text{(s)} + 2\text{H}_2\text{O(l)}$, $E_{\text{cell}} = 2.05 \text{ V}$

9. Resistance of cell is not due to vibrations of ion but actually it is due to collisions of ions.

11. $\kappa \propto C$

$$\text{Hence } \kappa_1 = a \times 0.1$$

$$\kappa_2 = a \times 0.01$$

$$\kappa_3 = a \times 0.005$$

$$\kappa_4 = a \times 0.0025$$

$$G = \frac{\kappa}{\text{cell constant}}$$

$$\text{So, } G_1 = \frac{a \times 0.1}{1} = 0.1 \text{ a} ; \quad G_2 = \frac{a \times 0.01}{10} = 0.001 \text{ a}$$

$$G_3 = \frac{a \times 0.005}{.5} = 0.001 \text{ a} ; \quad G_4 = \frac{a \times 0.0025}{25} = 0.0001 \text{ a}$$

$$\text{Hence } G_1 > G_2 = G_3 > G_4$$

13. $\lambda_{\text{eq}}^\circ = \frac{\lambda_m^\circ}{V_f}$

V_f for cation/anion – charge; V_f for salt = total cationic/anionic charge

$$\text{Also, } \lambda_m^\circ (\text{Al}_2(\text{SO}_4)_3) = 2 \lambda_m^\circ (\text{Al}^{3+}) + 3 \lambda_m^\circ (\text{SO}_4^{2-})$$

$$\& \lambda_{\text{eq}}^\circ (\text{Al}_2(\text{SO}_4)_3) = \lambda_{\text{eq}}^\circ (\text{Al}^{3+}) + \lambda_{\text{eq}}^\circ (\text{SO}_4^{2-})$$

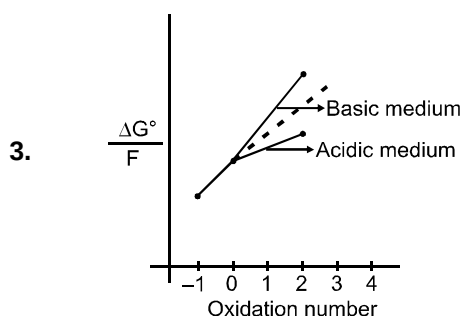


14. $\text{Li}^+ \text{Na}^+ \text{K}^+ \text{Rb}^+ \text{Cs}^+$
 degree of Hydration decreases
 Size of ions decreases
 ionic mobility increases
 $\text{H}^+_{(\text{aq})}$ has smallest size therefore show maximum mobility.

PART - IV

1. From given Latimer diagrams, $\text{Cl}_2 - \text{Cl}^-$ is independent of H^+ concentration.

2. $\Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ$, using this $E^\circ = \frac{0.42 + 1.36}{2} \text{ V} = 0.89 \text{ V}$



4. As $\frac{\Delta G^\circ}{F}$ is low, stability is higher.

5. As $\frac{\Delta G^\circ}{F}$ is low, stability is higher so, +2 and 0 state is more stable than +1.

6. $\lambda_m^C = \lambda_m^\infty - b\sqrt{C}$

when $C_1 = 4 \times 10^{-4}$ $\lambda_m^C = 107$

and when $C_2 = 9 \times 10^{-4}$ $\Lambda_m = 97$

so $107 = \lambda_m^\infty - b \times 2 \times 10^{-2}$... (1)

$97 = \lambda_m^\infty - b \times 3 \times 10^{-2}$... (2)

$b = 1000$

$\Lambda_m = \lambda_m^\infty - b\sqrt{C} \Rightarrow \lambda_m^\infty = \Lambda_m + b\sqrt{C} = 107 + 10^3 \times 2 \times 10^{-2}$

$\lambda_m^\infty = 127 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$

7. For $25 \times 10^{-4} \text{ (M) NaCl}$ solution

$\Lambda_m = \lambda_m^\infty - b\sqrt{C} \Rightarrow \Lambda_m = 127 - 10^3 (25 \times 10^{-4})^{1/2}$

$\Lambda_m = 127 - 10^3 \times 5 \times 10^{-2} \Rightarrow \Lambda_m = 77$

But $\Lambda_m = \frac{K \times 1000}{M}$ $K = \left(\frac{\ell}{a}\right) \times \frac{1}{R}$

$\Lambda_m = \left(\frac{\ell}{a}\right) \times \frac{1}{R} \times \frac{1000}{M}$

$\Lambda_m = [\text{Cell constant}] \times \frac{1000}{R \times M}$

$\Rightarrow 77 = [\text{Cell constant}] \times \frac{1000}{1000 \times 25 \times 10^{-4}}$

Cell constant = $77 \times 25 \times 10^{-4} = 0.1925 \text{ cm}^{-1}$



8. For Na_2SO_4 solution

$$K = \left(\frac{\ell}{a}\right) \times \frac{1}{R} = \frac{0.1925}{400} = 4.81 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\Lambda_m = \frac{K \times 1000}{M} = \frac{4.81 \times 10^{-4} \times 1000}{\frac{5}{2} \times 10^{-3}}$$

$$\Lambda_m (\text{Na}_2\text{SO}_4) = 192.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

9. At the equivalence point the concentrations will be $[\text{Br}^-] = 100 \text{ mol/m}^3$, $[\text{Na}^+] = 100 \text{ mol/m}^3$
Therefore $\kappa_{\text{total}} = \kappa_{\text{Br}^-} + \kappa_{\text{Na}^+} = 1.2 \text{ Sm}^{-1} = 12 \times 10^{-1} \text{ Sm}^{-1}$.

EXERCISE # 3

PART - I

1. MnO_4^- ion can oxidise both Fe^{2+} to Fe^{3+} as well as Cl^- to Cl_2 . So $\text{Fe}(\text{NO}_3)_2$ cannot be estimated quantitatively with MnO_4^- ion in HCl .

E°_{cell} for the cell $\text{Pt}, \text{Cl}_2(\text{g}) (1 \text{ atm}) | \text{Cl}^-(\text{aq}) || \text{MnO}_4^-(\text{aq}) | \text{Mn}^{2+}(\text{aq})$ is equal to $(1.51 - 1.4) = 0.11 \text{ V}$.

2. $E + 0.03 = E^\circ - \frac{0.06}{2} \log \frac{[\text{Zn}^{2+}]}{0.5}$.

$$E = E^\circ - \frac{0.06}{2} \log \frac{[\text{Zn}^{2+}]}{C}. \quad C = 0.05 \text{ M}.$$

3. $\text{Zn} | \text{Zn}^{2+} (0.01 \text{ M}) || \text{Fe}^{2+} (0.001 \text{ M}) | \text{Fe}$, $E = 0.2905$.
cell reaction, $\text{Zn} + \text{Fe}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Fe}$.

$$0.2905 = E^\circ - \frac{0.0591}{2} \log \frac{0.01}{0.001}.$$

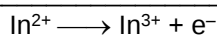
$$E^\circ = 0.32 \text{ Volt}.$$

At equilibrium, $E_{\text{cell}} = 0$.

$$0 = 0.32 - \frac{0.0591}{2} \log K_{\text{eq}}$$

$$K_{\text{eq}} = 10^{0.32/0.0295}.$$

4. $\text{In}^+ \longrightarrow \text{In}^{3+} + 2e^-$, 0.42 volt .
 $\text{In}^{2+} + e^- \longrightarrow \text{In}^+$, -0.4 volt .

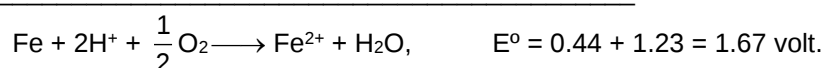


$$E^\circ = 0.44 \text{ volt}.$$

$$E^\circ_{\text{cell}} = 0.15 + 0.44 = 0.59 \text{ volt}.$$

$$0 = 0.59 - \frac{0.059}{1} \log K. \Rightarrow K = 10^{10}.$$

5. $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2e^-$, 0.44 V .
 $2\text{H}^+ + \frac{1}{2} \text{O}_2 + 2e^- \longrightarrow \text{H}_2\text{O}$, 1.23 V .



$$\Delta G^\circ = -2 \times 1.67 \times 96500 = -322.3 \text{ kJ}.$$



6. $2\text{Ag}^+ + \text{C}_6\text{H}_{12}\text{O}_6 + \text{H}_2 \longrightarrow 2\text{Ag(s)} + \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}^+$, $E^\circ = 0.8 - 0.05 = 0.75 \text{ volt.}$
 $0 = 0.75 - \frac{0.0592}{2} \log K.$
 $\ln K = 2.303 \times \log K = 2.303 \times 25.34 = 58.38.$
7. $[\text{H}^+] = 10^{-11} \text{ M.}$
 $E_{\text{oxide}} = -0.05 - \frac{0.0591}{2} \log(10^{-11})^2 = -0.05 + 0.65$
 or, $\Delta H = 0.65 \text{ volt.}$
8. Standards electrode potential does not depend upon on concentration.
9. $\text{AgBr(s)} \rightleftharpoons \text{Ag}^+ + \text{Br}^-$
 $(S + 10^{-7}) \times S = K_{\text{SP}} = 12 \times 10^{-14}.$
 $S = 3 \times 10^{-7} \text{ M.}$
 $[\text{Ag}^+] = 4 \times 10^{-7} \text{ M} ; [\text{Br}^-] = 3 \times 10^{-7} \text{ M} ; [\text{NO}_3^-] = 10^{-7} \text{ M.}$
 $K_{\text{total}} = \Lambda^\circ_{(\text{Ag}^+)} \Lambda^\circ_{(\text{Ag}^+)} + \Lambda^\circ_{\text{Br}^-} \Lambda^\circ_{\text{Br}^-} + \Lambda^\circ_{(\text{NO}_3^-)} \Lambda^\circ_{(\text{NO}_3^-)}$
 $\Lambda^\circ_{\text{KCl}} = \Lambda^\circ_{\text{K}^+} + \Lambda^\circ_{\text{Cl}^-}.$
 $K_{\text{KCl}} = 4 \times 10^{-4} \times 6 \times 10^{-3} + 3 \times 10^{-4} \times 8 \times 10^{-3} + 1 \times 10^{-4} \times 7 \times 10^{-3}.$
 $K_{\text{KCl}} = 24 + 24 + 7. \Rightarrow K_{\text{KCl}} = 55 \text{ Scm}^{-1}.$
10. Mol of NaCl = $4 \times 0.5 = 2 \text{ mol.}$
 No. of mole of Cl_2 evolved = $\frac{1}{2} \times \text{mol of NaCl} = \frac{1}{2} \times 2 = 1 \text{ mol.}$
11. Taking the 1 : 1 molar combination of Na–Hg amalgam.
 weight = $2 \times 23 + 2 \times 200 = 446 \text{ g.}$
12. $2\text{Na}^+ + 2\text{e}^- \longrightarrow 2\text{Na.}$
 No. of Faraday required = 2.
 $\therefore$ total charge = $2 \times 96500 = 193000 \text{ coulomb.}$
13. $\text{Cl}_2 + 2\text{I}^- \longrightarrow \text{I}_2 + 2\text{Cl}^-.$
 $E^\circ = 1.36 + (-0.54) = 0.82 \text{ V (+ve). Spontaneous.}$
14. $\text{Mn}^{3+} + \text{e}^- \longrightarrow \text{Mn}^{2+}, \quad 1.50 \text{ volt.}$
 $2\text{H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-, \quad 1.23 \text{ volt.}$
-
- $4\text{Mn}^{3+} + 2\text{H}_2\text{O} \longrightarrow 4\text{Mn}^{2+} + \text{O}_2 + 4\text{H}^+, \quad E_{\text{cell}} = 1.5 - 1.23 = 0.27 \text{ volt. (+ve).}$
 Mn^{3+} will oxidise $\text{H}_2\text{O}.$
15. Faraday law equivalents of H_2 produced = $\frac{I \times t (\text{sec})}{96500}$
 $0.01 \times 2 = \frac{10 \times 10^{-3} \times t}{96500} = 96500 \times 2 = t$
 $19.3 \times 10^4 \text{ sec} = t$
16. The species having less reduction potential with respect to NO_3^- ($E^\circ = 0.96 \text{ V}$) will be oxidised by NO_3^- .
 These species are V, Fe, Hg.
17. $\text{M(s)} | \text{M}^+ (\text{aq}, 0.05 \text{ M}) || \text{M}^+ (\text{aq}, 1 \text{ M}) | \text{M(s)}$
 Anode : $\text{M(s)} \longrightarrow \text{M}^+ (\text{aq}) + \text{e}^-$
 Cathode : $\text{M}^+ (\text{aq}) + \text{e}^- \longrightarrow \text{M(s)}$
-
- $\text{M}^+ (\text{aq}) |_{\text{c}} \rightleftharpoons \text{M}^+ (\text{aq}) |_{\text{a}}$



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{1} \log \frac{M^{+}(\text{aq})|_a}{M^{+}(\text{aq})|_c}$$

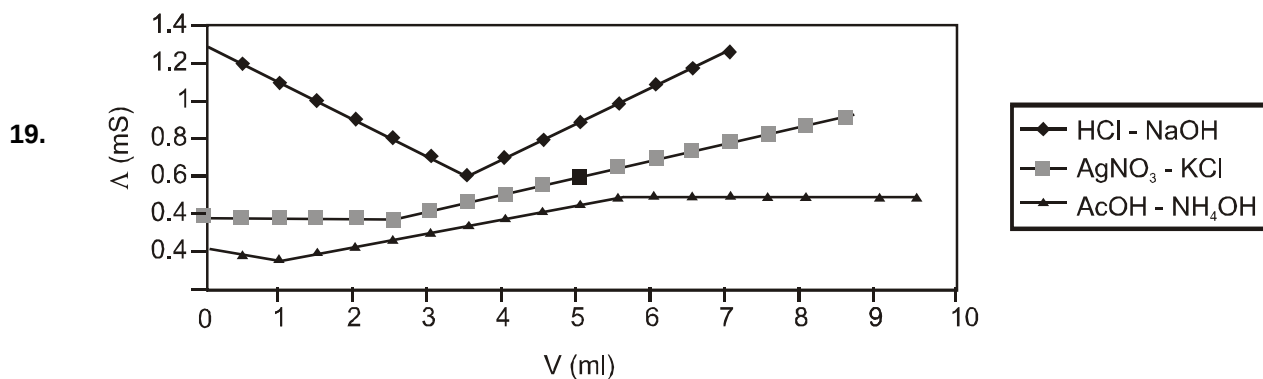
$$= 0 - \frac{0.0591}{1} \log \left\{ \frac{0.05}{1} \right\}$$

$$= +ve = 70 \text{ mV and hence } \Delta G = -nFE_{\text{cell}} = -ve.$$

18. $E_{\text{cell}} = \frac{-0.0591}{1} \log \left\{ \frac{0.0025}{1} \right\} = -\frac{0.0591}{1} \log \left\{ \frac{0.05}{20} \right\}$

$$= 70 \text{ mV} + \frac{0.0591}{1} \log 20 = 140 \text{ mV}.$$

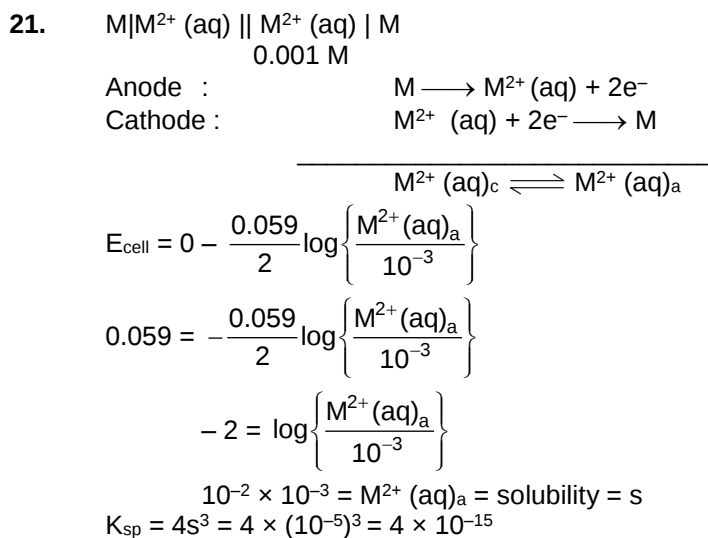
Typical titration curves



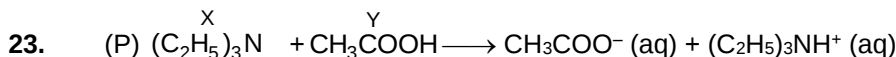
20. $E = E^{\circ} - \frac{0.059}{4} \log \frac{[\text{Fe}^{2+}]^2}{[\text{H}^{+}]^4 \text{P}_{\text{O}_2}}$

$$= 1.67 - \frac{0.06}{4} \log \frac{(10^{-3})^2}{(10^{-3})^4 \times 0.1} = 1.67 - \frac{0.03}{2} \log 10^7$$

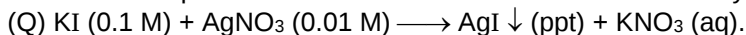
$$= 1.67 - \frac{0.03}{2} \times 7 = 1.67 - 0.105 = 1.565 = 1.57 \text{ V}.$$



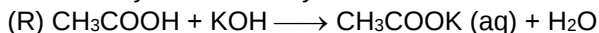
22. $\Delta G = -nFE_{\text{cell}} = -2 \times 96500 \times 0.059 \times 10^{-3} \text{ kJ/mole}$
 $= -11.4 \text{ kJ/mole}.$



As CH_3COOH is a weak acid, its conductivity is already less. On addition of weak base, acid-base reaction takes place and new ions are created. So conductivity increases.



As the only reaction taking place is precipitation of AgI and in place of Ag^+ , K^+ is coming in the solution, conductivity remain nearly constant and then increases.

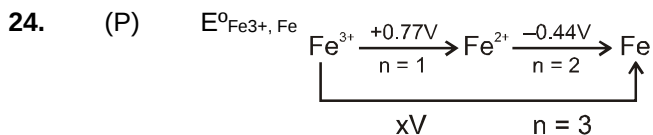


OH^- (aq) is getting replaced by CH_3COO^- , which has poorer conductivity. So conductivity decreases and then after the end point, due to common ion effect, no further creation of ions take place. So, conductivity remain nearly same.



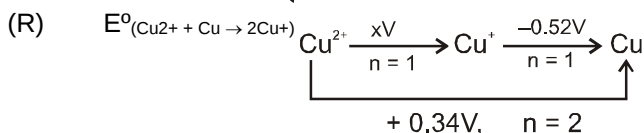
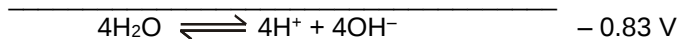
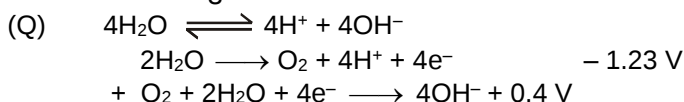
As H^+ is getting replaced by Na^+ conductivity dereases and after end point, due to OH^- , it increases.

So answer of 39 is : (P) – (3) ; (Q) – (4) ; (R) – (2); (S) – (1). Answer is (D).



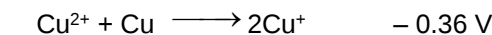
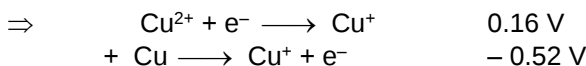
$$\Rightarrow 1 \times 0.77 + 2 \times (-0.44) = 3 \times x$$

$$\Rightarrow x = -\frac{0.11}{3} \text{ V} \sim -0.04 \text{ V}.$$

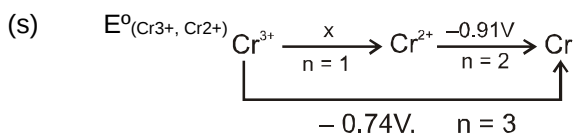


$$x \times 1 + 0.52 \times 1 = 0.34 \times 2$$

$x = 0.16 \text{ V.}$



However, in the given option, -0.18 V is printed.



$$x \times 1 + 2 \times (-0.91) = 3 \times (-0.74)$$

$$x - 1.82 = -2.22 \quad \Rightarrow \quad x = -0.4 \text{ V}$$

Hence, most appropriate is (D).

(P) – (3) ; (Q) – (4) ; (R) – (1) ; (S) – 2.

- 25.** Salt bridge is introduced to keep the solutions of two electrodes separate, such that the ions in electrode do not mix freely with each other. But it cannot stop the process of diffusion. It does not participate in the chemical reaction. However, it is not necessary for occurrence of cell reaction, as we know that designs like lead accumulator, there was no salt bridge, but still reactions takes place.



26. $m^+ \longrightarrow m^{3+} + 2e^-$
 $\Delta G^0 = -nFE^0$ For 1 mole of m^+
 $\Delta G^0 = -2 \times 96500 \times (-0.25) \text{ J}$
 $= + 48250 \text{ J/mole} = 48.25 \text{ KJ/mole}$
 Energy released by conversion of 1 mole of
 $x \longrightarrow y \quad \Delta G = -193 \text{ KJ}$
 Hence mole of m^+ convert
 $\frac{193}{48.25} = 4$

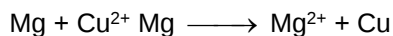
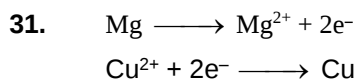
27. $\lambda_{X^-}^\circ \approx \lambda_{Y^-}^\circ$
 $\Rightarrow \lambda_{H^+}^\circ + \lambda_{X^-}^\circ \approx \lambda_{H^+}^\circ + \lambda_{Y^-}^\circ$
 $\Rightarrow \lambda_{HX}^\circ \approx \lambda_{HY}^\circ \quad (1)$
 Also $\frac{\lambda_m}{\lambda_m^\circ} = \alpha$, So $\lambda_m(HX) = \lambda_m^\circ \alpha_1$ and $\lambda_m(HY) = \lambda_m^\circ \alpha_2$
 (Where α_1 and α_2 are degrees of dissociation of HX and HY respectively.)
 Now, Given that
 $\lambda_m(HY) = 10 \lambda_m(HX)$.
 $\Rightarrow \lambda_m^\circ \alpha_2 = 10 \times \lambda_m^\circ \alpha_1$
 $\alpha_2 = 10 \alpha_1 \quad (2)$
 $K_a = \frac{C\alpha^2}{1-\alpha}$, but $\alpha \ll 1$, therefore $K_a = C\alpha^2$.
 $\Rightarrow \frac{K_a(HX)}{K_a(HY)} = \frac{0.01\alpha_1^2}{0.1\alpha_2^2} = \frac{0.01}{0.1} \times \left(\frac{1}{10}\right)^2 = \frac{1}{1000}$.
 $\Rightarrow \log(K_a(HX)) - \log(K_a(HY)) = -3. \quad \Rightarrow \quad pK_a(HX) - pK_a(HY) = 3.$

28. $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2} \log_{10} \frac{[M^{2+}][H^+]^2}{[M^{4+}]pH_2}$
 $0.092 = 0.151 - \frac{0.059}{2} \log_{10} 10^x$
 $\therefore x = 2$

29. $C = 0.0015M$ $\ell = 120 \text{ cm}$
 $G = 5 \times 10^{-7}S$ $a = 1 \text{ cm}^2$
 $G = \kappa \times \frac{a}{\ell}$
 $5 \times 10^{-7} = \kappa \times \frac{1}{120}$
 $\kappa = 6 \times 10^{-5} \text{ S cm}^{-1}$
 $\Lambda_m^c = \frac{\kappa \times 1000}{M} = \frac{6 \times 10^{-5} \times 1000}{0.0015}$
 $pH = 4$
 $[H^+] = 10^{-4} = c \alpha = 0.0015 \alpha$
 $\alpha = \frac{10^{-4}}{0.0015}$
 $\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} \Rightarrow \frac{10^{-4}}{0.0015} = \frac{6 \times 10^{-5} \times 1000}{\Lambda_m^0}$
 $\Lambda_m^0 = 6 \times 10^2 \text{ S cm}^2 \text{ mole}^{-1}$



30. $\Delta G = \Delta G^\circ + 2.303 RT \log_{10} Q$; $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$
 $= -2F(1.1) + 2.303 RT \log_{10} 10$
 $= 2.303 RT - 2.2 F$

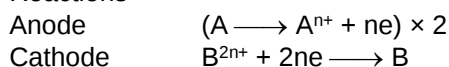
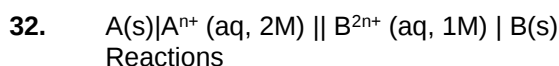


$$E = 2.67 = 2.7 - \frac{RT}{nF} \ln \frac{x}{1}$$

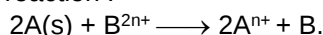
$$0.03 = \frac{300}{2 \times 11500} \ln x$$

$$2.3 = \ln x$$

$$x = 10$$



Overall reaction :



$$E = E^\circ - \frac{RT}{2nF} \ln Q$$

$$0 = E^\circ - \frac{RT}{2nF} \ln \frac{[A^{n+}]^2}{[B^{2n+}]}$$

$$E^\circ = \frac{RT}{2nF} \ln 4$$

Now $\Delta G^\circ = -2nFE^\circ = \frac{-2nFRT}{2nF} \ln 4 = -RT \ln 4.$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 2\Delta G^\circ = -T\Delta S^\circ$$

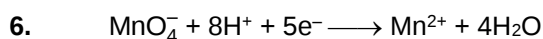
$$T\Delta S^\circ = \Delta G^\circ$$

$$\Delta S^\circ = \frac{\Delta G^\circ}{T} = \frac{-RT \ln 4}{T} = -R \ln 4$$

$$= -8.3 \times 2 \times 0.7 = -11.62 \text{ JK}^{-1}\text{mol}^{-1}$$

PART - II

5. Electrons flow from anode to cathode always.



$$E = 1.51 - \frac{0.059}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

Taking Mn^{2+} and MnO_4^- in standard state i.e. 1 M,

$$E = 1.51 - \frac{0.059}{5} \times 8 \log \frac{1}{[H^+]} = 1.51 - \frac{0.059}{5} \times 8 \times 3 = 1.2268 \text{ V}$$

Hence at this pH, MnO_4^- will oxidise only Br^- and I^- as SRP of Cl_2/Cl^- is 1.36 V which is greater than that for MnO_4^-/Mn^{2+} .

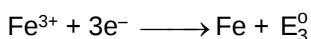
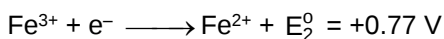
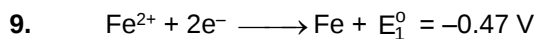


7. If a block of copper metal is dropped into a beaker containing solution of 1 M ZnSO_4 , no reaction will occur because $E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V}$

$$E_{\text{Cu}^{2+}/\text{Cu}}^0 = +0.34 \text{ V}$$

Hence Cu can't displace Zn from ZnSO_4 solution.

8. Fact



$$E_3^0 = \frac{n_1 E_1^0 + n_2 E_2^0}{n_1 + n_2} = \frac{2 \times (-0.47) + 1 \times (0.77)}{2 + 1} = -0.057 \text{ V}$$

10. $E_{\text{T}^{\ell}/\text{T}^{\ell+}}^0 = +0.34 \text{ V}$

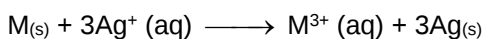
$$= E_{\text{A}^{\ell}/\text{A}^{\ell+}}^0 = +0.55 \text{ V}$$

Therefore $\text{T}^{\ell+}$ more stable

11. $E_{\text{Mn}^{2+}/\text{Mn}^{3+}}^0 = 1.57 \text{ V}$; $E_{\text{H}^+/\text{H}_2}^0 = 0 \text{ V}$

Mn^{2+} cannot reduce H^+ to H_2

12. Cell reaction :



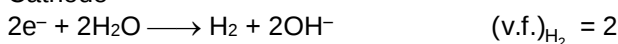
Applying Nernst equation :

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n} \log_{10} Q$$

$$\therefore 0.421 = (0.8 \times E_{\text{M}^{3+}/\text{M}}^0) - \frac{0.059}{3} \log_{10} \frac{0.001}{(0.01)^3}$$

$$\therefore E_{\text{M}^{3+}/\text{M}}^0 = 0.32 \text{ V}$$

13. Cathode

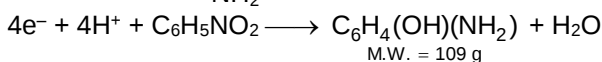
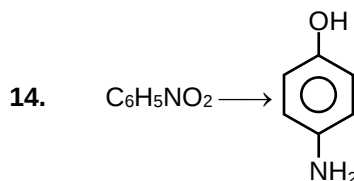


$$\text{mole} = \frac{i \times t}{\text{v.f.} \times 96500}$$

$$\frac{112}{22400} = \frac{i \times 965}{2 \times 96500}$$

$$\frac{1}{2} = \frac{i}{2}$$

$$i = 1 \text{ amp}$$



M.W. = 109 g

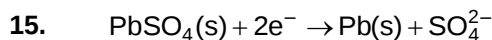




$$(v.f.) = 4 \quad W = ZIt = \frac{E}{F} \times I \times t \quad \left(E = \frac{M}{4} \right)$$

$$W = \frac{109 \times 9.65 \times 60 \times 60}{4 \times 96500}$$

$$W = 9.81 \text{ g}$$



For 2F current passed, PbSO_4 electrolyzed = 303g/mol

$$\text{For } 0.05F; \text{PbSO}_4 \text{ electrolyzed} = \frac{0.05 \times 303}{2} = 7.6 \text{ g}$$

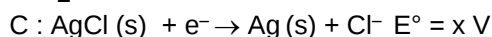
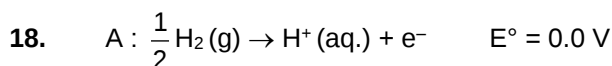
16. $\Delta G^\circ = -RT \ln K$

$$-2 \times 96000 \times 2 = -8 \times 300 \times \ln K$$

$$\text{or, } \ln K = 160$$

$$\text{or, } K = e^{160}$$

17. Higher the SOP, higher will be reducing power.



$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{1} \log \{[\text{H}^+][\text{Cl}^-]\}$$

$$0.92 = x - \frac{0.06}{1} \log (10^{-12})$$

$$0.92 = x + 0.72$$

$$x = 0.92 - 0.72 = 0.2 \text{ Volts}$$

19. Fact

20. $E^\circ_{\text{cell}} = E^\circ_{\text{Zn}(s)|\text{Zn}^{+2}} + E^\circ_{\text{Au}^{3+}/\text{Au}}$

$$= \text{SOP}_{\text{anode}} + \text{SRP}_{\text{cathode}}$$

$$= 0.76 \text{ V} + 1.40 \text{ V} = 2.16 \text{ V}$$

21. $E^\circ_{\text{cell}} = \frac{0.0591}{n} \log K_c = \frac{0.0591}{2} \log (1 \times 10^{16}) = 0.4728 \text{ V}$

22. $\Delta H = -nFE_{\text{cell}} + nFT \frac{dE}{dT}$

$$= -2 \times 96000 \times 2 + 2 \times 96000 \times 300 \times (-5 \times 10^{-4})$$

$$= -384000 - 28,800 = -412.8 \text{ kJ/mol}$$

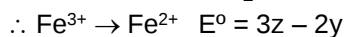
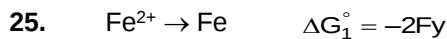
23. $\Lambda^\circ_m(\text{HA}) = \Lambda^\circ_m(\text{HCl}) + \Lambda^\circ_m(\text{NaA}) - \lambda^\circ(\text{NaCl})$

$$= 425.9 + 100.5 - 126.4 = 400$$

$$\Lambda^\circ_m = \frac{K \times 1000}{M} \Rightarrow \frac{5 \times 10^{-5} \times 10^3}{10^{-3}} = 50$$

$$\alpha = \frac{50}{400} = 0.125$$

24. Strongest oxidizing agent has highest value of SRP



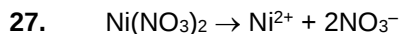
$$E_{\text{cell}}^\circ = E_{\text{Ag}^+|\text{Ag}}^\circ - E_{\text{Fe}^{3+}|\text{Fe}^{2+}}^\circ$$

$$= x - [3z - 2y] = x + 2y - 3z$$

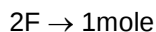
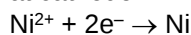
For given cell reaction

$$E_{\text{cell}}^\circ = x + 2y - 3z$$

26. $\Delta G^\circ = -nF E_{\text{cell}}^\circ = -2 \times 96000 \times 2.0 \times 10^{-3} = -384 \text{ kJ/mol}$

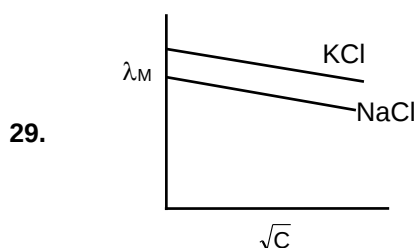


at cathode:



$$0.1F \rightarrow \frac{0.1}{2} = 0.05 \text{ mole}$$

28. Conductivity decreases on decreasing concentration of electrolyte.
Molar conductivity increases on decreasing concentration of electrolyte.

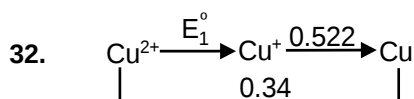


$$(\lambda_M^\circ)_{\text{K}^+} > (\lambda_M^\circ)_{\text{Na}^+}$$

Na^+ is more hydrated with respect to K^+ therefore KCl electrolyte have higher λ_M with respect to NaCl.

30. The metal ion with higher SRP value will have higher oxidising power.

31. Since acidic strength follows order $\text{HCOOH} > \text{C}_6\text{H}_5\text{COOH} > \text{CH}_3\text{COOH}$



$$2 \times 0.34 = E_1^\circ + 1 \times 0.522$$

$$E_1^\circ = 0.68 - 0.522 \Rightarrow E_1^\circ = 0.158 \text{ V}$$

33. Theory based.

34. From the given data

$$E_{\text{op}} = E_{\text{op}}^\circ - \frac{0.059}{4} \log [\text{H}^+]^4$$

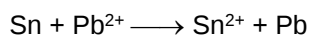
$$E_{\text{op}} = -1.23 - \frac{0.0591}{4} \log [\text{H}^+]^4$$

$$= -1.23 + 0.0591 \times \text{pH} = -1.23 + 0.0591 \times 5$$

$$= -1.23 + 0.2955 = -0.9345 \text{ V} = -0.93 \text{ V}$$



35. At Equilibrium state. $E_{\text{cell}} = 0$; $E^{\circ}_{\text{cell}} = 0.01 \text{ V}$

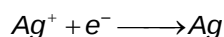


$$0 = 0.01 - \frac{0.06}{2} \log \left\{ \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} \right\}$$

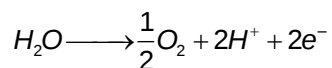
$$0.01 = \frac{0.06}{2} \log \left\{ \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} \right\}$$

$$\frac{1}{3} = \log \left\{ \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} \right\} \Rightarrow \frac{[\text{Sn}^{2+}]}{[\text{Pb}^{2+}]} = 10^{1/3} = 2.1544$$

36. $(n_{\text{Ag}})_{\text{deposit}} = \frac{108}{108} - 1 \text{ mole}$



1F charge is required to deposit 1 mole of Ag



2F charge deposit $\longrightarrow \frac{1}{2} \text{ mole}$

1F charge will deposit $\longrightarrow \frac{1}{4} \text{ mole}$

$$V_{\text{O}_2} = \frac{nRT}{P}$$

$$= \frac{1}{4} \times \frac{0.08314 \times 273}{1}$$

$$V_{\text{O}_2} = 5.674 \text{ L}$$

37. Theory based.