Exercise 5-1

1. (a) $Ag \longrightarrow Ag^{+} + e^{-} \,]\times 2$

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

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

(b) $Fe^{+2} \longrightarrow Fe^{+3} + e^{\ominus} \,]\times 5$

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

$5Fe^{+2} + 8H^{+} + MnO_4^{\ominus} \longrightarrow Fe^{+3} + Mn^{+2} + 4H_2O$

(c) $2Cl^{\ominus} \longrightarrow Cl_2 + 2e^{\ominus}$

$e^{\ominus} + Ag^{+} \longrightarrow Ag \,]\times 2$

$2Cl^{\ominus} + 2Ag^{+} \longrightarrow Cl_2 + Ag$

(d) $H_2 \longrightarrow 2H^{+} + 2e^{-}$

$2e^{\ominus} + Cd^{+2} \longrightarrow Cd$

$H_2 + Cd^{+2} \longrightarrow 2H^{+} + Cd$

Q.2 (a) $Zn | Zn^{+2} || Cd^{+2} | Cd$

(b) $Pt, H_2 | H^{+} || Ag^{+} | Ag$

(c) $Pt | Fe^{+2}, Fe^{+3} || H^{+}, Cr_2O_7^{-2}, Cr^{+3} | Pt$

Q.3 $$E^{\circ}_{Cell} = E^{\circ}_{Ce^{+4}|Ce^{+3}} + E^{\circ}_{Co|Co^{+2}}$$

$$1.89 = E^{\circ}_{Ce^{+4}/Ce^{+3}} + 0.28$$

$$E^{\circ}_{Ce^{+4}/Ce^{+3}} = 1.61 \text{ volt}$$

Q.4 $Cu^{+} \longrightarrow Cu^{+2} + e^{\ominus}$ $\quad E_1^{\circ} = -0.15$

$2e^{\ominus} + Cu^{+2} \longrightarrow Cu$ $\quad E_2^{\circ} = 0.34$

$e^{-} + Cu^{+} \longrightarrow Cu$ $\quad E^{\circ} = ?$

$$E^{\circ} = \frac{1 \times (-0.15) + 2(0.34)}{1}$$

$E^{\circ} = \underline{0.53 \text{ volt}}$

$\Rightarrow$ for disproportion of Cu^{+}

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

$$E^{\circ} = E^{\circ}_{Cu^{+}/Cu^{+2}} + E^{\circ}_{Cu^{+}/Cu}$$

$= -0.15 + 0.53$

$E^{\circ} = 0.38$

Q.5.

$$2e^{\ominus} + Fe^{+2} \longrightarrow Fe \qquad E_1^{\circ} = -0.44$$

$$e^{\ominus} + Fe^{+3} \longrightarrow Fe^{+2} \qquad E_2^{\circ} = 0.77$$

$$3e^{\ominus} + Fe^{+3} \longrightarrow Fe$$

$$E^{\circ}_{Fe^{+3}/Fe} = \frac{n_1 E_1^{\circ} + n_2 E_2^{\circ}}{n}$$

$$= \frac{2 \times (-0.44) + 1 \times (0.77)}{3}$$

$$= -0.03666$$

Q. 6

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

$$E = 0.1 - \frac{.059}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$

$$E = 0.1 - \frac{.059}{2} \log \frac{10^{-3}}{10^{-1}}$$

$$E = 0.1 + .059 \Rightarrow E = 0.159$$

Q. 7

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

$$E_{cell} = (.14 + (-.13)) - \frac{.059}{2} \log \frac{1}{10^{-3}}$$

$$E_{cell} = -.01 - .059 \Rightarrow E = -0.069 \text{ volt}$$

As E_{cell} is negative it means cell representation is incorrect

Q. 8

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

$$0 = +0.34 - \frac{.059}{2} \log \frac{1}{[Cu^{+2}]}$$

$$\log [Cu^{+2}] = -\frac{.68}{.059}$$

Q.9

$$E^{\circ}_{I^{\ominus}|AgI|Ag} = E^{\circ}_{Ag^{+}|Ag} + \frac{.059}{n} \log K_{sp}$$

$$E^{\circ}_{I^{\ominus}|AgI|Ag} = 0.7991 + \frac{.059}{1} \times (-16.07)$$

$$= -0.149$$

$$\simeq -0.15$$

Q.10 $2e^{\ominus} + Zn^{+2} \longrightarrow Zn$

$$E = -0.76 - \frac{.059}{2} \log \frac{1}{[Zn^{+2}]}$$

Let zinc salt is ZnX

$$ZnX \longrightarrow Zn^{+2} + X^{-2}$$

0.1	$-$	$-$
$0.1-x$	x	x

$$x = 0.1 \times \frac{20}{100} = 1/50$$

$$E = -0.76 - \frac{.059}{2} \log 50$$

$$E = -.81015$$

Q.11 $0.44 + 0.337 = \frac{.059}{2} \log K_{eq}$

$\log K_{eq} = 26.3389$

$K_{eq} = 10^{26.3389} = 2.18 \times 10^{26}$

Q.12 $\mu = \frac{dE^\circ}{dT} = \frac{\Delta S^\circ}{nF}$

$.02 = \frac{\Delta S^\circ}{2 \times 96500}$

$\Delta S^\circ = 3860$ Joule/Kelvin

$\Delta S^\circ = 3.86$ KJ/Kelvin

Q.13

$E_1^\circ = \frac{1 \times 0.55 + 2 \times 2.26}{3} = 1.69$ volt

$MnO_4^{\ominus} \xrightarrow{0.55} MnO_4 \xrightarrow{2.26} MnO_2 \xrightarrow{0.96} Mn^{+3} \xrightarrow{1.66} Mn^{+2}$

$E_2^\circ = \frac{0.96 \times 1 + 1.66 \times 1}{2}$

$E_2^\circ = 1.31$ volt

$E_1^\circ + E_2^\circ = 1.69 + 1.31 = 3$ volt

Q.14 $e^{\ominus} + H^{+}_{(aq.)} \longrightarrow \frac{1}{2} H_{2(g)}$

$$E = 0 - \frac{.059}{1} \log \frac{P_{H_2}^{1/2}}{[H^+]}$$

$P_{H_2} = 1$ atm

$$E = -\frac{.059}{1} \log \frac{1}{[H^+]}$$

$$E = -.059\,(pH)$$

~~E = .059 x~~

$$-0.413 = -.059\,(pH)$$

$$pH = 7$$

Q. 15. $Zn \longrightarrow Zn^{+2} + 2e^{\ominus}$

$2e^{\ominus} + Zn^{+2} \longrightarrow Zn$

$$E = 0 - \frac{.059}{2} \log \frac{(.01)}{(0.1)}$$

$E = .0295$ Volt

Q.16. $\frac{1}{2}H_2 \longrightarrow H^+ + e^\ominus$

$e^\ominus + H^+ \longrightarrow \frac{1}{2}H_2$

$E = 0 - \frac{.059}{1} \log x$

$0.2364 = -.059 \log x$

$x = 10^{-4}$ so $pH = 4$

Electrolytic cell

(17) (a) $\quad Eq.\ Cl^{\ominus} = \text{mole of electron}$

$$\frac{3.55}{35.5} \times 1 = n_{e^{\ominus}}$$

$$n_{e^{\ominus}} = 0.1 \text{ mole}$$

$$\text{Number of electrons} = 0.1 \times 6 \times 10^{23}$$

$$= 6 \times 10^{22} \text{ electrons}$$

(b) $\quad Eq.\ Cu^{+2} = \text{mole of electron}$

$$\frac{1}{63.5} \times 2 = n_e$$

$$\text{Number of } e^{\ominus} = \frac{2}{63.5} \times 6 \times 10^{23}$$

$$= 1.89 \times 10^{22} \text{ electrons.}$$

(c) Eq. Al^{+3} = mole of $e^{\ominus}$

$$\frac{2.7}{27} \times 3 = n_{e^{\ominus}}$$

Number of electrons $= 0.3 \times 6 \times 10^{23}$

$= 1.8 \times 10^{23}$ electrons

(18) (a) Eq. of Al^{+3} = number of faradays

0.25×3 = number of faradays

number of faradays = 0.75

(b) Eq. (SO_3) = number of faradays

$$\frac{27.6}{80} \times 2 = \text{number of faradays}$$

number of faradays = 0.69

(c) Eq. Cu^{+2} = number of faradays

$1.1 \times 0.5 \times 2$ = number of faradays

Number of faradays = 1.1 faraday

(19) Eq. Zn = Eq. (Ag) = 0.5

$n_{Zn} \times 2 = n_{Ag} \times 1 = 0.5$

mass of Ag $= 0.5 \times 108$
$= 54$ gm

mass of Zn $= 0.25 \times 65$
$= 16.25$ gm

(20) $Eq.(MnO_2) = \frac{It}{96500} \times \frac{85}{100}$

$\frac{1000}{87} \times 2 = \frac{25.5 \times t}{96500} \times \frac{85}{100}$

$t = \frac{2 \times 965 \times 10^7}{87 \times 25.5 \times 85} = 2 \times 5.12 \times 10^{-3} \times 10^7$

$= 10.24 \times 10^4$ second

(21) $NaCl + H_2O \longrightarrow \frac{1}{2}H_2 + \frac{1}{2}Cl_2 + NaOH$

$Eq.\ Cl_2 = \frac{It}{96500}$

$\Rightarrow n_{Cl_2} \times 2 = \frac{30 \times 3600}{96500}$

$n_{Cl_2} = 0.56$ mole

Volume of Cl_2 at 1 atm, 273 Kelvin temp

$$= 0.56 \times 22.4 = 12.544 \text{ lit}$$

produced mole of NaOH $= 2 \times 0.56$

$$= 1.12 \text{ mol}$$

mass of NaOH $= 1.12 \times 40$

$$= 44.8 \text{ gm}$$

Q.22 $\quad Eq.\ H_2 = Eq.\ O_2$

$$\frac{P(0.224)}{RT} \times 2 = \frac{P}{RT}(V_{O_2}) \times 4$$

$$V_{O_2} = 0.112 \text{ litre}$$

Q.23 $\quad Eq.\ (Al) =$ no. of faradays

$$\left(\frac{x}{27}\right)(3) = \text{no. of faradays}$$

no. of faradays $= \frac{x}{9}$

cost of $\frac{x}{9}$ faraday = x rupees.

cost of one faraday = $\frac{x}{x/9}$ = 9 rupees

Eq. (Mg) = number of faradays

$\frac{x}{24} \times 2$ = number of faradays

number of faradays = $\frac{x}{12}$

cost of $\frac{x}{12}$ faradays = $\frac{x}{12} \times 9$

$= \frac{3x}{4}$ rupees

Q. 24 Eq. (M) = $\frac{It}{96500}$

$$\frac{1.95}{\text{molar mass of M}} \times 2 = \frac{10 \times 330}{96500}$$

molar mass of M = 114

Eq. (Cu) = number of faraday

$$\frac{1.95}{63.5} \times 2 = \frac{Q}{96500}$$

Q = 5926 coulomb

(25.) $Eq. Ni = \frac{It}{96500}$

$n_{Ni} \times 2 = \frac{5 \times 20 \times 60}{96500}$

$n_{Ni} = 0.03108$ mol

mass of Ni $= 0.03108 \times 58.8$

$= 1.827$ gm

$\simeq 1.83$ gm

Q.26. concentration of $Ni(NO_3)_2$ remain constant in solution
Because we are using Nickel electrodes due to this at anode oxidation of Ni will occur in form of Ni^{+2} and this Ni^{+2} will deposit in form of Ni on cathode so ultimately concentration of $Ni(NO_3)_2$ will not change.

Q.27. $\lambda_{eq} = \frac{K \times 1000}{N}$

$\lambda_{eq} = \frac{\frac{1}{200} \times 0.88 \times 1000}{.01}$

$\lambda_{eq} = 440$ S cm^2 Eq^{-1}

(28)

$$\lambda_{eq} = \frac{k \times 1000}{M}$$

$$4 = \frac{k \times 1000}{0.1}$$

$$k = 4 \times 10^{-4}\ \Omega^{-1} cm^{-1}$$

$$\rho = \frac{1}{k} = \frac{1}{4 \times 10^{-4}} = \frac{10000}{4} = 2500\ \Omega\ cm.$$

(29)

(i) $k = \frac{1}{R} \cdot \frac{l}{A}$

$$8 \times 10^{-7} = \frac{1}{R} \cdot (2/4)$$

$$R = \frac{10^{7}}{16} = 6.25 \times 10^{5}\ \Omega$$

(ii) $I = \frac{V}{R} = \frac{1}{10^{7}/16} = 1.6 \times 10^{-8}$ amp.

(30) $k = \frac{1}{800} = 1.25 \times 10^{-3}\ \Omega^{-1} cm^{-1}$

$$\lambda_{eq} = \frac{k \times 1000}{N} = \frac{1.25 \times 10^{-3} \times 1000}{.01} = 125\ \Omega^{-1} cm^{2} eq^{-1}$$

31.

$$\lambda_m = \frac{k \times 1000}{M}$$

$$\lambda_m = \frac{\frac{1}{.005} \times 1000}{\frac{2.08/208}{0.5}} = 10^7 \; S\,cm^2 mol^{-1}$$

$$\lambda_{eq} \times n\text{-factor} = \lambda_m$$

$$\lambda_{eq} \times 2 = 10^7$$

$$\lambda_{eq} = 5 \times 10^6 \; Ohm^{-1} cm^2 Eq^{-1}$$

32. $$\lambda^o_m (AgBr) = 140 + 130 - 110$$

$$= 160 \; S\,cm^2 mol^{-1}$$

$$k_{solute} = (8.075 \times 10^{-7}) - (0.75 \times 10^{-7})$$

$$k_{solute} = 7.325 \times 10^{-7}$$

$$\lambda^o_m = \frac{k_{solute} \times 1000}{S}$$

$$160 = \frac{7.325 \times 10^{-7} \times 10^3}{S}$$

$$S = 4.578 \times 10^{-6} \; \frac{mol}{lit}$$

$$S = 4.578 \times 10^{-6} \times (188) \; gm/lit$$

$$S = 8.6 \times 10^{-4} \; gm/lit$$

Q(33.) $\alpha = \frac{200}{400} = \frac{1}{2} = 0.5$

$HF \rightleftharpoons H^+ + F^\ominus$

$C - C\alpha \quad C\alpha \quad C\alpha$

$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{2 \times 10^{-3} \times 1/4}{1/2} = 10^{-3}$

Q.34 $\Lambda_m^\infty(CH_3COOH) = \Lambda_m^\infty(CH_3COONa) + \Lambda_m^\infty(HCl) - \Lambda_m^\infty(NaCl)$

$= 100 + 425 - 125$

$= 400 \ S\,cm^2\,mol^{-1}$

$\Lambda_{eq} \times n\text{-factor} = \Lambda_m$

$48 \times 1 = \Lambda_m$

$\alpha = \frac{48}{400} = 0.12$

Q.35 $\lambda_m^\infty(Ba(OH)_2) = \lambda_m^\infty(BaCl_2) + 2\lambda_m^\infty(NaOH) - 2\lambda_m^\infty(NaCl)$

$= 280 \times 10^{-4} + 2 \times 240 \times 10^{-4} - 2 \times 125 \times 10^{-4}$

$= 5.1 \times 10^{-2} \ mho\,cm^2\,mol^{-1}$