SOLUTIONS

TOPIC : ELECTROCHEMISTRY.

Exercise (LEVEL-I)

(1) Ans [1] : $A^{+n} + ne^- \rightarrow A$, For the reaction $E = E^0 - \frac{0.0591}{n} \log \frac{1}{[A^{+n}]}$

As concencentration of $[A^{+n}] \uparrow$, $E \uparrow$.

(3) Ans [4] : $E^0_{H^+/\frac{1}{2}H_2} = 0.0\ V$ & $E^0_{Cu^{+2}/Cu} = +0.34\ V$.

Hydrogen electrode is more reactive than copper electrode.

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

(5) Ans[4] $E^0_{Ag^+/Ag} = +0.80\ V$. (maximum). It will be easily reduced.

(6) Ans[2]. Zn is more reactive than H_2 because E^0_{red} 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^0_{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.

(13) Ans[3]: E^0_{red} for (I) is maximum negative.

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

(16) Ans[1]: more will be reducing power if E^0_{red} is more negative (lower)

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

(19) Ans [2]: $\overset{+7}{Mn}O_4^- \rightarrow Mn^{+2}$, change in oxidation state is 5.

Charge required = 5F.

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

(25) Ans[3]: $E = E^{\circ} - \frac{RT}{nF} \ln Q_c$ is a Nernst's equation.
At equilibrium $E = 0$, $\therefore$ $E^{\circ} = \frac{RT}{nF} \ln K_c$

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

(27) Ans[3]: $Al^{+3} + 3e^{-} \longrightarrow Al$, 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]: $HCl(aq) \longrightarrow H^{+}(aq) + Cl^{-}(aq)$.

(33) Ans[1]:

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} = \frac{\frac{1}{250} \times 1.15 \times 1000}{1} \ Scm^2 eq^{-1}$$
$$= 4.6 \ Scm^2 eq^{-1}$$

(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] : $w = ZQ \therefore Z = w/Q \Rightarrow$ Z is having units = g/c

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

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

(7) Ans. (2) : $E = E^0 - \frac{0.0591}{n} \log Q_c$; $E = -2.36 - \frac{0.0591}{1} \log \frac{1}{0.1} = -2.41$ V.

(8) Ans (3) : $E^0_{cell} = E^0_{ox} + E^0_{red} = +0.25 + 1.50 = 1.75$ V

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

$$\frac{w_1}{w_2} = \frac{E_1}{E_2} = \frac{(56/2)}{(56/3)} = 3/2$$

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

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

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

Charge required for 4g H_2 = 4F (∵ $E_{H_2} = 1$)

or $4 \times 96500 = I * t$ or $t = \frac{4 \times 96500}{3 \times 3600}$ hrs ≈ 36 hrs.

(14) Ans[1] : $E^0 = \frac{0.0591}{2} \log \frac{[A^{+2}]}{[B^+]^2} = \frac{0.0591}{2} \log K_c$

$\therefore E^0 = \frac{0.0591}{2} \log 10^{12} = 0.0591 \times 6$ V $= 0.36$ V

(15) Ans[1] : $E^0_{A^-/A} = -0.24$V and $E^0_{B/B^{-2}} = +1.25$ V $\therefore E^0_{cell}$ = max.

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

(19) Ans[1] : $w = \frac{E \times I \times t}{96500} \therefore E = \frac{w \times 96500}{I \times t} = \frac{2.977 \times 96500}{10800} = 26.6$

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**.

$Ag^+ + 1e^- \rightarrow Ag$, $Ca^{+2} + 2e \rightarrow Ca$, $Al^{+3} + 3e^- \rightarrow Al$.

1 F = 1 mole of Ag   2F = 1 mole of Ca   3F = 1 mole of Al.

∴ 3F = 3 mole   3F = 3/2 " "   3F = 1 mole " "

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

(22) Ans[3]: $W = \frac{E \times I \times t}{96500}$ or $E = \frac{W \times 96500}{I \times t} = \frac{1.8 \times 96500}{3 \times 50 \times 60} g = 19.3$

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

$\Delta G_1 = \Delta G_2 + \Delta G_3$

$-n_1 F E_1 = -n_2 F E_2 - n_3 F E_3$

or $n_1 E_1 = n_2 E_2 + n_3 E_3$

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]: : $E_2 - E_1^\circ = -\frac{0.0591}{2} \log \frac{1}{0.1} + 0 = -0.030\,V$ $\left[\begin{matrix} C_1 = 1M \\ C_2 = 0.1M \end{matrix}\right]$

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

$\Lambda^0_{NH_4OH} = \Lambda^0_{NH_4Cl} + \Lambda^0_{NaOH} - \Lambda^0_{NaCl}$

$= (149.74 + 248.1 - 126.4)\, S\,cm^2 eq^{-1} = 271.44$

(27) Ans[3] : $\alpha = \frac{\Lambda^v}{\Lambda^\infty} = \frac{50}{250} = 0.20$

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

or $E^\circ = (0.5105 + 0.03)\,V = 0.54\,V$.

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

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

(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]: $\frac{\omega_{Cu}}{\omega_{H_2}} = \frac{E_{Cu}}{E_{H_2}}$, ∴ $W_{Cu} = \frac{E_{Cu}}{E_{H_2}} \times \omega_{H_2} = \frac{(63.5/2) \times 0.504\,g}{(2/2)}$

$= 31.75 \times 0.504\,g = 16\,g$.

Previous Years Questions

Questions asked in 2013:

(1) Ans [2] : $H_2 \rightarrow 2H^+ + 2e^-$, $E_{ox} = E^0_{ox} - \frac{0.0591}{2} \log[H^+]^2$

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

$= 0.0591 \times 10\ V = 0.591\ V$

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

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

TOPIC 1: Electrolytes and electrolytic conductance

(1) Ans[3]: F_2 and I^-

(2) Ans [2] : $\Lambda^0_{m, CH_3COOH} = \Lambda^0_{m, CH_3COONa} + \Lambda^0_{HCl} - \Lambda^0_{NaCl}$

$= 91 + 425.9 - 126.4 = 390.5\ Scm^2 mol^{-1}.$

(3) Ans [3] : $\because E^0_{I_2/2I^-} < E^0_{Fe^{+3}/Fe^{+2}}$, I^- will be oxidised to I_2

(5) Ans[3] : $Mg^{+2} + 2e^- \rightarrow Mg$, $RX + Mg \xrightarrow{ether} RMgX$

Moles of G.R. formed = mole of Mg deposited

$= \frac{1}{2 \times 96500} \times 9.65 = 5 \times 10^{-5}$

(6) Ans[4]: At cathode : H_2 and at anode : O_2

(7) Ans[3]: Potassium hexacyanoferrate(II) is $K_4[Fe(CN)_6]$. It gives 5 ions (max.). As a result conductivity is maximum.

(8) Ans [3] : $X(NO_3)_3 \rightarrow X^{+3}$ while $Y(NO_3)_2 \rightarrow Y^{+2}$

$\frac{M_X}{M_Y} = \frac{1}{2}$ (given), $\frac{W_X}{W_Y} = \frac{E_X}{E_Y} = \frac{M_X/3}{M_Y/2} = \frac{M_X}{M_Y} * \frac{2}{3} = \frac{1}{2} \times \frac{2}{3} = \frac{1}{3}$

(10) Ans[2]: Ionic mobility increases because the attraction force between ions decreases on dilution.

(12) Ans[1]: $\Lambda^0_{eq, CH_3COOH} = \Lambda^0_{H^+} + \Lambda^0_{CH_3COO^-} = 315 + 35 = 350$

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

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

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

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

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

[20] Ans[2] : $W = Z \times Q$, $\frac{W_1}{W_2} = \frac{Z_1}{Z_2} \Rightarrow \frac{Z_1}{Z_2} = \frac{0.375}{0.300} = 1.25$

(23) Ans[2]. : $Al^{+3} + 3e^- \rightarrow Al$

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

(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 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 $H_2 = \frac{1.12}{22400} = 5 \times 10^{-5}$, charge required $= 96500 \times 2 \times 5 \times 10^{-5}$ C $= 1.93 \times 5$ C.

Current required per second $= 9.65$ A

(29) Ans[2] : $\lambda^o_m Ba(OH)_2 = \lambda^o_{BaCl_2} + 2\lambda^o_{NaOH} - 2\lambda^o_{NaCl}$

$= (280 + 496 - 252) \times 10^{-4} = 524 \times 10^{-4}\ S\,cm^2 mol^{-1}$.

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

$= 3.29 \times 9.65\ g = 31.75\ g$.

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

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

(36) Ans[2] : Mole of $AgNO_3 = 0.125$ = mole of Ag^+

charge required $= 0.125 \times 96500 C = 12062.5 C$.

$\because I \times t = 12062.5 \quad \therefore t = \frac{12062.5}{241.25}$ sec $= 50$ 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]. : $\Lambda_{eq} = \frac{K \times 1000}{N} = \frac{1.25 \times 1000}{0.1 \times 2.5 \times 10^3} = 5\ S\,cm^2 eq^{-1}$.

(47) Ans[1] : mole of Ca deposited = $\frac{25\times10^{-3}\times60}{2\times96500}$

No. of Ca atoms deposited = $\frac{25\times10^{-3}\times60}{2\times96500}\times6.022\times10^{23} = 4.68\times10^{18}$

(53) Ans[3] : $\frac{W_{O_2}}{W_{Ag}} = \frac{E_{O_2}}{E_{Ag}} = \frac{8}{108}$ $\therefore W_{O_2} = \frac{8}{108}\times0.108 = 10^{-3}\times8g$.

$n_{O_2} = 8\times10^{-3}/32 = 2.5\times10^{-4}$ $\therefore V_{H_2} = 2.5\times10^{-4}\times22400\ ml = 5.6ml$.

Topic 2 : Electrochemical series, Electrode potential and EMF.

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

(3) Ans[4] : $Z > X > Y$.

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

(6) Ans[1]. : $E^\circ = \frac{0.0591}{2}\log K_{eq}$ or $\log K_{eq} = \frac{2\times E^\circ}{0.0591} = \frac{2\times0.59}{0.059} = 20$

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

(8) Ans[2]. : $\Delta G^\circ = -nFE^\circ = -2\times96500\times0.46\ J$.

(9) Ans[3] : $E = E^\circ - \frac{0.0591}{2}\log Q_c$ or $\log K_c = \frac{2E^\circ}{0.0591} = \frac{2\times1.2}{0.0591} = 40.6$

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

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

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

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

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

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

$= 0.34 - (0.0591\times9.5)$

$= -0.22V$

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

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

(29) Ans[4] : NO_3^- is reduced as compared (in preference) of H_3O^+

[32] Ans[2] : $M^+ + X^- \longrightarrow MX$ is the spontaneous reaction.

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

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

(38) 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) Ans [1]: max. electrical work $= nFE^0 = 2 \times 1.1 \times 96500\ J = 212.3\ kJ$.

(40) Ans[4]: $Sn^{+4} + 2e^- \longrightarrow Sn^{+2}$; $E = E^0 - \frac{0.0591}{2} \log \frac{[Sn^{+2}]}{[Sn^{+4}]} = E^0 - \frac{0.0591}{2} \log \frac{0.10}{0.01}$

$= E^0 - \frac{0.0591}{2}$

(44) Ans [2]: $\underset{P_1}{H_2} \rightarrow 2H^+ + 2e^-$, $2H^+ + 2e^- \longrightarrow \underset{P_2}{H_2}$

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

(45) Ans[2]: $E = E^0 - \frac{0.0591}{2} \log \frac{[Tl^+]^2}{[Cu^{+2}]}$, $E \uparrow$ as $[Cu^{+2}] \uparrow$.

(46) Ans [3]: $\Delta G = -nFE$ or $-827 \times 10^3 = -6 \times 96500 \times E$ or $E = 1.428$

E for 1 mole of $Al_2O_3 = 1.428 \times \frac{3}{2} = 2.14\ V$.

(47) Ans [2]: $\Delta G^0 = -nFE^0 = -2 \times 96500 \times 1.104\ J = -213072\ J$

(48) Ans [2]: $E = E^0 - \frac{0.0591}{n} \log \frac{1}{[Cu^{+2}]} = 0.34 - \frac{0.0591}{2} \log \frac{1}{0.01}$

$= (0.34 - 0.06)\ V = 0.28\ V$

Topic 3

(1) Ans [1]: $2Br^- + Cl_2 \rightarrow 2Cl^- + Br_2$

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

(11) Ans[3] = $\eta = \Delta G / \Delta H$.

(16) Ans[2]: $E^0_{Mg^{+2}/Mg}$ is more negative than $E^0_{Fe^{+2}/Fe}$.
Mg is converted into Mg^{+2} readily.

(18) Ans[3]: $2H_2 + O_2 \longrightarrow 2H_2O$