HINTS & SOLUTIONS

EXERCISE - 1
Single Choice

2. $E_{cell} = 0.29 - \frac{0.059}{2} \log \frac{0.01 \times (0.01)^2}{(0.01)^2 \times 1}$ or

E_{cell} **= 0.35 volt**

3. $E^\circ_{cell} = 1.89$; $E^\circ_{Ce^{4+}/Ce^{3+}} + E^\circ_{Co/Co^{2+}} = E + 0.277 \Rightarrow E =$ **1.62 V**

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

$\therefore$ Cu^{2+} can be reduced by H_2.

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

$= 0.713$ volt.

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. $E_1 = E^\circ - \frac{RT}{nF} \ln 2$

$E_2 = E^\circ - \frac{R \times 2T}{nF} \ln 1 = E^\circ$

$\therefore$ $E_2 > E_1$

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

11. $\frac{\lambda^\circ_{Cl^-}}{\lambda^\circ_{k^+} + \lambda^\circ_{Cl^-}} = 0.505$ or

$\lambda^\circ_{Cl^-} = 0.505 \times 130 = 65.65$ $Scm^2\,eq^{-1}$.

$\lambda^\circ_{k^+} = F \times U_{K^+}$ or

$U_{K^+} = \frac{(130 - 65.65)}{96500}$ $cm^2\ volt^{-1}\ sec^{-1}$.

$=$ **6.67×10^{-4} $cm^2\ volt^{-1}\ sec^{-1}$.**

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

16. $-0.413 = 0 - 0.059 \log \frac{1}{[H^+]}$ or

$\frac{0.414}{0.059} = -\log H^+ = pH$ or **pH = 7**

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

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.

19. $Ag \longrightarrow Ag^+ + e^-$

$E_1 = E_{oxid} + E_{calomel}$

$= E' - \frac{0.0591}{1} \log K_{sp_1} + E_{calomel}$

$E_2 = E' - \frac{0.0591}{1} \log K_{sp_2} + E_{calomel}$

$E_2 - E_1 = 0.177 = 0.0591 \log \frac{K_{sp_1}}{K_{sp_2}}$

$\frac{K_{sp_1}}{K_{sp_2}} =$ **10^3**.

20. $AgNO_3$ **At cathode :**

$Ag^+ + e^- \longrightarrow Ag(s)$

At anode :

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

$\therefore$ At cathode pH will increase.

23. $E_{cell} = 0.77 - \frac{0.059}{1} \log \frac{1.5}{0.015} =$ **0.652 V**

26. $H^+ + Cl^- + NaOH \longrightarrow Na^+ + Cl^- + H_2O$ to conductance I^{st} decreases since no. of ions decreases after end point it increases.

27. Lower standard reduction potential related metal ions can displace higher standard reduction potential related metal ions.

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

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

$H_2 = 2$ mole

$O_2 = 1$ mole Total volume $= 3 \times 22.4 = \mathbf{67.2\ L.}$

29. $AgCl + e^- \longrightarrow Ag + Cl^- \quad E° = 0.2\ V$

$Ag \longrightarrow Ag^+ + e^- \quad E° = -0.79\ V$

$AgCl \xrightarrow{e^-} Ag^+ + Cl^- \quad E° = -0.59\ V$

$$E° = \frac{0.059}{n}\log K \quad \Rightarrow \quad -0.59 = \frac{0.059}{1}\log K_{SP}$$

$\Rightarrow K_{SP} = 10^{-10}$

Now solubility of AgCl in 0.1 M $AgNO_3$

$S(S + 0.1) = 10^{-10} \Rightarrow S = 10^{-9}$ mol/L

Hence 1 mole dissolves in 10^9 L solution

hence in 10^6 L amount that dissolves in 1 m mol.

30. $Q = 10 \times 4825 = 48250\ C$

$$\text{no. of faraday} = \frac{48250}{96500} = 0.5$$

$$Ag + \frac{1}{2}Cu^{++} \longrightarrow Ag^+ + \frac{1}{2}Cu$$

2.00 2.00

2–0.25 2 + 0.50

$$E_{cell} = E°_{Cell} - \frac{0.0591}{1}\log\frac{[Ag^+]}{[Cu^{++}]^{1/2}}$$

$$E_1 = E°_{Cell} - \frac{0.0591}{1}\log\frac{2.00}{(2.00)^{1/2}}$$

$$E_2 = E°_{Cell} - \frac{0.0591}{1}\log\frac{2.50}{(1.75)^{1/2}}$$

$$\Delta E = E_2 - E_1 = \frac{0.0591}{1}\left[\log\sqrt{2} - \log\frac{2.50}{\sqrt{1.75}}\right]$$

$$= \frac{0.0591}{1}[\log 1.41 - \log 1.88]$$

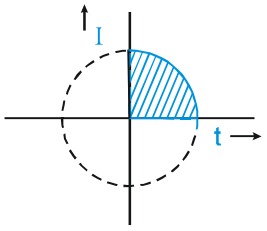
$$= \frac{0.0591}{1}[0.1492 - 0.2742] = -\frac{0.0591}{1} \times 0.125$$

$= -0.00738$ V.

32. $$E_{cell} = E°_{cell} - \frac{0.059}{2}\log\frac{[Sn^{2+}]}{[Ag^+]^2}$$

Ag^+ increase, E_{cell} increase.

34.



$$Q = \frac{\pi(25)}{4}C = \frac{\pi \times 25}{4 \times 96500}F$$

$$\therefore \quad m = \frac{108}{1} \times \frac{\pi \times 25}{4 \times 96500}\ g = 0.02197\ g = 21.97\ mg \simeq 22\ mg$$

35. $CH_3COOH + NaOH \longrightarrow Na^+ + CH_3COO^- + H_2O$ to conductance Ist increases slowly since no. of ions increases after end point it increases sharply due to OH^- ions.

36. Ionic compounds in molten state are conductor of electricity because of free ions.

37. $$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log_{10}\frac{[Cu^{2+}]_{cathode}}{[Cu^{2+}]_{anode}}$$

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

$$E_{cell} = -\frac{0.0591}{2}\log_{10}\frac{0.08}{0.12} = +5.2\ mV.$$

38. $H^+ + e^- \longrightarrow \frac{1}{2}H_2.$ $E = 0 - \frac{.0591}{1}\log_{10}\frac{1}{[H^+]}$

$= +0.591\log_{10}[H^+].$

$E_1 = 0$ {pH = 0}.

$E_2 = +0.0591\log_{10}[10^{-7}] = -.0591 \times 7$ {at pH = 7}

$= -0.41$ V.

39. $E_{cell} \Rightarrow E^0_{Sn^{4+}/Sn^{2+}} + E^0_{Fe^{2+}/Fe^{3+}} \Rightarrow 0.15 — 0.77.$

40. After deposition of Cu^{2+} ions. H^+ ion from the H_2O molecule will be discharged at cathode as its SRP is higher than of Fe^{2+} and Zn^{2+}.

41. $$E_{cell} = E^0_{cell} - \frac{0.0591}{1}\log_{10}[H^+]\,[Cl^-] \quad \text{and}$$

$$E'_{cell} = E^0_{cell} - \frac{0.0591}{1}\log_{10}100[H^+]\,[Cl^-].$$

$E'_{cell} - E_{cell} = -2 \times 0.0591 = -0.1182.$

42. $$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log_{10}\frac{P_{Cl_{2(anode)}}}{P_{Cl_{2(cathode)}}}$$

$$= 0 - \frac{0.0591}{2}\log_{10}\frac{P_1}{P_2}$$

If $P_1 < P_2$, $E_{cell} = +$ ve (spontaneous)

43. $E_{cell} = E^0_{cell} - \frac{0.0591}{1}\log_{10}\frac{[H^+]_{anode}}{[H^+]_{cathode}}$

$= -\frac{0.0591}{1}\log_{10}\frac{10^{-2}}{10^{-3}} = -$ ve (non spontaneous).

44. $\alpha = \frac{\Lambda^C_\infty}{\Lambda^\infty_m}$

45. $E^o_{Pb^{2+}/Pb} > E^o_{Fe^{2+}/Fe}$

So, Fe will oxidise and Pb^{2+} will reduce.

46. For same charge passed mole of H_2 produced = 2 × moles of O_2 produced.

47. Number of moles of Cu^{2+} discharged from anode = number of moles of Cu^{2+} deposited at cathode.

48. $E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log_{10}\frac{1}{[Cu^{2+}]}$.

49. Active metal has lower E^o_{Red} than E^o_{Red} of hydrogen so can not be reduced by hydrogen.

50. It is spontaneous change so no number of faraday is required.

51. $E_{H_2/H^+} = -\frac{0.0591}{1}\log_{10}\frac{\sqrt{pH_2}}{[H^+]}$;

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

52. At equilibrium

$$E^0_1 = +\frac{0.0591}{1}\log_{10}\frac{[Cu^+]^2}{[Cu^{++}]}$$

$$= \frac{0.0591}{1}\log\frac{10^{-4}}{2.02} = -0.254$$

$E^0_1 = E^0_{Cu^{2+}/Cu^+} - E^0_{Cu^+/Cu}$ and

$E^0_{Cu^{+2}/Cu} = \frac{E^0_{Cu^{+2}/Cu^+} + E^0_{Cu^+/Cu}}{2}$

so $E^0_1 = 2E^0_{Cu^{+2}/Cu} - 2E^0_{Cu^+/Cu}$

$E^0_{Cu^+/Cu} = 0.457$

$E^0_{Cu/Cu^+} = -0.457$

53. Let x gm of Zn deposit on 9 gm of Hg

% of Zn in Amalgam $= \frac{x}{9+x} \times 100 = 25$

$\therefore x = 3$gm

Eq. of Zn $= \frac{3 \times 2}{65.4}$

Current $= \frac{6}{65.4} \times \frac{96500}{1000} = 8.85$ amp.

54. Metal having more value of SRP will deposit first, but Mg does not deposition aqueous solution.

56. $ClO_3^- + 2H_2O + 4e \longrightarrow ClO^- + 4OH^-$; ΔG_1°

$ClO^- + H_2O + e \longrightarrow \frac{1}{2}Cl_2 + 2OH^-$; ΔG_2°

$\frac{1}{2}Cl_2 + e \longrightarrow Cl^-$; ΔG_3°

$ClO_3^- + 3H_2O + 3e \longrightarrow Cl^- + 6OH^-$; ΔG°

$\therefore \quad \Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ + \Delta G_3^\circ$

$-6FE^\circ = -4F \times 0.54 - 1F \times 0.45 - 1F \times 1.07$

$\therefore \quad E^\circ = +\frac{3.68}{6} = +0.61$ V

57. Considering the cell reaction

$H_2 + 2e \longrightarrow 2H^+$

$Hg_2^{2+} + 2e \longrightarrow 2Hg(\bullet) + 2Cl^-(aq)$

$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P = 2 \times 96500 \times 3.4 \times 10^{-4}$

$= 65.223$ J/K/mole

58. 90 gm Hg has 10 gm Na

$\therefore$ 10 gm Hg $= \frac{10}{90} \times 10 = \frac{10}{9}$ gm Na

$\therefore$ weight of Na $= \frac{M}{n} \times \frac{i \times t}{96500}$

$\frac{10}{9} = \frac{23}{1} \times \frac{10 \times t}{96500}$ [$\because Na^+ + e \longrightarrow Na$]

$\therefore t = \frac{10 \times 96500}{9 \times 10 \times 23} = 7.77$ min

60. pH changes from 0 to 7.

$\therefore$ $[H^+]$ changes from 1 to 10^{-7} M.

Accordingly $E_{red.}$ decreases by $0.059 \log 10^{-7}$ i.e. $0.059 \times (-7)$ $= -0.41$ volt.

61. $m\,(\text{theoretical}) = \dfrac{63.5\times 0.1\times 7200}{96500} = 0.4738\ g$

$\therefore \quad \%\ \text{efficiency} = \dfrac{0.3745}{0.4738}\times 100 = 79\ \%$

62. $\dfrac{m_X}{m_Y} = \dfrac{\frac{A_X}{2}\times Q}{\frac{A_Y}{1}\times Q} \Rightarrow \dfrac{m_X}{m_Y} = 1 \Rightarrow A_X = 2A_Y$

63. $\Delta G = -nF\,E_{cell}$ is maximum work.

64. $Q = ne = it$

$n = \dfrac{1\times 60}{1.6\times 10^{-19}} = 3.74\times 10^{20}$

65. $R = \dfrac{1}{k}\dfrac{1}{A}$ The k is halved while the A is doubled.
Hence R remains 50 Ω.

66. $\Delta G^0_{\text{cell reaction}} = 2(-130.79) - 2(-109.56) = -42.46\ kJ/mole$

(for $H_2 + 2AgCl \longrightarrow 2Ag + 2H^+ + 2Cl^-$)

$\therefore \quad E^0_{cell} = \dfrac{-42460}{-2\times 96500} = +0.220\ V$

Now $E_{cell} = +0.220 + \dfrac{0.059}{2}\log\dfrac{1}{(0.01)^4} = 0.456\ V = 456\ mV.$

67. $\Lambda_m = \Lambda_m^\infty - b\sqrt{c}$

$260 = \Lambda_m^\infty - 0.5\,b \quad \ldots\ldots (1)$

$250 = \Lambda_m^\infty - b \quad \ldots\ldots (2)$

On solving (1) & (2), we get

$\Lambda_m^\infty = 270\ \Omega^{-1}\,cm^2\,mol^{-1}$

68. at anode $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

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

69. $\dfrac{W_1}{E_1} = \dfrac{W_2}{E_2}\ ;\ \dfrac{4}{12} = \dfrac{W_{Ag}}{108}\ ;\ W_{Ag} = 36$

70. $Al^{3+} + 3e^- \longrightarrow Al$; So, mole of $e^- = 3$.

71. $\dfrac{W_1}{E_1} = \dfrac{W_2}{E_2}$

$\dfrac{W_{Cu}}{\frac{63.5}{2}} = \dfrac{0.504}{\frac{2}{2}}$

$W_{Cu} = 0.504\times 63.5 = 31.8\ gm.$

72. $K = \dfrac{1}{R}\left(\dfrac{1}{a}\right) \Rightarrow 0.0112 = \dfrac{1}{55}\left(\dfrac{1}{a}\right) \Rightarrow \dfrac{1}{a} = 0.616$

74. $ne^- = it$

$n = \dfrac{5\times 200}{1.6\times 10^{-19}}$

75. $\dfrac{W}{E} = \dfrac{it}{96500} \Rightarrow \dfrac{3}{E} = \dfrac{9.95\times 10\times 60}{96500} \Rightarrow E = 48.5$

77. $\dfrac{W}{71}\times 2 = \dfrac{2\times 30\times 60}{96500}\ ;\quad W = 1.32\ gm.$

78. Reduction take place at cathode.

79. $\dfrac{9\times 10^{-3}}{27}\times 3 = \dfrac{9.65\times t}{96500}\ ;\quad t = \dfrac{30}{27}\times 9 = 10\ sec.$

80. Anode $\left\{\begin{matrix} 2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^- \\ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \end{matrix}\right\}$

Cathode $\{2H_2O \rightarrow H_2 + 2OH^- - 2e^-\}\times 3.$

Net : $2H_2SO_4 + 8H_2O \rightarrow H_2S_2O_8 + O_2 + 3H_2 + 6H^+ + 6OH^-$

Hence ratio of n_{O_2} and n_{H_2} is 1 : 3.

81. 1 gm equivalent = 1 mole e^- = 96500 coulomb charge.

82. At anode : $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$ (not SO_4^{2-})

At cathode : $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ (not Na^+).

83. Daniel cell is copper -zinc electrochemical cell where Cu^{2+} deposit at copper cathode.

84. Cell notation is anode || cathode.

85. $E_{Cell} = E^\circ_{Cell} - \dfrac{0.059}{1}\log\dfrac{1}{[Cl^-]_a\,[Ag^+]_c}\ ;$

At $[Ag^+]_c = [Ag^+]_a$ equilibrium will achieve and $K = K_{sp} = [Ag^+]_a[Cl^-]_a$

86. $EMF = E^\circ_{cathode} - E^\circ_{anode} = 0.76 - 0.41 = 0.35.$

EXERCISE - 2

Part # I : Multiple Choice

3. $Fe^{2+} + 2e^- \longrightarrow Fe\ [\text{in } FeSO_4]$;

$Fe^{3+} + 3e^- \longrightarrow Fe\ [\text{in } Fe_2(SO_4)_3]$

$Fe^{3+} + 3e^- \longrightarrow Fe\ [\text{in } Fe(NO_3)_3]$

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

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

5. (A, B) At Cathode :

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

$2\,Br^- + \longrightarrow Br_2 + 2e^-$

$Cu^{2+} + 2Br^- \longrightarrow Br_2 + Cu(s).$

6. 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

$$\text{Anode} = \frac{2.68\times 3600}{96500} \times \frac{63.5}{2} = \mathbf{3.174\ g.}$$

8. During the working of cell E_{Cell} decreases ΔG increases, spontaneity decreases at equilibrium

$Q = K_C, E_{Cell} = 0.$

9. $Fe^{2+} + Fe^{2+} \longrightarrow Fe^{3+} + Fe$ (non spontaneous)

10. (A) $E_{Cell} = E^o_{Cell} - \frac{0.059}{2} \log \frac{[Ag^+]^2}{[Cu^{2+}]}$

(B) $E_{Cell} = E^o_{Cell} - \frac{0.059}{2} \log \frac{[H^+]^2}{[Zn^{2+}]}$

(D) $E_{Cell} = E^o_{Cell} - \frac{0.059}{2} \log \frac{[H^+]^2}{[Zn^{2+}]}$

11. (C) $\frac{1}{2}H_2 \longrightarrow H^+ + e^-$

$e^- + AgCl \longrightarrow Ag + Cl^-$

$AgCl + \frac{1}{2}H_2 \longrightarrow Ag + H^+ + Cl^-$

(D) $\frac{1}{2}H_2 \longrightarrow H^+ + e^-$

(KCl is neutral solution where $[H^+] = 10^{-7}$ M)

$AgCl + e^- \longrightarrow Ag + Cl^-$

$\frac{1}{2}H_2 + AgCl \longrightarrow Ag + H^+ + Cl^-$

12. In highly alkaline medium OH^- ion get oxidise in preference to H_2O

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

$$E^o_{Cl^-/AgCl/Ag} = E^o_{Ag^+/Ag} - \frac{0.059}{1} \log \frac{1}{K_{sp}}$$

E^o_{Red} of active metal is lower than E^o_{Red} of hydrogen so not reduced by hydrogen.

13. $E_{M/M^{+n}} = E^0_{M/M^{+n}} - \frac{0.059}{n} \log M^{n+}$

$[M^{n+}] \uparrow,\ E_{M/M^{n+}} \downarrow,\ E_{M^{n+}/M} \uparrow.$

14. $2Cu^{+1} \longrightarrow Cu + Cu^{+2}$

$2Cu^{+1} + 2e \longrightarrow 2Cu$

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

$2Cu^{+1} \longrightarrow Cu^{+2} + Cu$

$\therefore\ E^\circ \frac{2\times 0.521 + 2(-0.337)}{2} = 0.184$

Part # II : Assertion & Reason

2. $E^o_{H^+/H_2} > E^o_{Na^+/Na}$

so, that H_2 gas will have more tendency to get deposit.

3. Mole of $O_2 \times 4 = 2$ $(H_2O \longrightarrow O_2 + 4H^+ + 4e^-)$

Mole of $O_2 = 0.5$

volume of O_2 at S.T.P. = 11.2 Lt.

6. $Pt, Cl_2 \,|\, Cl^-(aq) \,||\, Cl^-(aq) \,|\, Cl_2(g), Pt.$

Anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$ (R.H.S.)

Cathode : $Cl_2 + 2e^- \longrightarrow 2Cl^-$ (L.H.S.)

$$E_{cell} = 0 - \frac{RT}{nF} \ln \frac{[Cl^-]_{L.H.S}}{[Cl^-]_{R.H.S}}$$

$$E_{cell} = \frac{RT}{nF} \ln \frac{[Cl^-]_{R.H.S}}{[Cl^-]_{L.H.S}}$$

8. Number of ions per unit volume is linearly decreases in strong electrolyte but not is weak electrolyte.

10. S.O.P. of Cu is greater then S.O.P. of water ($H_2O \rightarrow O_2$) and S.R.P. of Cu is greater than S.R.P. of water ($H_2O \rightarrow H_2$).

11. Molar conductivity of weak electrolyte at infinite dilution can not be determined by experimentally. It can be calculate by Kohlrausch law.

EXERCISE - 3

Part # I : Matrix Match Type

1. (A) $E_{cell} = -\frac{0.059}{2}\log\frac{(P_{H_2})_c[H^+]_a^2}{(P_{H_2})_a[H^+]_c^2}3$,

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

(B) cell reaction $Ag^+ + Cl^- = AgCl(s)$

$E_{cell} = E^0_{cell} - \frac{0.059}{1}\log\frac{1}{[Ag^+]_c[Cl^-]_a}$

$= E^0_{cell} - \frac{0.059}{1}\log\frac{1}{0.01\times 0.1} = E^0_{cell} - 0.059\times 3$

but $E^0_{cell} = \frac{0.059}{1}\log\frac{1}{Ksp} = 0.059\times 10$

so $E_{cell} = 0.059\times 10 - 0.059\times 3$

$E^0_{cell} \neq 0$ 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 $E^0_{cell} = 0$.

Part # II : Comprehension

Comprehension # 1 :

1. $E_{cell} = E^0_{cell} - \frac{2.303RT}{nF}\log\frac{(Zn^{+2})}{(Cu^{+2})}$

$= 0.76 + 0.34 - \frac{2.303\times 8.31\times 200}{2\times 96500}\log\frac{2}{0.2} = 1.08$ volt.

2. $Cu^{+2} + 4\,NH_3 \rightleftharpoons [Cu(CH_3)_4]^{+2}$

0.2 1 0

x 1–0.8 0.2

$k_f = 4.0\times 10^{11} = \frac{0.2}{x\times(0.2)^4} = \frac{1}{x\times(0.2)^3}$

$x = \frac{10^{-11}}{(0.2)^3\times 4}$

$x = 3.125\times 10^{-10}$ $[Cu^{+2}] = 3.125\times 10^{-10}$

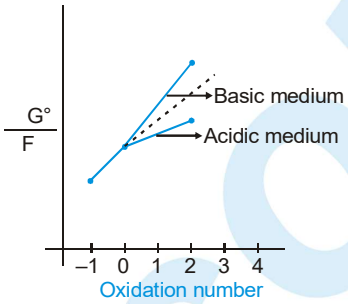
$E_{cell} = 0.75 + 0.34 - \frac{0.0591}{2}\log\frac{2}{3.125\times 10^{-10}}$

$= 1.1 - \frac{0.0591}{2}(10 - 0.194) = 1.1 - 0.29 = 0.81$ volt

Comprehension # 2 :

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.



Comprehension # 4 :

1. $\lambda_m^C = \lambda_m^\infty - b\sqrt{C}$

when $C_1 = 4\text{ x }10^{-4}$ $\lambda_m^C = 107$

and when $C_2 = 9\text{ x }10^{-4}$ $\lambda_m = 97$

so $107 = \lambda_m^\infty - b\text{ x }2\text{ x }10^{-2}$ ... (1)

$97 = \lambda_m^\infty - b\text{ x }3\text{ x }10^{-2}$ ... (2)

$b = 1000$

$\lambda_m = \lambda_m^\infty - b\sqrt{C}$

$\lambda_m^\infty = \lambda_m + b\sqrt{C} = 107 + 10^3\text{ x }2\text{ x }10^{-2}$

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

2. For $25\text{ x }10^{-4}$ (M) NaCl solution

$\lambda_m = \lambda_m^\infty - b\sqrt{C}$

$\lambda_m = 127 - 10^3\,(25\text{ x }10^{-4})^{1/2}$

$\lambda_m = 127 - 10^3\text{ x }5\text{ x }10^{-2}$

$\lambda_m = 77$

But $\lambda_m = \frac{K\text{ x }1000}{M}$ $K = \left(\frac{1}{a}\right)\text{ x }\frac{1}{R}$

$\lambda_m = \left(\frac{1}{a}\right)\text{ x }\frac{1}{R}\text{ x }\frac{1000}{M}$

$\lambda_m = [\text{Cell constant}]\text{ x }\frac{1000}{R\text{ x }M} \Rightarrow 77 = [\text{Cell constant}]$

$\text{x }\frac{1000}{1000\text{ x }25\text{ x }10^{-4}}$

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

3. For Na_2SO_4 solution

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

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

$$\lambda_m (Na_2SO_4) = 192.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

EXERCISE - 4
Subjective Type

2. If cell is taken to be conc cell, $E^o_{cell} = 0$

Anode : $Ag \longrightarrow Ag^+_a + e^-$

Cathode : $Ag^+_c + e^- \longrightarrow Ag$

$$Ag^+_c \rightleftharpoons Ag^+_a$$

From Nernst eq,

$$E_{cell} = E^o_{cell} - \frac{0.059}{1} \log \frac{[Ag^+]_a}{[Ag^+]_c}$$

$$\Rightarrow \quad 0 = 0 \quad - \frac{0.059}{1} \log \frac{[Ag^+]_a}{[Ag^+]_c}$$

$$\therefore [Ag^+]_a = [Ag^+]_c \Rightarrow \frac{K_{sp} \text{ of AgBr}}{[Br^-]} = \frac{K_{sp} \text{ of AgCl}}{[Cl^-]}$$

or, $\frac{5 \times 10^{-13}}{10^{-10}} = \frac{[Br^-]}{[Cl^-]} = \frac{[Br^-]}{[Cl^-]} = \frac{1}{200}$.

4. $E^o_1 = \frac{-[4 \times 1.47 + 1 \times 1.6]}{-5} = 1.496 \text{ V}$

$E^o_1 = \frac{-[5 \times 1.496 + 1.07]}{-6} = 1.425 \text{ V}$

6. Anode : $[Co(CN)_6]^{3-} + e^- \longrightarrow [Co(CN)_6]^{4-}$

$E^0_{SRP} = -0.83 \text{ V}.$

Cathode : $Co^{3+} + e^- \longrightarrow Co^{2+}$

$E^0_{SRP} = 1.82 \text{ V}.$

So overall cell reaction is,

$$Co^{3+} + [Co(CN)_6]^{4-} \longrightarrow Co^{2+} + [Co(CN)_6]^{3-}.$$

$$E^0_{cell} = E^0_c - E^0_a = 1.82 - (-0.83) = 2.65 \text{ V}.$$

$$E_{Cell} = E^0_{cell} - \frac{0.059}{1} \log \frac{[Co^{2+}][Co(CN)_6]^{3-}}{[Co^{3+}][Co(CN)_6]^{4-}}.$$

Now, $Co^{2+} + 6CN^- \rightleftharpoons [Co(CN)_6]^{4-}$

$K_{f_1} = 1 \times 10^{19}.$

$Co^{3+} + 6CN^- \rightleftharpoons [Co(CN)_6]^{3-} \qquad K_{f_2}$

at equilibrium, $E_{Cell} = 0$

$$E^0_{cell} = \frac{0.059}{1} \log \frac{K_{f_2}}{K_{f_1}} \quad ; \quad \text{solving we get } K_f = 10^{63.915}$$

7.

	MnO_4^-	+ $8H^+$	+ $5e^-$ ⟶	Mn^{2+}	+ H_2O.
Initially	0.1	0.8		0	0
After	0.1–0.1×0.9	0.8–0.09×8		0.09	0.09
reaction	0.10–0.09	0.8–0.72		0.09	0.09
	0.01	0.08		0.09	0.09

$$E = E^o - \frac{0.059}{5} \log_{10} \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

$$= 1.51 - \frac{0.059}{5} \log_{10} \frac{(0.09)}{(0.01)(0.08)^8} = \mathbf{1.39 \text{ V}}.$$

8. $K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow \frac{1}{6} = \frac{\alpha^2}{1-\alpha}$

$$\Rightarrow \alpha = \frac{-1 \pm \sqrt{(1)^2 + 4 \times 6 \times 1}}{12} = \frac{-1 \pm \sqrt{1+24}}{12} = \frac{1}{3}$$

$$\therefore [IO_3^-] = 1 \times \frac{1}{3} = \frac{1}{3} \text{ M}$$

$$\Rightarrow [Ag^+] = \frac{3 \times 10^{-8}}{\frac{1}{3}} = 9 \times 10^{-8} \text{ M}$$

Now $2Ag + Zn^{+2} \xrightarrow{2e^-} 2Ag^+ + Zn$

Gives $E = -1.56 + \frac{0.059}{2} \log \frac{1}{(9 \times 10^{-8})^2} = -1.144 \text{ V}$

$= -1144 \text{ mV}$

Ans. 1144

11. $K_{water} = 2.56 \times 10{-}5 \text{ sec cm}^{-1}$

$K_{NaCl(aq)} = 3.1 \times 10^{-5} \text{ sec cm}^{-1}.$

$$149.9 = \frac{(3.1 - 2.56) \times 10^{-5} \times 1000}{M} \quad \text{or}$$

$$M = \frac{5.4 \times 10^{-3}}{149.9} \approx 3.6 \times 10^{-5} \text{ mole/L}$$

or $\frac{500}{58.5 \times V} = 3.6 \times 10^{-5} \text{ mole/L}$ or

$V = \frac{500 \times 10^5}{58.5 \times 3.6}$ Liter $= \mathbf{2.37 \times 10^5 \text{ Liter Ans.}}$

12. $CuSO_4$ 100 ml, M molar.

$$\frac{\text{At cathode}}{Cu^{2+} + 2e^-} \longrightarrow Cu\ ] \times 2$$

$$\frac{\text{At Anode}}{2H_2O} \longrightarrow O_2 + 4H^+ + 4e^-$$

Over all,

$2Cu^{2+} + 2H_2O \longrightarrow 2Cu(s) + O_2 + 4H^+$

$pH = 1 \Rightarrow [H^+] = 0.1 \Rightarrow H^+ = 0.01$ mole

$Q = 0.01$ mole of $e^- = 0.01 \times 96500$ coulomb

$= 965$ coulomb.

$\therefore$ duration of electrolysis with 100% efficiency $= \frac{Q}{i}$

$= \frac{965}{0.965} = 1000$ sec.

$\therefore$ duration of electrolysis with 80% efficiency

$= \frac{1000}{0.8}$ sec $= 1250$ sec.

Cu deposited $= \frac{0.01}{2}$ mole $= 5$ m mole.

$2Cu^{2+} + 4I^- \longrightarrow Cu_2I_2 + I_2$

1.4 m mole 0.7 m mole

$I_2 + 2\,Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

0.04×35

0.7 m mole = 1.4 m mole

$\therefore$ Initial conc. of $CuSO_4 = \frac{5+1.4}{100} = \frac{6.4}{100} = 0.064$ M.

14. Charge passed = 0.01 Faraday

At the anode $\left(H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-\right)$ with 90 % efficiency 0.01×0.9 F have been used and will produce

$\frac{1}{4} \times 0.01 \times 0.9$ mole of O_2 i.e. 0.00225 mol O_2.

At the cathode $2H_2O \xrightarrow{+2e^-} H_2 + 2OH^-$

moles of H_2 produced $= \frac{0.01 \times 0.8}{2}$ mol $= 0.004$ mol

Total moles produced of gases $= 0.004 + 0.00225 = 0.00625$ mol

vol. at STP $= 0.00625 \times 22400$ mL $= 140$ mL **Ans. 140**

15. $[Ag(NH_3)_2]^+ \longrightarrow Ag^+ + 2NH_3$, $K_d = 6 \times 10^{-8}$,

$\Delta G_1^0 = -RT \ln 6 \times 10^{-8}$.

$Ag^+ + e^- \longrightarrow Ag$,

$E^o = 0.799$ volt, $\Delta G_2^0 = -1 \times 0.799 \times F$.

$[Ag(NH_3)_2]^+ + e^- \longrightarrow Ag(s) + 2NH_3$,

$\Delta G^o = \Delta G_1^0 + \Delta G_2^0$

$-1 \times E^o \times F = -RT \ln 6 \times 10^{-8} - 1 \times 0.799 \times F$.

$E^o = 0.373$ volt.

16. $M = \frac{0.624 \times 1000}{249.5 \times 100} = 0.025$

$\frac{1}{A} = 153.7\ m^{-1}$. $R = 520\ \Omega$

$M = \frac{K \times 1000}{M}$, $R = \frac{1}{KA}$

or $R = \frac{1}{K} \times G^*$ or $K = \frac{G^*}{R} = \frac{153.7}{520}$

or $K = 0.29557\ Scm^{-1} = 0.29557\ Scm^{-1}$

$M = \frac{2.955 \times 10^{-3} \times 1000}{0.025} = 118.2\ Scm^2\ mol^{-1}$ Ans.

17. $E = 0 - \frac{0.0591}{2} \log \frac{0.1 \times 1.8 \times 10^{-5}}{[H^+]^2_{NH_3}}$

$\frac{[OH^-]^2}{0.01} = 1.8 \times 10^{-5} \Rightarrow [H^+]^2 = \frac{(10^{-14})^2}{1.8 \times 10^{-7}}$

$\Rightarrow E = -0.46$ volt.

18. $K = 1.342\ sec^{-1}$ $R = 170.5\ \Omega$ $A = 1.86 \times 10^{-4}$ sec.m.

$R = \frac{\delta l}{A} = \frac{1}{KA}$ or

$\bullet = RKA = 170.5 \times 1.342 \times 1.86 \times 10^{-4} = \mathbf{4.25 \times 10^{-2}\ m.}$

19. $E^o = 0.7991 + \frac{0.0591}{1} \log K_{SP} = 0.0791 - 0.0591 \times pK_{SP}$

$= -0.149$ volt.

20. $H_2 + 2H^+(C) + 2e^-$.

$2Ag^+(0.8\ M) + 2e^- \longrightarrow 2Ag$.

$H_2(g) + 2Ag^+(0.8\ M) \longrightarrow 2H^+(C) + 2Ag$,

$E^o = 0 + 0.8 = 0.8$ volt.

$$0.982 = 0.8 - \frac{0.0591}{2}\log\frac{[H^+]^2}{1\times(0.8)^2} \quad \text{.....(i)}$$

$$K_{a(HOCN)} = \frac{[H^+]^2}{1.3\times10^{-3} - [H^+]} \quad \text{.....(ii)}$$

From equation (i) and (ii).

$K_{a(HOCN)} = 6.74 \times 10^{-4}$.

21. $T\bullet^+ \longrightarrow T\bullet^{3+} + 2e^-$.

$2Co^{3+} + 2e^- \longrightarrow 2Co^{2+}$.

$T\bullet^+ + 2Co^{3+} \longrightarrow T\bullet^{3+} + 2Co^{2+}$,

---

2.5	5	0	0
x	2x	2.5	5

$E^o = -1.25 + 1.84 = 0.59$ volt.

$$0 = 0.59 - \frac{0.059}{2}\log\frac{2.5\times5^2}{x\times(2x)^2}.$$

$$\frac{2.5\times(5)^2}{4x^3} = 10^{20}.$$

$[T\bullet^+] = 10^{-8}\ M$, $[Co^{3+}] = 2\times10^{-8}\ M$.

22. (A) M = Zn & X = Ni

$E^o_{cell} = -0.25 + 0.76 = 0.51$ V

$$E_{cell} = 0.51 - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Ni^{2+}]}$$

$$= 0.51 - \frac{0.059}{2}\log\frac{0.01}{1} = 0.569\ V$$

(B) $Zn^{2+} = 1M$.

$Ni^{2+} + Zn(s) \rightleftharpoons Zn^{2+}(aq) + Ni(s)$

initial conc.	1	0.01
conc. after time 't'	0.01	1

$$E_{cell} = 0.51 - \frac{0.059}{2}\log\frac{1}{0.01} = 0.451 \text{ volt.}$$

(C) circuit is disconnected & cell voltage = 0

23. $\lambda^o_c = F \times \mu_c$

$= 96500$ coulomb $\times\ 6.6\times10^{-4}\ cm^2\ volt^{-1}\ sec^{-1}$

$= 96500$ Siemen $\times\ 6.6\times10^{-4}\ cm^2$

$= 96500 \times 6.6\times10^{-4}\ Scm^2\ mole^{-1}$

$\lambda^o_a = F\times\mu_a = 96500\times5.7\times10^{-4}\ Scm^2\ mole^{-1}$

$\lambda^o_{NH_4ClO_4} = 96500\times10^{-4}\times(6.6+5.7)$

$=$ **118.695 Scm² mol⁻¹ Ans.**

24. Equivalent of metal = Equivalents of I_2 = Equivalents of hypo.

0.617 / equivalent weight $= 46.3\times0.124\times10^{-3}$

$\Rightarrow$ Eq. wt. = 107.47.

25. $K = \frac{K_1+K_2}{2} \Rightarrow K = \frac{1}{2}\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \Rightarrow K = 0.0165\ S\,cm^{-1}$.

25. $\Lambda^\infty = \frac{\Lambda_{eq}}{\Lambda^\infty_{eq}} = \frac{1.4}{391} = 3.58\times10^{-3}$, $K = C\alpha^2 = 1.64\times10^{-7}$.

27. $Cu^{2+} + H_2O \longrightarrow Cu(s) + 2H^+ + \frac{1}{2}O_2$.

moles of electricity = 0.01.

$\therefore$ moles of Cu^{2+} consumed $= \frac{0.01}{2}$.

and moles of O_2 liberated $= \frac{0.01}{4}$

$\therefore$ mass of solution decreased

$$= \left(\frac{0.01}{2}\times63.5\right) + \left(\frac{0.01}{4}\times32\right) = 0.3175 + 0.08 = 0.3975.$$

$\therefore$ mass of resulting solution $= 10 - 0.3975 = 9.6$ gm.

equivalent of acid formed = 0.01.

28. (i) Equivalents of Ag^+ = Equivalent of O_2.

1 = equivalent of O_2.

$\therefore$ mass of $O_2 = \frac{1}{4} = \frac{PV}{RT}$.

$$V = \frac{1}{4}\times\frac{0.0821\times298\times760}{750} = 6.2 \text{ lit.}$$

(ii) moles of $O_2 = \frac{\text{equivalent of } O_2}{4}$

$$= \frac{8\times10^{22}/6.023\times10^{23}}{4} = 0.0332.$$

$$V = \frac{0.0332\times0.0821\times298\times760}{750} = 0.823 \text{ lit.}$$

29. Equivalents of Cu deposited $= \frac{31.75\times2}{63.5} = 1$

equivalents of NaOH formed $= 0.6\times0.6$.

% yield of NaOH = 60%.

30. $Pb^{2+} + 2e^- \longrightarrow Pb$

$$E^0_{Pb^{2+}/Pb} = E^0_{Pb^{2+}/Pb} - \frac{0.0591}{2}\log\frac{1}{0.1} = -0.1555 \text{ volt}$$

$E_{cell} = E_{Pb^{2+}/Pb} - E_{T\lambda^+/T\lambda}$

$0.443 = -0.1555 - E_{T\lambda^+/T\lambda}$

$E_{T\lambda^+/T\lambda} = -0.5985V$

$T\bullet^+ + e^- \longrightarrow T\bullet$

$E_{T\lambda^+/T\lambda} = E^0_{T\lambda^+/T\lambda} - 0.059 \log \frac{1}{(Tl^+)}$

$-0.5985 = -0.336 + 0.059 \log (T\bullet^+)$

$T\bullet^+ = 3.55 \times 10^{-5}\,M$

$Ksp = [T\bullet^+][Br^-] = 3.55 \times 10^{-5} \times 0.1 = 3.55 \times 10^{-6}\,M^2$

$= 355 \times 10^{-8}\,M^2$

31. $Fe(s) + Sn^{2+}(aq.) \rightleftharpoons Fe^{2+}(aq) + Sn(s)$ $\quad E^0_{cell} = 0.30V$

$Zn(s) + Fe^{2+}(aq.) \rightleftharpoons Zn^{2+}(aq.) + Fe(s)$ $\quad E^0_{cell} = 0.32V$

If above cells are connected in parallel then first cell will get charged up and second cell will get discharged so net cell reaction will be.

$Fe_2^{2+}(aq.) + Fe_1^{2+}(aq.) \rightleftharpoons Zn^{2+}(aq.) + Sn^{2+}(aq.)$

t = 0	1M	1M	1M	1M
t(aq.)	(1 – x)	(1 – x)	(1 + x)	(1 + x)

$E^0_{net} = 0.02$

$\Delta G^0_{net} = -nF E^0_{net}$

$E = 0.3 - \frac{0.059}{2} \log \frac{[Fe^{2+}]}{[Sn^{2+}]}$.

$\Rightarrow E = 0.32 - \frac{0.059}{2} \log \frac{[Z^{2+}]}{[Fe^{2+}]}$

$= -2 \times 96500 \times 0.02$ J/mole

So, $-2.30\,RT \log K_{eq.} = -2 \times 96500 \times 0.02$

$\log K_{eq.} = \frac{2 \times 96500 \times 0.02}{6433} = 0.6 \Rightarrow K_{eq.} = 4$

$\frac{(1+x)^2}{(1-x)^2} = 4 \Rightarrow \frac{(1+x)}{(1-x)} = 2 \Rightarrow x = \frac{1}{3}$

So, $[Fe^{2+}]$ in the first cell $= [Fe^{2+}]$ in the second cell $= \frac{2}{3}$ M = **667 mmoles/L**

32. $E = E° + RTF^{-1} \ln \frac{[X^-]}{K_a[HX][Cl^-]}$

$\Rightarrow E - E° + RTF^{-1} \ln \frac{[HX][Cl^-]}{[X^-]}$ $RTF^{-}\bullet n \frac{1}{K_a}$

$\Rightarrow \bullet n \frac{1}{K_a} = \frac{96500}{8.315 \times 298}(0.2814)$

$\Rightarrow K_a = 1.74 \times 10^{-5}$ Hence Ans. 174

33. $\Lambda^\infty_m = 350 + 198 = \frac{0.58 \times 10^{-7} \times 1000}{M}$

$\Rightarrow M = 1.06 \times 10^{-7}$ and $K_w = M^2 = 1.12 \times 10^{-14}$.

34. $Cu^{2+} + e^- \longrightarrow Cu^+$ $\quad E° = 0.15$ $\Delta G° = -F \times 0.15$

$Cu^+ + e^- \longrightarrow Cu$ $\quad E° = 0.50$ $\Delta G° = -F \times 0.50$

$Cu^{2+} + 2e^- \longrightarrow Cu$ $\quad \Delta G° = -F \times 0.65$

$= -2 \times F \times E°_{Cu^{2+}/Cu}$

$E°_{Cu^{2+}/Cu} = 0.325$

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

$E°_{cell} = 0.5 - 0.15 = 0.35$ volt.

So, disproportionation is possible

35. As cell reaction is

1st cell : $Zn + 2AgCl \longrightarrow ZnCl_2 + 2Ag$

2nd cell : $ZnCl_2 + 2Ag \longrightarrow 2AgCl + Zn$

Overall $\quad ZnCl_2(C_2) \longrightarrow ZnCl_2(C_1)$

$E = \frac{RT}{2F} \ln \left(\frac{0.5}{0.02}\right) V = \left[\frac{0.059}{2} \log \left(\frac{0.5}{0.02}\right)\right] V = 42\,mV$

EXERCISE - 5

Part # I : AIEEE/JEE-MAIN

1. $E°_{cell} = 0.77 + 0.14 = 0.91$ volt.

2. $\overset{0}{\wedge}_{NaBr} = 126 + 152 - 150 =$ **128 S cm² mol⁻¹.**

3. $Zn + 2H^+_{(aq)} \longrightarrow Zn^{2+}(aq) + H_2(g)$

$E = E° - \frac{0.0591}{2} \log \frac{[Zn^{2+}]pH_2}{[H^+]^2}$

Adding H_2SO_4 means increasing H^+ and therefore E_{cell} will increase and reaction will shift to forward direction.

4. $Cr^{2+} | Cr^{3+} = +0.41V$ $\quad Mn^{2+} | Mn^{3+} = -1.57V$

$Fe^{2+} | Fe^{3+} = -0.77V$ $\quad Co^{2+} | Co^{3+} = -1.97V$

As Cr will have maximum oxidation potential value, therefore its oxidation will be easiest.

5. Difluoroacetic acid will be strongest acid due to electron withdrawing effect of two fluorine atoms so as it will show maximum electrical conductivity.

6. $Al^{3+} + 3e^- \longrightarrow Al.$

$\frac{5.12 \times 10^3}{27} = 189.62$ mol.

Charge $= 189.62 \times 3 \times 96500 =$ **5.489×10^7 coulomb.**

7. $CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$

From the reaction,

$$\Lambda^0_{CH_3COONa} + \Lambda^\circ_{HCl} = \Lambda^0_{CH_3COOH} + \Lambda^\circ_{NaCl} \quad \text{or}$$

$$\Lambda^0_{CH_3COOH} = \Lambda^0_{CH_3COONa} + \Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl}$$

Thus to calculate the value of $\Lambda^0_{CH_3COOH}$ one should know the value of Λ°_{NaCl} along with $\Lambda^0_{CH_3COONa}$ and Λ°_{HCl}.

8. $0.152 = -0.8 - \frac{0.059}{1}\log K_{SP}$; **log KSP = – 16.11.**

9. $C = 0.1\ M, \quad R = 100\ \Omega$

$K = 1.29\ Sm^{-1} = \frac{1}{100} \times \frac{1}{A}$.

$0.02\ M, \quad R = 520\ \Omega$.

$$K = \frac{1}{520} \times 129$$

$$\text{Å}_M = \frac{\frac{1}{520}\times 129}{1000 \times 0.02} = \mathbf{124 \times 10^{-4}\ Sm^2 mol^{-1}.}$$

or $K = G\sigma = \frac{r}{R} = 1\ \sigma = KR.$

$\sigma = 1.29 \times 100 = 129.$

For other concentration

$r = 129.$

$$K' = \frac{\sigma}{R} = \frac{129}{520};$$

$$\Lambda_M = \frac{1000\,K}{M} = \frac{1000\times 129}{0.02\times 500} = \mathbf{5\ Cm^2\ mol^{-1}.}$$

10. According to Kohlrausch's law the molar conductivity at infinite dilution (Λ°) for weak electrolyte CH_3COOH is

$\Lambda^\circ_{CH_3COOH} = \Lambda^\circ_{CH_3COONa} + \Lambda^\circ_{HCl} - \Lambda^\circ_{NaCl}$

So for calculating the value of $\Lambda^\circ_{CH3COOH}$, value of Λ°_{NaCl} should also be known.

11. $0 = +1.1 - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$; $\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = 37.3.$;

$\frac{[Zn^{2+}]}{[Cu^{2+}]} = \mathbf{10^{37.3}}$ **Ans.**

12. $E_{cell} = E^0_{cell} - \frac{0.059}{6}\log\frac{[Cr^{+3}]^2}{[Fe^{+2}]^3}$

$= 0.3 - \frac{0.056}{6}\log\frac{(0.1)^2}{(0.01)^3} = 0.3 - 0.04 = 0.26\ V$

13. $Fe^{3+} + 3e^- \longrightarrow Fe \qquad \Delta G_1 = -3 \times F \times E^0_{Fe^{3+}/Fe}$

$Fe^{2+} \longrightarrow Fe \qquad \Delta G_2 = -2 \times F \times E^0_{Fe^{2+}/Fe}$

$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad \Delta G = \Delta G_1 - \Delta G_2$

$\Delta G = 3 \times 0.036F - 2 \times 0.439 \times F = -1 \times E^0_{(Fe^{3+}/Fe^{+2})} \times F$

$E^0_{(Fe^{3+}/Fe^{+2})} = 2 \times 0.439 - 3 \times 0.036$

$= 0.878 - 0.108 = 0.770\ V$

14. $\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2$

$\Delta_r G = +966\ kJ\ mol^{-1} = 966 \times 10^3\ J\ mol^{-1}$

$\Delta G = -nFE_{cell}$

$966 \times 10^3 = -4 \times 96500 \times E_{cell}$

$E_{cell} = 2.5\ V$

15. $2H^+(aq) + 2e^- \longrightarrow H_2(g)$

$$E_{red} = E^\circ_{red} - \frac{0.0591}{n}\log\frac{P_{H_2}}{(H^+)^2};$$

$$E_{red} = 0 - \frac{0.0591}{2}\log\frac{2}{(1)^2}; \qquad E_{red} = -\frac{0.0591}{2}\log 2$$

$\therefore$ E_{red} is found to be negative for (3) option.

16. $X + Y^{2+} \longrightarrow X^{2+} + Y$

For reaction to be spontaneous E° must be positive.

$E^\circ_{Zn/Zn^{+2}} + E^\circ_{Ni^{2+}/Ni} = 0.76 + (-0.23) = +0.53$ (positive)

17. Higher the SRP, better is oxidising agent

Hence MnO_4^- is strongest oxidising agent.

18. $E^\circ_{MnO_4^-/Mn^{+2}} = 1.51V$ ..... (i)

$E^\circ_{Cl_2/Cl^-} = 1.36V$ .....(ii)

$E^\circ_{Cr_2O_7^{-2}/Cr^{+3}} = 1.33V$ .....(iii)

$E^\circ_{Cr^{+3}/Cr} = -0.74V$ .....(iv)

Since Cr^{+3} is having least reducing potential, so chromium is the best reducing agent.

19. $B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$

moles of O_2 required = 3x moles of B_2H_6

$$= 3 \times \frac{27.6}{27.6} = 3 \Rightarrow \frac{I \times t}{96500} = \text{moles of } O_2 \times 4$$

$$\frac{100 \times t}{96500} = 3 \times 4 \quad \Rightarrow \quad t = \frac{3\times 4 \times 96500}{100}\ \text{sec.} = 3.2\ \text{hours.}$$

Part # II : IIT-JEE ADVANCED

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

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

$E^\circ = 0.32$ Volt.
At equilibrium, $E_{cell} = 0$.

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

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

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

$In^{2+} \longrightarrow In^{3+} + e^-$
$E^\circ = 0.44$ volt.

$E^\circ_{cell} = 0.15 + 0.44 = 0.59$ volt.

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

$K = 10^{10}$.

3. $Fe \longrightarrow Fe^{2+} + 2e^-$, 0.44 V.

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

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

$\Delta G^\circ = -2 \times 1.67 \times 96500 = -322.3$ kJ.

4. **(a)** $\Delta G^\circ_r = -109 + 129 - 77 = -57$ kJ/mol
Cell representation : $Ag\,|\,AgCl\,||\,Cl^-|\,Ag^+\,|\,Ag$.
$-1 \times 96500 \times E^\circ = -57 \times 10^3$.
$E^\circ = 0.59$ volt.

$$0 = 0.59 - \frac{0.059}{1}\log\frac{1}{K_{SP}}.$$

$\log K_{SP} =$ **-10.**

(b) $Zn \longrightarrow Zn^{2+} + 2e^-$, 0.76 volt.
$2Ag^+ + 2e^- \longrightarrow 2Ag$, 0.80 volt.

$Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag$, $E^\circ_{cell} = 1.56$ volt.

$$n_{Zn} = \frac{6.539\times10^{-2}}{65.39} = 10^{-3}\ \text{mol},$$

$[Ag^+] = \sqrt{K_{sp}} = 10^{-5}$ M.

$$0 = 1.56 - \frac{0.059}{2}\log K$$

$n_{Ag^+} = 10^{-5} \times 0.1 = 10^{-6}$ M.
$n_{Ag} = 10^{-6}$ mol. $\Rightarrow$ **$\log K = 52.8$.**

5. $2Ag^+ + C_6H_{12}O_6 + H_2 \longrightarrow 2Ag(s) + C_6H_{12}O_7 + 2H^+$,
$E^\circ = 0.8 - 0.05 = 0.75$ volt.

$$0 = 0.75 - \frac{0.0592}{2}\log K.$$

$\ln K = 2.303 \times \log K = 2.303 \times 25.34 = 58.38$.

6. $[H^+] = 10^{-11}$ M.

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

or, $\Delta H = 0.65$ volt.

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

8. $AgBr\,(s) \rightleftharpoons Ag^+ + Br^-$
$(S + 10^{-7}) \times S = K_{SP} = 12 \times 10^{-14}$.
$S = 3 \times 10^{-7}$ M.
$[Ag^+] = 4 \times 10^{-7}$ M ; $[Br^-] = 3 \times 10^{-7}$ M ; $[NO_3^-] = 10^{-7}$ M.
$K_{total} = \lambda^\circ_{(Ag^+)}\,\lambda^\circ_{(Ag^+)} + \lambda^\circ_{Br^-}\,\lambda^\circ_{Br^-} + \lambda^\circ_{(NO_3^-)}\lambda^\circ_{(NO_3^-)}$
$\lambda^\circ_{KCl} = \lambda^\circ_{K^+} + \lambda^\circ_{Cl^-}$.
$K_{KCl} = 4 \times 10^{-4} \times 6 \times 10^{-3} + 3 \times 10^{-4} \times 8 \times 10^{-3} + 1 \times 10^{-4} \times 7 \times 10^{-3}$.
$K_{KCl} = 24 + 24 + 7$. **$K_{KCl} = 55\ Scm^{-1}$.**

9. Mol of NaCl $= 4 \times 0.5 = 2$ mol.
No. of mole of Cl_2 evolved $= \frac{1}{2} \times$ mol of NaCl $= \frac{1}{2} \times 2 =$ **1 mol.**

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

11. $2Na^+ + 2e^- \longrightarrow 2Na$.
No. of Faraday required $= 2$.
$\therefore$ total charge $= 2 \times 96500 =$ **193000 coulomb.**

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

13. $Mn^{3+} + e^- \longrightarrow Mn^{2+}$, 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.

14. 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 $= t$

15. 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.

16. M (s) | M^+ (aq, 0.05 M) || M^+ (aq, 1 M) | M(s)

Anode : $M(s) \longrightarrow M^+(aq) + e^-$

Cathode : $M^+(aq) + e^- \longrightarrow M(s)$

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

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

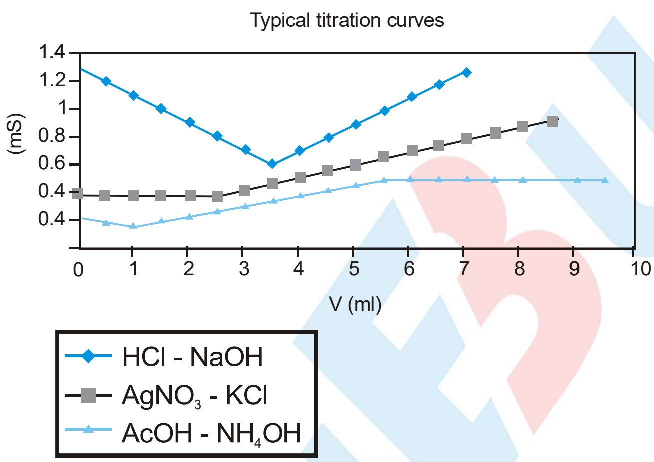
$$= 0 - \frac{0.0591}{1} \log \left\{\frac{0.05}{1}\right\}$$

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

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

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

18.



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

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

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

20. 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

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

21. $\Delta G = -nFE_{cell} = -2 \times 96500 \times 0.059 \times 10^{-3}$ kJ/mole
$= -11.4$ kJ/mole.

22. **(P)** $\underset{X}{(C_2H_5)_3N} + \underset{Y}{CH_3COOH} \longrightarrow CH_3COO^-(aq) + (C_2H_5)_3NH^+(aq)$

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↓ (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 decreases 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 decreases 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).

23. **(P)** $E^o_{Fe^{3+}, Fe}$ $\quad Fe^{3+} \xrightarrow[n=1]{+0.77V} Fe^{2+} \xrightarrow[n=2]{-0.44V} Fe$, overall $Fe^{3+} \rightarrow Fe$: xV, n = 3

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

$\Rightarrow x = -\frac{0.11}{3} \text{ V} \simeq -0.04 \text{ V}.$

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

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \quad -1.23\ V$

$+$

$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad +0.4\ V$

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

(R) $E^\circ_{(Cu^{2+} + Cu \rightarrow 2Cu^+)}$

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

$+0.34V, \quad n = 2$

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

$x = 0.16\ V.$

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

$+$

$Cu \longrightarrow Cu^+ + e^- \quad -0.52\ V$

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

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

(S) $E^\circ_{(Cr^{3+},\ Cr^{2+})}$

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

$-0.74V, \quad n = 3$

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

$x - 1.82 = -2.22$

$\Rightarrow$ $x = -0.4\ V$

Hence, most appropriate is (D).

(P) – (3) ; (Q) – (4) ; (R) – (1) ; (S) – 2.

24. **6**

Concentration = 0.0015 M

[HA]

$l = 120\ cm \qquad G = 5 \times 10^{-7}\ S = R \times A/l$

$A = 1\ cm^2$

$P^H = -\log(H^+) = -\log(H^+) = -\log(0.0015\ \alpha) = 4$

$$\alpha = \frac{1}{15}$$

$$\lambda_M^C = \frac{K \times 1000}{[HA]} = \frac{5\times10^{-7} \times 120 \times 1000}{0.0015} \times 10^4 = 40$$

$$\alpha = \frac{\lambda_M^C}{\lambda_M^\infty} = \frac{1}{15}$$

$\lambda_M^\infty = 600 = Z \times 10^2\ S\ cm^{-1} \quad \Rightarrow Z = 6$ Ans.

25. $Zn(s) + Cu^{+2}_{eq} \longrightarrow Cu(s)$

$x \qquad\qquad 10\ x$

$\Delta G = -2.2\ F\ (1.1) + RT \ln(10)$

$= -2.2\ F + 2.303\ RT$

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

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

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

$E = 2.67 = 2.7 - \frac{RT}{nF} \ln\frac{x}{1} \Rightarrow 0.03 = \frac{300}{2\times11500} \ln x$

$2.3 = \bullet nx \Rightarrow X = 10$

27. (i) $2Cu(s) + \frac{1}{2}O_2(g) \longrightarrow Cu_2O(s)\ ;\ \Delta G^\circ = -78000\ J/mol$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)\ ;\ \Delta G^\circ = -178000\ J/mol$

(i) – (ii) then

$2Cu(s) + H_2O\ (g) \longrightarrow Cu_2O\ (s) + H_2(g)$

$\Delta G^\circ = -78000 + 178000 = 100000\ J/mol$

Now for the above reaction

$$\Delta G = \Delta G^\circ + RT \ln\left(\frac{P_{H_2}}{P_{H_2O}}\right) \geq 0$$

$10^4(\ln P_{H_2} - \ln P_{H_2O}) \geq -10^5$

$\ln P_{H_2} \geq -10 + \ln P_{H_2O}$

$\geq -10 + 2.3 \log(0.01)$

$\ln P_{H_2} \geq -10 + 4.6$

$\ln P_{H_2} \geq -14.6$

$\therefore$ Minimum $\ln P_{H_2} = -14.6$

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

Reactions

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

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

Overall reaction :

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

$$E = E^\circ - \frac{RT}{2nF} \ln Q$$

$$0 = E^\circ - \frac{RT}{2nF} \ln\frac{[A^{n+}]^2}{[B^{2n+}]}$$

$$E^\circ = \frac{RT}{2nF} \ln 4$$

Now

$$\Delta G^\circ = -2nFE^\circ = \frac{-2nFRT}{2nF} \ln 4 = -RT \ln 4$$

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

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

$$\Delta S^\circ = \frac{\Delta G^\circ}{T} = \frac{-RT \ln 4}{T} = -R \ln 4$$

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

MOCK TEST

1. (B)

$$ClO_3^- + 2H_2O + 4e \longrightarrow ClO^- + 4OH^- \quad ; \Delta G_1^\circ$$

$$ClO_3^- + 2H_2O + 4e \longrightarrow ClO^- + 4OH^- \quad ; \Delta G_2^\circ$$

$$\frac{1}{2}Cl_2 + e \longrightarrow Cl^- \quad ; \Delta G_3^\circ$$

$$ClO_3^- + 3H_2O + 3e \longrightarrow Cl^- + 6OH^- \quad ; \Delta G^\circ$$

2. (B)

Considering the cell reaction

$$H_2 + 2e \longrightarrow 2H^+$$

$$Hg_2^{2+} + 2e \longrightarrow 2Hg(l) + 2Cl^-(aq)$$

$$\Delta S = nF = \left(\frac{\partial E}{\partial T}\right)_P = 2 \times 96500 \times 3.4 \times 10^{-4}$$

$$= 65.223 \text{ J/K/mole}$$

3. (A)

$$2Ag^+ + H_2 \; f \quad 2H^+ + 2Ag$$

$$E = E^\circ - \frac{0.0591}{2}\log\frac{(H^+)^2}{P_{H_2} \times (Ag^+)^2}$$

$$0.222 = 0.7995 - \frac{0.0591}{2}\log\frac{1}{(Ag^+)^2}$$

$$(Ag^+) = 10^{-9.8}$$

$$Ksp = (Ag^+)(Cl^-) = (10^{-9.8}) \times (1) = 10^{-9.8}$$

4. (B)

5. (A)

Cell reaction

Cathode : $H_2O(l) + \frac{1}{2}O_2(g) + 2e^- \longrightarrow 2OH^-(aq)$

Anode : $H_2g \longrightarrow 2H^+(aq.) + 2e^-$

$$H_2O(l) + \frac{1}{2}O_2(g) + H_2(g) \longrightarrow 2H^+(aq.) + 2OH^-(aq.)$$

Also we have

$$H_2g + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta G^\circ_f = -237.2 \text{ kJ/mole}$$

$$H_2O(l) \longrightarrow H^+(aq.) + OH^-(aq.) \quad \Delta G^\circ = 80 \text{ kJ/mole}$$

Hence for cell reaction

$\Delta G^\circ = -77.20$ kJ/mole

So, $E^\circ = -\frac{\Delta G^\circ}{nF} = \frac{77200}{2 \times 96500} = 0.40$ V

6. (B)

$$H^+ + e^- \Rightarrow \frac{1}{2}H_2(g)$$

$$E_1 = 0 - 0.0591 \log \frac{1}{(H^+)_1}$$

$$E_1 = 0 + 0.0591 \log [H^+]_1$$

$$= -0.0591 \, pH_1$$

$$E_2 = -0.0591 \, pH_2$$

$$pH_1 = pk_a + \log\frac{\text{Salt}}{\text{Acid}}$$

$$pH_1 = pk_a + \log\frac{a}{b} \quad \text{..... (1)}$$

$$pH_2 = pk_a + \log\frac{b}{a} \quad \text{..... (2)}$$

Add (1) & (2)

$$pH_1 + pH_2 = 2\,pk_a$$

$$2pk_a = -\frac{E_1}{.0591} - \frac{E_2}{.0591}$$

$$pk_a = -\left[\frac{E_1 + E_2}{0.118}\right]$$

7. (D)

$$E_{Cell} = -\frac{0.0591}{1}\log\frac{[H^+]_a}{[H^+]_c}$$

For E_{Cell} to be highest $[H^+]_a$ should be lower and $[H^+]_c$ should be higher and that why anode compartment should be more basic and cathodic compartment should be acidic.

8. (C)

pH changes from 0 to 7.

$\therefore$ $[H^+]$ changes from 1 to 10^{-7} M.

Accordingly E_{red} decreases by 0.059 log 10^{-7}

i.e. $0.059 \times (-7) = -0.41$ volt

9. (A)

Anode : $\frac{1}{2}H_2 \longrightarrow H^+ + 1e^-$

Cathode : $AgCl + 1e^- \longrightarrow Ag + Cl^-$

Net : $\frac{1}{2}H_2 + AgCl \xrightarrow{1e^-} H^+ + Ag + Cl^-$

$$E_{Cell} = +0.222 + \frac{0.059}{1}\log\frac{1}{[H^+][Cl^-]}$$

$$= +0.222 + 0.059\log\frac{[OH^-]}{[10^{-14}][Cl^-]}$$

$= +0.222 + 0.059\,(14) \quad = +\,1.048$ volt

10. (A)

$$m(\text{theoretical}) = \frac{63.5\times0.1\times7200}{96500} = 0.4738\ g$$

$$\therefore \quad \%\ \text{efficiency} = \frac{0.3745}{0.4738}\times100 = 79\%$$

11 (A)

$$\frac{8.7}{8.7}\times96500 = 4.825\times10^{-3}\times t$$

$\Rightarrow \quad t = 2\times10^8$ sec

12. (A)

$$R = \frac{1}{k}\frac{1}{A}$$

The k is halved while the A is double. Hence R remains 50 Ω.

13. (B)

$AgCl + 1e^- \longrightarrow Ag + Cl^- \qquad E° = 0.2$ V

$Ag \longrightarrow Ag + 1e^- \qquad E° = -0.79$ V

$AgCl \xrightarrow{1e^-} Ag^+ + Cl^- \qquad E° = -0.59$ V

$$E° = \frac{0.059}{n}\log K \quad \Rightarrow \quad -0.59 = \frac{0.059}{1}\log K_{SP}$$

$\Rightarrow \quad K_{SP} = 10^{-10}$

Now solubility of AgCl in 0.1 M $AgNO_3$

$S\,(S + 0.1) = 10^{-10} \quad \Rightarrow \quad S = 10^{-9}$ mol/L

Hence 1 mole dissolves in 10^9 L solution

hence in 10^6 L amount that dissolves in s 1 m mol.

14. (B)

15. (B)

Reaction is $H_C^+ \xrightarrow{1e^-} H_A^+$

$$\therefore \quad E = \frac{0.059}{1}\log\frac{2.1\times10^{-4}}{1.8\times10^{-5}} = 0.0629\ V$$

16. (A)

$$E^0_{Br^-/AgBr/Ag} = E^0_{Ag^+} + \frac{0.059}{1}\log K_{SP}AgBr = E^0_{Ag^+/Ag} - 0.7257$$

and $E^0_{Cl^-/AgCl/Ag} = E^0_{Ag^+/Ag} + \frac{0.059}{1}\log K_{SP}AgCl = E^0_{Ag^+/Ag} - 0.59$

Now cell reaction is

$Ag + Br^- \longrightarrow AgBr + 1e^-$

$AgCl + 1e^- \longrightarrow Ag + Cl^-$

$Br^- + AgCl \xrightarrow{1e^-} Cl^- + AgBr$

$$0 = (0.7257 - 0.59) + \frac{0.059}{1}\log\frac{[Br^-]}{[Cl^-]}$$

$$\Rightarrow \quad \frac{[Br^-]}{[Cl^-]} = 0.005$$

17. (A)

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{c}$$

$260 = \Lambda_m^\infty - 0.5\,b$ ..... (1)

$250 = \Lambda_m^\infty - b$ ..... (2)

On solving (1) & (2), we get

$\Lambda_m^\infty = 270\ \Omega^{-1}\ cm^2\ mol^{-1}$

18. (B)

If reduction potential of metal ion is greater then O_2/H_2O couple, the ion is stable in water.

So Co^{3+} is stable in water.

19. (B)

$$\alpha = \frac{\lambda_m}{\lambda_m^\infty} = \frac{7.8}{390} = 0.02$$

$\Rightarrow K_a(CH_3COOH) = C\alpha^2 = 0.04\times(4.8)$

$\Rightarrow pK_a\ 6 - \log 2^4 = 6 - 4\times0.3 = 4.8$

$\Rightarrow pK_b\ (=H_3COO^-) = 14 - pK_a = 9.2$

20. (A, B, D)

21. (A, C)

$$2Cu^{+1} \longrightarrow Cu + Cu^{+2}$$

$$2Cu^{+1} + 2e \longrightarrow 2Cu$$

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

$$2Cu^{+1} \longrightarrow Cu^{+2} + Cu$$

$$\therefore \quad E^\circ \frac{2\times 0.521 + 2(-0.337)}{2} = 0.184$$

22. (A)

23. (B, C, D)

The SRP should be high for a species to be a good oxidising agent.

24. (C)

Conductivity is high due to $[H^+]$

25. (A)

Anode : $\left\{\begin{matrix} 2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^- \\ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \end{matrix}\right\}$

Cathode : $\{2H_2O \rightarrow H_2 + 2OH^- - 2e^-\} \times 3$

Net : $2H_2SO_4 + 8H_2O \rightarrow H_2S_2O_8 + O_2 + 3H_2 + 6H^+ + 6OH^-$

Hence ratio of n_{O_2} and n_{H_2} is 1 : 3.

26. (C)

27. (D)

28. The cell for oxidation reaction is,

$Pt \mid O_2 \mid H^+, H_2O \parallel MnO_4^-, Mn^{+2}, H^+ \mid Pt$

$$\therefore \quad E^0_{cell} = E^0_{MnO_4^-, Mn^{+2}, H^+ \mid Pt} - E^0_{H^+ \mid O_2 \mid Pt}$$

$$= 1.51 - 1.223 = 0.287\ V$$

Therefore true. **Ans. True**

29. True

30. True

$$\lambda^\infty = \lambda^\infty_{H^+} + \lambda^\infty_{C_2H_5O} = 400$$

$$\therefore \quad \lambda = K \times \frac{1000}{C} \qquad [C = \text{concentration of } C_2H_5OH]$$

$$\therefore \quad C = \frac{4\times 10^{-10} \times 1000}{400}$$

$$\therefore \quad K_{alcohol} = [H^+]\,[OC_2H_5] = (10^{-9})^2$$

$$\therefore \quad pk_{alcohol} = -\log(10^{-18}) = 18$$

31. False

The oxidation number is not changing for Ag.

32. (A)

33. (C)

34. (B)

At the equivalence point the concentrations will be $[Br^-] = 100\ m^3$, $[Na^+] = 100\ m^3$

Therefore $K_{total} = K_{Br} + K_{Na} = 1.2\ Sm^{-1} = 12 \times 10^{-1}\ Sm^{-1}$

35. (A)

$$E^0_{cell} = E^0_{Fe^{3+}/Fe^{2+}} - E^0_{Fe(CN)_6^3/Fe(CN)_6^4}$$

$$= +0.77\ V - 0.36\ V = +0.41\ V$$

The reaction is

$$Fe(CN)_6^{4-}(aq) + Fe^{3+}(aq) \rightarrow Fe(CN)_6^{3-}(aq) + Fe^{2+}(aq)$$

36. (C)

$$E^0_{cell} = E^0_{Br_2/Fe} - E^0_{Fe^{3+}/Fe^{2+}}$$

$$= +1.07\ V - 0.77 = +0.30\ V$$

If cyanide ions are added, the left hand half cell would change its e.m.f. to $E^0_{Fe(CN)_6^3/Fe(CN)_6^4} = +0.36$. There for the e.m.f. would change to 0.71 V.

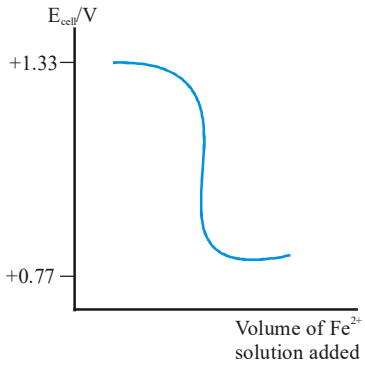
37. (B)

After one drop of iron (II) solution is added the beaker will contain a mixture of $Cr_2O_7^{2-}$, Cr^{3+} and Fe^{3+} ions. The e.m.f. will be near to $E^{(-)}_{Cr_2O_7^{2-},Cr^{3+}} = +1.33V$. At the end of the titration there will be Cr^{3+}, Fe^{2+} and Fe^{3+} ions. The e.m.f. will be near to $E^{(-)}_{Fe^{3+}/Fe^{2+}} = +0.77V$

The reaction is :

$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

The apparatus would be like that in figure. The graph is shown in figure.



38. (B)

560 mL of H_2 gas $= \frac{560}{22400}$ moles of H_2 gas $\frac{1}{4}\times10^{-1}$

moles of H_2 gas $\frac{1}{2}\times10^{-1}$ moles of electrons

$= \frac{1}{2}\times10^{-1}\times96500$ C of electrical charge $= 4825$ C

So, electrical current $= \frac{4825}{600} = 8.04$ A .

39. (D)

$\Delta G^\circ = -nFE^\circ_{cell} = -2\times96500\times1.2288$ J/mole

$= -237.1584$ kJ/mole

So thermodynamic efficiency $= \frac{237.1584}{285} = 0.83$

40. (C)

41. (A)

42. (A)

43. (B)

$Ag^+ + NaCl \rightarrow AgCl + Na^+$

44. (B)

SRP zinc $= -0.76$

SRP iron $= -0.44$

SRP copper $= +0.34$ (highest) ;

hence only copper deposits, others do not.

45. (A)

Increasing voltage would cause deposition of Fe^{+2} and Zn^{+2} also to occur.

46. (B)

Water (pure) is a poor electrical conductor.

47. (A→q,s) ; (B→ p) ; (C→ p) ; (D→ q,r)

48. (A→s) ; (B→ r) ; (C→ p) ; (D→ q)

Factual question.

49. 40

50. 42

as cell reaction is

1st cell : $Zn + 2AgCl \longrightarrow ZnCl_2 + 2Ag$

2nd cell : $ZnCl_2 + 2Ag \longrightarrow 2AgCl + Zn$

Overall $ZnCl_2(C_2) \longrightarrow ZnCl_2(C_1)$

$$E = \frac{RT}{2F}\ln\left(\frac{0.5}{0.02}\right)V = \left[\frac{0.059}{2}\log\left(\frac{0.5}{0.02}\right)\right]V = 42 \text{ mV}$$

51. $Fe(s) + Sn^{2+}(aq.) \textcircled{3} Fe^{2+}(aq.) + Sn(s)$ $E^0_{cell} = 0.30V$

$Zn(s) + Fe^{2+}(aq.) \textcircled{3} Zn^{2+}(aq.) + Fe(s)$ $E^0_{cell} = 0.32V$

If above cells are connected in parallel then first cell will get charged up and second cell will get discharged so net cell reaction will be

$Fe_2^{2+}(aq.) + Fe_1^{2+}(aq.) \textcircled{3} Zn^{2+}(aq.) + Sn^{2+}(aq.)$

$E^0_{net} = 0.02$

t = 0	1M	1M	1M	1M
t(aq.)	(1–x)	(1–x)	(1+x)	(1+x)

$\Delta G^0_{net} = -nfE^0_{net}$

$= -2\times96500\times0.02$ J/mole

So, $-2.30\,RT\log k_{eq} = -2\times 96500\times 0.02$

$$\log\, k_{eq} = \frac{2\times 96500\times 0.02}{6433} = 0.6$$

$k_{eq} = 4$

$$\frac{(1+x)^2}{(1-x)^2} = 4 \Rightarrow \frac{(1+x)}{(1-x)} = 2 \Rightarrow x = \frac{1}{3}$$

So, concentration of Fe^{2+} ions in the first cell

= concentration of Fe^{2+} ions in the second cell = $\frac{2}{3}$M

= 667 mmoles/L

52. $E = E° + RTF^{-1}\ln\frac{[X^-]}{K_a[HX][Cl^-]}$

$$\Rightarrow\ E - E° + RTF^{-1}\ln\frac{[HX][Cl^-]}{[X^-]}\ RTF^{-}\ 1n\frac{1}{K_a}$$

$$\Rightarrow\ 1n\frac{1}{K_a} = \frac{96500}{8.135\times 298}(0.2814)$$

$\Rightarrow\ K_a = 1.74\times 10^{-5}$ Hence **Ans. 174**

53. Anode : $\frac{1}{2}H_2 \longrightarrow H^+ + 1e^-$

Cathode : $\frac{1}{2}H_2O + \frac{1}{4}O_2 + 1e^- \longrightarrow OH^-$

Net : $\frac{1}{2}H_2 + \frac{1}{4}O_2 + \frac{1}{2}H_2O \xrightarrow{1e^-} H^+ + OH^-$

$$\Delta S° = \frac{-1\times 96500(0.3900 - 0.4000)}{-20} = -48.25\frac{J}{K}$$

Now,

$\frac{1}{2}H_2 + \frac{1}{4}O_2 \longrightarrow \frac{1}{2}H_2O \quad \Delta S° = \frac{-193}{2}J/K = -96.5\ J/K$

$H^+ + OH^- \longrightarrow \frac{1}{2}H_2 + \frac{1}{4}O_2 + \frac{1}{2}H_2 \quad \Delta S° = +48.25\ J/K$

Add : $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$

$\Delta S° = -48.25\ J/K = -48250\ mJ/K$

54. $K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow \frac{1}{6} = \frac{\alpha^2}{1-\alpha}$

$$\Rightarrow \alpha = \frac{-1\pm\sqrt{(1)^2+4\times 6\times 1}}{12} = \frac{-1\pm\sqrt{1+24}}{12} = \frac{1}{3}$$

$\therefore\ [IO_3^-] = 1\times\frac{1}{3} = \frac{1}{3}$M

$$\therefore\ [Ag^+] = \frac{3\times 10^{-8}}{\frac{1}{3}} = 9\times 10^{-8}\,M$$

Now $2Ag + Zn^{+2} \xrightarrow{2e^-} 2Ag^+ + Zn$

Gives $E = -1.56 + \frac{0.059}{2}\log\frac{1}{(9\times 10^{-8})^2} = -1.144V$

= –1144 mV Ans.