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.

C-2. $SO_4^{2-} + 4e^- \rightarrow \frac{1}{2} S_2O_3^{2-}$

$-4 \times E^o \times F = 2 \times 0.936\ F + 2 \times 0.576\ F$

$E^o = -\frac{2 \times 0.936 + 2 \times 0.576}{4} = -0.756$ volt

C-3. $Mn^{3+} + e^- \longrightarrow Mn^{2+}$ 1.5 volt

$Mn^{3+} \longrightarrow MnO_2 + e^-$ – 1 volt

$2H_2O + Mn^{3+} \longrightarrow MnO_2 + 4H^+ + e^-$.

$2Mn^{3+} + 2H_2O \longrightarrow MnO_2 + 4H^+ + Mn^{2+}$.

$2Mn^{3+} \longrightarrow Mn^{2+} + MnO_2$, $E^o = 1.5 - 1 = 0.5$ volt.

$\Delta G = -1 \times 0.5 \times 96500 = -48.25$ KJ.

C-4. $2Al_2O_3$ (melt) $\longrightarrow 2Al_2O_3(s)$, $\Delta G_1^o = -2 \times 16$

$2Al_2O_3(s) \longrightarrow 4Al(l) + 3O_2(g)$, $\Delta G_2^o = 2 \times 1269$

$3C + 3O_2 \longrightarrow 3CO_2$, $\Delta G_3^o = -3 \times 395$

$2Al_2O_3$ (melt) $+ 3C \longrightarrow 4Al$ (l) $+ 3CO_2(g)$,

$\Delta G^o = \Delta G_1^o + \Delta G_2^o + \Delta G_3^o = -32 + 2 \times 1269 - 3 \times 395 = 1321$ kJ

$\Delta G^o = -nFE^o \Rightarrow 1321 \times 10^3 = -12 \times E^o \times 96500$

$E^o = -1.14$ volt

D-1. $H_2 \rightarrow 2H^+ + 2e^-$

0.1M and $P_{H_2} = 1$ atm

$E_{oxidation} = 0 - \frac{0.0591}{2} \log (P_{H_2})^2 = +0.0591 \times 1 = 0.0591$ volt

D-3. $Cu^{2+} + 2e^- \longrightarrow Cu$,

pH = 14, $[H^+] = 10^{-14}$ M $[OH^-] = 1$ M $\Rightarrow [Cu^{2+}] \times 1^2 = 1 \times 10^{-19} \Rightarrow [Cu^{2+}] = 1 \times 10^{-19}$ M

$E = 0.34 - \frac{0.0591}{2} \log \frac{1}{10^{-19}} = 0.34 - \frac{0.0591}{2} \times 19 = -0.2214$ volt

D-4. $(M \longrightarrow M^{n+}_{(0.02M)} + ne^-) \times 2$

$(2H^+ + 2e^- \longrightarrow H_2) \times n$

$2M + 2nH^+ \longrightarrow 2M^{n+} + nH_2$

$0.81 = (0.76 + 0) - \frac{0.0591}{2n} \log \frac{(0.02)^2}{(1)^{2n}} \Rightarrow (0.81 - 0.76) = \frac{0.0591}{2n} \log 4 \times 10^{-4}$

$n = -\frac{0.0591}{2 \times 0.5} \times \log 4 \times 10^{-4} = -0.591\ (-4 + 0.6) = 2.$

D-5. (a) $Zn + 2Ag^+$ (aq) $\rightleftharpoons$ Zn^{2+} (aq) $+ 2Ag(s)$

(b) $E^o = 0.8 - (-0.76) = 1.56$ V

(c) $1.6 = 1.56 - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Ag^+]^2}$ or $1.356 = \log \frac{[Ag^+]^2}{[Zn^{2+}]}$

or $\log \frac{[0.1]^2}{[Zn^{2+}]} = 1.356$ or $\frac{0.01}{[Zn^{2+}]} = 22.7$

or $[Zn^{2+}] = \frac{0.01}{22.7} = 4.4 \times 10^{-4}$ M

D-6. $\overset{+5}{N}O_3^- + 2H^+ + e^- \longrightarrow \overset{+4}{N}O_2 + H_2O$; 0.79 volt

$\overset{+5}{N}O_3^- + 8H^+ + 6e^- \longrightarrow NH_3OH^+ + 2H_2O$; 0.731 volt

$E = 0.79 - \frac{0.0591}{1} \log \frac{1}{[H^+]^2} = 0.731 - \frac{0.0591}{6} \log \frac{1}{[H^+]^8}$

$0.79 + 2 \times \frac{0.0591}{2} \log [H^+] = 0.731 + \frac{0.0591}{6} \times 8 \times \log [H^+]$

$0.059 = 0.059 (2 - \frac{8}{6})$ pH $\Rightarrow$ pH $= \frac{6}{4} = 1.5$

D-7. $E^o_{Zn\,/\,Zn2+} = 0.76$ volt $E^o_{Cu\,/\,Cu2+} = -0.34$ volt

$CuSO_4 + Zn \longrightarrow ZnSO_4 + Cu.$

$O = (0.76 + 0.34) - \frac{0.0591}{2} \boxed{\log\left(\frac{Zn^{2+}}{Cu^{2+}}\right)}$ $\Rightarrow$ $\log \left(\frac{Zn^{2+}}{Cu^{2+}}\right) = 37.22$

F-1. $Cu^{2+} + 2e^- \longrightarrow Cu$

No. of Faraday required = 2 F $= 2 \times 6.023 \times 10^{23} = 12.04 \times 10^{23}$

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

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

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

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

F-6. $Ag^+ + e^- \longrightarrow Ag$ $\frac{0.54}{108} = 5 \times 10^{-3}$ mol

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$n_{H_2} = 2.5 \times 10^{-3}$, $V_{H_2} = 22.4 \times 2.5 \times 10^{-3} = 56.0$ mL

F-7. With Ni electrode, cathode reaction, $Ni^{2+} + 2e^- \longrightarrow Ni$, Anode reaction, $Ni \longrightarrow Ni^{2+} + 2e$

No. Change in molarity of solution.

F-8. $Cd^{2+} + 2e^- \longrightarrow Cd.$

Cd required for 2g of Hg = $\frac{12 \times 2}{88} = 0.2727$ g.

$t = \frac{2 \times 96500 \times 2727}{112.4 \times 5} = 93.65$ Sec.

F-9. $2HSO_4^- \longrightarrow S_2O_8^{2-} + 2e^- + 2H^+$ $\quad i = \dfrac{2 \times 96500}{60 \times 60 \times 0.75}$ i = 71.48 Amp.

G-1. $CH_4 + 10OH^- \longrightarrow CO_3^{2-} + 7H_2O + 8e^-$

No. of Faradays required = $\dfrac{80 \text{ x } 3600 \text{ x } 0.96}{96500}$

Hence mol. of CH_4 required = $\dfrac{1}{8} \text{ x } \dfrac{80 \text{ x } 3600 \text{ x } 0.96}{96500}$

$V_{CH_4} = \dfrac{1}{8} \text{ x } \dfrac{80 \text{ x } 3600 \text{ x } 0.96}{96500}$ x 22.4 L = 8.356 x 0.96 = 8.02 L **Ans.** 8

H-1. $K = \dfrac{1}{245} \times \dfrac{4}{7}$ = **2.332×10^{-3} mho cm^{-1}.**

$\Lambda_m = \dfrac{2.33 \times 10^{-3} \times 1000}{0.1}$ **= 23.32 mho cm^2 mol^{-1}.**

H-2. $\Lambda_{eq} = 97.1$ Scm^2 eq^{-1}, C = 0.1 N
A = 1.5 cm^2, l = 0.5 cm

$\Lambda_{eq} = \dfrac{1000 \times \left(\frac{1}{R} \times \frac{\ell}{A}\right)}{C} \quad \Rightarrow \quad 97.1 = \dfrac{1000}{0.1} \times \dfrac{1}{R} \times \dfrac{0.5}{1.5}$

$R = 34.33\ \Omega \quad \Rightarrow \quad i = \dfrac{V}{R} = \dfrac{5}{34.33} = 0.1456$ amp

H-3. C = 0.1 N, $\quad K = 1.12 \times 10^{-2}$ Scm^{-1}, $\quad R = 65\Omega$

$K = \dfrac{1}{R} \times \dfrac{\ell}{A} \qquad \dfrac{\ell}{A}$ = cell constant = $1.12 \times 10^{-2} \times 65 = 0.728$ cm^{-1}

I-1. $\Lambda^\circ_m(NH_4Cl) = 150 = \Lambda^\circ_m(NH_4^+) + \Lambda^\circ_m(Cl^-)$
$\Lambda^\circ_{OH^-} = 198, \quad \Lambda^\circ_{Cl^-} = 76, \quad \Lambda_m(NH_4OH) = 9.6, \quad C = 0.01$
$\Lambda^\circ_m(NH_4OH) = 150 - 76 + 198 = 272$

$\alpha = \dfrac{\Lambda_m(NH_4OH)}{\Lambda^\circ_m(NH_4OH)} = \dfrac{9.6}{272} = 0.0353$

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

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

I-4. $K_{AgCl} = 2.28 \times 10^{-6}$ Scm^{-1}, $\quad 138.3 = \dfrac{1000 \times 2.28 \times 10^{-6}}{S}$

$S = 1.65 \times 10^{-5}$ and $\quad K_{sp} = (S)^2 = 2.72 \times 10^{-10}$ 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. $E_{cell} = E°_{Ni / Ni2+} + E°_{Ag^+ / Ag}$
$= 0.25 + 0.80 =$ **1.05 Volt.**

B-1. E^0 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. $E^0_{Cu^{2+}/Cu} = 0.34$ $E^0_{Fe^{2+}/Fe} = -0.44$ 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 $AgNO_3$, $Pb(NO_3)_2$ so can't be used along these electrolyte.

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

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

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

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

D-2. $H_2(Pt)\ (1\ atm)\ |H_3O^+|\ |\ Ag^+_{(xM)}\ |\ Ag$

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

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

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

$\log x = -1.7$

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

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

D-3. $Zn \longrightarrow Zn^{2+}_{(C_1)} + 2e^-$

$Zn^{2+}_{(C_2)} + 2e^- \longrightarrow Zn$

$Zn^{2+}_{(C_2)} \rightleftharpoons Zn^{2+}_{(C_1)}$

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

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

D-4. $H_{2_{(p_1)}} \longrightarrow 2H^+ + 2e^-$

$2H^+ + 2e^- \longrightarrow H_{2_{(p_2)}}$

$X_{2_{(p_1)}} \longrightarrow X_{2_{(p_2)}}$

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

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

D-5. $H_2 \longrightarrow 2H^+_{(10^{-2}M)} + 2e^-$

$2H^+_{(10-3\ M)} + 2e^- \longrightarrow H_2$

$2H^+_{(10^{-3}M)} \longrightarrow 2H^+_{(10^{-2}M)}$

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

$E \rightarrow$ – ve (Non spontaneaous).

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 Volt.**

If connected in reverse direction,E = 0.0178 volt.

E-1. At anode $Ag \longrightarrow Ag^+ + e^-$

At cathode $Ag^+ + e^- \longrightarrow Ag$

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 -

Anode : $H_2O \longrightarrow 4H^+ + 4e^- + O_2$

Cathode : $\{Cu^{++}_{(aq)} + 2e^- \longrightarrow Cu(s)\} \times 2$

Net cell reaction $2Cu^{++}$ aq. $+ 2H_2O \longrightarrow 4H^+ + 2Cu(s) + O_2 \uparrow$

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

$\therefore$ (B) is answer

F-1. $8H^+ + 5e^- + MnO_4^- \longrightarrow Mn^{+2} + 4H_2O$

(1 mole)

5 mole e^- = 5 Faraday.

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

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

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

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

F-4. $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

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

n_{OH^-} formed = 0.1 mol

nNaOH = 0.1 mol $\equiv$ **4 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

$Pb(s) + PbO_2(s) + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O.$

G-2. H_2–O_2 fuel cell

At anode : $2OH^- + H_2 \longrightarrow 2H_2O + 2e^-$

At cathode : $2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$

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. $K_a = 25\times10^{-6}$ $\wedge_{eq} = 19.6$ Scm^2 eq^{-1}, C = 0.01

$K_a = 0.01 \times \alpha^2 \quad \Rightarrow \quad \alpha = \sqrt{\frac{25\times10^{-6}}{10^{-2}}} = 5 \times 10^{-2}$

$\alpha = 5 \times 10^{-2} = \frac{19.6}{\overset{\circ}{\wedge}_{eq}} \quad \Rightarrow \quad \overset{\circ}{\wedge}_{eq} = \frac{19.6}{5\times10^{-2}} = 392$ Scm^2 eq^{-1}.

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

Normality = 2×10^{-3} M

Molarity = $\frac{2\times10^{-3}}{2} = 10^{-3}$ M

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

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

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

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

I-5. $\wedge_{m,BaSO_4} = (x_1 + x_2\, x - 2x_3) \quad \Rightarrow \quad \wedge_{eq.,BaSO_4} = \frac{\wedge_{eq.,BaSO_4}}{n - factor}$

$\wedge_{eq.,BaSO_4} = \frac{(x_1 + x_2 - 2x_3)}{2}$

PART - III

1. (A) $E^o_{Zn^{2+}/Zn} > E^o_{Mg^{2+}/Mg}$ so E^o_{cell} = –ve

(B) $E^o_{Ag^+/Ag} > E^o_{Zn^{2+}/Zn}$ so E^o_{cell} = +ve

(C) $E^o_{Ag^+/Ag} > E^o_{Zn^{2+}/Zn}$ so E^o_{cell} = 0 (at equilibrium)

(D) $E^o_{Ag^+/Ag} > E^o_{Fe^{2+}/Fe}$ so E^o_{cell} = +ve

2. (A) $E_{cell} = -\frac{0.059}{2} \log \frac{(P_{H_2})_c [H^+]_a^2}{(P_{H_2})_a [H^+]_c^2}$,

$E^0_{cell} = -\frac{0.059}{2} \log \frac{0.01 \times (0.1)^2}{(0.1) \times (1)^2} = \frac{0.059}{2} \times 3$ = +ve

(B) Cell reaction $Ag^+_c\ (10^{-2}) \rightarrow Ag^+_a\ (10^{-9})$

$E_{cell} = E^0_{cell} - \frac{0.059}{1} \log \frac{10^{-9}}{10^{-2}} = E^0_{cell} + \frac{0.059}{1} \times 7 > 0$

$E^0_{cell} \neq 0$ and not conc. cell

(C) $E_{cell} = 0 - \frac{0.059}{2} \log \frac{[Cu^{+2}]_a}{[Cu^{+2}]_c} = -\frac{0.059}{2} \log \frac{0.1}{0.01}$ = – ve

(D) $E_{cell} = -\frac{0.059}{2} \log \frac{[Cl^-]_c}{[Cl^-]_a} = \frac{0.059}{2} \log \frac{0.1}{0.1} = 0$

And $E^0_{cell} = 0$.

EXERCISE # 2

PART - I

1. As $E^o_{Cu^{2+}} \longrightarrow Cu = 0.337\ V > E^0_{H^+/H_2}$

$\therefore$ 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 reaitive 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. $E_1 = E^o - \frac{R\ T}{n\ F} \ln 2$

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

$\therefore \quad E_2 > E_1$

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

For E_{cell} to be +ve and maximum

$\frac{C_1}{C_2} < 1$ or $C_1 < C_2$ Give $C_2 = 1M$.

$\therefore$ C_1 should be the minimum conc. of H^+. $\therefore$ (B) is the right answer.

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

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

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

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

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

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

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

11. At Cathode : $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$] × 2

At Anode : $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

H_2 = 2 mole

O_2 = 1 mole Total volume = 3 × 22.4 **= 67.2 L.**

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

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

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

15. Rusting reaction of Fe is -

$2H^+ + Fe + \frac{1}{2} O_2 \longrightarrow Fe^{2+} + H_2O$

PART - II

1. (A) H_4XeO_6 has more SRP, so better oxidizing agent then F_2
(B) O_3 has more SRP, so will oxidize Cl_2
(C) $E^o_{ClO_4^-/ClO_3^-}$ is more in acidic medium than in basic medium
(D) $E^o_{[Fe(CN)_6]^{3-}|[Fe(CN)_6]^{4-}} = 0.36$ V
Hence $[Fe(CN)_6]^{4-}$ can be easily oxidized by ClO^-, Ce^{4+} Br_2O^- but not by Li^+
(E) $E^o_{ClO^-/Cl^-(OH^-)}$ is more than $E^o_{BrO^-/Br^-}$ and $E^o_{ClO_4^-/ClO_3^-(OH^-)}$ so true.
(F) Ce^{4+} can't oxidize Cl_2 in acidic medium.

2. $H_2 \longrightarrow 2H^+ + 2e^-$
1 atm $\quad 10^{-10}$

$$E_{H_2/H^+} = 0 - \frac{0.059}{2}\log\frac{\left(10^{-10}\right)^2}{1} \Rightarrow \qquad E_{H_2/H^+} = +0.59\,V$$

3. $Cu^{2+} + 4NH_3 \longrightarrow [Cu(NH_3)_4]^{2+}$
1 $\quad$ a $\quad$ 0
0 $\quad$ 2 $\quad$ 1

$$K_f = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}]\ [NH_3]^4}$$

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

Now, $\quad E_{Cell} = E^0_{Cell} - \dfrac{0.059}{2}\ \log\ \dfrac{[Zn^{2+}]}{[Cu^{2+}]} = 1.1 - \dfrac{0.059}{2}\ \log\ \dfrac{1}{6.25\times10^{-14}} = 0.71$ V.

4. $\lambda_m = \dfrac{K\times1000}{M}$

$200 = \dfrac{K\times1000}{0.04}$

$K = \dfrac{200\times0.04}{1000} = 8 \text{ x } 10^{-3}$ S cm^{-1}.

$K = \left(\dfrac{\ell}{9}\right) \text{ x } \dfrac{1}{R}$

$8 \text{ x } 10^{-3} = \left[\dfrac{8}{4}\right] \text{ x} \dfrac{1}{R}$

$R = \dfrac{2}{8\times10^{-3}} = \dfrac{1}{4}\text{x } 10^3\ \Omega$.

Again $\Rightarrow V = IR$

So $\quad I = \dfrac{V}{R} = \dfrac{10}{\left(\frac{1}{4}\times10^3\right)} = 4 \text{ x } 10^{-2}$A.

5. $K_{sol} = K_{Ba^{2+}} + K_{Ag^+} + K_{NO_3^-}$

$$5.3 = \frac{\lambda^o_{Ba^{2+}}\times[Ba^{2+}]}{10^{-3}} + \frac{\lambda^o_{Ag^+}\times[Ag^+]}{10^{-3}} + \frac{\lambda^o_{NO_3^-}\times[NO_3^-]}{10^{-3}}$$

$$\therefore\ 5.3 = \frac{13\times10^{-3}\times0.1}{10^{-3}} + \frac{6\times10^{-3}\times0.2}{10^{-3}} + \frac{\lambda^{o}_{(NO_3^-)}\times0.4}{10^{-3}}$$

$$\therefore\ \lambda^{o}_{(NO_3^-)} = 7\times10^{-3}\times1000\ Sm^2mol^{-1} = 7\ Sm^2\ mol^{-1}$$

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

$HA + aq \rightleftharpoons H^+ + A^-$

$C\alpha \quad C\alpha$

$C\alpha - C\alpha$

$[H^+| = C\alpha = 0.01\times0.01 = 10^{-4}$

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

7. $\lambda^0 = \frac{1000\times(\kappa_{sol} - \kappa_{H_2O})}{S}$

$$138 = \frac{1000\times(3.4-2.02)\times10^{-6}}{S}$$

$S = 1\times10^{-5}$

8. $\lambda^{o}_{m}\ (H_2O) = \frac{\lambda^{o}_{m(Ba(OH)_2)} + 2\lambda^{o}_{m(HCl)} - \lambda^{o}_{m(BaCl_2)}}{2}$

$= 5.5\times10^{-2}\ S\ m^2\ mol^{-1}.$

Now, in SI units,

$$\lambda^{o}_{m} = \frac{K\times10^{-3}}{M} \qquad \therefore\ \lambda^{o}_{m\ (H2O)} = \frac{K\times10^{-3}}{[H_2O]diss}$$

$$5.5\times10^{-2} = \frac{5.5\times10^{-6}\times10^{-3}}{[H_2O]diss}$$

$[H_2O]\ diss = [H^+] = [OH^-] = 10^{-7}\ M$

For equilibrium : $H_2O \rightleftharpoons H^+ + OH^-$

Dissociation constant $K = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7}\times10^{-7}}{\left(\frac{1000}{18}\right)}$

$= 1.8\times10^{-16}$

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

1. Lower S.R.P. containing ion can displace higher S.R.P. containing ion.

2. $\Delta G^0 = -nFE^0_{cell}$

If E^0_{cell} = +ve then $\Delta G° = -$ve and reaction is spontaneous.

4.

(A) Anode $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

(B) Anode $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

(C) Anode $Cu \longrightarrow Cu^{2+} + 2e^-$

(D) Anode $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

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

Increase in mass of cathode = decrease in mass of Anode = $\frac{2.68 \times 3600}{96500} \times \frac{63.5}{2}$ = **3.174 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. $Fe^{2+} + 2e^- \longrightarrow Fe$ [in $FeSO_4$] ; $Fe^{3+} + 3e^- \longrightarrow Fe$ [in $Fe_2(SO_4)_3$]
$Fe^{3+} + 3e^- \longrightarrow Fe$ [in $Fe(NO_3)_3$]

Amount of Fe deposited in $FeSO_4 = \frac{Q}{96500} \times \frac{56}{2}$

Amount of Fe deposited in $Fe_2(SO_4)_3 = \frac{Q}{96500} \times \frac{56}{3}$

8. **Anode :** Pb(s)
Cathode : $PbO_2(s)$
H_2SO_4(conc.) about 38% solution of H_2SO_4 is taken.
Anode : $Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$
$Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s)$
$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4 + 2e^-$
most of the $PbSO_4(s)$ ppt sticks to the lead rod.
Cathode : $2e^- + 4H^+ + PbO_2(s) \longrightarrow Pb^{2+}(aq) + 2H_2O(\ell)$
$Pb^{2+}(aq) + SO_4^{2-}(aq) + 4H^+ + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(\ell)$
$PbSO_4(s)$ sticks to cathode rod.
Over all reaction : $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(\ell)$, $E_{cell} = 2.05$ V

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

11. $\kappa \alpha c$

Hence $\kappa_1 = a \times 0.1$
$\kappa_2 = a \times 0.01$
$\kappa_3 = a \times 0.005$
$\kappa_4 = a \times 0.0025$

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

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

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

Hence $G_1 > G_2 = G_2 > G_4$

13. $\lambda^\circ_{eq} = \frac{\lambda^\circ_m}{Vf}$

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

Also, $\lambda^\circ_m (Al_2(SO_4)_3) = 2\ \lambda^\circ_m (Al^{3+}) + 3\ \lambda^\circ_m (SO_4^{2-})$

& $\lambda^\circ_{eq} (Al_2(SO_4)_3) = \lambda^\circ_{eq} (Al^{3+}) + \lambda^\circ_{eq} (SO_4^{2-})$

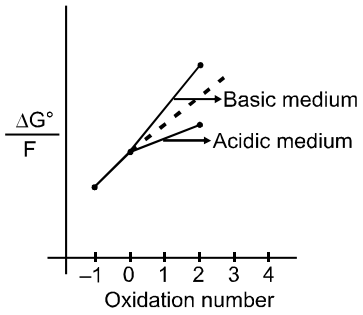
14. Li^+ Na^+ K^+ Rb^+ Cs^+
degree of Hydration decreases
Size of ions decreases
ionic mobility increases
$H^+_{(aq)}$ has smallest size therefore show maximum mobility.

PART - IV

1. From given latimer diagrams.$Cl_2 - Cl^-$ is independent of H^+ cocentration.

2. $\Delta G^0 = \Delta G_1^0 + \Delta G_2^0$, using this $E^0 = \frac{0.42 + 1.36}{2}$ V = 0.89 V

3.



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

5. As $\frac{\Delta G^o}{F}$ 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

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

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

7. For 25×10^{-4} (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 $\Lambda_m = \frac{K \times 1000}{M}$ $K = \left(\frac{\ell}{a}\right) \times \frac{1}{R}$

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

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

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

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

8. For Na_2SO_4 solution

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

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

Λ_m (Na_2SO_4) = 192.4 ohm^{-1} cm^2 mole^{-1}

9. At the equivalence point the concentrations will be [Br^-] = 100 mol/m^3, [Na^+] = 100 mol/m^3
Therefore $\kappa_{total} = \kappa_{Br^-} + \kappa_{Na^+}$ = 1.2 Sm^{-1} = **12** × 10^{-1} 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 $Fe(NO_3)_2$ cannot be estimated quantitatively with MnO_4^- ion in HCl.
E^o_{Cell} for the cell Pt, Cl_2(g) (1 atm) | Cl^- (aq) | | MnO_4^- (aq) | Mn^{2+} (aq). is euqal to (1.51 – 1.4) = 0.11 V.

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

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

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

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

E^o = 0.32 Volt.
At equilibrium, E_{cell} = 0.

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

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

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

$In^{2+} \longrightarrow In^{3+} + e^-$

E^o = 0.44 volt.
E^o_{cell} = 0.15 + 0.44 = 0.59 volt.

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

5. $Fe \longrightarrow Fe^{2+} + 2e^-$, 0.44 V.
$2H^+ + \frac{1}{2} O_2 + 2e^- \longrightarrow H_2O$, 1.23 V.

$Fe + 2H^+ + \frac{1}{2} O_2 \longrightarrow Fe^{2+} + H_2O$, E^o = 0.44 + 1.23 = 1.67 volt.

ΔG^o = – 2 × 1.67 × 96500 = – 322.3 kJ.

6. $2Ag^+ + C_6H_{12}O_6 + H_2 \longrightarrow 2Ag(s) + C_6H_{12}O_7 + 2H^+$, $E^o = 0.8 - 0.05 = 0.75$ 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. $[H^+] = 10^{-11}$ M.

$E_{oxide} = -0.05 - \frac{0.0591}{2} \log(10^{-11})^2 = -0.05 + 0.65$

or, $\Delta H = 0.65$ volt.

8. Standards electrode potential does not depend upon on concentration.

9. $AgBr(s) \rightleftharpoons Ag^+ + Br^-$

$(S + 10^{-7}) \times S = K_{SP} = 12 \times 10^{-14}$.

$S = 3 \times 10^{-7}$ M.

$[Ag^+] = 4 \times 10^{-7}$ M ; $[Br^-] = 3 \times 10^{-7}$ M ; $[NO_3^-] = 10^{-7}$ M.

$K_{total} = \Lambda^o_{(Ag+)}\ \Lambda^o_{(Ag+)} + \Lambda^o_{Br-}\ \Lambda^o_{Br-} + \Lambda^o_{(NO3-)}\ \Lambda^o_{(NO3-)}$

$\Lambda^o_{KCl} = \Lambda^o_{K+} + \Lambda^o_{Cl-}$.

$K_{KCl} = 4 \times 10^{-4} \times 6 \times 10^{-3} + 3 \times 10^{-4} \times 8 \times 10^{-3} + 1 \times 10^{-4} \times 7 \times 10^{-3}$.

$K_{KCl} = 24 + 24 + 7. \quad \Rightarrow \quad$ **$K_{KCl} = 55\ Scm^{-1}$.**

10. Mol of NaCl = $4 \times 0.5 = 2$ mol.

No. of mole of Cl_2 evolved = $\frac{1}{2}$ × mol of NaCl = $\frac{1}{2} \times 2 =$ **1 mol.**

11. Taking the 1 : 1 molar combination of Na–Hg amalgam.
weight = $2 \times 23 + 2 \times 200 = 446$ g.

12. $2Na^+ + 2e^- \longrightarrow 2Na$.
No. of Faraday required = 2.
$\therefore$ total charge = $2 \times 96500 =$ **193000 coulomb.**

13. $Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$.
$E^o = 1.36 + (-0.54) =$ **0.82 V (+ ve). Spontaneous.**

14. $Mn^{3+} + e^- \longrightarrow Mn^{2+}$, 1.50 volt.
$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$, 1.23 volt.

$4Mn^{3+} + 2H_2O \longrightarrow 4Mn^{2+} + O_2 + 4H^+$, $E_{cell} = 1.5 - 1.23 =$ **0.27 volt. (+ ve).**

Mn^{3+} will oxidise H_2O.

15. Faraday law equivalents of H_2 produced $= \frac{I \times t\ (sec)}{96500}$

$0.01 \times 2 = \frac{10 \times 10^{-3} \times t}{96500} = 96500 \times 2 = t$

19.3×10^4 sec = t

16. The species having less reduction potential with respect to NO_3^- ($E^o = 0.96$ V) will be oxidised by NO_3^-. These species are V, Fe, Hg.

17. M (s) | M^+ (aq, 0.05 M) || M^+ (aq, 1 M) | M(s)
Anode : $M(s) \longrightarrow M^+(aq) + e^-$
Cathode : $M^+(aq) + e^- \longrightarrow M(s)$

$M^+(aq)|_c \rightleftharpoons M^+(aq)|_a$

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

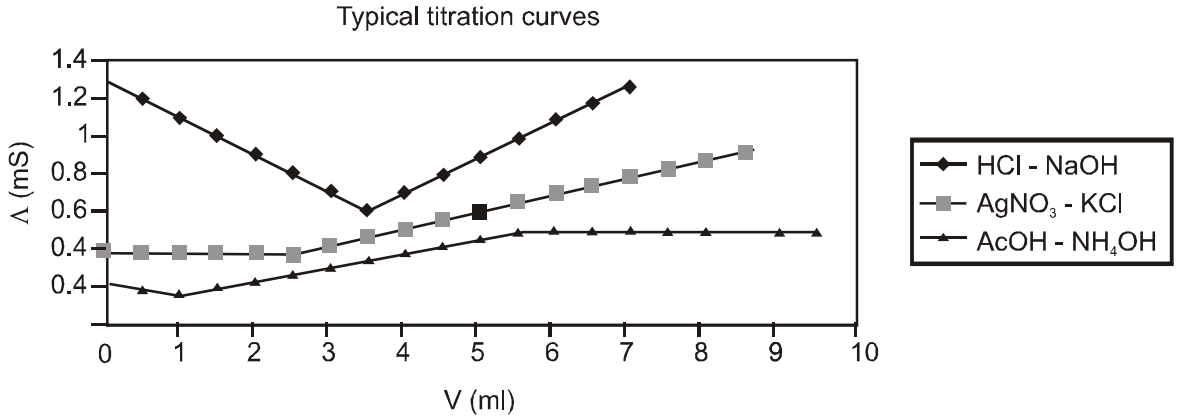
$$= 0 - \frac{0.0591}{1} \log \left\{\frac{0.05}{1}\right\}$$

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

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

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

19.



20. $E = E^o - \frac{0.059}{4} \log \frac{[Fe^{2+}]^2}{[H^+]^4 P_{O_2}}$

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

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

21. $M|M^{2+}(aq) \,||\, M^{2+}(aq)|M$
0.001 M

Anode : $M \longrightarrow M^{2+}(aq) + 2e^-$

Cathode : $M^{2+}(aq) + 2e^- \longrightarrow M$

$$M^{2+}(aq)_c \rightleftharpoons M^{2+}(aq)_a$$

$$E_{cell} = 0 - \frac{0.059}{2} \log \left\{\frac{M^{2+}(aq)_a}{10^{-3}}\right\}$$

$$0.059 = -\frac{0.059}{2} \log \left\{\frac{M^{2+}(aq)_a}{10^{-3}}\right\}$$

$$-2 = \log \left\{\frac{M^{2+}(aq)_a}{10^{-3}}\right\}$$

$10^{-2} \times 10^{-3} = M^{2+}(aq)_a$ = solubility = s

$K_{sp} = 4s^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15}$

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

= – 11.4 kJ/mole.

23. (P) $\overset{X}{(C_2H_5)_3N} + \overset{Y}{CH_3COOH} \longrightarrow CH_3COO^-\,(aq) + (C_2H_5)_3NH^+\,(aq)$

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.

(Q) KI (0.1 M) + $AgNO_3$ (0.01 M) $\longrightarrow$ AgI $\downarrow$ (ppt) + KNO_3 (aq).

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.

(R) $CH_3COOH + KOH \longrightarrow CH_3COOK\,(aq) + H_2O$

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

(S) $NaOH + HI \longrightarrow NaI\,(aq) + H_2O$

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).

24. (P) $E^o_{Fe3+, Fe}$

$$Fe^{3+} \xrightarrow[n=1]{+0.77V} Fe^{2+} \xrightarrow[n=2]{-0.44V} Fe$$

$Fe^{3+} \rightarrow Fe$: xV, n = 3

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

$\Rightarrow$ $x = -\dfrac{0.11}{3}\,V \sim -0.04\,V.$

(Q) $4H_2O \rightleftharpoons 4H^+ + 4OH^-$

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad -1.23\,V$$
$$+\ O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- + 0.4\,V$$

$$4H_2O \rightleftharpoons 4H^+ + 4OH^- \qquad -0.83\,V$$

(R) $E^o_{(Cu2+ + Cu \to 2Cu+)}$

$$Cu^{2+} \xrightarrow[n=1]{xV} Cu^{+} \xrightarrow[n=1]{-0.52V} Cu$$

$Cu^{2+} \rightarrow Cu$: + 0.34V, n = 2

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

$x = 0.16$ V.

$\Rightarrow$ $Cu^{2+} + e^- \longrightarrow Cu^+ \qquad 0.16\,V$

$+\ Cu \longrightarrow Cu^+ + e^- \qquad -0.52\,V$

$Cu^{2+} + Cu \longrightarrow 2Cu^+ \qquad -0.36\,V$

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

(s) $E^o_{(Cr3+, Cr2+)}$

$$Cr^{3+} \xrightarrow[n=1]{x} Cr^{2+} \xrightarrow[n=2]{-0.91V} Cr$$

$Cr^{3+} \rightarrow Cr$: – 0.74V, n = 3

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

$x - 1.82 = -2.22 \qquad \Rightarrow \qquad x = -0.4\,V$

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 occurence 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^+

$\Delta G^0 = -2 \times 96500 \times (-0.25)$ J

$= +48250$ J/mole $= 48.25$ KJ/mole

Energy released by conversion of 1 mole of

$x \longrightarrow y \qquad \Delta G = -193$ KJ

Hence mole of m^+ convert

$$\frac{193}{48.25} = 4$$

27. $\lambda^\circ_{X^-} \approx \lambda^\circ_{Y^-}$

$\Rightarrow \lambda^\circ_{H^+} + \lambda^\circ_{X^-} \approx \lambda^\circ_{H^+} + \lambda^\circ_{Y^-}$

$\Rightarrow \lambda^\circ_{HX} \approx \lambda^\circ_{HY}$ (1)

Also $\frac{\lambda_m}{\lambda_m^\circ} = \alpha$, So $\lambda_m(HX) = \lambda^\circ_m \alpha_1$ and $\lambda_m(HY) = \lambda^\circ_m \alpha_2$

(Where α_1 and α_2 are degrees of dissociation of HX and HY respectively.)

Now, Given that

$\lambda_m(HY) = 10\, \lambda_m(HX)$.

$\Rightarrow \lambda^\circ_m \alpha_2 = 10 \times \lambda^\circ_m \alpha_1$

$\alpha_2 = 10\, \alpha_1$ (2)

$K_a = \frac{C\alpha^2}{1-\alpha}$, but $\alpha << 1$, therefore $K_a = C\alpha^2$.

$$\Rightarrow \frac{K_a(HX)}{K_a(HY)} = \frac{0.01\alpha_1^2}{0.1\alpha_2^2} = \frac{0.01}{0.1} \times \left(\frac{1}{10}\right)^2 = \frac{1}{1000}.$$

$\Rightarrow \log(K_a(HX)) - \log(K_a(HY)) = -3. \qquad \Rightarrow pK_a(HX) - pK_a(HY) = 3.$

28. $E_{cell} = E°_{cell} - \frac{0.059}{2} \log_{10} \frac{[M^{2+}][H^+]^2}{[M^{4+}]pH_2}$

$0.092 = 0.151 = \frac{0.059}{2} \log_{10} 10^x$

$\therefore x = 2$

29. $C = 0.0015M \qquad \ell = 120$ cm

$G = 5 \times 10^{-7}$s $\qquad a = 1$ cm^2

$$G = \kappa \times \frac{a}{\ell}$$

$$5 \times 10^{-7} = \kappa \times \frac{1}{120}$$

$\kappa = 6 \times 10^{-5}$ s cm^{-1}

$$\Lambda_m^c = \frac{\kappa \times 1000}{M} = \frac{6 \times 10^{-5} \times 1000}{0.0015}$$

pH = 4

$[H^+] = 10^{-4} = c\,\alpha = 0.0015\,\alpha$

$$\alpha = \frac{10^{-4}}{0.0015}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^o} \Rightarrow \frac{10^{-4}}{0.0015} = \frac{\frac{6 \times 10^{-5} \times 1000}{0.0015}}{\Lambda_m^o}$$

$\Lambda_m^o = 6 \times 10^2$ s cm^2 mole^{-1}

30. $\Delta G = \Delta G^\circ + 2.303\ RT \log_{10} Q\ ;\ Q = \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$

$= -2F(1.1) + 2.303\ RT \log_{10} 10$

$= 2.303\ RT - 2.2\ F$

31. $Mg \longrightarrow Mg^{2+} + 2e^-$

$Cu^{2+} + 2e^- \longrightarrow Cu$

$Mg + Cu^{2+}\ Mg \longrightarrow Mg^{2+} + Cu$

$E = 2.67 = 2.7 - \dfrac{RT}{nF}\ell$ ɣ

ɪ

$0.03 = \dfrac{300}{2\times 11500}\ \ell nx$

$2.3 = \ell nx$

$X = 10$

32. $A(s)|A^{n+}(aq, 2M) \,||\, B^{2n+}(aq, 1M)\,|\,B(s)$

Reactions

Anode $(A \longrightarrow A^{n+} + ne) \times 2$

Cathode $B^{2n+} + 2ne \longrightarrow B$

Overall reaction :

$2A(s) + B^{2n+} \longrightarrow 2A^{n+} + B.$

$E = E^o - \dfrac{RT}{2nF}\ell$

$O = E^o - \dfrac{RT}{2nF}\ell\ \dfrac{[A^{n+}]^2}{[B^{2n+}]}$

$E^o = \dfrac{RT}{2nF}\ell$

Now $\Delta G^o = -2nFE^o = \dfrac{-2nFRT}{2nF}\ell = -RT\ell n4.$

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

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

$\Delta S^o = \dfrac{\Delta G^o}{T} = \dfrac{-RT\ell}{T} = -R\ell n4$

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

PART - II

5. Electrons flow from anode to cathode always.

6. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

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

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

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

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 $E^o_{Zn^{2+}/Zn} = -0.76$ V

$E^o_{Cu^{2+}/Cu} = +0.34$ V

Hence Cu can't displace Zn from $ZnSO_4$ solution.

8. Fact

9. $Fe^{2+} + 2e^- \longrightarrow Fe + E^o_1 = -0.47$ V

$Fe^{3+} + e^- \longrightarrow Fe^{2+} + E^o_2 = +0.77$ V

$Fe^{3+} + 3e^- \longrightarrow Fe + E^o_3$

$$E^o_3 = \frac{n_1E^o_1 + n_2E^o_2}{n_1 + n_2} = \frac{2\times(-0.47) + 1\times(0.77)}{2+1} = -0.057V$$

10. $E^o_{T\ell\ \ell} = +0.34V$

$= E^o_{A\ell\ \ell} = +0.55V$

Therefore $T\ell^+$ more stable

11. $E^o_{Mn^{2+}/Mn^{3+}} = 1.57V$; $E^o_{H^+/H_2} = OV$

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

12. Cell reaction :

$M_{(s)} + 3Ag^+(aq) \longrightarrow M^{3+}(aq) + 3Ag_{(s)}$

Applying Nernst equation :

$$E_{cell} = E^o_{cell} - \frac{0.059}{n}\log_{10} Q$$

$$\therefore \quad 0.421 = (0.8 \times E^o_{M^{3+}/M}) - \frac{0.059}{3}\log_{10}\frac{0.001}{(0.01)^3}$$

$$\therefore \quad E^o_{M^{3+}/M} = 0.32V$$

13. Cathode

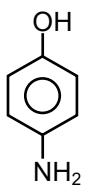
$2e^- + 2H_2O \longrightarrow H_2 + 2OH^-$ $\qquad (v.f.)_{H_2} = 2$

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

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

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

i = 1 amp

14. $C_6H_5NO_2 \longrightarrow$ 

$4e^- + 4H^+ + C_6H_5NO_2 \longrightarrow \underset{\text{M.W. = 109 g}}{C_6H_4(OH)(NH_2)} + H_2O$

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

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

W = 9.81 g

15. $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}$

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

For 0.05F; $PbSO_4$ electrolyzed = $\frac{0.05 \times 303}{2}$ = 7.6g

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

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

or, $\ln K = 160$

or, $K = e^{160}$

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

18. A : $\frac{1}{2}H_2(g) \rightarrow H^+(aq.) + e^-$ $\qquad E° = 0.0$ V

C : $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$ $\quad E° = x$ V

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

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

$0.92 = x + 0.72$

$x = 0.92 - 0.72 = 0.2$ Volts

19. Fact

20. $E°_{cell} = E°_{Zn(s)|Zn^{+2}} + E°_{Au^{3+}/Au}$

$= SOP_{anode} + SRP_{cathode}$

= 0.76 V + 1.40 V = 2.16V

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

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

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

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

23. $\Lambda°_m(HA) = \Lambda°_m(HCl) + \Lambda°_m(NaA) - \lambda°(NaCl)$

$= 425.9 + 100.5 - 126.4 = 400$

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

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

24. Strongest oxidizing agent has highest value of SRP

25. $Fe^{2+} \rightarrow Fe \qquad \Delta G_1^\circ = -2Fy$

$Fe^{3+} \rightarrow Fe \qquad \Delta G_2^\circ = -3Fz$

$\therefore Fe^{3+} \rightarrow Fe^{2+} \quad E^o = 3z - 2y$

$E^\circ_{cell} = E^0_{Ag^+|Ag} - E^0_{Fe^{3+}|Fe^{2+}}$

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

For given cell reaction

$E^\circ_{cell} = x + 2y - 3z$

26. $\Delta G^o = -nF E^\circ_{Cell} = -2 \times 96000 \times 2.0 \times 10^{-3} = -384$ kJ/mol

27. $Ni(NO_3)_2 \rightarrow Ni^{2+} + 2NO_3^-$

at cathode:

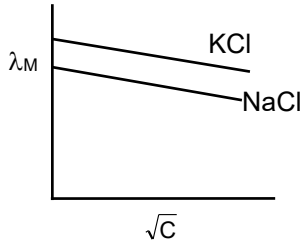
$Ni^{2+} + 2e^- \rightarrow Ni$

$2F \rightarrow 1$mole

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

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

29.



$(\lambda^0_M)_{K^+} > (\lambda^0_M)_{Na^+}$

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 $HCOOH > C_6H_5COOH > CH_3COOH$

32. $Cu^{2+} \xrightarrow{E_1^\circ} Cu^+ \xrightarrow{0.522} Cu$ (0.34)

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

$E_1^\circ = 0.68 - 0.522 \Rightarrow E_1^\circ = 0.158\,V$

33. Theory based.

34. From the given data

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

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

$= -1.23 + 0.0591 \times pH = -1.23 + 0.0591 \times 5$

$= -1.23 + 0.2955 = -0.9345\ V = -0.93\ V$

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

$Sn + Pb^{2+} \longrightarrow Sn^{2+} + Pb$

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

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

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

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

$Ag^{+} + e^{-} \longrightarrow Ag$

1F charge is required to deposit 1 mole of Ag

$H_2O \longrightarrow \frac{1}{2} O_2 + 2H^{+} + 2e^{-}$

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

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

$$V_{O_2} = \frac{nRT}{P}$$

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

$V_{O_2} = 5.674$ L

37. Theory based.