

SOLUTIONS
TOPIC : ELECTROCHEMISTRY.

Exercise (LEVEL-I)

(1) Ans [1] : $A^{+n} + ne^- \rightarrow A$, For the reaction $E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[A^{+n}]}$
 As concentration of $[A^{+n}] \uparrow$, $E \downarrow$.

(3) Ans [4] : $E_{H^+/ \frac{1}{2} H_2}^{\circ} = 0.0 \text{ V}$ & $E_{Cu^{+2}/ Cu}^{\circ} = +0.34 \text{ V}$.

Hydrogen electrode is more reactive than copper electrode.

(4) Ans [1] : Anode is negative because it is electron rich or active.

(5) Ans [4] $E_{Ag^+/ Ag}^{\circ} = +0.80 \text{ V}$. (maximum). It will be easily reduced.

(6) Ans [2]. Zn is more reactive than H_2 because $E_{Zn^{+2}/ Zn}^{\circ}$ for Zn^{+2}/ Zn is more negative than $H^+/ \frac{1}{2} H_2$.

(7) Ans [3]. $Ag^+ + Cl^- \rightarrow AgCl(s)$, ppt.

(8) Ans [3]: E_{red}° for Mg and Al is more negative. As a result the value of discharge potential is high.

(9) Ans [1]: At cathode H^+ or H_2O and at anode OH^- or H_2O are discharged.

(10) Ans [1]: Attraction force b/w ions decreases by which they become free to move more.

(11) Ans [2] : C_2H_5OH is not ionised in water.

(12) Ans [3] : E_{red}° for (I) is maximum negative.

(14) Ans [4] : $Zn + Fe^{+2} \rightarrow Zn^{+2} + Fe$.

(16) Ans [1] : more will be reducing power if E_{red}° is more negative (lower).

(18) Ans [1] : $Cu + 2Ag^+ \rightarrow Cu^{+2} + 2Ag$
 (Blue)

(19) Ans [2] : $MnO_4^- \rightarrow Mn^{+2}$, change in oxidation state is 5.
 Charge required = 5F.

(20) Ans[1]: Crystalline NaCl have lattice of ions where they cannot move to pass the charge.

(25) Ans[3]: $E = E^\circ - \frac{RT}{nF} \ln Q_c$ is a Nernst's equation.

At equilibrium $E=0$, $\therefore E^\circ = \frac{RT}{nF} \ln K_e$.

(26) Ans[4]: Electrical circuit is not completed through the solution.
As a result, ions will start moving randomly.

(27) Ans[3]: $Al^{+3} + 3e^- \rightarrow Al$, Three mole electrons are required.

(30) Ans[2]: The electrode potential for SHE is assumed to be zero.

(31) Ans[4]: Degree of ionisation increases as temperature increases.

(32) Ans[4] : $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$.

$$(33) \text{ Ans[1]}: \quad k_{eq} = \frac{k \times 1000}{N} = \frac{\frac{1}{250} \times 1.15 \times 1000}{1} \text{ S cm}^2 \text{ eq}^{-1} \\ = 4.6 \text{ S cm}^2 \text{ eq}^{-1}$$

(35) Ans [3]: NaCl(aq).

(38) Ans[4] : $Mg > Ca > Ba > K$. K is most reactive and Mg is least.

(40) Ans [1]: Lower will be the value of E°_{red} , more will be the reactivity of the element.

LEVEL - II

(1) Ans [3] : H_2 at cathode and O_2 at anode.

(4) Ans [3] : $\omega = ZQ \quad \therefore \quad Z = \omega/Q \Rightarrow Z$ is having units = g/c

(5) Ans [4] : Charge on one mole of electrons = $1F \approx 965000C$.
This charge deposits amount of a substance equal to 1 g-equivalent.

(6) Ans (1) : $Fe^{+3} + 1e^- \rightarrow Fe^{+2}$. 1F charge is required.

(7) Ans. (2) : $E = E^{\circ} - \frac{0.0591}{n} \log K_c ; \quad E = -2.36 - \frac{0.0591}{1} \log \frac{1}{0.1} = -2.41 V$.

(8) Ans (3) : $E_{cell}^{\circ} = E_{Ox}^{\circ} + E_{red}^{\circ} = +0.25 + 1.50 = 1.75 V$

(11) Ans (4) : $Fe^{+2} + 2e^- \rightarrow Fe$ and $Fe^{+3} + 3e^- \rightarrow Fe$

$$\frac{\omega_1}{\omega_2} = \frac{E_1}{E_2} = \frac{(56/2)}{(56/3)} = 3/2$$

(12) Ans [3] : $\frac{\omega_{Cu}}{\omega_{H_2}} = \frac{E_{Cu}}{E_{H_2}}$ or $\frac{\omega_{Cu}}{0.50} = \frac{(63.6/2)}{(2/2)}$

$$\text{or } \omega_{Cu} = \frac{63.6}{2} \times 0.5 \text{ g} = 15.9 \text{ g.}$$

(13) Ans [1] : $2H_2O \rightarrow 2H_2 + O_2$ 2 mole or 4g H_2 is obtained if
36g water = 2mole 36g water is decomposed.

charge required for 4g $H_2 = 4F$ ($\because E_{H_2} = 1$)

$$\text{or } 4 \times 96500 = I \times t \quad \text{or } t = \frac{4 \times 96500}{3 \times 3600} \text{ hrs} \approx 36 \text{ hrs.}$$

(14) Ans [1] : $E^{\circ} = \frac{0.0591}{2} \log \frac{[A^{+2}]}{[B^+]^2} = \frac{0.0591}{2} \log K_c$

$$\therefore E^{\circ} = \frac{0.0591}{2} \log 10^{12} = 0.0591 \times 6 V = 0.36 V$$

(15) Ans [1] : $E_{A^-/A}^{\circ} = -0.24 V$ and $E_{B^-/B^2}^{\circ} = +1.25 V \quad \therefore E_{cell}^{\circ} = \text{max.}$

(18) Ans [2] : $E = E^{\circ} - \frac{0.0591}{2} \log \frac{1}{[H^+]^2} = 0 - \frac{0.0591}{2} \log \frac{1}{10^{20}} = -0.591 V.$

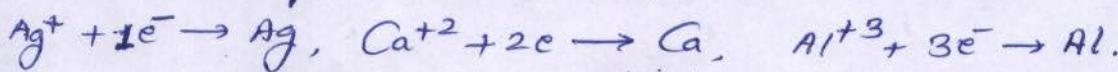
(19) Ans [1] : $\omega = \frac{EXIxt}{96500} \quad \therefore E = \frac{\omega \times 96500}{IXt} = \frac{2.977 \times 96500}{10800} = 26.6$

valency of the metal or charge on ion = $M/E = \frac{106.4}{26.6} = +4$

LEVEL-II

(1) Ans [3]: H_2 is

(20) molar ratio of the metals deposited = 6:3:2.



$$1F = 1 \text{ mole of Ag} \quad 2F = 1 \text{ mole of Ca} \quad 3F = 1 \text{ mole of Al.}$$

$$\therefore 3F = 3 \text{ mole} \quad 3F = \frac{3}{2} " \quad 3F = 1 \text{ mole } "$$

$$\therefore \text{molar ratio} = 3 : \frac{3}{2} : 1 \text{ or } 6 : 3 : 2.$$

(22) Ans[3]: $W = \frac{EXIxt}{96500} \quad \text{or} \quad E = \frac{W \times 96500}{Ixt} = \frac{1.8 \times 96500}{3 \times 50 \times 60} \text{ J} = 19.3$

(23) Ans[3]: $\text{Cu}^{+2} \xrightarrow{\Delta G_1} \text{Cu}^+ \xrightarrow{\Delta G_2} \text{Cu} \quad \Delta G_1 = \Delta G_2 + \Delta G_3$

$$-\eta FE_1 = -n_2 FE_2 - n_3 FE_3$$

$$\text{or} \quad n_1 E_1 = n_2 E_2 + n_3 E_3$$

$$\text{Now } E_3 = \frac{n_1 E_1 - n_2 E_2}{n_3} \approx \frac{2 \times 0.34 - 0.153}{1} = +0.527$$

(24) Ans[3]: $E_2 - E_1^\circ = -\frac{0.0591}{2} \log \frac{1}{0.1} + 0 = -0.030 \text{ V} \quad [G = 1M, C_2 = 0.1M]$

(26) Ans[2]: By using Kohlrausch's law -

$$\Lambda_{\text{NH}_4\text{OH}}^\circ = \Lambda_{\text{NH}_4\text{Cl}}^\circ + \Lambda_{\text{NaOH}}^\circ - \Lambda_{\text{NaCl}}^\circ$$

$$= (149.74 + 248.1 - 126.4) \text{ Scm}^2 \text{ eq}^{-1} = 271.44$$

(27) Ans[3]: $\alpha = \frac{\Lambda^\circ}{\Lambda^\circ \text{ at } 25^\circ} = \frac{50}{250} = 0.20$

(29) Ans[1]: $E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Zn}^{+2}]}{[\text{Ni}^{+2}]} \quad \text{or} \quad E^\circ = E + \frac{0.0591}{2} \log \frac{10}{1}$

$$\text{or} \quad E^\circ = (0.5105 + 0.03) \text{ V} = 0.54 \text{ V.}$$

(31) Ans[2]: $E = E^\circ - \frac{0.0591}{2} \log \frac{[\text{Sn}^{+2}]}{[\text{Ag}^+]^2}, \text{ As } [\text{Ag}^+] \uparrow, E_{\text{cell}} \uparrow.$

(32) Ans[3]: Amount of charge passed = $2 \times 96500 \times 0.1 \text{ C} = 19300 \text{ C.}$

(34) Ans[2]: More the value of E_{red}° , more will be discharging capacity.

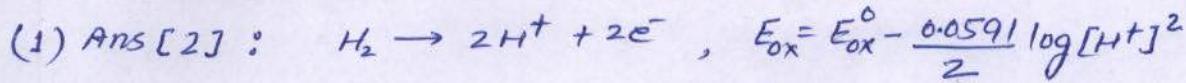
Sequence of deposition of metals: Ag, Hg, Cu

(35) Ans[2]: $\frac{W_{\text{Cu}}}{W_{\text{H}_2}} = \frac{E_{\text{Cu}}}{E_{\text{H}_2}}, \therefore W_{\text{Cu}} = \frac{E_{\text{Cu}} \times W_{\text{H}_2}}{E_{\text{H}_2}} = \frac{(63.5/2) \times 0.504 \text{ J}}{(2/2)}$

$$= 31.75 \times 0.504 \text{ J} = 16 \text{ g.}$$

Previous Years Questions

Questions asked in 2013:

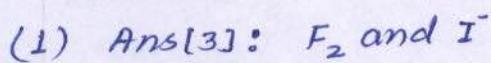


$$E_{ox} = 0 - \frac{0.0591}{2} \times 2 \log[H^+]$$

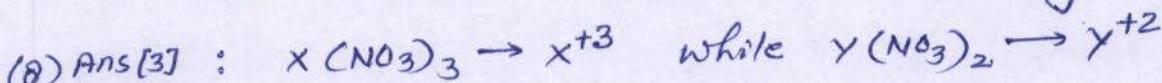
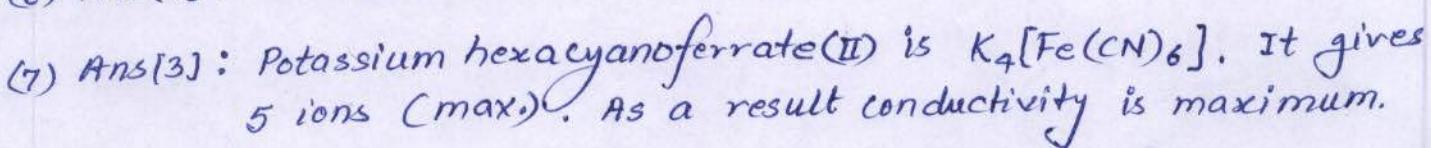
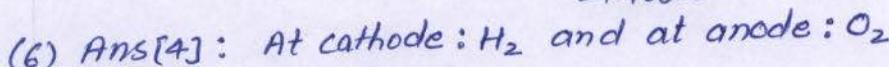
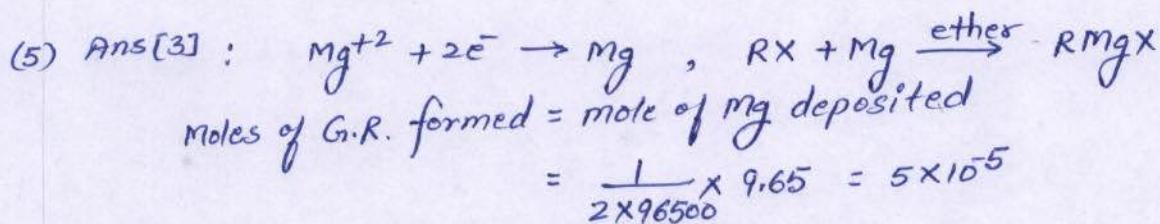
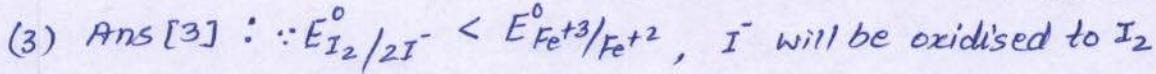
$$(2) \text{Ans [3]} : \alpha = \frac{9.54}{238} \times 100\% = 4.008\%$$

$$(3) \text{Ans [1]} : E_{cell} = E_{ox} + E_{red} = +0.76 + 0.34 = 01.10V.$$

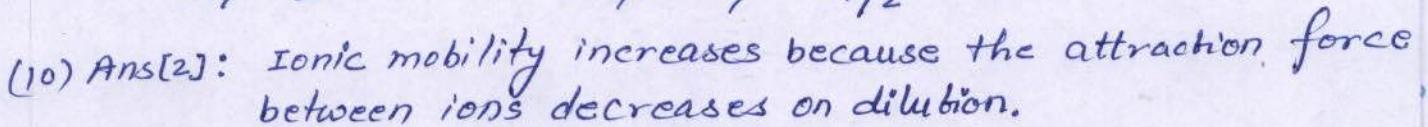
TOPIC 1: Electrolytes and electrolytic conductance



$$(2) \text{Ans [2]} : \Lambda_{m, CH_3COOH}^\circ = \Lambda_{m, CH_3COONa}^\circ + \Lambda_{HCl}^\circ - \Lambda_{NaCl}^\circ \\ = 91 + 425.9 - 126.4 = 390.5 \text{ Scm}^2 \text{ mol}^{-1}$$



$$\frac{M_X}{M_Y} = \frac{1}{2} \text{ (given)}, \quad \frac{w_X}{w_Y} = \frac{E_X}{E_Y} = \frac{M_X/3}{M_Y/2} = \frac{M_X}{M_Y} \times \frac{2}{3} = \frac{1}{2} \times \frac{2}{3} = \frac{1}{3}$$



$$(12) \text{Ans [1]} : \Lambda_{eq, CH_3COOH}^\circ = \Lambda_{H^+}^\circ + \Lambda_{CH_3COO^-}^\circ = 315 + 35 = 350$$

$$(15) \text{Ans [1]} : w = \frac{E \times Q}{96500} \quad \therefore Q = \frac{w \times 96500}{E} = \frac{50 \times 96500 \times 3}{27} g = 536111 \text{ g.}$$

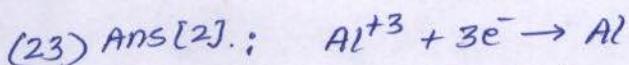
$$(16) \text{Ans [2]} : K = \frac{1}{R} \times G^* = \frac{1}{250} \times 1.15 \text{ } \Omega^{-1} \text{ cm}^{-1} = 0.0046 \text{ Scm}^2.$$

$$\text{Now } \Lambda_{eq} = \frac{K \times 1000}{N} = \frac{0.0046 \times 1000}{1} = 4.6 \text{ Scm}^2 \text{ eq}^{-1}.$$

(18) Ans[4] : $A_m = \frac{K \times 1000}{M} = \frac{0.0248 \times 1000}{0.2} = 124 \text{ S cm}^2 \text{ mol}^{-1}$.

(19) Ans[2] : K decreases on increasing dilution because number of ions per unit volume of solution decreases.

(20) Ans[2] : $w = Z \times Q$, $\frac{w_1}{w_2} = \frac{Z_1}{Z_2} \Rightarrow \frac{Z_1}{Z_2} = \frac{0.375}{0.300} = 1.25$



$$W_{\text{Al}} = \frac{E \times I \times t}{96500} = \frac{9 \times 4 \times 10^4 \times 6 \times 3600}{96500} \text{ g} = 8.1 \times 10^4 \text{ g.}$$

(24) Ans[4] : $\alpha = \frac{8}{400} = 0.020$, Now $K_a = \frac{c\alpha^2}{1-\alpha} \approx c\alpha^2 = \frac{1}{32} \times (0.020)^2 = \frac{4 \times 10^{-4}}{32} = 1.25 \times 10^{-5}$.

(26) Ans[2] : mole of $\text{NaCl} = \frac{6.5 \times 0.9}{58.5} = 0.1$
mole of NaOH formed = 0.1, volume of CH_3COOH required = 100 ml.

(27) Ans[1] : mole of $\text{H}_2 = \frac{1.12}{22400} = 5 \times 10^{-5}$, charge required = $\frac{96500 \times 2 \times 5 \times 10^5 \text{ C}}{1.93 \times 5 \text{ C}}$

Current required per second = 9.65 A

(29) Ans[2] : $\lambda_m \text{ Ba(OH)}_2 = \lambda \text{ BaCl}_2 + 2\lambda \text{ NaOH} - 2\lambda \text{ NaCl}$
 $= (280 + 496 - 252) \times 10^4 = 524 \times 10^4 \text{ S cm}^2 \text{ mol}^{-1}$

(30) Ans[2] : Amount of Cu deposited by 1F = $3.29 \times 10^4 \times 9.6500 \times 10^4 \text{ g.}$
 $= 3.29 \times 9.65 \text{ g} = 31.75 \text{ g.}$

Atomic mass = $31.75 \times 2 = 63.5$.

(32) Ans[3] : $\text{Mn}^{+7} \rightarrow \text{Mn}^{+2}$, charge required = 5F. = $4.83 \times 10^5 \text{ C}$

(36) Ans[2] : Mole of $\text{AgNO}_3 = 0.125$ = mole of Ag^+

$$\text{charge required} = 0.125 \times 96500 \text{ C} = 12062.5 \text{ C.}$$

$\therefore I \times t = 12062.5 \quad \therefore t = \frac{12062.5}{241.25} \text{ sec} = 50 \text{ sec.}$

(39) Ans[4] : speed of H^+ ion is maximum.

(42) Ans[2] : Mole of Ni deposited = $\frac{96.5 \times 18 \times 60}{2 \times 96500} = 0.54$.

Mole of Ni^{+2} in 500 ml = $1 - 0.54 = 0.46$, Molarity after electrolysis = 0.92 M.

(46) Ans[2] : $N_{eq} = \frac{K \times 1000}{N} = \frac{1.25 \times 1000}{0.1 \times 2.5 \times 10^3} = 5 \text{ S cm}^2 \text{ eq}^{-1}$.

$$(47) \text{ Ans[1]} : \text{ mole of Ca deposited} = \frac{25 \times 10^3 \times 60}{2 \times 96500}$$

$$\text{No. of Ca atoms deposited} = \frac{25 \times 10^3 \times 60}{2 \times 96500} \times 6.022 \times 10^{23} = 4.68 \times 10^{18}$$

$$(53) \text{ Ans[3]} : \frac{W_{\theta_2}}{W_{Ag}} = \frac{E_{\theta_2}^\circ}{E_{Ag}} = \frac{8}{108} \quad \therefore W_{\theta_2} = \frac{8}{108} \times 0.108 = 10^3 \text{ g} \times 8 \text{ g}$$

$$n_{\theta_2} = 8 \times 10^3 / 32 = 2.5 \times 10^4 \quad \therefore V_{H_2} = 2.5 \times 10^4 \times 22400 \text{ ml} = 5.6 \text{ ml.}$$

Topic 2: Electrochemical series, Electrode potential and EMF.

$$(1) \text{ Ans[1]} : \Delta G^\circ = -nFE^\circ \quad \therefore \Delta G^\circ > 0 \quad \& \quad \Delta G^\circ = -RT \ln K_{eq} \Rightarrow K_{eq} < 1.$$

$$(3) \text{ Ans[4]} : Z > X > Y.$$

$$(4) \text{ Ans[3]} : E_{\text{cell}} = E_{\text{ox}}^\circ + E_{\text{red}}^\circ = 0.74 + 0.15 = +0.89 \text{ V.}$$

$$(6) \text{ Ans[1]} : E^\circ = \frac{0.0591}{2} \log K_{eq} \quad \text{or} \quad \log K_{eq} = \frac{2 \times E^\circ}{0.0591} = \frac{2 \times 0.59}{0.0591} = 20$$

$$\Rightarrow K_{eq} = 10^{20}$$

$$(8) \text{ Ans[2]} : \Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 0.46 \text{ J.}$$

$$(9) \text{ Ans[3]} : E = E^\circ - \frac{0.0591}{2} \log Q_c \quad \text{or} \quad \log Q_c = \frac{2E^\circ}{0.0591} = \frac{2 \times 1.2}{0.0591} = 40.6$$

$$(12) \text{ Ans[1]} : E^\circ = (2.37 - 0.45) = 1.92$$

$$1.92 = 1.92 - \frac{0.0591}{2} \log \frac{(x)}{(0.01)} \quad \text{or} \quad \log \frac{x}{0.01} = 0 = \log 1$$

$$\text{or} \quad \frac{x}{0.01} = 1 \quad \text{or} \quad \boxed{x = 0.01}$$

$$(16) \text{ Ans[4]} : [Cu^{+2}] [OH^-]^2 = 10^{19}$$

$$\because pH = 14 \quad \therefore pOH = 0 \quad \text{or} \quad [OH^-] = 10^0 = 1 \text{ M.}$$

$$[Cu^{+2}] = 10^{19} \text{ M.} \quad \Rightarrow \quad E = 0.34 - \frac{0.0591}{2} \log \frac{1}{[Cu^{+2}]} = 0.34 - \frac{0.0591}{2} \log \frac{1}{10^{19}}$$

$$= 0.34 - (0.0591 \times 9.5)$$

$$= -0.22 \text{ V}$$

$$(24) \text{ Ans[2]} : E = E^\circ - \frac{0.0591}{2} \log [Zn^{+2}] [Cl^-]^2$$

$$(26) \text{ Ans[2]} : E = 0.337 - \frac{0.0591}{2} \log \frac{[H^+]^2}{[Cu^{+2}]} = 0.337 - \frac{0.0591}{2} \log \frac{(10^2)^2}{0.10} = +0.427 \text{ V}$$

(29) Ans[4]: NO₃ is reduced as compared (in preference) of H₃O⁺

[32] Ans[2]: M⁺ + x⁻ → M+x is the spontaneous reaction.

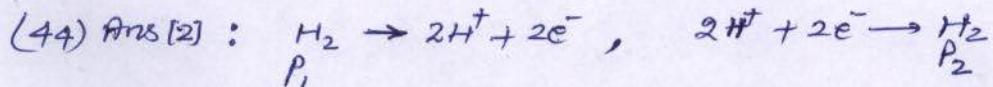
$$(33) \text{ Ans[1]} : E = 0 - \frac{0.0591}{n} \log \frac{[Ag^+]_{L.C.}}{[Ag^+]_{H.C.}} : \text{For concentration cell.}$$

$$E = 0 - \frac{0.0591}{1} \log \frac{0.01}{1} = 0.12 \text{ V.}$$

$$(38) \text{Ans [1]: } E = 0 - \frac{0.0591}{2} \log \frac{(H^+)^2_{L.C.}}{(H^+)^2_{H.C.}} = - \frac{0.0591}{2} \times 2 \log \frac{10^6}{10^3} = 0.0591 \times 3 V = 0.1773 V$$

$$(39) \text{Ans [1]: } \text{max. electrical work} = nFE^\circ = 2 \times 1.1 \times 96500 J = 212.3 \text{ kJ.}$$

$$(40) \text{Ans [4]: } Sn^{+4} + 2e^- \rightarrow Sn^{+2} ; E = E^\circ - \frac{0.0591}{2} \log \frac{[Sn^{+2}]}{[Sn^{+4}]} = E^\circ - \frac{0.0591}{2} \log \frac{0.10}{0.01} = E^\circ - \frac{0.0591}{2}$$



$$E = 0 - \frac{0.0591}{2} \log_{10} \frac{(1/P_1)}{(1/P_2)} = - \frac{RT}{2F} \ln \frac{P_2}{P_1} = \frac{RT}{2F} \ln \frac{P_1}{P_2}$$

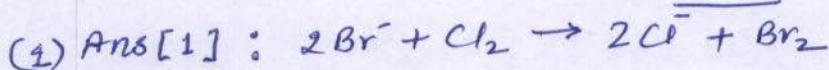
$$(45) \text{Ans [2]: } E = E^\circ - \frac{0.0591}{2} \log \frac{[Cu^{+2}]^2}{[Cu^{+2}]} , E \uparrow \text{as } [Cu^{+2}] \uparrow.$$

$$(46) \text{Ans [3]: } \Delta G = -nFE \text{ or } -0.27 \times 10^3 = -6 \times 96500 \times E \text{ or } E = 1.428 \\ E \text{ for 1 mole of } Al_2O_3 = 1.428 \times \frac{3}{2} = 2.14 \text{ V.}$$

$$(47) \text{Ans [2]: } \Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.104 \text{ J} = -213072 \text{ J}$$

$$(48) \text{Ans [2]: } E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[Cu^{+2}]} = 0.34 - \frac{0.0591}{2} \log \frac{1}{0.01} = (0.34 - 0.06)V = 0.28 \text{ V}$$

Topic 3



(4) Ans [4]: H_2SO_4 is consumed.

$$(11) \text{Ans [3]: } \eta = \frac{\Delta G}{\Delta H}$$

(16) Ans [2]: $E^\circ_{Mg^{+2}/Mg}$ is more negative than $E^\circ_{Fe^{+2}/Fe}$.
Mg is converted into Mg^{+2} readily.

