

UNIT # 08 (PART - II)

ELECTROCHEMISTRY

EXERCISE # 1

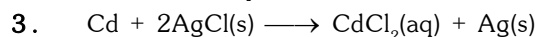
3. $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$
- $$E_{\text{cell}} = E - \frac{0.059}{1} \log \left[\frac{1}{0.1} \right] /$$
- $$= E_{\text{red}} - 0.059$$
4. $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$
- $$V_1 = 1, \quad C_1 = 1 \text{ M}$$
- $$V_2 = 10, \quad C_2 = 0.1 \text{ M}$$
- $$E_{\text{cell}} = E - \frac{0.0591}{2} \log \frac{1}{1} \quad E_{\text{cell}} = E$$
- $$E_{\text{cell}} = E - \frac{0.0591}{2} \log \left[\frac{1}{0.1} \right]$$
- $$= E - 0.059/2 = E - 0.030$$
5. $\text{H}_2 \longrightarrow 2\text{H}^+ + 2e^-$
- $$\text{pH} = 1, [\text{H}^+] = 10^{-1} \quad E = 0$$
- $$E = \frac{0.0591}{2} \log \frac{[\text{H}_2]}{[\text{H}^+]^2} = \frac{0.0591}{2} \log \left[\frac{1}{10^{-1}} \right]^2$$
- $$= \frac{0.0591}{2} \times 2 = 0.0591 \text{ V}$$
6. $E = E_{\text{cell}} - \frac{0.0591}{n} \log \left[\frac{P}{R} \right] \quad 1 = \left[\frac{P}{R} \right]$
10. $\text{Fe}^{3+} + 3e^- \longrightarrow \text{Fe} \quad \Delta G_1 = -nF E_{\text{cell}} = -3F E_{\text{cell}}$
- $$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe} \quad \Delta G_2 = -2F E_{\text{cell}}$$
- $$\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+} \quad \Delta G_3 = -F E_{\text{cell}}$$
- required $\therefore \Delta G_3 = \Delta G_1 - \Delta G_2$
- $$-F E_{\text{cell}} = -3F E_{\text{cell}} + 2F E_{\text{cell}}$$
- $$-E_{\text{cell}} = -3(-0.036) + 2(-0.440)$$
- $$-E_{\text{cell}} = -0.772 \quad E_{\text{cell}} = +0.772 \text{ V}$$
11. $2\text{H}^+ + 2e^- \longrightarrow \text{H}_2 \quad \text{pH} = 10, [\text{H}^+] = 10^{-10}$
- $$E = 0$$
- $$E_{\text{red}} = \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}(\text{g})} = \frac{0.0591}{2} \times 2 \log [10^{-10}]$$
- $$= \frac{0.0591}{2} \times 2 \times [-10] = -0.591 \text{ V}$$
12. $E_{\text{cell}} = E_{\text{cathod}} - E_{\text{anode}} = 0.80 - (-0.25) = 1.05 \text{ V}$
14. $E_{\text{cell}} = E_{\text{cathod}} - E_{\text{anode}} = 1.50 - (-0.25) = 1.75 \text{ V}$
18. $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2e^-$
- $$W = Z I t = \frac{71}{2 \times 96500} \times 2 \times 2.5 \times 60 = 0.110 \text{ g}$$
19. $E_{\text{cell}} = 0.29 - \frac{0.0591}{2} \log \frac{[\text{Cl}^-]^2 [\text{Br}_2]}{[\text{Br}^-]^2 [\text{Cl}_2]}$
- $$= 0.29 - \frac{0.0591}{2} \log \frac{[10^{-2}]^2 [10^{-2}]}{[10^{-2}]^2 [1]}$$
- $$= 0.29 + \frac{0.0591}{2} \quad 2 = 0.349 \approx 0.35 \text{ V}$$
20. 1 F ion discharge = $\frac{56}{2} \times 3$
- $$3 \text{ F} \longrightarrow 84 \text{ g}$$
22. $\text{Ag}^+, \quad \text{Cu}^{2+}, \quad \text{Au}^{3+}$
- $$\frac{1}{1} : \frac{1}{2} : \frac{1}{3}$$
- $$= 6 : 3 : 2$$
23. $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad 0.80 = E_{\text{Ag}^+/\text{Ag}} - E_{\text{H}_2/\text{H}^+}$
- $$0.80 = E_{\text{Ag}^+/\text{Ag}} - 0$$
- $$E_{\text{oxidation}} = -E_{\text{red}} = -0.80 \text{ V}$$
25. $\Delta G = -nF E_{\text{cell}} \quad (\because 1 \text{ F} = 96500 \text{ C})$
- $$= -2 \quad 0.360 \quad 96500 = -69480 \text{ J} = -69.48 \text{ kJ}$$
26. $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} = 5\text{F}$
27. $\text{Cu}^+ + e^- \longrightarrow \text{Cu} \quad \Delta G_1 = -F E = -FX_1$
- $$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu} \quad \Delta G_2 = -2F E = -2FX_2$$
- $$\text{Cu}^{2+} + e^- \longrightarrow \text{Cu}^+ \quad \Delta G_3 = -F E$$
- $$\Delta G_3 = \Delta G_2 - \Delta G_1 \quad -FE = -2FX_2 + FX_1$$
- $$E = 2X_2 - X_1$$
31. $W = Z I t \quad 0.275 = \frac{\text{at.} \times 14 \times 965}{2 \times 96500}$
- $$0.550 \quad 100 = \text{at.} \quad \text{at.} = 55$$
33. $\frac{w_1}{w_2} = \frac{(E_1)_{\text{Ag}}}{(E_2)_{\text{metal}}} \quad \frac{0.5094}{0.2653} = \frac{\left(\frac{\text{at.}}{\text{v.f.}} \right)_{\text{Ag}}}{\left(\frac{\text{at.}}{\text{v.f.}} \right)_{\text{metal}}}$
- $$\frac{0.5094}{0.2653} = \frac{(\text{v.f.})_{\text{Ag}}}{1} \quad \text{v.f.} = 1.9 \approx 2$$
34. $\frac{1}{2} \text{H}_2 + \text{AgI} \longrightarrow \text{H}^+ + \text{Ag} + \text{I}^- \quad E = 0$
- $$\frac{1}{2} \text{H}_2 \longrightarrow \text{H}^+ + e^- \quad E = 0.151$$
- $$0.151 = - \frac{0.059}{1} \log (\text{H}^+) = 0.059 \quad \text{pH}$$
- $$\text{pH} = \frac{0.151}{0.059} = 2.5$$
35. $\text{AgI} + e^- \longrightarrow \text{Ag} + \text{I}^- \quad E = -0.151$
- $$\text{Ag}^+ + e^- \longrightarrow \text{Ag} \quad E = 0.799$$
-
- $$\text{AgI} \rightleftharpoons \text{Ag}^+ + \text{I}^- \quad E = -0.151 - 0.799$$
- $$E = -0.95 \quad E = E - \frac{0.0551}{1} \log K_{\text{sp}}$$
- $$-16.074 = \log_{10} K_{\text{sp}} \quad 10^{-16.074} = K_{\text{sp}}$$
- $$7.91 \quad 10^{-17} = K_{\text{sp}}$$

$$2. \quad \Delta G = -nFE = \Delta H - T\Delta S$$

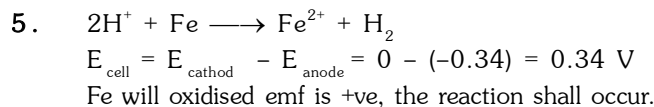
$$= -2F \quad 0.695 = \Delta H - 273 \Delta S \quad \dots (i)$$

$$= -2F \quad 0.6753 = \Delta H - 298 \Delta S \quad \dots (ii)$$

Solve both equation.



$$W = \frac{E}{96500} \times I \times t = \frac{63.5 \times 2.68 \times 3600}{2 \times 96500} = 3.174 \text{ g}$$



$$7. \quad W = Z I t = \frac{40}{96500} \times 9.65 \times 10^3 = 4 \text{ g}$$

$$8. \quad \Delta G = -nFE = \Delta H - T\Delta S \quad -nF \frac{dE}{dT} = 0 - \Delta S$$

$$nF \frac{dE}{dT} = \Delta S \quad \dots (i)$$

$$E = 1.1028 - 0.641 \quad 10^{-3} T + 0.72 \quad 10^{-5} T^2$$

$$\frac{dE}{dT} = -0.641 \quad 10^{-3} + 1.44 \quad 10^{-5} T$$

at 25 C

$$\frac{dE}{dT} = 3.6502 \quad 10^{-3}$$

from eq. (i)

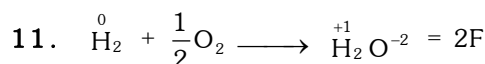
$$2 \quad F \quad 3.6502 = \Delta S \quad \Delta S = -54.23 \text{ EU}$$

$$9. \quad E = \frac{0.0591}{2} \log K \quad 1.1 \quad 2 = 0.06 \log K$$

$$36.22 = \log K \quad 10^{36.22} = K_f$$

$$8.314 \quad 10^{36} = K$$

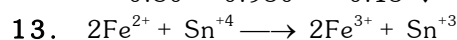
$$10. \quad E_{\text{cell}} = 0.80 - \frac{0.0591}{1} \log \left[\frac{1}{10^{-3}} \right] = 0.623 \text{ V}$$



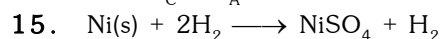
$$12. \quad 0 = (E_C - E_A) - \frac{0.0591}{1} K_{\text{sp}}$$

$$E_C = -0.80 - 0.0591 (-17 + \log 8.3)$$

$$= -0.80 + 0.950 = -0.15 \text{ V}$$



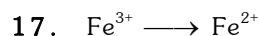
$$E = E_C - E_A = 0.15 - 0.77 = -0.62 \text{ V}$$



$$0.236 = E - \frac{0.0591}{n} \log \frac{1}{1}$$

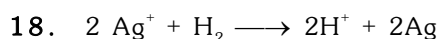
$$-nFE = \Delta G$$

$$\Delta G = -2 \quad 96500 \quad 0.236 = 45.55 \text{ kJ}$$



$$E_{\text{cell}} = 0.770 \text{ V} - \frac{0.0591}{1} \log \frac{1.5}{0.015}$$

$$= 0.770 - 0.059 \quad 2 = 0.652 \text{ V}$$



$$1.023 = (E_C - E_A) - \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2} [\text{Ag}^+]^2}$$

$$1.023 = 0.799 - 0 - \frac{0.591 \times 2}{2} \log [\text{H}^+] + \frac{0.591 \times 2}{2} \log [\text{X}]^2$$

$$0.294 = 0.06 \quad 5.5 + \frac{0.06}{2} \log [\text{X}]^2 - 0.036 = 0.03 \log_{10} [\text{X}]^2$$

$$-0.036 = 0.6 \log_{10} [\text{X}]$$

$$0.6 = \log_{10} [\text{X}]$$

$$19. \quad w = Z I t \quad w = \frac{E}{96500} \times I \times t$$

$$\frac{w}{t} = \frac{200.6 \times 2 + 71}{2 \times 96500} \times I \quad \frac{44}{3600} = \frac{236.1}{96500} \times I$$

$$I = 5 \text{ Amp.}$$

$$20. \quad K_a = 25 \quad 10^{-6}$$

$$\Delta_{\text{eq}} = 19.6 \text{ s cm}^2 \text{ eq}^{-1}$$

$$C = 0.1 \text{ M} \quad \alpha = \sqrt{\frac{K_a}{C}} = \frac{\Lambda_{\text{eq}}^{\text{C}}}{\Lambda_{\text{eq}}^{\infty}}$$

$$\sqrt{\frac{25 \times 10^{-6}}{0.01}} = \frac{19.6}{\Lambda_{\text{eq}}^{\infty}}$$

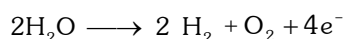
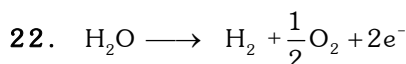
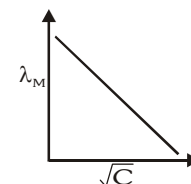
$$\frac{5 \times 10^{-6}}{0.01} = \frac{19.6}{\Lambda_{\text{eq}}^{\infty}}$$

$$\Lambda_{\text{eq}}^{\infty} = 392$$

$$21. \quad \Lambda_M = \Lambda_M^{\circ} - A \sqrt{C}$$

$$\lambda = C - mx$$

slope = -ve



$$\text{gases } [\text{H}_2 + \text{O}_2] = 2 \quad 22.4 + 22.4 = 67.2$$

$$23. \quad \Lambda_{\infty}^1 = \Lambda_{\text{BaCl}_2}^{\infty} = \frac{1}{2} \Lambda_{\text{eq Ba}^{2+}}^{\infty} + \Lambda_{\text{eq Cl}^-}^{\infty} \quad \dots \dots \dots (i)$$

$$\Lambda_{\infty}^2 = \Lambda_{\text{H}_2\text{SO}_4}^{\infty} = \Lambda_{\text{eq H}^+}^{\infty} + \frac{1}{2} \Lambda_{\text{eq SO}_4^{2-}}^{\infty} \quad \dots \dots \dots (ii)$$

$$\Lambda_{\infty}^3 = \Lambda_{\text{HCl}}^{\infty} = \Lambda_{\text{H}^+}^{\infty} + \Lambda_{\text{Cl}^-}^{\infty} \quad \dots \dots \dots (iii)$$

$$\Lambda_{\text{eq BaCl}_2}^{\infty} = \frac{1}{2} \Lambda_{\text{eq Ba}^{2+}}^{\infty} + \frac{1}{2} \Lambda_{\text{eq SO}_4^{2-}}^{\infty} \quad \dots \dots \dots (iv)$$

$$\text{eq. (4)} = \text{eq (i)} + \text{eq (ii)} - \text{eq (iii)}$$

$$= \Lambda_{\infty}^1 + \Lambda_{\infty}^2 - \Lambda_{\infty}^3$$

$$24. \quad w = Z I t$$

$$w = ZQ$$

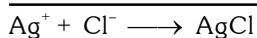
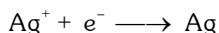
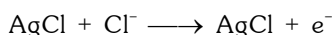
$$w \propto Z$$

$$26. \quad \text{Cost} = \frac{5 \text{ paise}}{\text{KWH}} \quad \text{hour} \quad 15 \text{ amp} \quad 110$$

$$= \frac{5}{10^3 \times wH} \times 15 \times 110 = \frac{66000}{10^3} = 66 \text{ paise}$$

28. $\text{Ag} + \text{Cl}^- \longrightarrow \text{AgCl} + e^-$
 $E = E^\circ + 0.0591 \log [\text{Cl}^-]$
 $-0.25 = E^\circ + 0.0591 \log 0.1$ $E^\circ = -0.1909$

Now for reaction



$$E = E_{\text{Ag}/\text{AgCl}/\text{Cl}^-} + E_{\text{Ag}^+/\text{Ag}} + 0.0591 \log K_{\text{sp}}$$

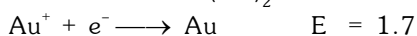
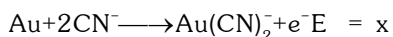
$$0 = -0.1909 + 0.799 + 0.0591 \log K_{\text{sp}}$$

$$K_{\text{sp}} = 5.13 \times 10^{-11}$$

29. Given $\text{Au}^{+3} + 3e^- \longrightarrow \text{Au}$ $E_1 = 1.5$



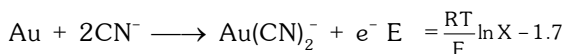
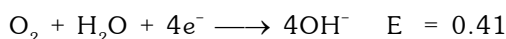
so for reaction



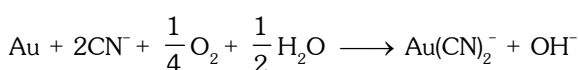
$$0 = x + 1.7 - \frac{RT}{F} \ln X - 1.7$$

$$x = \frac{RT}{F} \ln X - 1.7$$

For reaction



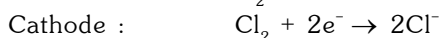
so for reaction



$$E = 0.41 + \frac{RT}{F} \ln X - 1.7 = -1.29 + \frac{RT}{F} \ln X$$

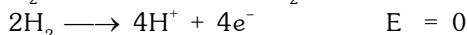
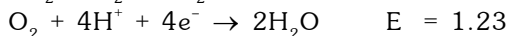
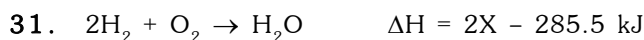
$$\Delta G = -nFE \quad (n = 1)$$

$$\Delta G = 1.29 F - RT \ln X$$



$$E = E^\circ - 0.0591 \log [\text{H}^+] [\text{Cl}^-]$$

on increasing concentration by 10 E will increase by a factor of $-0.0591 \log 100 = -0.0591 \times 2 = -0.1182 \text{ V}$



for reaction :



$$\Delta G = -nFE = -4 \times 96500 \times 1.23 = -474780$$

$$\Delta G = \Delta H - T\Delta S \quad -474780 = -571000 - 298\Delta S$$

$$\Delta S = -322.8 \text{ J/K}$$

32. $\lambda_M = \frac{K \times 1000}{M}$

$$k = \frac{1}{R} \left(\frac{\ell}{a} \right) = \frac{1}{50} \left(\frac{2.2}{4.4} \right) = \frac{1}{100} = 0.01$$

$$\lambda_M = \frac{0.01 \times 1000}{0.5} = 20 \text{ S cm}^2 \text{ mole}^{-1}$$

$$= 20 \times 10^{-4} \text{ S m}^2 \text{ mole}^{-1} = 0.002 \text{ S m}^2 \text{ mole}^{-1}$$

33. $k_a = 1.69 \times 10^{-5} = C\alpha^2 = 0.01 \alpha^2 = \alpha = 0.04$

$$\alpha = \frac{\lambda_M}{\lambda_M^\infty} \Rightarrow \lambda_M = 0.04 \times 380$$

$$\lambda_M = 15.2 \text{ S cm}^2 \text{ mole}^{-1} \quad \lambda_M = \frac{k \times 1000}{M}$$

$$15.2 = \frac{k \times 1000}{0.01}$$

$$k = 1.52 \times 10^{-4} \text{ S cm}^{-1}$$

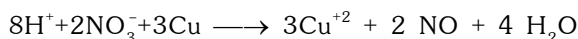
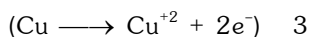
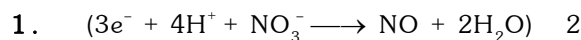
$$k = 1.52 \times 10^{-2} \text{ S cm}^{-1}$$

ELECTROCHEMISTRY

EXERCISE # 3

COMPREHENSION BASED QUESTIONS

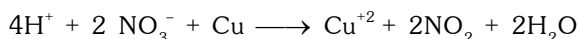
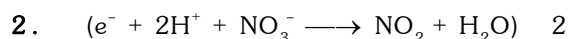
Comprehension # 1



$$E = 0.96 - 0.34 - \frac{0.0591}{6} \log \frac{[\text{NO}]^2 [\text{Cu}^{+2}]^3}{[\text{NO}_3^-]^2 [\text{H}^+]^8} \dots (i)$$

$$\text{since } [\text{HNO}_3] = 1 \text{ M so } [\text{H}^+] = [\text{NO}_3^-] = 1$$

$$E = 0.62 - \frac{0.0591}{6} \log (10^{-3})^2 (0.1)^3 = 0.70865$$



$$E = 0.79 - 0.34 - \frac{0.0591}{2} \log \frac{[\text{NO}_2]^2 [\text{Cu}^{+2}]}{[\text{NO}_3^-]^2 [\text{H}^+]^4} \dots (ii)$$

$$\text{Let } [\text{HNO}_3] = x \text{ M so } [\text{H}^+] = [\text{NO}_3^-] = x$$

equation (i) & (ii)

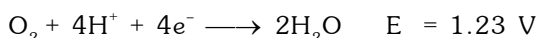
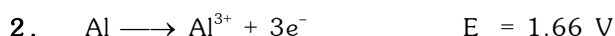
$$0.62 - \frac{0.0591}{2} \log \frac{10^{-9}}{x^{10}} = 0.45 - \frac{0.0591}{2} \log \frac{10^{-7}}{x^6}$$

$$0.17 = \frac{0.0591}{6} [-9 - 10 \log x] - \frac{0.0591}{2} [-7 - 6 \log x]$$

$$0.0518 = 0.0788 \log x$$

$$x = 10^{0.657} \text{ M}$$

Comprehension # 2



$$\therefore E_{\text{cell}} = 2.89 \text{ V}$$

1. Cell constant (सेल नियतांक) = $\frac{1}{a} = \frac{4}{7} \text{ cm}^{-1}$
 specific conductance = conductance cell constant
 (विशिष्ट चालकता) = (चालकता सेल नियतांक)

$$= \frac{1}{\text{resistance}} \times \frac{1}{a} = \frac{1}{245} \times \frac{4}{7} = 2.332 \times 10^{-3} \text{ mho cm}^{-1}$$

equivalent conductance = sp. cond. volume (cc)
 (तुल्यांकी चालकता) = (विशिष्ट चालकता आयतन (cc))
 (containing 1 eq. of the substance)
 $= 2.332 \times 10^{-3} \times 10000$ (for N/10 solution,
 $V = 10,000 \text{ cc}$) = 23.32 mho cm^2

2. Let K_1 and K_2 be the specific conductances of the solutions A and B respectively and the constant of the cell be x.

(माना कि K_1 तथा K_2 विलयनों क्रमशः A तथा B की विशिष्ट चालकताएँ हैं, तथा सेल का नियतांक x है।)

- ∴ For solution A : sp. conductance = conductance cell constant

$$K_1 = \frac{1}{50} \times x \dots\dots\dots(i)$$

For solution B : sp. conductance

$$K_2 = \frac{1}{100} \times x \dots\dots\dots(ii)$$

When equal volumes of A and B are mixed, both the solutions get doubly diluted ; hence their individual contribution towards the sp. conductance

of the mixture will be $\frac{K_1}{2}$ and $\frac{K_2}{2}$ respectively and the sp. conductance of the mixture will be

$\frac{1}{2}(K_1 + K_2)$. (जब A तथा B के समान आयतनों को मिलाया जाता है, तो दोनों विलयन दुगुने तनु हो जाते हैं। अतः मिश्रण की विशिष्ट चालकता के लिए इनका पृथक-पृथक सहयोग

क्रमशः $\frac{K_1}{2}$ तथा $\frac{K_2}{2}$ होगा तथा मिश्रण की विशिष्ट चालकता $\frac{1}{2}(K_1 + K_2)$ होगी)

- ∴ For the mixture : $\frac{1}{2}(K_1 + K_2) = \frac{1}{R} \times x \dots\dots\dots(iii)$
 (R is the resistance of mixture)

From equations (i),(ii)and(iii),we get $R=66.67 \text{ ohms}$.

3. Since the electrodes of the cell are just half dipped, the effective area will be 5 sq cm.

(चूँकि सेल के इलेक्ट्रोड आधे डूबे हुए हैं अतः प्रभावी क्षेत्रफल 5 sq cm. होगा।)

$$\text{Cell constant} = \frac{1}{a} = \frac{1.5}{5} = 0.3 \text{ cm}^{-1}$$

Specific conductance = conductance cell constant

$$= \frac{1}{\text{resistance}} \times \text{cell constant} = \frac{1}{50} \times 0.3 = \frac{3}{500} \text{ mho cm}^{-1}$$

Equivalent conductance = specific conductance volume ... (8)

$$= \frac{3}{500} \times 20000 = 120 \text{ mho cm}^2$$

$$(0.05 \text{ N} = \text{N}/20 \therefore V = 20,000 \text{ cc})$$

4. Let the volume of the vessel be V cc. (माना पात्र का आयतन V cc है)

Number of equivalent of NaCl (NaCl के तुल्यांकी की

$$\text{संख्या}) = \frac{\text{wt. in grams (ग्राम में भार)}}{\text{eq. weight (तुल्यांकी भार)}}$$

$$= \frac{500}{58.5} = 8.547$$

- ∴ volume of water (cc) containing 1 eq. of NaCl = $\frac{V}{8.547}$

(1 तुल्यांक NaCl युक्त जल का आयतन (cc))

The sp. cond. of the NaCl solution (only due to presence of Na^+ and Cl^- ions)

(NaCl विलयन की विशिष्ट चालकता (केवल Na^+ तथा Cl^- आयनों की उपस्थिति के कारण))

$$= 3.10 \times 10^{-5} - 2.56 \times 10^{-5} = 0.54 \times 10^{-5}$$

$$\therefore \Lambda_{\text{NaCl}} = 0.54 \times 10^{-5} \times \frac{V}{8.547}$$

since the vessel is big, the resulting solution may be supposed to be dilute.

(चूँकि पात्र बड़ा है अतः माना कि परिणामी विलयन तनु हो सकता है)

$$\therefore \Lambda_{\text{NaCl}} = \Lambda_{\text{NaCl}}^\circ$$

$$0.54 \times 10^{-5} \times \frac{V}{8.547} = 149.9$$

$$V = 2.37 \times 10^8 \text{ cc.}$$

5. Cell constant = $\frac{0.50}{1.50} = \frac{1}{3}$
 Specific conductance

$$= \frac{\text{equivalent conductance}}{\text{volume (cc) containing 1 eq.}}$$

$$= \frac{97.1}{10,000} \quad (\text{for } 0.1 \text{ N solution } V = 10,000 \text{ cc})$$

$$= 0.00971 \text{ mho cm}^{-1}$$

Conductance = specific conductance / cell constant

$$\frac{0.00971}{1/3} = 0.02913 \text{ mho}$$

$$\therefore \text{resistance} = \frac{1}{0.02913} \text{ ohm}$$

$$\therefore \text{current in amp} = \frac{\text{potential difference (volt)}}{\text{resistance (ohm)}}$$

$$(\text{Ohm's law}) = \frac{5}{1/0.02913} = 0.1456 \text{ ampere.}$$

6. From Kohlrausch's law, we have,

$$\begin{aligned}\Lambda_{\text{NH}_4\text{ClO}_4}^{\circ} &= \lambda_{\text{NH}_4^+}^{\circ} + \lambda_{\text{ClO}_4^-}^{\circ} = \text{Fu}_{\text{NH}_4^+}^{\circ} + \text{Fu}_{\text{ClO}_4^-}^{\circ} \\ &= F(u_{\text{NH}_4^+}^{\circ} + u_{\text{ClO}_4^-}^{\circ}) = 96500(6.6 \times 10^{-4} + 5.7 \times 10^{-4}) \\ &= 118.67 \text{ mho cm}^2\end{aligned}$$

7. We have

$$u_{\text{H}^+} = \frac{\lambda_{\text{H}^+}^{\circ}}{F} = \frac{349.8}{96500} = 3.62 \times 10^{-3} \text{ cm}^2 \text{ volt}^{-1} \text{ s}^{-1}$$

$$u_{\text{Na}^+} = \frac{\lambda_{\text{Na}^+}^{\circ}}{F} = \frac{50.11}{96500} = 5.20 \times 10^{-4} \text{ cm}^2 \text{ volt}^{-1} \text{ s}^{-1}$$

Further, we know that

$$u = \frac{\text{ionic velocity (cm/s)}}{\text{pot. diff. (volt)/distance between the electrodes (cm)}}$$

$$\therefore \text{velocity of H}^+ = 3.62 \times 10^{-3} \times \frac{2}{5} = 1.45 \times 10^{-3} \text{ cms}^{-1}$$

$$\text{velocity of Na}^+ = 5.20 \times 10^{-4} \times \frac{2}{5} = 2.08 \times 10^{-4} \text{ cms}^{-1}$$

$$8. \Lambda_{\text{NH}_4\text{Cl}}^{\circ} = \lambda_{\text{NH}_4^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}$$

$$\therefore \lambda_{\text{NH}_4^+}^{\circ} = \Lambda_{\text{NH}_4\text{Cl}}^{\circ} - \lambda_{\text{Cl}^-}^{\circ} = 150 - 76 = 74$$

$$\therefore \Lambda_{\text{NH}_4\text{OH}}^{\circ} = \lambda_{\text{NH}_4^+}^{\circ} + \lambda_{\text{OH}^-}^{\circ} = 74 + 198 = 272$$

Further,

$$\text{degree of dissociation (वियोजन की मात्रा)} = \frac{\Lambda_c}{\Lambda^{\circ}} =$$

$$\frac{9.6}{272} = 0.0353$$

9. Suppose water contains X moles per L (or X eq. / L) of H⁺ ions (or OH⁻ ions)

(माना कि जल के प्रति लीटर में H⁺ आयनों (या OH⁻ आयन) के X मोल (या X eq. / L) उपस्थित हो)

\therefore X equivalents of H⁺ ions are produced from X eq. of water

(X तुल्यांक जल से X तुल्यांक H⁺ आयन बनते हैं)

\therefore volume (cc) containing 1 eq. of water which dissociated into its ions = $\frac{1000}{X}$

(एक तुल्यांक जल युक्त आयतन (cc) जो इसके आयनों में

वियोजित होता है)

\therefore eq. conductance of water = sp. cond. V

$$= 5.8 \times 10^{-8} \times \frac{1000}{X}$$

Since water dissociates feebly, i.e., water may be considered to be a dilute solution of H⁺ and OH⁻ ions,

(चुंकि जल अल्प मात्रा में वियोजित होता है अर्थात् जल H⁺ तथा OH⁻ का तनु विलयन हो सकता है)

$$\Lambda_{\text{H}_2\text{O}} = \Lambda_{\text{H}_2\text{O}}^{\circ} = \lambda_{\text{H}^+}^{\circ} + \lambda_{\text{OH}^-}^{\circ}$$

$$5.8 \times 10^{-8} \times \frac{1000}{X} = 350 + 198 = 548$$

$$\therefore X = 1.0 \times 10^{-7}$$

$$\therefore [\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7}$$

For the equilibrium, $\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-$

$$\text{Equilibrium constant (K)} = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

$$K_w = K [\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-] = 1.0 \times 10^{-7} \times 1.0 \times 10^{-7} = 1 \times 10^{-14}$$

$$\therefore K = \frac{K_w}{[\text{H}_2\text{O}]} = \frac{1 \times 10^{-14}}{55.5} = 1.8 \times 10^{-16} \text{ mole/L}$$

$$\left([\text{H}_2\text{O}] = \frac{1000}{18} = 55.5 \text{ mole/L} \right)$$

$$10. \text{Degree of dissociation (x)} = \frac{\Lambda_c}{\Lambda_0} = \frac{7.36}{390.7} = 0.0188$$

For the equilibrium

$$0.05 \quad 0 \quad 0 \quad \text{Initial conc. (moles/litre)}$$



$$0.05(1-x) \quad 0.05x \quad 0.05x \quad \text{Equilibrium concentration (for CH}_3\text{COOH, 0.05 N = 0.05 M)}$$

$$K_a = \frac{0.05x \times 0.05x}{0.05(1-x)}$$

since x is very small,

$$K_a = 0.05x^2 = 0.05 \quad (0.0188)^2 = 1.76 \times 10^{-5} \text{ mole/L}$$

11. For equilibrium,



If the solubility of AgCl in water is, say, x moles / L or x eq. / L,

(यदि AgCl की जल में विलेयता, x मोल/ L या x तुल्यांक/ L है, तो)

$$K_{sp} = x \cdot x = x^2$$

$$\therefore \text{volume containing 1 eq. of AgCl} = \frac{1000}{x}$$

$$\Lambda_{\text{AgCl}} = \text{sp. cond.} \quad V = 2.28 \times 10^{-6} \times \frac{1000}{x}$$

Since AgCl is sparingly soluble in water, $\Lambda_{\text{AgCl}} = \Lambda_{\text{AgCl}}^{\circ} = 138.3$

(चुंकि AgCl जल में अल्प विलेयशील होता है)

$$\therefore 2.28 \times 10^{-6} \times \frac{1000}{x} = 138.3$$

$$\text{or } x = 1.644 \times 10^{-5} \text{ eq./L or mole/L}$$

$$K_{sp} = x^2 = (1.644 \times 10^{-5})^2 = 2.70 \times 10^{-10} \text{ (mole/L)}^2$$

27. The overall battery reaction is
 $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 = 2\text{PbSO}_4 + 2\text{H}_2\text{O}$
 \therefore two moles of electrons are involved for the reaction of two moles of H_2SO_4 .

(दो मोल H_2SO_4 की अभिक्रिया के लिए दो मोल इलेक्ट्रॉन भाग लेते हैं)

- \therefore eq. wt. of H_2SO_4 = mol. wt. of H_2SO_4 = 98
 no. of eq. of H_2SO_4 present in 3.5 L of solution of a charged battery

(आवेशित बैटरी के 3.5 L विलयन में उपस्थित H_2SO_4 के तुल्यांको की संख्या)

$$= \frac{39}{98} \times \frac{1.294}{100} \times 3500 = 18.0235$$

No. of equivalents of H_2SO_4 present in 3.5 L of solution after getting discharged

(निरावेशन के पश्चात् 3.5 L विलयन में उपस्थित H_2SO_4 के तुल्यांको की संख्या)

$$= \frac{20}{98} \times \frac{1.139}{100} \times 3500 = 8.1357$$

Number of eq. of H_2SO_4 lost (H_2SO_4 के तुल्यांको की संख्या में कमी) = $18.0235 - 8.1357 = 9.8878$

- \therefore moles of electric charge produced by the battery = 9.8878 F

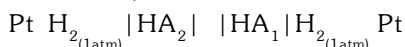
(बैटरी द्वारा उत्पन्न विद्युत आवेश के मोल)

$$= 9.8878 \times 96500 \text{ coulombs}$$

$$= 9.8878 \times 96500 \text{ amp-seconds}$$

$$= \frac{9.8878 \times 96500}{60 \times 60} \text{ amp-hours} = 265 \text{ amp-hours.}$$

35. The cell is,



$$\text{At L.H.S. : } E_{\text{H}^+/\text{H}} = E_{\text{OP}_{\text{H}^+/\text{H}}} + \frac{0.059}{1} \log_{10} [\text{H}^+]_2$$

$$\therefore -\log \text{H}^+ = \text{pH} \quad \therefore E_{\text{H}^+/\text{H}} = E_{\text{OP}_{\text{H}^+/\text{H}}} - 0.059 (\text{pH})_2$$

$$\text{At R.H.S. : } E_{\text{H}^+/\text{H}} = E_{\text{RP}_{\text{H}^+/\text{H}}} + \frac{0.059}{1} \log_{10} [\text{H}^+]_1$$

$$\therefore E_{\text{H}^+/\text{H}} = E_{\text{RP}_{\text{H}^+/\text{H}}} - 0.059 (\text{pH})_1$$



$$[\text{H}^+] = C \cdot \alpha = \sqrt{K_a \cdot C}$$

$$\therefore (\text{pH})_1 = \frac{1}{2} \text{p}K_{a1} - \frac{1}{2} \log_{10} C$$

$$\text{Similarly, } (\text{pH})_2 = \frac{1}{2} \text{p}K_{a2} - \frac{1}{2} \log_{10} C$$

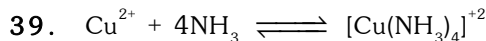
($\therefore C$ are same)

$$\therefore E_{\text{cell}} = E_{\text{OP}_{\text{H}^+/\text{H}}} + E_{\text{RP}_{\text{H}^+/\text{H}}}$$

for II for I

$$= 0.059 \left[\frac{1}{2} \text{p}K_{a2} - \frac{1}{2} \text{p}K_{a1} \right] = \frac{0.059}{2} [5 - 3]$$

$$= + 0.059$$



$$\therefore K_f = 1 \times 10^{12} = \frac{[\text{Cu}(\text{NH}_3)_4]^{+2}}{[\text{Cu}^{+2}][\text{NH}_3]^4} = \frac{1.0}{x(2.0)^4}$$

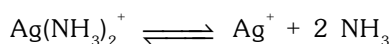
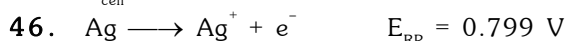
$$\therefore x = 6.25 \times 10^{-14} \text{ M}$$

Note that due to high value of K_f almost all of the Cu^{+2} ions are converted to $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion

$$\text{Now } E_{\text{cell}} = E_{\text{cell}} + \frac{0.059}{2} \log_{10} \frac{\text{Cu}^{2+}}{\text{Zn}^{+2}}$$

$$= 1.1 + \frac{0.059}{2} \log_{10} \left[\frac{6.25 \times 10^{-14}}{1} \right]$$

$$E_{\text{cell}} = 0.71 \text{ V}$$

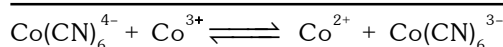
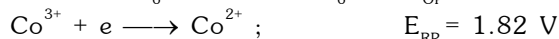
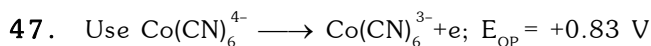


$$E_{\text{cell}} = E_{\text{cell}} + \frac{0.0591}{1} \log_{10} \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

$$0 = E_{\text{cell}} + \frac{0.0591}{1} \log(6 \times 10^{-8}) \Rightarrow E_{\text{cell}} = -0.426$$

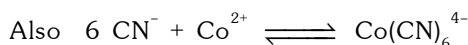
$$E_{\text{cell}} = E_{\text{C}}^\circ - E_{\text{A}}^\circ$$

$$-0.426 = E_{\text{C}}^\circ - 0.799 \Rightarrow E_{\text{C}}^\circ = 0.373 \text{ V}$$

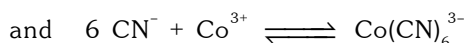


$$\text{and } E_{\text{cell}} = E_{\text{cell}} + \frac{0.059}{1} \log_{10} \frac{[\text{Co}^{3+}][\text{Co}(\text{CN})_6^{4-}]}{[\text{Co}^{2+}][\text{Co}(\text{CN})_6^{3-}]}$$

$$\text{or } E_{\text{cell}} = E_{\text{cell}} + \frac{0.059}{1} \log_{10} \frac{[\text{Co}^{3+}][\text{Co}(\text{CN})_6^{4-}][\text{CN}^-]^6}{[\text{Co}^{2+}][\text{Co}(\text{CN})_6^{3-}][\text{CN}^-]^6}$$



$$\text{and } K_{f1} = \frac{[\text{Co}(\text{CN})_6^{4-}]}{[\text{Co}^{2+}][\text{CN}^-]^6}$$



$$\text{and } K_{f2} = \frac{[\text{Co}(\text{CN})_6^{3-}]}{[\text{Co}^{3+}][\text{CN}^-]^6}$$

$$\therefore E_{\text{cell}} = E_{\text{cell}} + \frac{0.059}{1} \log_{10} \frac{K_{f1}}{K_{f2}}$$

$$0 = 0.83 + 1.82 + \frac{0.059}{1} \log_{10} \frac{10^{19}}{K_{f2}}$$

(At equilibrium $E_{\text{cell}} = 0$)

$$\therefore \frac{K_{f2}}{10^{19}} = 8.23 \times 10^{44}$$

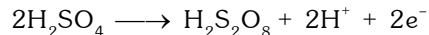
$$\therefore K_{f2} = 8.23 \times 10^{63}$$

1. $E = E_{\text{calomal}} + E_{\text{H}_2/\text{H}^+} - \frac{RT}{nF} \ln \frac{[\text{H}^+]^2}{P_{\text{H}_2}}$
- $$0.6885 = 0.28 - \frac{8.314 \times 313}{2 \times 96500} \ln \frac{[\text{H}^+]^2}{725} \quad 760$$
- $$[\text{H}^+] = 2.57 \times 10^{-7}$$
- pH = 6.6
2. For $\text{Fe}^{+3} + e^- \longrightarrow \text{Fe}^{+2}$ $E = 0.77$
 so Fe^{+3} will reduce to Fe^{+2}
 (अतः Fe^{+3} , Fe^{+2} में अपचयित होगा।)
 Faraday of current passed (प्रवाहित धारा का फैराडे)

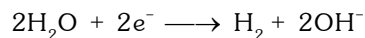
$$= \frac{1.25 \times 1.1 \times 3600}{96500} = 0.0513$$
 meq. of $\text{Fe}^{+2} = \text{meq. of KMnO}_4 \text{ required} = 51.3$
 (Fe^{+2} के मिली तुल्यांक = आवश्यक KMnO_4 के मिली तुल्यांक = 51.3)
 $51.3 = M \times 5 \times 25$
 $M = 0.41$
3. At cathode (कैथोड पर) :
 $\text{Sn}^{+2} + 2e^- \longrightarrow \text{Sn}$
 At anode (एनोड पर) :
 $\text{X} \longrightarrow \text{X}^{+n} + ne^-$
 Cell reaction (सेल अभिक्रिया) :
 $n \text{Sn}^{+2} + 2\text{X} \longrightarrow 2\text{X}^{+n} + n\text{Sn}$
 $E = -0.14 + 0.78 = 0.64$
- $$E = E^\circ - \frac{0.0591}{2n} \log \frac{[\text{X}^{+n}]^2}{[\text{Sn}^{+2}]^n}$$
- $$0.65 = 0.64 - \frac{0.0591}{2n} [\log 0.01 - \log (0.5)^n]$$
- $$0.01 = -\frac{0.0591}{2n} [-2 + n \log 2]$$
- $$0.03384 n = 2 - 0.3010 n$$
- $$0.6394 n = 2$$
- $$n = 3.12 \sim 3$$
- 4.(a) At cathode :
 $2e^- + \text{Cu}^{+2} \longrightarrow \text{Cu}$
 At anode :
 $2\text{H}_2\text{O} \longrightarrow 4\text{H}^+ + \text{O}_2 + 4e^-$
 Eq. of O_2 evolved = Eq. of Cu formed = 0.01
 (मुक्त O_2 के तुल्यांक = निर्मित Cu के तुल्यांक = 0.01)
 total loss in wt. (भार में कुल कमी) = $0.1 \times 8 + \frac{0.01 \times 63.5}{2} = 0.3975$
 wt. of resulting solution = $10 - 0.3975 = 9.6025\text{g}$
 (परिणामी विलयन का भार)
- (b) Eq. of $\text{H}^+ = 0.01$

5. In beginning (प्रारम्भ में) :

At anode :

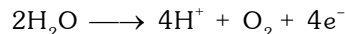


At cathode:

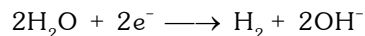


After some time (कुछ समय पश्चात्) :

At anode :



At cathode:



$$\text{moles of O}_2 \text{ evolved (मुक्त O}_2 \text{ के मोल)} = \frac{2.35}{22.4}$$

during this time moles of H_2 evolved (इस समय के

$$\text{दौरान मुक्त H}_2 \text{ के मोल)} = \frac{2 \times 2.35}{22.4}$$

volume of H_2 evolved with O_2 (O_2 के साथ मुक्त H_2

$$\text{का आयतन)} = \frac{2 \times 2.35}{22.4} \times 22.4 = 4.7 \text{ L}$$

volume of H_2 evolved with $\text{H}_2\text{S}_2\text{O}_8$ ($\text{H}_2\text{S}_2\text{O}_8$ के साथ मुक्त H_2 का आयतन) = $9.722 - 4.7 = 5.022 \text{ L}$

$$\text{moles of H}_2 \text{ evolved (मुक्त H}_2 \text{ के मोल)} = \frac{5.022}{22.4}$$

moles of $\text{H}_2\text{S}_2\text{O}_8$ formed (निर्मित $\text{H}_2\text{S}_2\text{O}_8$ के मोल)

$$= \frac{5.022}{22.4}$$

wt. of $\text{H}_2\text{S}_2\text{O}_8$ formed (निर्मित $\text{H}_2\text{S}_2\text{O}_8$ का भार) =

$$\frac{5.022}{22.4} \times 194 = 43.45 \text{ g}$$

6. At cathode only pure copper is deposited so % of

$$\text{Cu} = \frac{22.011}{22.26} \times 100 = 98.88\%$$

(कैथोड पर केवल शुद्ध कॉपर निक्षेपित होता है अतः Cu का %)

since Cu is getting deposited, iron will also get reduced because its SRP value is lesser than Cu. (चूंकि Cu निक्षेपित हो रहा है, आयरन भी अपचयित होगा क्योंकि इसका SRP मान Cu से कम होता है।)

Charge passed (प्रवाहित आवेश)

$$= 140 \times 482.5 = 67550 \text{ coulomb}$$

$$= \frac{67550}{96500} = 0.7 \text{ Faraday}$$

Faraday used for reduction of Cu (Cu के अपचयन

$$\text{के लिए प्रयुक्त फैराडे)} = \frac{22.011 \times 2}{63.5} = 0.69326$$

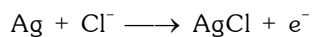
so Faraday used for iron (अतः : आयरन के लिए प्रयुक्त फ़ैराडे) = $0.7 - 69326 = 0.00674 \text{ F}$

mass of iron (आयरन का द्रव्यमान)

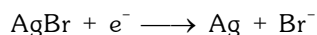
$$= \frac{0.00674 \times 56}{2} = 0.1887 \text{ g}$$

$$\% \text{ of Fe} = \frac{0.1887}{22.26} \times 100 = \mathbf{0.847 \%}$$

7. At anode :

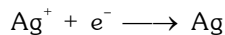
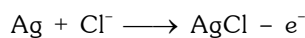


At cathode :



$$E = E_{\text{Ag/AgCl/Cl}^-} + E_{\text{Br}^-/\text{AgBr/Ag}} - 0.0591 \log \frac{[\text{Br}^-]}{[\text{Cl}^-]} \quad \dots(i)$$

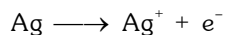
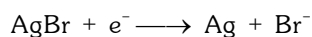
For reaction :



$$E = 0 = E_{\text{Ag/AgCl/Cl}^-} + E_{\text{Ag}^+/\text{Ag}} - 0.0591 \log \frac{1}{[\text{Ag}^+][\text{Cl}^-]}$$

$$E_{\text{Ag/AgCl/Cl}^-} = E_{\text{Ag}^+/\text{Ag}} - 0.0591 \log K_{\text{sp}} (\text{AgCl}) \quad \dots(ii)$$

for reaction



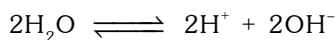
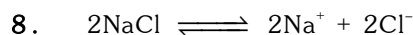
$$E = 0 = E_{\text{Br}^-/\text{AgBr/Ag}} + E_{\text{Ag}^+/\text{Ag}} - 0.0591 \log [\text{Ag}^+][\text{Br}^-]$$

$$E_{\text{Br}^-/\text{AgBr/Ag}} = E_{\text{Ag}^+/\text{Ag}} + 0.0591 \log K_{\text{sp}} (\text{AgBr}) \quad \dots(iii)$$

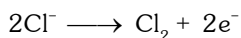
from equation (1), (2) & (3)

$$E = 0.0591 \log \frac{K_{\text{sp}} (\text{AgBr})}{K_{\text{sp}} (\text{AgCl})} - 0.0591 \log \frac{[\text{Br}^-]}{[\text{Cl}^-]}$$

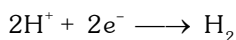
$$E = 0.0591 \log \frac{3.3 \times 10^{-13} \times 0.2}{2.8 \times 10^{10} \times 0.001} = - \mathbf{0.037 \text{ V}}$$



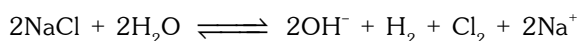
At anode :



At cathode :



Net reaction (कुल अभिक्रिया) :



$$1000 = \frac{35.5}{96500} \quad 25.62 \text{ t}$$

$$t = 175374.83 \text{ sec} = \mathbf{48.74 \text{ hr.}}$$

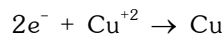
$$\text{moles of OH}^- = \frac{1000}{71} \times 2$$

$$\text{volume} = 20 \text{ L}$$

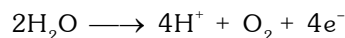
$$[\text{OH}^-] = \frac{2000}{71 \times 20} = \mathbf{1.408 \text{ M}}$$

9. In beginning (प्रारम्भ में)

At cathode :



At anode :



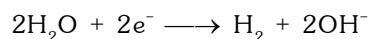
Eq. of O_2 = Eq. of Cu^{+2} (O_2 के तुल्यांक = Cu^{+2} के

$$\text{तुल्यांक}) = \frac{0.4 \times 2}{63.5} = 0.012598$$

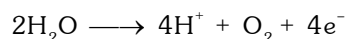
$$\text{vol of O}_2 = \frac{0.012598 \times 22400}{4} = 70.55 \text{ mL}$$

Later on (बाद में) :

At cathode :



At anode :



Faraday passed (प्रवाहित फ़ैराडे)

$$= \frac{1.2 \times 7 \times 60}{96500} = 0.00522$$

$$\text{moles of O}_2 = \frac{0.00522}{4}$$

$$\text{moles of H}_2 = \frac{0.00522}{2}$$

$$\text{Volume of O}_2 = \frac{0.00522}{4} \times 22400 = 29.24 \text{ mL}$$

$$\text{Volume of H}_2 = \frac{0.00522}{2} \times 22400 = 58.464 \text{ mL}$$

Total volume of O_2 (O_2 का कुल आयतन)

$$= 29.24 + 70.55 = \mathbf{99.79 \text{ mL}}$$

Total volume of H_2 (H_2 का कुल आयतन)

$$= \mathbf{58.464 \text{ mL}}$$

10. $w = \frac{108 \times 5 \times 2 \times 3600}{96500} = 40.29$

but since anode is 95% pure with Ag so along with silver some impurities will also come out so actual (लेकिन चूँकि ऐनोड Ag के साथ 95% शुद्ध है अतः सिल्वर के साथ कुछ अशुद्धियाँ भी आयेगी।)

$$\text{wt. coming out of anode is } \frac{40.29}{0.95} = 42.41 \text{ g}$$

(अतः ऐनोड का वास्तविक भार)

$$\text{weight of anode now} = 100 - 42.41 = \mathbf{57.58 \text{ g}}$$

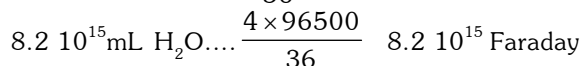
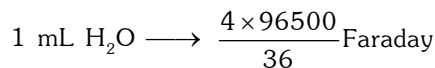
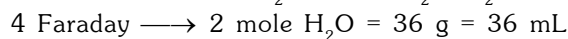
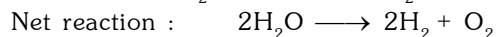
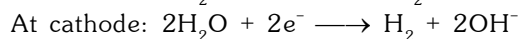
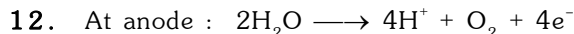
(अब ऐनोड का भार)

$$11. \text{ moles of } H_2O_2 = \text{moles of } H_2 = \frac{100}{34}$$

$$\text{wt. of } H_2 = \frac{100}{17} = Z \text{ it}$$

$$\frac{100}{17} = \frac{1 \times i \times 0.5 \times 3600}{96500}$$

$$i = 315.36 \text{ Amp.}$$



$$t = \frac{4 \times 96500 \times 8.2 \times 10^{15}}{36 \times 1.5 \times 10^{-6}} \text{ sec} = 5.861 \times 10^{13} \text{ sec.}$$

$$= 1.858 \times 10^6 \text{ years.}$$

$$13. E_{\text{cell}} = -0.0591 \log \frac{[H^+]_{\text{Anode}}}{[H^+]_{\text{Cathode}}}$$

$$-0.188 = -0.0591 \log \frac{1}{[H^+]_{\text{Cathode}}}$$

$$\text{pH} = 3.18 = 7 - \frac{1}{2} P^{\text{Kb}} - \frac{1}{2} \log C$$

$$3.18 = 7 - \frac{1}{2} P^{\text{Kb}} - \frac{1}{2} \log(1/32)$$

$$k_b = 7.15 \times 10^{-10}$$

$$k_b = \frac{k_w}{k_b} = \frac{10^{-14}}{7.15 \times 10^{-10}} = 1.39 \times 10^{-5}$$

$$h = \sqrt{\frac{k_h}{C}} = \sqrt{\frac{1.39 \times 10^{-5}}{1/32}} = 2.1 \times 10^{-2}$$

$$14. E = E - 0.0591 \log \frac{[H^+]}{[Ag^+]}$$

$$0.9 = E - 0.0591 \log \frac{0.1}{0.8}$$

$$E = 0.84662$$

On adding 40 mL of 0.05 M NaOH (0.05 M NaOH के 40 mL मिलाने पर)

$$[H^+] = \frac{3-2}{70} = \frac{1}{70}$$

now (अब)

$$E = E - 0.0591 \log \frac{[H^+]}{[Ag^+]}$$

$$E = 0.84662 - 0.0591 \log \frac{1}{70 \times 0.8}$$

$$E = 0.95 \text{ V}$$

$$15. \lambda_E = \text{Ionic mobility (आयनिक गतिशीलता)} \quad 96500$$

$$\lambda_M = \lambda_E \quad (\text{v.f.})$$

$$\text{For } K^+ \text{ ion v.f.} = 1 \text{ so}$$

$$\lambda_E = \lambda_M = 73.52$$

Ionic mobility (आयनिक गतिशीलता)

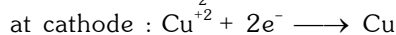
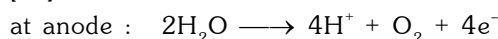
$$= \frac{73.52}{96500} = \frac{\text{speed}}{\text{potential gradient}} \left(\frac{\text{गति}}{\text{विभव प्रवणता}} \right)$$

$$\text{speed (गति)} (\mu) = \frac{73.52}{96500} \times \frac{6}{10} = 0.000457 \text{ cm/sec}$$

$$\text{distance (दूरी)} = \mu \quad t = 0.000457 \quad 7200 = 3.29 \text{ cm}$$

$$16. \text{ pH} = 1, [H^+] = 10^{-1} \text{ mole/lit}$$

$$[H^+] \text{ in } 100 \text{ mL} = 10^{-2} \text{ mole}$$



To produce 0.01 mole H^+ , we need 0.01 Faraday.

(0.01 मोल H^+ उत्पन्न करने के लिए, हमें 0.01 फ़ैराडे की आवश्यकता होती है।)

$$0.01 = \frac{0.965 \times 8 \times t}{96500} \Rightarrow t = 1250 \text{ sec.}$$

$$\text{eq. of } Cu^{+2} \text{ consumed (प्रयुक्त } Cu^{+2} \text{ के तुल्यांक)} = 0.01$$

$$\text{moles of } Cu^{+2} \text{ consumed (प्रयुक्त } Cu^{+2} \text{ के मोल)}$$

$$= \frac{0.01}{2} = 0.005$$

$$m \text{ moles of } I_2 = \frac{0.04 \times 35}{2}$$

$$m \text{ moles of } CuSO_4 = 0.04 \quad 35 = 1.4$$

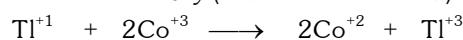
$$\text{total moles (कुल मोल)} = 0.005 + 0.0014 = 0.0064$$

$$\text{volume (आयतन)} = 100 \text{ mL} = 0.1 \text{ L}$$

$$[CuSO_4] = \frac{0.0064}{0.1} = 0.064 \text{ M}$$

$$17. \text{ moles of } Ti^{+1} \text{ initially (प्रारम्भ में } Ti^{+1} \text{ के मोल)} = 0.0025$$

$$\text{moles of } Co^{+3} \text{ initially (प्रारम्भ में } Co^{+3} \text{ के मोल)} = 0.005$$



$$0.0025 \quad 0.005 \quad 0.005 \quad 0.0025$$

since k value is very high almost all Ti^+ & Co^{+3} will convert into Ti^{+3} & Co^{+2} respectively.

(चूंकि k मान बहुत उच्च है लगभग सभी Ti^+ व Co^{+3} क्रमशः Ti^{+3} व Co^{+2} में परिवर्तित होंगे।)

$$E_{\text{cell}} = 1.84 - 1.25 = 0.59 = \frac{0.0591}{2} \log k$$

$$k = 10^{20}$$

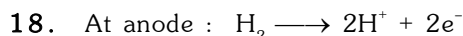
$$10^{20} = \frac{(0.005)^2 (0.0025)}{4 \times 10^{-3}}$$

$$x = 5.386 \times 10^{-10} \text{ mole}$$

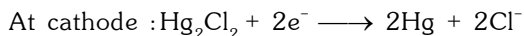
$$\text{total volume (कुल आयतन)} = 50 \text{ mL} = 0.05 \text{ L}$$

$$[Co^{+3}] = \frac{2 \times 5.386 \times 10^{-10}}{0.05} = 2 \times 10^{-8}$$

$$[Ti^+] = 10^{-8}$$



$$E = -0.699$$



$$E = 0.28$$

$$E_{\text{cell}} = -0.699 + 0.28 - \frac{0.0591}{2} \log [\text{H}^+]^2 [\text{Cl}^-]^2$$

$$E_{\text{cell}} = -0.419 + 0.0591 \text{ pH}$$

(a) $E_{\text{cell}} = -0.419 + 0.0591 \quad 5$

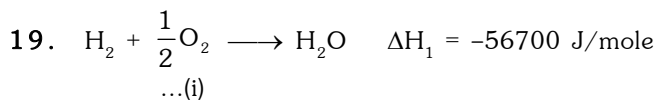
$$= -0.1235 \text{ V}$$

(b) $O = -0.419 + 0.0591 \text{ pH}$

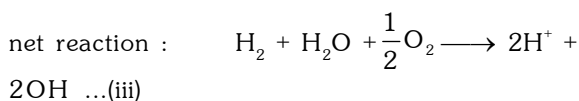
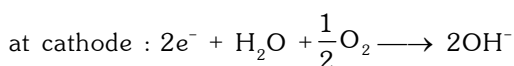
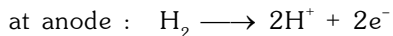
$$\text{pH} = 7.1$$

(c) $E_{\text{cell}} = -0.419 + 0.0591 \quad 7.5 = 0.2425$ is $E_{\text{cell}} > 0$ cell is spontaneous & **Calomal electrode** with work as cathode i.e. positive electrode.

($E_{\text{cell}} = -0.419 + 0.0591 \quad 7.5 = 0.2425$ $E_{\text{cell}} > 0$ सेल स्वतः है तथा कैलोमल इलेक्ट्रोड कैथोड अर्थात् धनात्मक इलेक्ट्रोड की तरह कार्य करेगा)



cell reaction :



equation (i) + (ii) = (iii)

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

$$\Delta H_1 - T\Delta S_1 + \Delta H_2 - T\Delta S_2 = -nFE$$

$$(\Delta H_1 + \Delta H_2) - T(\Delta S_1 + \Delta S_2) = -2FE$$

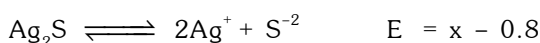
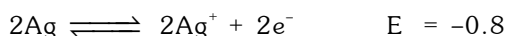
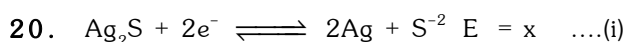
$$(\Delta H_1 + \Delta H_2) - T(\Delta S_{\text{net}}) = -2FE$$

$$\Delta S = nF \frac{dE}{dT} \quad \text{so} \quad E = - \frac{(\Delta H_1 + \Delta H_2)}{2F} + \frac{TDE}{dT}$$

$$E = - \frac{(-56700 + 2 \times 19050)}{2 \times 96500} + 298 (0.001158)$$

$$\Rightarrow E = 0.09637 + 0.345$$

$$= 0.4414 \text{ V}$$



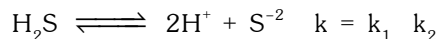
$$E = x - 0.8 - \frac{0.0591}{2} \log [\text{Ag}^+]^2 [\text{S}^{2-}]$$

$$0 = x - 0.8 - \frac{0.0591}{2} \log K_{\text{sp}}$$

$$x = 0.8 + \frac{0.0591}{2} \log 2 \quad 10^{-49} = -0.639$$

so for equation (i)

$$E = E - \frac{0.0591}{2} \log [\text{S}^{2-}] \quad \dots (ii)$$



$$1.1 \quad 10^{-21} = \frac{[\text{H}^+]^2 [\text{S}^{2-}]}{[\text{H}_2\text{S}]} = \frac{(10^{-3})^2 (\text{S}^{2-})}{(0.1)}$$

$$[\text{S}^{2-}] = 1.1 \quad 10^{-16}$$

putting this in equation (ii) (इसे समीकरण (ii) में रखने पर)

$$E = -0.639 - \frac{0.0591}{2} \log 1.1 \quad 10^{-16} = -0.1674 \text{ V}$$

21. $\lambda_{\text{M}} = \frac{k \times 1000}{M}$

$$(86 \quad 2 + 444) = \frac{(2.06 \times 10^{-6} - 4.1 \times 10^{-7}) \times 1000}{s}$$

$$s = 2.678 \quad 10^{-6}$$

$$K_{\text{sp}} = 4s^3 = 7.687 \quad 10^{-17}$$

22. For KCl

$$\lambda_{\text{M}} = \frac{k \times 1000}{M} \Rightarrow 138 \quad \frac{k \times 1000}{0.02}$$

$$k = 2.76 \quad 10^{-3} = \frac{1}{R} \left(\frac{\ell}{a} \right) = \frac{1}{85} \left(\frac{\ell}{a} \right)$$

$$(\ell/a) = 0.2346$$

$$\text{For } \text{H}_2\text{O} : k_{\text{H}_2\text{O}} = \frac{1}{9200} (\ell/a)$$

$$\text{For } \text{NaCl} : k_{\text{NaCl}} = \frac{1}{7600} (\ell/a)$$

$$\lambda_{\text{M}} = \frac{(k_{\text{NaCl}} - k_{\text{H}_2\text{O}}) \times 1000}{M}$$

$$126.5 = \frac{\left(\frac{1}{7600} - \frac{1}{9200} \right) \times 0.2346 \times 1000}{M}$$

$$M = 4.2438 \quad 10^{-5}$$

$$M = \frac{500}{58.5 \times V} = 4.2438 \quad 10^{-5}$$

$$V = 201400 \text{ L}$$

$$V = 2.014 \quad 10^5 \text{ L}$$