SOLUTION
EXERCISE # (O-I)

1. Chemical reaction produces electrical energy.

2. Reduction takes place at cathode (not anode) in galvanic cell.

3. Standard Hydrogen electrode is universally accepted as reference electrode at all temperatures and assigned a value of a0 Volt.

4. It is taken as reference, so electrode potential assumed to be zero.

5. Temperature can be varied also in standard Hydrogen Electrode.

6. $Zn^{2+}(aq) + 2e^{-} \longrightarrow Zn(s)$

7. E° is independent of balancing of reaction.

10. $E° = E^{o}_{Oxy^{n}} + E^{o}_{Red^{n}}$

$= E^{o}_{Sn/Cn^{2+}} + E^{o}_{Ag^{+}/Ag}$

$= 0.80 + 0.14 = 0.94$ Volt

11. $E° = E^{o}_{Oxy^{n}} + E^{o}_{Red^{n}}$

$= E^{o}_{Ni/Ni^{2+}} + E^{o}_{Au^{3+}/Au}$

$= 0.25 + 1.5 = 1.75$ Volt

12. $E°_{cell} = E°_{Co/Co^{2+}} + E°_{Ce^{4+}/Ce^{3+}}$

$E°_{Co/Co^{2+}} = -E°_{Co^{2+}/Co} = +0.28$ V

$1.89 = 0.28 + E°_{Ce^{4+}/Ce^{3+}}$

$E°_{Ce^{4+}/Ce^{3+}} = +1.61$ V

13. $E° = E^{o}_{Oxd^{n}} + E^{o}_{Red^{n}}$

For option A largest $E^{o}_{Cell} = 1.25 + 1.25 = 2.5$ V

For option B largest $E^{o}_{Cell} = 1.25 + 0.68 = 0.57$ V

For option C largest $E^{o}_{Cell} = 1.25 + 0.24 = 1.01$ V

For option D largest $E^{o}_{Cell} = 0.68 + 0.24 = 0.92$ V

$\Rightarrow$ Clearly, option A has largest E^{o}_{Cell}

14. $E_{cell} = E_{Oxy^n} + E_{Red^n}$

$= 0.4 + 0.8 = 1.2$

$\Delta G = -nFE = -2 \times 96500 \times 1.2 = -231.6$ KJ

15. $E^o_{Cell} = E^o_{Oxyd^n} + E^o_{Red^n}$

$E^o_{Cell} = E^o_{I/I_2} + E^o_{Fe^{+3}/Fe^{+2}}$

$= -0.536 + 0.771 = 0.235$ Volt

16. $Au^+ + e^- \longrightarrow Au(s)$ $E° = 1.69$ V ...(1) ; $\Delta G^°_1$

$Au^{3+} + 3e^- \longrightarrow Au(s)$ $E° = 1.40$ V ...(2) ; $\Delta G^°_2$

From (2) – (1)

$Au^{3+} + 2e^- \longrightarrow Au^+$ ...(3) ; $\Delta G^°_3$

$\Delta G^°_3 = \Delta G^°_2 - \Delta G^°_1$

$-2 \times F \times E° = -3 \times F \times 1.40 + 1 \times 1.69 \times F$

$E° = 1.255$ V

17. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$; $E° = 1.51$ volt

$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$; $E° = 1.23$ volt

Subtract

$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$; $E° = ?$

$$E° = \frac{5 \times 1.51 - 2 \times 1.23}{3} = \frac{7.55 - 2.45}{3} = \frac{5.09}{3} = 1.70 \text{ volt}$$

18. $E^o_{Cell} = -0.68 + 1.44 = 0.76$ V

$$E^o_{Cell} = \frac{0.0591}{1} \log Keq$$

$0.76 = 0.0591 \log Keq$

$\log Keq = 10^{12.86} = 7.6 \times 10^{12}$

19. $\frac{1}{2} H_2 + H^+ \dashrightarrow H^+ + \frac{1}{2} H_2$

10^{-3} M 10^{-8} M

$$E = 0 - \frac{0.0591}{1} \log \frac{10^{-8}}{10^{-3}}$$

$E = 0.295$ V

20. at eq^m $E = 0$

$$E^\circ = \frac{0.0591}{n}\log K_{eq}m$$

$$E^\circ = \frac{0.0591}{n}\log (4 \times 10^{12})$$

$$E^\circ = \frac{0.0591}{n} \times 12.6 = 0.3717 \text{ Volt}$$

21. $$E^\circ = \frac{0.0591}{n}\log Kc$$

$$E^\circ = \frac{0.0591}{2}\log 10^{12}$$

$E^\circ = 0.354$ V

22. $$E^\circ = \frac{0.0591}{n}\log K_{eq}$$

$$E^\circ = \frac{0.0591}{2}\log 10^{6}$$

$E^\circ = 0.177$ V

23. $A^{n+} + ne^- \dashrightarrow A \qquad E^\circ = -0.250$

To make this reaction spontaneous

$E_{cell} > 0$

$E_{red^n} + E_{oxy^n} > 0$

$-0.250 + E_{oxy^n} > 0 \quad \Rightarrow E_{oxy^n} > 0.25$ V

Therefore, metal D can displace A from it's aqueous sol^n

24. The metal with less reduction potential is strangest reducing agent.

25. Metal with lower reduction potential reduce metal with high reduction potential.

26. $2X^- + Y_2 \dashrightarrow 2Y^- + X_2 \qquad \Rightarrow X^-$ can reduce Y

$2Z^- + X_2 \dashrightarrow 2X^- + Z_2 \qquad \Rightarrow Z^-$ can reduce X

$2W^- + Y_2 \dashrightarrow X \qquad \Rightarrow W^-$ can not reduce Y but y can reduce W

Arrange Reduction potential $Z^- < X^- < Y^- < W^-$

So oxidation potential is reverse $Z^- < X^- < Y^- < W^-$

27. Oxidation reaction $\Rightarrow 2Cl^- \dashrightarrow Cl_2 + 2e^-$

Reduction reaction $\Rightarrow 2Ag^+ + 2e^- \dashrightarrow 2Ag$

net Cell reaction $2Ag^+ + 2Cl^- \dashrightarrow 2Ag + Cl_2$

NERNST EQUATION & ITS APPLICATIONS

28. By Nernst equation

$$E = E° - \frac{RT}{nF} In \frac{[M^+]}{[M^{n+1}]}$$

29. $2H^+ + 2e^- \longrightarrow H_2 \quad E° = 0$

0.1 M 1 atm

$$E = E° - \frac{0.0591}{n} \log \frac{PH_2}{[H^+]^2}$$

$$E = 0 - \frac{0.0591}{2} \log \frac{1}{(0.1)^2} = -0.059 \text{ V}$$

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

0.1

$$E = E^o_{Red^n} - \frac{0.0591}{1} \log \frac{1}{0.1}$$

$$E = E^o_{Red^n} - 0.059$$

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

$$E_1 = E° - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$$

$$E_2 = E° - \frac{0.0591}{2} \log \frac{100}{[Cu^{2+}]}$$

$E_2 - E_1 = 59 \times 10^{-3}$ V

32. $2H^+(eq) + 2e^- \longrightarrow H_2(g)$

Let $P_{H_2} = 1$ bar

$\therefore$ When pH = 0 $\Rightarrow [H^+] = 1$ M

$$E = E° - \frac{0.06}{2} \log 1 = E°$$

& when pH = ? $\Rightarrow [H^+] = 10^{-7}$ M

$$E = E° - \frac{0.06}{2} \log \frac{1}{(10^{-7})^2} = E° - 0.42$$

$\therefore$ Reduction potential decreases by 0.42 V

33. $2H^+(eq) + 2e^- \longrightarrow H_2(g)$

When $P_{H_2} = 1$ atm

$$E = E° - \frac{0.06}{2} \log \frac{1}{1^2} = E°$$

When $P_{H_2} = 100$ atm

$$E = E° - \frac{0.06}{2} \log \frac{100}{1^2} = E° - 0.06$$

34. $E = E^{o}_{Red^n} - \frac{0.0591}{2}\log\frac{[Sn^{2+}]}{[Ag^{+}]^2}$

If $[Sn^{2+}]\downarrow$ or $[Ag^{+}]$, then E

35. $2Ti + Cu^{2+} \longrightarrow 2Ti^{+} + Cu$

0.1 M 0.01 M

$E = E° - \frac{0.0591}{2}\log\frac{[Ti]^2}{[Cu^{2+}]}$

T E $\Rightarrow [Ti^{+}]\downarrow$ or $[Cu^{2+}]$

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

$E_1 = E° - \frac{0.0591}{2}\log\frac{[Cu^{2+}]}{[Ag^{2+}]^2}$

$E_2 = E° - \frac{0.0592}{2}\log\frac{[Cu^{2+}]\times 10}{[Ag^{2+}]^2\times 100}$

$E_2 - E_1 = 0.0295$ V

37. $E = E° - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Ni^{2+}]}$

$0.5105 = E° - \frac{0.0591}{2}\log 10$

E° = 0.54 Volt

38. $E = E° + \frac{0.0591}{2}\log\frac{0.1}{0.1}$

$E = 1.1 + \frac{0.0591}{2}\log 1$

E = 1.1 V

39. $Cl_2(g) + 2Br^{-}_{(eq)} \longrightarrow 2Cl^{-}(eq) + Br_{2\,(g)}$

$Q = \frac{[Cl^{-}]^2 P_{Br_2}}{P_{Cl_2}.[Br^{-}]^2} = \frac{(0.01)^2\times 0.01}{1\times(0.01)^2} = 0.01$

$E = E° - \frac{0.06}{2}\log(0.01)$

$= 0.29 - 0.03\log 10^{-2}$

= 0.35 V

CONCENTRATION CELL

40. $\frac{1}{2}H_2 + H^+ \longrightarrow H^+ + \frac{1}{2}H_2$

10^{-3} M $\quad$ 10^{-8} M

$E = 0 - \frac{0.0591}{1}\log\frac{10^{-8}}{10^{-3}}$

E = 0.295 V

41. Concentration cell has two equivalent half cell

42. $\Delta G < 0 \Rightarrow E > 0$

$E = E° - \frac{0.0591}{n}\log\frac{C_1}{C_2}$

If $C_2 > C_1 \Rightarrow E > 0$

METAL, METAL INSOLUBLE SALT- ION ELECTRODE

43. Pt(s) / H_2(g) , 1 bar / 1M HCl (aq) / AgCl (s) / Ag(s)

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

$E = E° - \frac{0.06}{1}\log[Ag^+]$

$-0.209 = -0.799 - \frac{0.06}{1}\log\frac{Ksp}{[Cl^-]}$

$-0.209 = -0.799 - \frac{0.06}{1}\log\frac{Ksp}{0.1}$

$\therefore$ Ksp = 10^{-11}

45. $E°_{I^-/AgI/Ag} = E_{Ag^+/Ag} + \frac{0.0591}{1}\log\frac{1}{Ksp}$

$= 0.8 - \frac{0.0591}{1}\log\frac{1}{8.3\times10^{-17}}$

$= 0.8 - 0.591\log\frac{10^{17}}{8.3}$

= −0.15 V

46. $\Delta S = nF\frac{dE}{dT}$

$\frac{dE}{dT} = \frac{\Delta S}{nF}$

47. efficiency = $\frac{\text{used energy}}{\text{total energy}} = \frac{\Delta G}{\Delta H} = \frac{nFE_{cell}}{\Delta H}$

48. efficiency = $\frac{|\Delta G|}{\Delta H} \times 100$

$84 = \frac{|\Delta G|}{285} \times 100$

$\Delta G = -84 \times 285 \times \frac{1}{100}$

$\Delta G = -239.4$ kJ

$\Delta G = -nFE$

$-239.4 \times 10^3 = -2 \times 96500 \times E$

E = 1.24 V

49. $\Delta S = nF\frac{dE}{dT}$

$= -2 \times 96500 \times 0.00065 = -125.45\ JK^{-1}$

50. AgCl, Hg_2Cl_2 and $PbCl_2$ are sparingly soluble so Cl^- will form ppt with silver mercury and lead , hence cannot be used.

51. AgCl and $PbCl_2$ are sparingly soluble so Cl^- will form ppt with silver and lead, hence can not be used

52. If cathode is removed from a electro chemical cell. The cell will be not be completed and polarity of anode end cup.

53. $Z = \frac{E}{96500}$

E = equivalent weight

$\because$ 96500 C liberates = E g

$\therefore$ 1 C will liberate = $\frac{E}{96500}$ g

54. $\frac{w_1}{E_1} = \frac{w_2}{w_2} \quad \Rightarrow \frac{w_1}{w_2} = \frac{E_1}{E_2}$

55. equivalent of charge = equivalent of substance deposited

= 1

1 equivalent of charge = 1 F = 96500 C

= charge of 1 mol e^-

56. $Z = \frac{E}{96500}$

E = 0.0006 × 96500 = 57.9

57. equivalent of substance = $\dfrac{9.65\times10\times60}{96500}$ = 0.06

58. equivalent of charge = $\dfrac{108}{108}\times 1 = 1$

= 1 F

59. $w \propto Q$

$$\frac{w_1}{w_2}=\frac{I_1t_1}{I_2t_2}$$

$$\frac{w_1}{w_2}=\frac{2\times2}{1\times4} \quad\Rightarrow\quad w_2 = w$$

60. $Sn^{n+} \longrightarrow Sn$

$n_f = 2$

equivalent of Sn = $\dfrac{9.65\times1000}{96500}$ = 0.1

$$\frac{5.95}{119}\times n = 0.1 \Rightarrow n = \frac{11.9}{5.95} = 2$$

61. Ag : Cu : Al = $1 : \dfrac{1}{2} : \dfrac{1}{3}$ = 6 : 3 : 2

62. $2H^+ + 2e^- \longrightarrow H_2$

$n_f = 2$

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

$n_f = 2$

$$\frac{w_1}{w_2}=\frac{E_1}{E_2}=\frac{2}{24}=\frac{1}{12}$$

$$\frac{3}{E} = 0.06 \quad\Rightarrow\quad E = \frac{3}{0.06} = 50$$

63. $Ni^{2+} + 2e^- \longrightarrow Ni$

$n_f = 2$

$Cr^{3+} + 3e^- \longrightarrow Cr$

$n_f = 3$

$$\frac{w_1}{w_2}=\frac{E_1}{E_2} \quad\Rightarrow \frac{0.3}{w_2}=\frac{59}{2}\times\frac{3}{52}$$

$$w_2 = \frac{0.3\times104}{177} = 0.17\text{ g}$$

64. $2H^+ + 2e^- \longrightarrow H_2$

$n_f = 2$

$$\frac{I \times 965}{96500} = \frac{112}{22400} \times 2 \Rightarrow I = 1 \text{ amp}$$

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

$2F = 1 \text{ mol } H_2O = \frac{1}{2} \text{ mol } O_2$

$2F = 2 \times 96500 \text{ C} = 1.93 \times 10^5 \text{ C}$

66. Equivalent of Ag = equivalent of $O_2 = \frac{0.108}{108} \times 1 = 0.001$

Moles of $O_2 = \frac{0.001}{4}$

Vol. of $O_2 = \frac{0.001}{4} \times 22700 = 5.675$ mL

67. $Mn_2O_4 \longrightarrow MnO_4^{2-}$

$n_f = 10$ $n_f = \frac{10}{8}$

Equivalent of charge = $\frac{10}{8} \times 1 = \frac{10}{8}$

$\frac{10}{8}$ Equivalent of charge = $\frac{10}{8} \times 96500$ C

68. equivalent of charge = equivalent of Ag

$$\frac{9.65 \times t}{96500} = \frac{80 \times 5 \times 10^{-3} \times 1.08}{108}$$

t = 40 sec

69. anode $2Br^- \longrightarrow Br_2 + 2e^-$

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

By product NaOH

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

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

By product NaOH

$\because$ $[H^+]$, So pH $\downarrow$

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

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

72. anode $2Cl^- \longrightarrow Cl_2 + 2e^-$

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

COMMERCIAL CELLS & CORROSION

73. Voltage of cell increases

74. $2PbSO_4(s) + 2H_2O(\ell) \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$

75. At high pH, The passive layer is formed and prevent corrosion

76. Resistance decrease with increase in temp as speed of ions increases

77. K, Molarity

78. $\lambda_m = \dfrac{K \times 1000}{N}$

N , $\lambda_m \downarrow$

79. $K = \dfrac{1}{50} \times \dfrac{2.2}{4.4} = 0.01 \text{ S cm}^{-1}$

$\lambda_m = \dfrac{K \times 1000}{M} = \dfrac{0.01 \times 1000}{50} = 0.2 \text{ S cm}^2 \text{ mole}^-$

80. $K = \dfrac{1}{40} \times 0.4 = 0.01 \text{ S cm}^{-1}$

$\lambda_m = \dfrac{K \times 1000}{N} = \dfrac{0.01 \times 1000}{0.01} = 1000 \text{ S cm}^2 \text{ mole}^{-1}$

81. $K = \dfrac{1}{200} \times 1.5 = 7.5 \times 10^{-3} \text{ S cm}^{-1}$

$\lambda_{eq} = \dfrac{K \times 1000}{N} = \dfrac{7.5 \times 10^{-3} \times 1000}{0.01} = 750 \text{ S cm}^2 \text{ eq}^{-1}$

82. $CH_3COOH \text{ (eq)} + NaOH \text{ (eq)} \longrightarrow CH_3COONa \text{ (eq)} + H_2O (\ell)$

0.015 × V	0.015 × V	0
0	0	0.015 × V

$\therefore \quad [CH_3COONa] = \dfrac{0.015 \times V}{2V} = \dfrac{0.015M}{2}$

$\Lambda_m = \dfrac{K \times 1000}{M} = \dfrac{6.3 \times 10^{-4} \times 1000}{0.015 / 2} = 84 \text{ S cm}^2 \text{ mole}^{-1}$

83. $\lambda_m \, NaNO_3 = \lambda_m \, NaCl + \lambda_m \, AgNO_3 - \lambda_m \, AgCl$

$= 110 + 115 - 120 = 105$

84. $\lambda_m^\infty \, BaCl_2 = \lambda_{eq} \, BaCl_2$

$= \lambda_{eq} \, Ba^{2+} + \lambda_{eq} \, Cl^- = 127 + 76 = 203 \text{ S cm}^2 \text{ eq}^{-1}$

85. $\alpha = \frac{\lambda_m}{\lambda_m^\infty} = \frac{80}{400} = \frac{1}{5}$

86. $\lambda_m = 10 \text{ S cm}^2 \text{ mole}^{-1}$

$\lambda_m^\infty = 200 \text{ S cm}^2 \text{ mole}^{-1}$

$\alpha = \frac{10}{200} = 0.05$

$[H^+] = c\alpha = 5 \times 10^{-2}$

pH = 2.2

87. $Ka = \frac{c\alpha^2}{1-\alpha} \Rightarrow \alpha = \sqrt{\frac{kc}{C}} = 0.04$

$\lambda_m = \lambda_m^\infty \times \alpha = 380 \times 10^{-4} \times 0.04 = 1.52 \times 10^{-3} \text{ S m}^2 \text{ mole}^{-1}$

$1.52 \times 10^{-3} = K/(1000 \times 0.01)$

$K = 1.52 \times 10^{-5} \text{ S m}^{-1}$

88. $\lambda_m^\infty = \frac{K \times 1000}{s}$

$s = \frac{3.06 \times 10^{-6} \times 10^3}{1.53} = 2 \times 10^{-3}$

$ksp = s^2 = 4 \times 10^{-6}$

89. $\Lambda_m^\infty = \frac{K}{1000 \times \text{Solubility}}$

$1.5 \times 10^{-4} \times 3 = \frac{9 \times 10^{-6}}{1000 \times S}$

$S = 2 \times 10^{-5}$

$Ksp = 3^3 \times S^4$

$= 27 \times (2 \times 10^{-5})^4 = 4.32 \times 10^{-18}$

EXERCISE # S-I

2. $3e^- + Cr^{3+} \longrightarrow Cr$ (i)

$OCl^- + H_2O + 3e^- \longrightarrow Cl^- + 2OH^-$ (ii)

$2Cr^{3+} + 3H_2O + 3OCl^- \longrightarrow 2Cr^{3+} + 3Cl^- + 6OH^-$ (iii)

(iii) = –2 × (i) + 3 × (ii)

$6E_3^o = -2 \times 3 \times E_1^o + 3 \times 2 \times E_2^o$

$E_3^o = 0.74 + 0.94 = 1.68$ V

3. $-0.15 = 1.20 + E^\circ_{Cl^-/Cl_2}$

$E^\circ_{Cl^-/Cl_2} = -1.35$ V

$E_{Cl_2/Cl^-} = 1.35$ V

4. $Fe^{2+} + 2e^- \longrightarrow Fe$ $\quad E_0 = 0.44$ V

$\Delta G_1 = -2 \times F \times (-0.44)$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $\quad E_0 = 0.77$ V

$\Delta G_2 = -1 \times F \times 0.77$

By adding above two reactions

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

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

$-3 \times F \times E_0 = 0.88F - 0.77F$

$E_0 = -\left(\frac{0.11}{3}\right) V = -0.0367$ V

5. $Cu^{2+} + e^- \longrightarrow Cu^+$ $\quad \Delta G_1 = -1 \times F \times 0.15$ ....(1)

$Cu^{+2} + 2e^- \longrightarrow Cu$ $\quad \Delta G_2 = -2 \times F \times 0.34$ ....(2)

$Cu^+ + e^- \longrightarrow Cu$ ....(3)

(3) =(2) - (1)

$\Delta G_3 = \Delta G_2 - \Delta G_1$

$= -0.68 F + 0.15 F$

$\Delta G_3 = -nFE_0 = -0.53 F$

$-1 \times F \times E_0 = -0.53 F$

$E_0 = 0.53$ V

6. $2e^- + 2H^+ + SO_4^{2-} \longrightarrow SO_3^{2-} + H_2O$ (i)

$3e^- + 3H^+ + SO_3^{2-} \longrightarrow \frac{1}{2} S_2O_3^{2-} + \frac{3}{2} H_2O$ (ii)

$4e^- + 5H^+ + SO_4^{2-} \longrightarrow \frac{1}{2} S_2O_3^{2-} + \frac{5}{2} H_2O$ (iii)

(iii) = (ii) + (i)

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

$4FE_3^o = 2FE_2^o + 2FE_1^o$

$E_3^o = \frac{E_1^o + E_2^o}{2} = \frac{-0.936 - 0.576}{2} = 0.756$ V

8. $Mn^{2+} \longrightarrow Mn^{3+} + e^-$ (i)

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

$2Mn^{2+} + 2H_2O \longrightarrow Mn^{2+} + MnO_2 + 4H^+$ (iii)

(iii) = (ii) – (i)

$E_3^o = E_2^o - E_1^o$

$0.5 = -1.0 + 1.5$

$E° > 0$, So reaction is spontaneous

$\Delta G° = -nFE° = -1 \times 96500 \times 0.5 = -48250$ J

9. At equilibrium $E = 0$

$$\Rightarrow E = E_0 - \frac{0.0591}{n} \log K = (-0.68 + 1.44) - \frac{0.0591}{1} \log K$$

$$0.76 = \frac{0.0591}{1} \log K$$

$$\log K = \frac{0.76 \times 1}{0.0591} = 12.859$$

$K = 10^{12} \times 10^{-0.859} = 7.6 \times 10^{12}$

10. (i) $E°_{cell} = 2.37 + 0.80$

$= 3.17$ V

$$E_0 = \frac{0.591}{2} \log K$$

$$3.17 = \frac{0.591}{2} \log K \quad \Rightarrow \quad \log K = \frac{6.34}{0.0591} = 107.275$$

$K = 10^{107.275}$

$= 10^{107} \times 10^{0.275}$

$= 1.88 \times 10^{107}$

(ii) $\Delta G = 2 \times 3.17 \times 96500$

$= -611810$ J

$= -611.8$ KJ

11. $E^o_{Cell} = E°\, Zn / Zn^{2+} + E°\, Cu^{2+} / Cu$

$= 0.76 + 0.34 = 1.1$ V

$$1.1 = \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\log \frac{[Zn^{2+}]}{[Cu^{2+}]} = 37.22$$

12. $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E° = -0.84$

$H_2 + 2e \rightarrow 2H^+$ $E° = 0$

$2H_2O \rightarrow 2H^+ + 2OH^-$ K^2

$$2 \times E^o = \frac{2.303RT}{F} \log K^2$$

$-0.84 = 0.06 \log K$

$\log K = -14$

$K = 10^{-14}$

13. $4 \times E°_{Sn|Sn^{4+}} = 2 \times E°_{Sn|Sn^{2+}} + 2 \times E°_{Sn^{2+}|Sn^{4+}}$

$$E°_{Sn|Sn4+} = \frac{0.136 - 0.154}{2} = -0.009 \text{ V}$$

$E°_{cell} = E°_{Sn|Sn^{4+}} + E°_{Cr_2O_7^{2-}|Cr^{3+}}$

$= -0.009 + 1.33 = 1.321$ V

14. $\Delta rG° = -nFE° = -12 \times 96500 \times 2.73$

$= -3161340$

$\Delta rG° = 4\ \Delta G_f^0\ [Al(OH)_4^-] - 6\ \Delta G_f^0\ H_2O - 4\ \Delta G_f^0\ OH^-$

$-3161.340 = 4 \times x - 6 \times (-237.2) - 4 \times (-157)$

$= 4x + 1423.2 + 628$

$x = -1303.13$ kJ

15. SRP value , oxidizing power $\downarrow$

Reducing power $\downarrow$

mg is best reducing agent.

16. SRP value , Reducing power $\downarrow$

SRP X > Z > Y

Reducing power Y > Z > X

17. Lower S.R.P. metal can displace higher S.R.P. metals ions from solution.

$E°\ Zn^{2+} / Zn = -0.763$ V

SRP value $\downarrow$, Reducing power $\uparrow$

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

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

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

$E°_{cell} = -0.8$

$$E_{cell} = -0.8 - \frac{0.06}{1} \log\frac{1}{1} = -0.8 < 0 \text{ (reaction will not spontaneous)}$$

19. (a) anode $Ag \longrightarrow Ag^+ + e^- \times 2$

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

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

(b) anode $Fe^{2+} \longrightarrow Fe^{3+} + e^- \times 5$

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

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

(c) anode $2Cl^- \longrightarrow Cl_2 + 2e^-$

Cathode $Ag^+ + e^- \longrightarrow Ag \times 2$

$2Cl^- + 2Ag^+ \longrightarrow Cl_2 + 2Ag$

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

Cathode $Cd^{2+} + 2e^- \longrightarrow Cd$

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

20. (a) $Zn\ (s) / Zn^{2+}\ (aq)\ ||\ Cd^{2+}\ (aq) / Cd\ (s)$

(b) $Pt / H_2\ (g) / H^+\ (aq)\ ||\ Ag^+\ (aq) / Ag\ (s)$

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

<u>NERNST EQUATION</u>

21. pH = 1 $[H^+] = 0.1$

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

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

$$E = -\frac{0.0591}{2}\log (0.1)^2 = 0.0591\ V$$

22. $E_{cell} = 0$

$$E_{cell} = E^0 - \frac{0.0591}{n}\log\frac{[Cu^{+2}]}{1}$$

$$E^0 = \frac{0.0591}{2}\log[Cu^{+2}] \qquad -0.34 = \frac{0.0591}{2}\log[Cu^{+2}]$$

$$\log[Cu^{+2}] = -\frac{0.68}{0.0591} = -11.501$$

$\log[Cu^{+2}] = -11.501$

$[Cu^{+2}] = 10^{-11.501}$

$= 2.97 \times 10^{-12}$ M

23. $E_{cell} = E_0 - \left(\frac{0.0591}{2}\log\frac{1}{[Zn^{+2}]}\right)$

$ZnSO_4 \longrightarrow Zn^{+2}$

$0.1\times0.8 \qquad 0.1\times0.2$

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

$$E_{cell} = -0.76 - \frac{0.0591}{2}\log\frac{1}{0.1\times0.2}$$

$= -0.76 - 0.03 \times 1.7 = -0.81V$

24. $Cu(OH)_2 \dashrightarrow Cu^{2+} + 2OH^-$

$[Cu^{2+}]$ at pH = 14

$[Cu^{2+}] \times [OH^-]^2 = 10^{-19}$

$[Cu^{2+}] \times (1)^2 = 10^{-19}$

$[Cu^{2+}] = 10^{-19}$ M

$Cu^+ + 2e^- \dashrightarrow Cu$

$$E = E^\circ - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]}$$

$$= 0.34 - \frac{0.0591}{2}\log 10^{19}$$

$$= 0.34 - \frac{0.0591}{2} \times 19 = -0.2214\ V$$

25. Daniel cell :- $Zn_{(s)}|ZnSO_{4_{m_1}}||Cu^{2+}{}_{m_2}|Cu_{(s)}$

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

$$E = E_0 - \frac{0.059}{n}\log 0 \quad \Rightarrow \quad E = E_0 - \frac{0.0591}{2}\log\frac{[Zn^{+2}]}{[Cu^{+2}]}$$

$$E = 1.1 - \frac{0.059}{2}\log\frac{001}{01}$$

$$= 1.1 - \frac{0.59}{2}\log 10^{-2} = 1.1 + 0.059 = 1.159\ V$$

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

$E^\circ_{cell} = 0.14V - 0.13V = 0.01V$

$$E_{cell} = E_0 - \frac{0.06}{2}\log\frac{[Sn^{+2}]}{[Pb^{+2}]}$$

$$= 0.01 - \frac{0.06}{2}\log\frac{1}{10^{-3}}$$

$$= 0.01 - \frac{0.06}{2}\times 3 = 0.01 - 0.09$$

$= -0.08$ V

$E_{cell} < 0 \Rightarrow$ incorrect

representation should be as

$\Rightarrow \quad Pb|Pb^{+2}||Sn^{+2}|Sn$

27. (i) anode $Zn \dashrightarrow Zn^{2+} + 2e^-$

Cathode $Ag^+ + e^- \dashrightarrow Ag \times 2$

$Zn + Ag \dashrightarrow Zn^{2+} + Ag$

(ii) $E^o_{Cell} = E° Zn / Zn^{2+} + E° Ag^{2+} / Ag$

$= 0.76 + 0.8 = 1.56$ V

(iii) $1.6 = 1.56 - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{(0.1)^2}$

$[Zn^{2+}] = 4 \times 10^{-4}$ M

(iv) IF 125 is added then

$As^+ + I^- \dashrightarrow AgI$

$[Ag]\downarrow$, $E_{Cell}\downarrow$

CONCENTRATION CELL

28. $E = 0 - \frac{0.0591}{2}\log\frac{[0.01]}{[0.1]} = -\frac{0.0591}{2}\log 10^{-1} = \frac{.0591}{2}\times 1 = 0.0295$ V

29. $H_2 \rightarrow 2H^+ + 2e^-$

$2H^+ + 2e^- \rightarrow H_2 = \frac{[H_a^+]^2 Pa}{[H_c^+]^2 Pc}$

$0.2367 = 0 - \frac{0.0591}{2}\log\left(\frac{x^2 \times 1}{1\times 1}\right)$

$8 = -\log x^2$

$-4 = \log x$

$\Rightarrow \quad x = 10^{-4}$

PH = 4

30. $E_{cell} = -\frac{0.0591}{2}\log\frac{[H^+]_a^2}{[H^+]_c^2}$

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

$2e^- + 2H^+ \rightarrow H_2^+$

$[H^+]_a = \sqrt{ka \times c} = \sqrt{10^{-3}c}$

$[H^+]_c = \sqrt{ka \times c} = \sqrt{10^{-3}c}$

$E_{cell} = -\frac{0.0591}{2}\log\frac{10^{-3}c}{10^{-5}\times c} = -\frac{0.0591}{2}\log 10^2 = -\frac{0.0591}{2}\times 2 = -0.0591$ V

31. $E_{cell} = -\frac{0.0591}{2}\log\frac{[H^+]_a^2}{[H^+]_c^2}$

$[OH]^- = \sqrt{k_b \times c} \Rightarrow \sqrt{10^{-9}\times 10^{-3}} = 10^{-6}$

$[H^+] = \frac{10^{-14}}{[OH]^-} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$

$[H^+] = \frac{50}{500} = 10^{-1}$

$E = -\frac{0.0591}{1}\log\frac{[10^{-8}]}{10^{-1}} = -0.059 \times \log(10^{-7}) = -0.0591 \times (-7) = 0.4137\ V$

METAL- METAL INSOLUBLE SALT- ION ELECTRODE

32. (a) anode $Cu \longrightarrow Cu^+ + 2e^-$

Cathode $2e^- + Hg_2Cl_2 \longrightarrow 2Hg + 2Cl^-$

$Cu^{2+} + Hg_2Cl_2 \longrightarrow Cu^{2+} + 2Hg + 2Cl^-$

(b) anode $IO_3^- + Ag \longrightarrow AgIO_3 + e^- \times 2$

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

$2Ag(s) + 2IO_3^- + Zn^{2+} \longrightarrow Zn + 2AgIO_3$

(c) anode $Mn + 2OH^- \longrightarrow Mn(OH)_2 + 2e^-$

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

$Mn + 2OH^- + Cu^{2+} \longrightarrow Mn(OH)_2 + Cu$

33. Ag | AgBr(s)| KBr (0.001M) || KCl (0.2M)|AgCl(s) |Ag,

Replacing above cell by

$Ag / Ag^+ || Ag^+ / Ag$

$E = 0 - \frac{0.06}{1}\log\frac{[Ag^+]_a}{[Ag^+]_c}$

$[Ag^+]_c = \frac{Ksp.AgCl}{[Cl^-]} = \frac{10^{-10}}{0.2} = 5 \times 10^{-10}\ M$

$[Ag^+]_a = \frac{Ksp.AgBr}{[Br^-]} = \frac{10^{-13}}{10^{-3}} = 10^{-10}$

$E = \frac{0.06}{1}\log\frac{5\times 10^{-10}}{10^{-10}} = 0.06 \times 0.7 = 0.42\ V$

34. Ag | Ag I | KI || Ag NO_3 | Ag

0.05 M 0.005 M

$$0.788 = 0 - \frac{0.0591}{1}\log\frac{[Ag^+]_a}{[Ag^+]_c}$$

$$0.788 = -\frac{0.0591}{1}\log\frac{[Ag^+]_a}{0.05}$$

$[Ag^+]_a = 2.5 \times 10^{-15}$

Ksp (AgI) $= 0.05 \times 2.5 \times 10^{-15}$

$= 1.125 \times 10^{-16}$

35. Ag |Ag Br(s) | Br^- || Cl^- | AgCl(s) | Ag(s)

Ag | Ag^+ || Ag^+ | Ag

$E^\circ_{cell} = 0$

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

$$[Ag^+]_a = \frac{Ksp.AgCl}{[Cl^-]} = \frac{1\times10^{-10}}{[Cl^-]}$$

$$[Ag^+]_c = \frac{Ksp.AgBr}{[Br^-]} = \frac{5\times10^{-13}}{[Br^-]}$$

$$E_{cell} = -\frac{0.0591}{1}\log\frac{10^{-10}}{5\times10^{-13}} \times \frac{[Br^-]}{[Cl^-]}$$

$$\frac{10^{-10}}{5\times10^{-13}}\frac{[Br^-]}{[Cl^-]} = 1$$

$$\frac{[Cl^-]}{[Br^-]} = \frac{1000}{5} = \frac{200}{1}$$

36. $2e^- + PbCl_2 \longrightarrow Pb + 2Cl^-$

$$E^\circ\ Cl^- / Pb(s) / Pb = E^\circ\ Pb^{2+} / Pb - \frac{0.06}{2}\log\frac{1}{Ksp}$$

$-0.27 = -0.12 + 0.03 \log Ksp$

$\log Ksp = -5$

$Ksp = 10^{-5}$

37. $e^- + AgI\ (s) \longrightarrow Ag + I^-$

$$E^\circ_{I^- / AgI / Ag} = E^\circ_{Ag^+ / Ag} - \frac{0.06}{1}\log\frac{1}{Ksp}$$

$= 0.8 - 0.06 \times 16$

$= 0.8 - 0.96 = -0.10$ V

38. (a) $2Cl^- \longrightarrow Cl_2 + 2e^-$

nf = 2

Equivalent of charge = Equivalent of Cl_2

$$= \frac{355}{71} \times 2 = 0.1$$

Mole of electron = 0.1

No. of electron = 0.1 Na

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

$n_f = 2$

Equivalent of charge = Equivalent of Cu= 2

Mole of electron = 2 x 6 × 10^{23}

(c) $Al^{3+} + 3e^- \longrightarrow Al$

$n_f = 3$

Equivalent of charge = Equivalent of Al= $\frac{2.7}{27} \times 3 = 0.3$

Mole of electron = 0.3 × NA = 1.8 × 10^{23}

39. (a) equivalent of Al = 0.25 × 3 = 0.75

equivalent of charge = 0.75

1 equivalent charge = 1 F

0.75 equivalent charge = 0.75 F

(b) equivalent of charge = equivalent of SO_3^{2-}= $\frac{27.6}{80} \times 2 = 0.69$

0.69 equivalent charge = 0.69 F

(c) equivalent of charge = equivalent of Cu= 1.1 × 0.5 × 2 = 1.1

equivalent charge = 1.1 F

40. 0.5 mole electron = 0.5 F charge

equivalent of charge = equivalent of Zn= equivalent of Ag = 0.5

Moles of Zn × 2 = 0.5

Moles of Zn = $\frac{1}{4}$

Amount of Zn deposited = 65 × $\frac{1}{4}$ = 16.25 g

Moles of Ag × 2 = 0.5

Amount of Ag deposited = 108 × 0.5 = 54 g

41. $Pd^{n+} \dashrightarrow Pd$

$n_f = n$

equivalent of Pd = equivalent of charge

$$\frac{2.977}{106.4} \times n = \frac{3 \times 3600}{96500}$$

$n = 4$

42. $2e^- + 2H_2O \dashrightarrow H_2 + 2OH^-$

$n_f = 2$

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

$n_f = 4$

43. equivalent of Al = $\frac{x}{27} \times 3 = \frac{x}{9}$

$\frac{x}{9}$ Equivalent is produced by coast = x Rs

1 equivalent will cost = 9 Rs

Equivalent of Mg = $\frac{x}{24} \times 2 = \frac{x}{12}$

Cost to produce $\frac{x}{12}$ equivalent Mg = $\frac{x}{12} \times 9 = 0.75$ x Rs

44. $CrO_2(aq) + 6H^+ (aq) + 6e^- \dashrightarrow Ce(s) + 3H_2O$

$n_f = 6$

(i) equivalent of Cr = equivalent of charge = $\frac{24125}{96500} = 0.25$

Moles of Cr × 6 = 0.25

Moles of Cr = $\frac{1}{24}$

Moles of Cr = $\frac{1}{24} \times 52 = 2.16$ g

(ii) equivalent of charge = equivalent of Cr

$$\frac{12.5 \times t}{96500} = \frac{1.5}{52} \times 6$$

t = 1336.15 sec

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

$$\frac{3}{63.2} \times 2 = \frac{3 \times 2 \times 60 \times 60}{96500} \times \eta$$

$\eta = 0.4221$

% η = 42.21 %

46. $Mn^{2+} \longrightarrow MnO_2$

$nf = 2$

equivalent of MnO_2 = equivalent of charge

$$\frac{25.5 \times t}{96500} \times 0.85 = \frac{1000}{87} \times 2$$

$t = 1.023 \times 10^5$ sec

47. $2HSO_4^- \longrightarrow S_2O_3^{2-} + 2H^+ + 2e^-$

$nf = 2$

equivalent of Ni = equivalent of charge

$$\frac{Q \times 60 \times 60}{96500} \times 0.75 = 1 \times 2$$

$$Q = \frac{2 \times 96500}{3600 \times 0.75} = 71.48 \text{ C}$$

48. (1) molten NaCl

anode $2Cl^- \longrightarrow S_2O_3^{2-} + 2H^+ + 2e^-$

cathode $Na^+ + e^- \longrightarrow Na$

(2) NaCl (aq)

anode $2Cl^- \longrightarrow 2Cl_2 + 2e^-$

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

(3) Na_2SO_4 (aq) with pt electrode

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

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

(4) $AgNO_3$ (aq) with pt electrode

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

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

(5) $CuSO_4$ (aq) with inest electrode

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

cathode $Cu^+ + 2e^- \longrightarrow Cu$

(6) $CuSO_4$ (aq) with Cu electrode

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

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

49. $2Cl^- \longrightarrow Cl_2 + 2e^-$

$n_f = 2$

equivalent of Cl_2 = equivalent of charge

moles of $Cl_2 \times 2 = \frac{30 \times 60 \times 60}{96500}$

moles of Cl_2 = 0.5%

vol. of Cl_2 produced at 1 atm , 273 K = 0.56 × 22.4 = 12.531

equivalent of NaOH = 1.12

moles of NaOH = 1.12

50. equivalent of Cu = $\frac{31.75}{63.5} \times 2 = 1$

equivalent of NaOH = equivalent of Cu

= 1

Amount of NaOH = 1 × 40 = 40 g

Actual amount of NaOH obtained = 0.6 × 1 = 0.6 mole

% efficiency = $\frac{0.6}{1} \times 100 = 60\%$

51. $Ni^{2+} \longrightarrow Ni$

$n_f = 2$

equivalent of Ni = equivalent of charge= $\frac{5 \times 20 \times 60}{96500}$

Moles of Ni = $\frac{6000}{96500} \times \frac{1}{2}$

Amount of Ni = $\frac{6000}{96500} \times \frac{1}{2} \times 58.5 = 1.82$ g

52. If active electrodes are used of a metal. Then same metal is oxidized at anode and reduced at cathode so these is no change in concentration of electrolytic solution.

53. $K = \frac{1}{R}\frac{\ell}{a}$

$1.342 = \frac{1}{170.5} \times \frac{\ell}{1.86 \times 10^{-4}}$

$\ell = 1.342 \times 170.5 \times 1.86 \times 10^{-4}$

$= 4.25 \times 10^{-2}$ m

54. N = 0.01N, R = 200Ω, $(\ell/A) = 0.88\ cm^{-1}$

$K = \left(\frac{1}{200}\right) \times 0.88$

$\Lambda_m = \left(\frac{1}{200}\right) \times \frac{0.88 \times 1000}{0.01} = 440\ Scm^2\ mol^{-1}$

55. $BaCl_2$ K = 0.005 ohm⁻ cm^{-1}

Morality = $\frac{2.08}{500\,cm^3} = \frac{2.08}{0.5} = 4.16M$

$\Lambda_m = \frac{0.005 \times 1000}{4.16} = \frac{5}{4.16} = 1.2$

$\Lambda_m = \frac{0.005 \times 1000}{0.02} = \frac{5}{0.02} = 250$ Scm^2mol^{-1}

$\Lambda_{eq} = \frac{250}{2}$ =125 $Seq^{-1}\ cm^2$

56. $K = \frac{1}{\rho} = \frac{1}{800}$ = 0.00125 5cm^{-1} = 1.25 × 10^{-3} mho cm^{-1}

$\Lambda_{eq} = \frac{K}{N \times 1000} = \frac{250}{2}$ $Seq^{-1}\ m^2$

$\Lambda_{eq} = \Lambda_m = 0.0125$ $Seq^{-1}\ m^2$

57. $\Lambda_m = 4 = \frac{K \times 1000}{0.1}$

K = 0.4 × 10^{-3}= 0.0004 Scm^{-1}

Resistivity = $\frac{1}{K} = \frac{1}{0.0004}$ = 2500 ohm cm.

58. $\left(\frac{\ell}{A}\right) = \frac{2cm}{4cm^2} = \left(\frac{1}{2}\right)cm^{-1}$

K = 8 × 10^{-7} Scm^{-1}

(i) $R = \rho\left(\frac{\ell}{A}\right)$

$R = \left(\frac{1}{K}\right)\left(\frac{\ell}{A}\right)$

$R = \left(\frac{1}{8 \times 10^{-7}}\right) \times \left(\frac{1}{2}\right) = \frac{100}{16} \times 10^5$ = 6.25 × 10^5 ohm

(ii) V = iR ⇒ $i = \frac{1}{6.25 \times 10^5}$ = 1.6 × 10^{-6} amp.

59. $\Lambda^\infty_{Ba(OH)_2} = \Lambda^\infty_{BaCl_2} + 2\Lambda^\infty_{NaOH} - 2\Lambda^\infty_{NaCl}$

= 280 × 10^{-4} + 2(240 × 10^{-4}) – (125 × 10^{-4}) × 2 = 510 × 10^{-4}

60. $\Lambda^\infty_{m(CH_3COOH)} = \Lambda^\infty_{m(CH_3COONa)} + \Lambda^\infty_{mHCl} - \Lambda^\infty_{mNaCl}$ = 425 + 100 – 125 = 400 $Scm^2\ mol^{-1}$

For CH_3COOH ⇒ N = M

$\Lambda^\infty_{eq} = \Lambda^\infty_m = 48$

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

α % = 12

61. $\alpha = \frac{\Lambda_{eq}}{\Lambda_{eq}^{\infty}} = \frac{120}{150} = 0.8$

62. HF $\rightarrow$ H^+ + A^-

$C(1-\alpha)$ $\quad C\alpha \quad C\alpha$

C = 0.002M

$\alpha = \frac{\Lambda_m}{\Lambda_m^{\infty}} = \frac{200}{400} = 0.5$

$K = \frac{C\alpha^2}{1-\alpha} = \frac{0.002(0.5)^2}{1-0.5} = 10 \times 10^{-4}$

63. $K = 1.12 \times 10^{-6}$ ohm^{-1} cm^{-1}

$\lambda^{\infty}_{N(AgCl)} = 54 + 58 = 112$ Scm^2/eq

$112 = \frac{1.12 \times 10^{-6} \times 10^3}{S}$

$s = \frac{1.12 \times 10^{-6} \times 10^3}{112}$

$s = 10^{-5}$

$AgCl \rightarrow Ag^+ + Cl^-$

Solubility product = $s^2 = 10^{-10}$ mol/ltr

64. $K_{AgBr} = 8.75 \times 10^{-7} - 0.75 \times 10^{-7} = 8 \times 10^{-7}$

$\Lambda^{\infty}_{m(AgBr)} = \Lambda^{\infty}_{m(AgNO_3)} + \Lambda^{\infty}_{m(KBr)} - \Lambda^{\infty}_{m(KNO_3)}$ = 130+140 – 110 = 160

For sparsely soluble like AgBr $\Rightarrow \alpha = 1$

$A^{\infty}_{(AgBr)} = \Lambda_{m(AgBr)}$

$160 = \frac{8 \times 10^{-7} \times 1000}{s}$

$s = \frac{8 \times 10^{-4}}{160} = 5 \times 10^{-6}$ M = $188 \times 5 \times 10^{-6}$ g/L = 9.48×10^{-4} g/L

65. $\Lambda^{\infty}_{H_2O} = 3.5 \times 10^{-2} + 2 \times 10^{-2} = 5.5 \times 10^{-}$

$K = 5.5 \times 10^{-6}$ Sm^{-1}

$\Lambda^{\infty}_{H_2O} = \frac{5.5 \times 10^{-6}}{1000 \times M} = 5.5 \times 10^{-2}$

$M = \frac{5.5 \times 10^{-6}}{10^3 \times 5.5 \times 10^{-2}}$

$[H^+] = 10^{-7}$

$P^H = 7$

$k_w = 10^{-14}$

EXERCISE # (O-II)

1. $\frac{dE^\circ}{dT}$ = –0.000648 Volt K^{-1}

$\Delta G^\circ = -nFE$

$\Delta G^\circ = -2 \times 96500 \times 0.6753$

$\Delta G^\circ = -130332.9$ J

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

$-130332.9 = \Delta H^\circ + 298 \times 0.000648 \times 2 \times 96500$

$\Delta H^\circ = -167.6$

2.

Cell-1	Cell-2	Cell-3	
Product	O_2	Cl_2	H_2
n-Factor	4	2	2
Equivalent from the given resistance	1	3/4	1/4
Mol	1/4	3/8	1/8
Volume ratio	2	3	1

6. Specie giving higher reduction potential can oxidize the specie having lower reduction potential.

7. The metal with less reduction potential is strangest reducing agent.

8. At cathode : $2H^+(aq) + 2e^- \longrightarrow H_2\,(g)$

At anode : $Ag(s) + Cl^-\,(aq) \longrightarrow AgCl\,(s) + e^-$

Overall cell rxn : $2Ag(s) + 2H^+\,(aq) + 2Cl^-\,(aq) \longrightarrow H_2(g) + 2AgCl\,(s)$

$$Q = \frac{P_{H_2}}{[H^+]^2[Cl^-]^2}$$

$$E = E^\circ - \frac{0.06}{2}\log Q$$

With increase in value of Q, EMF of cell decrease.

10. (A) : During electrolysis Cu at anode will oxidise as well as Cu^{2+} of solution will reduce at cathode.

(B) : During electrolysis

At cathode : $2H^+(g) + 2e^- \longrightarrow H_2(g)$

At anode : $H_2O\,(\ell) \longrightarrow \frac{1}{2}O_2\,(g) + 2H^+(g) + 2e^-$

(C) : During electrolysis

At cathode : $Na^+ + e^- \longrightarrow Na$

At anode : $2OH^- \longrightarrow \frac{1}{2}O_2\,(g) + H_2O\,(\ell) + 2e^-$

(D) : During electrolysis

At cathode : $2H^+ (aq) + 2e^- \dashrightarrow H_2 (g)$

At anode : $2Cl^- (aq) \dashrightarrow Cl_2 (g) + 2e^-$

11. $H_2O (\ell) \dashrightarrow H_2(g) \quad + \quad \frac{1}{2} O_2(g)$

At cathod At anode

Mole of H_2O electrolyzed = $\frac{270}{18}$ = 15 mole

Equivalent of H_2O electrolyzed = 15 × 2 = 30

Equivalent of H_2 gas released = Equivalent of O_2 gas released = 30

mole of H_2 gas = $\frac{30}{2}$ = 15 mole

mole of O_2 gas = $\frac{30}{4}$ = 7.5 mole

Volume of O_2 gas = 7.5 × 22.4 L = 168 L

Total volume of gas = (15 + 7.5) × 22.4 = 504 L

Faraday of electricity consumed = 30 × $\frac{100}{75}$ = 40 F

12. $2H_2SO_4 + Pb(s) + PbO_2 (s) \longrightarrow 2PbSO_4(aq) + 2H_2O (\ell)$

15. Cathode : $Cr_2O_7^{2-} + 6e^- + 14 H^+ \longrightarrow 2Cr^{+3} + 7H_2O$

Anode : $[Sn^{2+} \longrightarrow Sn^{+4} + 2e^-] \times 3$

Net cell reaction : $Cr_2O_7^{2-} + 3Sn^{+2} + 14 H^+ \longrightarrow 3 Sn^{+4} + 2Cr^{+3} + 7H_2O$

	$Cr_2O_7^{2-}$	$3Sn^{+2}$	$14 H^+$	$3 Sn^{+4}$	$2Cr^{+3}$	$7H_2O$
Initial conc.	1M	1M	10^{-1} M	–	–	–
At completion	$\frac{2}{3}$ M	–	10^{-1} M	1M	$\frac{2}{3}$ M	–

Moles of Cr^{+3} = $\frac{2}{3} \times 3 = 2$

16. Cathode : $Cr_2O_7^{2-} + 6e^- + 14 H^+ \longrightarrow 2Cr^{+3} + 7H_2O$

Anode : $[Sn^{2+} \longrightarrow Sn^{+4} + 2e^-] \times 3$

Net cell reaction : $Cr_2O_7^{2-} + 3Sn^{+2} + 14 H^+ \longrightarrow 3 Sn^{+4} + 2Cr^{+3} + 7H_2O$

	$Cr_2O_7^{2-}$	$3Sn^{+2}$	$14 H^+$	$3 Sn^{+4}$	$2Cr^{+3}$	$7H_2O$
Initial conc.	1M	1M	10^{-1} M	–	–	–
At completion	$\frac{2}{3}$ M	–	10^{-1} M	1M	$\frac{2}{3}$ M	–

$$E_{Cr_2O_7^{-2}/Cr^{+3}} = E^o_{Cr_2O_7^{-2}/Cr^{+3}} \frac{-0.06}{6} \log \frac{[Cr^{+3}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$= 1.33 - 0.01 \log \frac{(2/3)^2}{(2/3)(10^{-1})^{14}} = 1.191 \quad \text{Ans.}$$

17. $Cr_2O_7^{2-} + 3\,Sn^{+2} + 14\,H^+ \longrightarrow 3\,Sn^{+4} + 2\,Cr^{+3} + 7\,H_2O$

$$E = (1.33 - 0.15) - \frac{0.06}{6}\log\frac{(0.2)^3(1)^2}{(0.2)^1(0.1)^3(1)^{14}}$$

$= 1.164$ V

25. Cells whose cell reaction does not involve any specie whose active mass changes with progress of reaction gave constant value of EMF.

26. Lower the value of reduction potential higher will be reducing power.

(A): During electrolysis of dil HCl

At cathode: $2e^- + H_2O\,(\ell) \longrightarrow H_2\,(g) + 2OH^-$

At anode: $2H_2O\,(\ell) \longrightarrow O_2\,(g) + 4H^+ + 4e^-$

(B) During electrolysis of dil NaCl

At cathode: $2e^- + H_2O\,(\ell) \longrightarrow H_2\,(g) + 2OH^-$

At anode: $2H_2O\,(\ell) \longrightarrow O_2\,(g) + 4H^+ + 4e^-$

(C) : During electrolysis of conc. NaCl

At anode: $2Cl^- \longrightarrow Cl_2\,(g) + 2e^-$

At cathode: $2H_2O\,(\ell) \longrightarrow O_2\,(g) + 4H^+ + 4e^-$

(D) : During electrolysis of $AgNO_3$

At cathode : $2Ag^+\,(aq) + e^- \longrightarrow Ag$

At anode : $2H_2O\,(\ell) \longrightarrow O_2\,(g) + 4H^+ + 4e^-$

EXERCISE # (S-II)

1. $5 \times E_1^\circ = 0.54 \times 4 + 0.45 \times 1$

$E_1^\circ = 0.522$ V

$6E_2^\circ = 0.54 \times 4 + 0.45 \times 1 + 1.07 \times 1$

$E_2^\circ = 0.613$ V

2. M/M^{n+} (0.02 M) || H^+(1M) / H_2(g) 1 atm

$M \longrightarrow M^{n+} + ne^-$

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

$$M + nH^+ \longrightarrow M^{n+} + \frac{n}{2}H_2$$

$$0.81 = 0.76 - \frac{0.06}{n}\log\frac{[M^{n+}](P_{H_2})^{n/2}}{[H^+]^n}$$

$$0.81 = 0.76 - \frac{0.06}{n}\log\frac{0.02\times 1}{1}$$

$$\frac{0.06}{n}\log 0.02 = -0.05$$

$$n = -\frac{6}{5}\log 0.02$$

$$n = \frac{6}{5}\log 50 = 2$$

3. $$E = 0 - \frac{0.0591}{2}\log\frac{[Zn^{2+}]_a}{[Zn^{2+}]_c}$$

$$= -\frac{0.0591}{2}\log\frac{10}{1}$$

$= -\ 0.0295$ V

4. $H_{2a} \longrightarrow 2H_a^+ + 2e^-$

$2H_c^+ + 2e^- \longrightarrow H_{2c}$

$$E = E^\circ - \frac{0.0501}{2}\log Q$$

$$Q = \frac{[H^+]_a^2\,(P_{H2})_c}{[H^+]_c^2\,(P_{H2})_a}$$

$(P_{H_2})_a = (P_{H_2})_c = 1$ atm

$[H^+]_a = \sqrt{Ka,\ CH_3COOH \times C}$

$= \sqrt{1.8 \times 10^{-5} \times 0.1}$

$[OH^-]_c = \sqrt{1.8 \times 10^{-5} \times 0.01}$

$[H^+]_c = \dfrac{10^{-14}}{\sqrt{1.8 \times 10^{-5} \times 0.01}}$

$E = 0 - \dfrac{0.0591}{2} \log \dfrac{(1.8)^2 \times 10^{-13}}{10^{-28}}$

$= -0.45$ V

5. (i) at anode

$Fe(s) + 2OH^- \longrightarrow FeO(s) + H_2O(\ell) + 2e^-$

at cathode

$Ni_2O_3(s) + H_2O(\ell) + 2e^- \longrightarrow 2\ NiO(s) + 2OH^-$

$Fe(s) + Ni_2O_3(s) \longrightarrow FeO\ (s) + 2\ NiO(s)$

(ii) E°_{cell} = 0.87 + 0.4 = 1.27 v

(iii) $\Delta G = -nFE^\circ$

$= -2 \times 96500 \times 1.27 = -2.45$ kJ

$|\Delta G| = 2.45$ kJ

6. $Ag\ |Ag^+||\ Ag^+\ |\ Ag$

$[Ag^+]_a = \dfrac{Ksp._{\ AgCl}}{[Cl^-]} = \dfrac{2.8 \times 10^{-10}}{0.2}$

$[Ag^+]_c = \dfrac{Ksp_{\ AgBr}}{[Br^-]} = \dfrac{3.3 \times 10^{-13}}{0.001}$

$E_{cell} = 0 - \dfrac{0.0591}{1} \log \dfrac{2.8 \times 10^3 \times 0.001}{0.2 \times 3.3}$

$= -0.0591 + \log 4.24$

$= -0.037$ V

$E^\circ_{Pb\ |PbCl_2|\ Cl^-} = E^\circ_{Pb\ |\ Pb^{2+}} - \dfrac{0.0591}{2} \log K_{sp}$

$0.268 = 0.126 - \dfrac{0.0591}{2} \log K_{sp}$

$K_{sp} = 1.536 \times 10^{-5}$

7. $C_6H_5\underset{n_f=6}{\overset{+3}{NO_2}} \longrightarrow C_6H_5\overset{-3}{NH_2}$

Equivalent of charge= Eq. of $C_6H_5NO_2$

= 0.1 × 6 = 0.6

$0.6 = \frac{Q}{96500} \times 0.2$

Q = 115,800 C

E = Q × V = 115,800 × 3 J =347.4 kJ

8. Mass of Ag deposited = 80 × 5 × 10^{-4} × 10.8 J

= 0.432

Eq. of Ag = $\frac{0.432}{108} = 0.004$

$0.004 = \frac{2 \times t(sec)}{96500}$

t(sec) = $\frac{0.004 \times 96500}{2}$ = 193 sec

9. (i) Eq. of Cu deposit = Eq. of charge = 0.01

Mole of Cu deposit = $\frac{0.01}{2}$

Mass of Cu deposit = $\frac{0.01}{2} \times 63.5$ = 0.3175

Mass of Cu remaining = 10 – 0.3175 = 9.6825 g

(ii) Eq. of charge = Eq. of H_2O electrolysed

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

$n_f = 1$

Equivalent of H^+ = 0.01

10. Amount of Cd deposited

$\frac{x}{x+2} \times 100 = 12$

x = $\frac{24}{88}$

$\frac{24}{88} \times \frac{2}{112.4} = \frac{5 \times t(sec)}{96500}$

t = 93.65 sec

11. at cathode

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

at anode

$2SO_4^{2-} \longrightarrow S_2O_8^{2-} + 2e^-$

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

Eq of H_2 = Eq of $S_2O_8^{2-}$ + Eq of O_2

$$\frac{9.722}{22.7} \times 2 = \frac{2.35}{22.7} \times 4 + \frac{w \times 2}{194}$$

w = 42.874 g

12. Eq of charge/year = $\frac{1.5 \times 10^6 \times 3.15 \times 10^7}{96500}$ = 4.9×10^8

Eq of charge = Eq of H_2O

$n_{H_2O} \times 2 = 4.9 \times 10^8$

$n_{H_2O} = 2.45 \times 10^8$

V(L) = $\frac{2.45 \times 10^8}{55.5}$ = 4.41×10^6 L/year

t = $\frac{8.2 \times 10^{12}}{4.41 \times 10^6}$ = 2×10^6 year

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

$$97.1 = \frac{K \times 1000}{0.1}$$

K = 97.1×10^{-4} Scm^{-1}

$$K = \frac{\ell}{a} \cdot \frac{1}{R}$$

$$97.1 \times 10^{-4} = \frac{1}{R} \times \frac{0.5}{1.5}$$

$$R = \frac{10^4}{97.1 \times 3} = 34.24\ \Omega$$

$$I = \frac{V}{R} = \frac{5}{34.24} = 0.146 \text{ amp}$$

14. $K_{total} = K_{SrSO_4} + K_{H_2O}$

$1.482 \times 10^{-4} = K_{SrSO_4} + 1.5 \times 10^{-6}$

$K_{SrSO_4} = 148.2 \times 10^{-6} - 1.5 \times 10^{-6}$

$= 146.7 \times 10^{-6}$ s cm^{-1}

$\lambda_m^\infty = \lambda_m^\infty Sr^{2+} + \lambda_m^\infty SO_4^{2-}$

$= 139.28$ s cm^2 mol^{-1}

$$\lambda_m^\infty = \frac{K \times 1000}{S} \Rightarrow s = \frac{146.7 \times 10^{-6} \times 10^3}{139.28}$$

s = 1.053×10^{-3} M

= $1.053 \times 10^{-3} \times 183.6$ g/L

= 0.1934 g/L

EXERCISE # (JEE–MAINS)

13. Since $S_2O_8^{2-}$ has highest value of reduction potential among given species therefore $S_2O_8^{2-}$ is strongest oxidizing agent.

14. $Fe^{+2}_{(aq)} + Ag^{+}_{(aq)} \longrightarrow Fe^{+3}_{(aq)} + Ag_{(s)}$

$E^{o} = E^{0}_{Ag^+/Ag} - E^{0}_{Fe^{+3}/Fe^{+2}}$

Now Eqn.1: $Fe^{+2} + 2e^- \longrightarrow Fe, E^{o} = y$

$\Delta G^{o} = -2Fy$

Eqn.2: $Fe^{+3} + 3e^- \longrightarrow Fe, E^{o} = z$

$\Delta G^{o} = -3Fz$

Eqn.2 – Eqn. 1, We get

$Fe^{+3} + e^- \longrightarrow Fe^{+2}, (E^{o})^1$

$\Delta G^{o} = -3Fz + 2Fy$

$\Rightarrow$ $-1 \times F \times (E^{o})^1 = -3Fz + 2Fy$

$\Rightarrow$ $(E^{o})^1 = E^{0}_{Fe^{+3}/Fe^{+2}} = 3z - 2y$

Now $E^{o} = E^{0}_{Ag^+/Ag} - E^{0}_{Fe^{+3}/Fe^{+2}}$

$= x - (3z - 2y)$

$= x - 3z + 2y$

15. $\Delta G^\circ = -nFE^\circ$

$= -2 \times 96000 \times 2$

$= -384000 \text{ J} = -384 \text{ kJ}$

16. Reaction at cathode

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

0.1 mole

Deposited moles of Ni = $\frac{0.1}{2} = 0.05$

17. Conductivity increases with increasing concentration of electrolyte and molar conductivity decreases with increasing concentration of electrolyte.

18. $\lambda_m = \lambda_m^{o} - A\sqrt{C}$

value of A will be same for NaCl and KCl

So Slope for both curve will be same.

But λ_m^{o} for KCl > λ_m^{o} for NaCl

So λ_m KCl > λ_m NaCl

(for a given Concentration)

19. oxidising power $\propto$ S.R.P value.

$\Rightarrow$ correct order is : $Bi^{+3} < Ce^{+4} < Pb^{+4} < CO^{+3}$

$E^{\circ}_{red} \Rightarrow$ oxidising power

20. As, Acidic Strength $\propto$ Ka

$\Rightarrow$ order of Acidic Strength or ka is A > C > B

As, Acidic Strength () $\Rightarrow$ ka() $\Rightarrow$ electrical conductivity ()

21. Anode

$PbSO_4 + 2e^- \longrightarrow Pb(s) + SO_4^{2-}$

Equivalent of $PbSO_4$ electrolysed = 0.05

Moles of $PbSO_4 = \frac{0.05}{2}$

Mass of $PbSO_4 = \frac{0.05}{2} \times 303 = 7.6$ g

22. $E^{\circ}_{cell} = 2V$

As, $\Delta G^{\circ} = -nF\, E^{\circ}_{cell}$ ... (1)

and also, $\Delta G^{\circ} = -RT\ln K_C$ ....(2)

Equating (1) and (2)

$\cancel{-} nFE^{\circ}_{aq} = \cancel{-} RT\ln K_C$

$2 \times 96000 = 8 \times 300 \ln K_C$

$\Rightarrow$ $K_C = e^{160}$

$\Rightarrow$ Correct option is 3

23. SRP , Oxidising power ↑

Reducing power ↓

24. Cell reaction :

$$H_{2(g)} + 2AgCl_{(s)} \longrightarrow 2H^+_{(eq)} + 2Ag_{(s)} + 2Cl^-_{(eq)}$$

$$Q_C = \frac{[H^+]^2[Cl^-]^2}{P_{H_2}} = \frac{(10^{-6})^2\,(10^{-6})^2}{1} = 10^{-24}$$

$$E = E^{\circ} - \frac{0.06}{n}\log Q$$

$$0.92 = E^{\circ} - \frac{0.06}{2}\log 10^{-24}$$

$E^{\circ} = 0.2V$

25. $E^\circ_{cell} = \left(E^\circ_{ox}\right)_{anode} + \left(E^\circ_{red}\right)_{cathode}$

$= 0.76 + \left(E^\circ_{red}\right)_{cathode}$

A electrode having maximum SRP will produce maximum E°_{cell}

26. $K_C \rightarrow 10 \times 10^{15}$

$E^\circ_{Cell} \rightarrow ?$

$\Delta G^\circ = -nF\ E^\circ_{Cell}$ ...(1)

Also, $\Delta G^\circ - RT\ln K_C$ ...(2)

Equate (1) and (2)

$\cancel{-}\ nF\ E^\circ_{Cell} = \cancel{-}\ RT\ln K_C$

$\Rightarrow \quad 2 \times E^\circ_{Cell} = \dfrac{2.303RT}{F} \log 10^{16}$

27. $\Delta S^\circ = nF\dfrac{dE^\circ}{dT}$

$\Delta G^\circ = -nFE^\circ$

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

$\Delta S^\circ = -2 \times 96000 \times 5 \times 10^{-4} = -96.5$ J

$\Delta G^\circ = -2 \times 96000 \times 2 = -384$ kJ

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

$-384 = \Delta H^\circ - \dfrac{300 \times (-96.0)}{1000}$

$\Delta H^\circ = -384 - 28.8 = -412.8$ kJ mol^{-1}

28. $\Lambda^\infty_{m_{HA}} = \Lambda^\infty_{m_{HCl}} + \Lambda^\infty_{m_{NaA}} - \Lambda^\infty_{m_{NaCl}}$

$= 425.9 + 100.5 - 126.4 = 400$

$\Lambda_m = \dfrac{K \times 1000}{M} = \dfrac{5 \times 10^{-5} \times 1000}{0.001} = 50$

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

Moles of O_2 required $= 3\times$ moles of $B_2H_6 = 3$

$\dfrac{I \times t}{96500}$ = moles of $O_2 \times 4 = 12 \Rightarrow t = 3.2$hrs

30. SRP , Oxidising power $\uparrow$

Reducing power $\downarrow$

31. Catnode : $2e^- + 2H_2O \rightarrow H_2 + 2OH^-$

$n_f = 2$

Anode : $\begin{array}{l} CH_2 - COO^- \\ | \\ CH_2 - COO^- \end{array} \rightarrow CH_2 = CH_2 + 2CO_2 + 2e^-$

$n_f = 2$ $\quad n_f = 1$

Total equivalent of gases ($CH_2 = CH_2$, CO_2, H_2) = 0.2 + 0.2 + 0.2 = 0.6

Total moles of gases = $\frac{0.2}{2} + 0.2 + \frac{0.2}{2} = 0.4$

Total Vol. of gases = 0.4 × 22.4 = 8.96 L

32. $Cu + ZnSO_4 \dashrightarrow X$

No reaction Cu lies below Zn in electro chemical series.

33. $Cu^{2+} + 2e^- \rightarrow Cu$

2F $\quad$ 1 mole = 63.5 g.

34. if $E_{ext} > E°$ Then electron flow from cathode to anode

35. $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

$$E = 1.51 - \frac{0.06}{5}\log\frac{[H^+]^8 f}{[H^+]^8 i}$$

$$E = 1.51 - \frac{0.06}{5}\log\frac{(10^{-3})^8}{(10^{-7})^8}$$

$$E = 1.51 - \frac{0.06}{5} \times 32 = 1.126 \text{ V}$$

So it will oxidize Br^- & I^-

36. κ = 1.4 S/m.

R = 50 Ω

M = 0.2

$$\kappa = \frac{1}{R} \times \frac{\ell}{A}$$

$$\Rightarrow \frac{\ell}{A} = 1.4 \times 50 \text{ m}^{-1}.$$

$$\kappa = \frac{1}{R} \times \frac{\ell}{A} = \frac{1}{280} \times 1.4 \times 50 = 0.25 \text{ Sm}^{-1}$$

$$\lambda = \frac{\kappa}{1000 \times M} = \frac{0.25}{1000 \times 0.5} = 5 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$$

37. $\lambda_c = \lambda_\infty - B\sqrt{C}$

38. Higher the SRP, better is oxidising agent

Hence MnO_4^- is strongest oxidising agent

39. $X + Y^{2+} \rightarrow X^{2+} + Y$

For reaction to be spontaneous E° must be positive.

40. $2H^+ (aq) + 2e^- \rightarrow H_2 (g)$

$E_{red} = E^{o}_{red} - \frac{0.0591}{n} \log \frac{P_{H_2}}{(H^+)^2}$; $E_{red} = 0 - \frac{0.0591}{2} \log \frac{2}{(1)^2}$; $E_{red} = -\frac{0.0591}{2} \log 2$

E_{red} is found to be negative for (3) option

41. $\kappa = 1.3$ S/m.

$R = 50\ \Omega$

$M = 0.2$

$$\kappa = \frac{1}{R} \times \frac{\ell}{A}$$

$$\Rightarrow \frac{\ell}{A} = 1.3 \times 50 \text{ m}^{-1}.$$

$$\kappa = \frac{1}{R} \times \frac{\ell}{A} = \frac{1}{260} \times 1.3 \times 50 = 0.25 \text{ Sm}^{-1}$$

$$\lambda = \frac{\kappa}{1000 \times M} = \frac{0.25}{1000 \times 0.4} = 6.25 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}$$

42. $\frac{2}{3} Al_2O_3 \rightarrow \frac{4}{3} Al + O_2$

$\Delta_rG = +966$ kJ mol^{-1} = 966×10^3 J mol^{-1}

$\Delta G = -nFE_{cell}$

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

$E_{cell} = 2.5$ V

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

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

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $\Delta G_3 = \Delta G_1 - \Delta G_2$

$\Delta G_3 = 3 \times 0.036F - 2 \times 0.439 \times F = -1 \times E^0 (Fe^{3+}/Fe^{+2}) \times F$

$E^0 (Fe^{3+}/Fe^{+2}) = 2 \times 0.439 - 3 \times 0.036 = 0.878 - 0.108 = 0.770$ V

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

$$= 0.3 - \frac{0.059}{6} \log \frac{(0.1)^2}{(0.01)^3} = 0.3 - 0.04 = 0.26 \text{ V}$$

45. $0 = +1.1 - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$

$\log = 37.3\,\frac{[Zn^{2+}]}{[Cu^{2+}]} \Rightarrow \frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{37.3}$

46. $0.152 = -0.8 - \frac{0.059}{1}\log K_{sp}$ $\Rightarrow \log K_{sp} = -16.11$

47. $C = 0.1$ M, $R = 100\ \Omega$

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

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

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

$\lambda_M = \frac{\frac{1}{520}\times 129}{1000\times 0.02} = 124\times 10^{-4}\ Sm^2mol^{-1}$

48. $CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$ From the reaction,

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

Thus to calculate the value of one should know the value of Λ^o_{NaCl} along with and Λ^o_{HCl}.

50. $\frac{5.12\times 1000}{27}\times 3 = \frac{Q}{96500}$

$Q = 54897\times 10^3 C = 5.4897\times 10^7 C$

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

52. $\lambda°_{HOAC} = \lambda°_{NaOAC} + \lambda°_{HCl} - \lambda°_{NaCl}$

$= 91 + 426.2 - 126.5 = 390.7$

53. $E° = E°_{Sn/Sn^{2+}} + E°_{Fe^{3+}/Fe^{2+}} = 0.14 + 0.77 = 0.91$ V

54. $E° = \frac{0.06}{n}$ 10 g Keq

$0.591 = \frac{0.0591}{1}$ 10 g Keq

$Keq = 10^{10}$

55. $\lambda°m\ NaBr = \lambda°m\ KBr + \lambda°m\ NaCl - \lambda°m\ KCl = 152 + 126 - 150 = 12\ Scm^2\ mol^{-1}$

56. $Zn(s) + 2H^+(eq) \longrightarrow Zn^{2+}(eq) + H_2(g)$

On adding H_2SO_4, equilibrium shift to right

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

$[H^+]\uparrow$, $E\uparrow$

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

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

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

58. SRP ↑, Oxidising power ↑

Reducing power ↓

59. SRP ↑, Oxidising power ↑

Reducing power ↓

60.

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 1.10 - \frac{0.0591}{2}\log\frac{1}{0.1} = 1.07V$$

61. number of equivalent of of electrons = $\frac{9650}{96500} = 0.1 mole$

number of equivalent of of Ag = $0.1 mole$

EXERCISE # (JEE-ADVANCED)

1. $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$

$K_a = \dfrac{c\alpha^2}{1-\alpha}$

$K_a = \dfrac{c(\Lambda_m/\Lambda_m^\circ)^2}{1-(\Lambda_m/\Lambda_m^\circ)}$

$K_a = \dfrac{c\Lambda_m^2}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m)}$

$K_a\Lambda_m^\circ 2 - K_a\Lambda_m^\circ\Lambda_m = c\Lambda_m^2$

$\dfrac{K_a\Lambda_m^\circ}{\Lambda_m} - K_a\Lambda_m^\circ = c\Lambda_m$

$\dfrac{K_a\Lambda_m^{\circ 2}}{\Lambda_m} = c\Lambda_m + K_a\Lambda_m^\circ$

$\dfrac{1}{\Lambda_m} = \left(\dfrac{c\Lambda_m}{K_a\Lambda_m^{\circ 2}}\right) + \dfrac{1}{\Lambda_m^\circ}$

$P = \dfrac{1}{\Lambda_m^\circ}$

$S = \dfrac{1}{K_a\Lambda_m^{\circ\ 2}}$

$\frac{P}{S} = \left(\dfrac{\frac{1}{\Lambda_m^\circ}}{\frac{1}{K_a\Lambda_m^{\circ 2}}}\right) = K_a\Lambda_m^\circ$

2. (1)

$MnO_4^-(aq) + 4H^+ + 3e \rightarrow MnO_2(s) + 2H_2O; E^\circ = 1.68\ V$

$\Delta G_1^o = -3F(1.68) = -5.04\ F$

(2)

$MnO_2(s) + 4H^+ + 2e \rightarrow Mn^{2+} + 2H_2O; E^\circ = 1.21\ V$

$\Delta G_2^o = -2F(1.21) = -2.42F$

(3)

$Mn^{2+}(aq) + 2e \rightarrow Mn(s); E^\circ = -1.03\ V$

$\Delta G_3^o = -2F(-1.03) = +2.06F$

Adding (1), (2) and (3),

$MnO_4^-(aq) + 8H^+ + 7e \longrightarrow Mn(s) + 4H_2O$

$\Delta G = \Delta G_1^o + \Delta G_2^o + \Delta G_3^o$

$= (-5.04 - 2.42 + 2.06)F$

$-7FE^\circ = -5.4\ F$

$E^\circ = 0.77\ V$

3. $\lambda_m = \lambda_m^o - A\sqrt{C}$

For electrolyte Z_mX_n and from given curve

$\lambda_m(Z_mX_n) = \lambda_m^o(Z_mX_n) - A\sqrt{C}$

$-A = \frac{336 - 339}{0.04 - 0.01} = -\frac{3}{0.03}$

$\Rightarrow A = 100$

$\therefore$ For $\lambda_m = 336 \text{ S cm}^2 \text{ mol}^{-1}$

$\Rightarrow 336 = \lambda_m^o(Z_mX_n) - 100 \times 0.04$

$\lambda_m^o = 336 + 4 = 340 \text{Scm}^2 \text{ mol}^{-1}$

$Z_mX_n \rightarrow mZ^{n+} + nXX^-$

$\therefore 50\text{ m} + 80\text{n} = 340$

$\Rightarrow 5\text{ m} + 8\text{n} = 34 \ldots \text{ (i)}$

$U_mY_p \rightarrow mUO^p + pYP^{m-}$

$\therefore 25\text{m} + 100\text{p} = \lambda_m^o\left(U_mY_p\right) = 250$

$\Rightarrow \text{m} + 4\text{p} = 10 \ldots \text{ (ii)}$

$\therefore 100\text{ m} + 80\text{n} = 440$

$\Rightarrow 5\text{ m} + 4\text{n} = 22 \ldots \text{ (iii)}$

From equation (i) and (iii)

$n = 3$

$m = 2$

From equation (ii)

$p = 2$

$\therefore m + n + p = 2 + 3 + 2 = 7$

4. $E_{cell}^0 = 1.23 \text{ volt}$

$\Delta G^0 = -nFE_{cell}^0 \{-2 \times 96500 \times 1.23\}J$

Since, Work derived from this fuel cell $= 70/100 \times (-\Delta G^\circ \text{ cell}) \times 1.0 \times 10^{-3} = x\text{ J}$

Since insulated vessel, hence $q = 0$

From equation, for monoatomic gas,

$w = \Delta U \Rightarrow x = nC_{V,m}\Delta T$

$\left\{C_{V,m} = \frac{3R}{2}\right\}$

Or

$70/100 \times 2 \times 96500 \times 1.23 \times 10^{-3} = 1 \times 3/2 \times 8.314 \times \Delta T$

$\Delta T = 13.32$

5 & 6. Solution for Questions 5 and 6.

Molar conductivity of HX at infinite dilution

Λ_m^{∞}

$= 4 \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$

Molar conductivity of HX at conc. $c_1 = y \times 10^2 \text{ S cm}^2 \text{ mol}^{-1}$

$$\alpha_1 = \frac{\Lambda_m^{c_1}}{\Lambda_m^{\infty}} = \frac{y \times 10^2}{4 \times 10^2} = \frac{y}{4}$$

On 20 times dilution of the solution of HX

$$\alpha_2 = \frac{\Lambda_m^{c_2}}{\Lambda_m^{\infty}} = \frac{3y \times 10^2}{4 \times 10^2} = \frac{3y}{4} \quad \left[c_2 = \frac{c_1}{20}\right]$$

$$\frac{\alpha_1}{\alpha_2} = \frac{1}{3} \Rightarrow \alpha_2 = 3\alpha_1$$

$HX \rightleftharpoons H^+ + X^-$

$c_1(1-\alpha_1) \; c_1\alpha_1 \; c_1\alpha_1$

$$K_a = \frac{c_1\alpha_1^2}{1-\alpha_1} = \frac{c_2\alpha_2^2}{1-\alpha_2} = \frac{c_1(3\alpha_1)^2}{20(1-3\alpha_1)}$$

$$\frac{1}{1-\alpha_1} = \frac{9}{20(1-3\alpha_1)}$$

$20 - 60\alpha_1 = 9 - 9\alpha_1$

$\Rightarrow \alpha_1 = 11/51 = 0.215$

$Y = 4\alpha_1 = 0.086$

7. $Mg\,(s) + Cu^{2+}\,(aq) \longrightarrow Cu\,(s) + Mg^{2+}\,(aq)$

Initially : $E = 2.7 = E° - \frac{RT}{2 \times F}\ell n\left(\frac{1}{1}\right) \Rightarrow E° = 2.7$

When : $[Mg^{2+}] = x$

$$E = 2.67 = 2.7 - \frac{300}{2 \times 11500} \times \ell n\left(\frac{x}{1}\right)$$

$\ell n\ x = 2.3 \Rightarrow x = 10$

8. $2A\,(s) + B^{2n+}\,(aq) \longrightarrow 2A^{n+}\,(aq) + B(s)$

Given $\Delta H° = 2\Delta G°$

$\because \quad \Delta G° = \Delta H° - T\Delta S°$

$\therefore \quad \Delta G° = 2\,\Delta G° - T\Delta S°$

$\Delta G° = T\Delta S°$

$\because \quad \Delta G = \Delta G° + RT\,\ell n\,Q = 0$

$$\Delta G° = -8.3 \times 300 \times \ell n\left(\frac{2^2}{1}\right) = 300 \times \Delta S°$$

$\Delta S° = -\,8.3 \times \ell n\,4 = -8.3 \times 2 \times 0.7 = -11.62 \text{ J/K}$

9. $\kappa = G \times \dfrac{\ell}{A} = 5 \times 10^{-7} \times \dfrac{120}{1} = 6 \times 10^{-5}\ \text{Scm}^{-1}$

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

$\because \Lambda_m = \dfrac{K \times 1000}{0.0015} = \dfrac{6 \times 10^{-5} \times 1000}{0.0015} = 40\ \text{Scm}^2\text{mol}^{-1}$

$\because \quad \alpha = \dfrac{\Lambda_m}{\Lambda_m^\infty} \Rightarrow \Lambda_m^\infty = \dfrac{\Lambda_m}{\alpha}$

$\therefore \quad \Lambda_m^\infty = \dfrac{40}{\dfrac{10^{-4}}{0.0015}} = 6 \times 10^2$

$\therefore \quad Z = 6$

10. $Zn\,(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}\,(aq) + Cu\,(s)$

$Q_c = \dfrac{[Zn^{2+}]}{[Cu^{2+}]} = 10$

$\Delta G° = -2 \times F \times 1.1$

$\Delta G = \Delta G° + RT\ \ell n\, Q = -2.2\ F + RT\ \ell n\ 10 = 2.303\ RT - 2.2\ F$

11. $H_2(g) + M^{4+}(aq) \longrightarrow 2H^+(aq) + M^{2+}(aq)$

$Q = \dfrac{[H^+]^2[M^{2+}]}{P_{H_2}[M^{4+}]} = \dfrac{1 \times [M^{2+}]}{1 \times [M^{4+}]} = 10^x$

$E = 0.092 = 0.151 - \dfrac{0.059}{2}\log 10^x \quad \Rightarrow x = 2$

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

$\Delta G^0 = -nFE^0$ For 1 mole of M^+

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

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

Energy released by conversion of 1 mole of

$X \longrightarrow Y \qquad \Delta G = -193$ KJ

Hence mole of M^+ convert $= \dfrac{193}{48.25} = 4$

13. $\lambda^{\circ}_{X^-} \approx \lambda^{\circ}_{Y^-}$

$\Rightarrow \quad \lambda^{\circ}_{H^+} + \lambda^{\circ}_{X^-} \approx \lambda^{\circ}_{H^+} + \lambda^{\circ}_{Y^-}$

$\Rightarrow \quad \lambda^{\circ}_{HX} \approx \lambda^{\circ}_{HY}$ (1)

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

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

Now, Given that

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

$\Rightarrow \quad \lambda^{\circ}_m \alpha_2 = 10 \times \lambda^{\circ}_m \alpha_1$

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

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

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

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

$\Rightarrow \quad pK_a (HX) - pK_a (HY) = 3$.

14. Salt bridge is introduced to keep the solutions of two electrodes separate, such that the ions in electrode do not mix freely with each other. But it cannot stop the process of diffusion.
It does not participate in the chemical reaction. However, it is not necessary for occurence of cell reaction, as we know that designs like lead accumulator, there was no salt bridge, but still reactions takes place.

15. (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 $\downarrow$ (ppt) + KNO_3 (aq).

As the only reaction taking place is precipitation of AgI and in place of Ag^+, K^+ is coming in the solution, conductivity remain nearly constant and then increases.

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

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

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

As H^+ is getting replaced by Na^+ conductivity dereases and after end point, due to OH^-, it increases.

So answer of 39 is : (P) – (3) ; (Q) – (4) ; (R) – (2) ; (S) – (1). Answer is (D).

16. (P) $E^{o}_{Fe3+, Fe}$ $Fe^{3+} \xrightarrow[n=1]{+0.77V} Fe^{2+} \xrightarrow[n=2]{-0.44V} Fe$

xV n = 3

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

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

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

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

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

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

(R) $E^{o}_{(Cu2+ + Cu \longrightarrow 2Cu+)}$ $Cu^{2+} \xrightarrow[n=1]{xV} Cu^{+} \xrightarrow[n=1]{-0.52V} Cu$

+ 0.34V, n = 2

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

$x = 0.16\ V.$

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

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

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

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

(S) $E^{o}_{(Cr3+, Cr2+)}$ $Cr^{3+} \xrightarrow[n=1]{x} Cr^{2+} \xrightarrow[n=2]{-0.91V} Cr$

– 0.74V, 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.

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

$= -11.4$ kJ/mole.

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

0.001 M

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

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

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

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

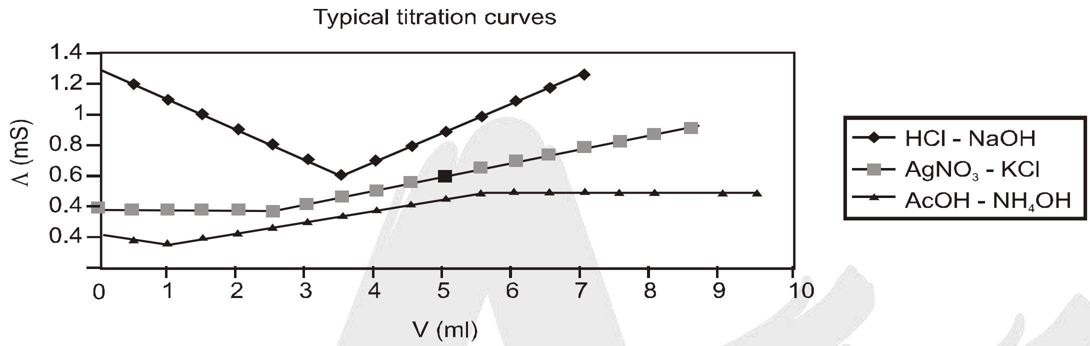
$$0.059 = -\frac{0.059}{2}\log\left\{\frac{M^{2+}(aq)_a}{10^{-3}}\right\}$$

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

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

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

19.



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

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

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

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

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

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

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

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

$$= 0 - \frac{0.0591}{1}\log$$

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

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

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

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

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

$t = 19.3 \times 10^4$ sec

25. $Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$.

$E^o = 1.36 + (-0.54) = 0.82$ V (+ ve). Spontaneous.

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

So Mn^{3+} will oxidise H_2O.

27. Mol of NaCl = 4 × 0.5 = 2 mol.

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

28. Taking the 1 : 1 molar combination of Na–Hg amalgam.

weight = 2 × 23 + 2 × 200 = 446 g.

29. $2Na^+ + 2e^- \longrightarrow 2Na$.

No. of Faraday required = 2.

∴ total charge = 2 × 96500 = 193000 coulomb.

30. $2Ag^+ + C_6H_{12}O_6 + H_2 \longrightarrow 2Ag(s) + C_6H_{12}O_7 + 2H^+$, $E^o = 0.8 + 0.05 = 0.85$ volt.

$$0 = 0.85 - \frac{0.0592}{2} \log K.$$

ln K = 2.303 × log K = 2.303 × 28.71 = 66.13

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

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

or, $\Delta H = 0.65$ volt.

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

33. $AgBr\ (s) \longrightarrow Ag^+ + Br^-$

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

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

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

$K_{total} = \Lambda_{Ag^+} + \Lambda_{Br^-} + \Lambda_{NO_3^-}$

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

$K_{total} = 24 + 24 + 7$.

$K_{total} = 55\ Scm^{-1}$.

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

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

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

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

35. (a) $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

$\Delta G^o_{rxn} = -109 - (-129) - 79$

$= -57$ kJ/mole

$\Delta G° = -nFE°$

$-57 \times 100 = -1 \times 96500 \times E°$

$E° = 0.591$ V

$\Delta G° = -RT\,\ell n \frac{1}{Ksp} = -57 \times 100$

log Ksp = –10

(b) $2Ag^+(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$

$E° = 0.8 + 0.76 = 1.56$ V

$E° = \frac{0.06}{2} \log Kq = 1.56$

$Kq = 10^{52}$

36. $Zn + Fe^{2+} \longrightarrow Fe + Zn^{2+}$

$Q = \frac{0.1}{0.01} = 10$

$E = E° - \frac{0.0591}{2} \log Q$

$0.2905 = E° - \frac{0.0591}{2} \log(10)$

$E° = 0.32$

$E° = \frac{0.0591}{2} \log K = 0.32$

$K = 10^{0.32/0.0295}$

37. $In^+ \longrightarrow In^{3+} + 2e^-$, $E° = 0.42$ V

$In^{2+} + e \longrightarrow In^+$, $E° = -0.4$ V

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

$E^o = 0.44$ V

$E^o_{cell} = 0.15 + 0.44 = 0.59$ V

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

$K = 10^{10}$.

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

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

40. MnO_4^- ion can oxidise both Fe^{2+} to Fe^{3+} as well as Cl^- to Cl_2. So $Fe(NO_3)_2$ cannot be estimated quantitatively with MnO_4^- ion in HCl.

E^{o}_{Cell} for the cell Pt, $Cl_2(g)$ (1 atm) | Cl^- (aq) | | MnO_4^- (aq) | Mn^{2+} (aq). is euqal to (1.51 – 1.4) = 0.11 V.

41. Disproportionate reaction

42. conductance $\propto \frac{1}{\text{Hydrated radius of ion}}$

44. (i) $H_2(g) + 2AgCl(s) \longrightarrow 2Ag(s) + 2H^+(aq) + 2Cl^-(aq)$

(ii) $\Delta G° = \Delta H° - T\Delta S° = -nFE°$

At 15°C : $\Delta H° - 288 \times \Delta S° = -2 \times 96500 \times 0.23$

At 35°C : $\Delta H° - 308 \times \Delta S° = -2 \times 96500 \times 0.21$

On solving

$\Delta H° = -49587$ J/mole

$\Delta S° = -96.5$ J/mole-K

45. E°cell = 0.33 + 0.44 = 0.77 Volt

since E°cell is positive therefore reaction is spontaneous.

46. Let initially $[Cu^{2+}]$ = C M

$\therefore$ moles of Cu^{2+} in the solution = $\frac{C \times 250}{1000}$ = 0.25 C moles

After electrolysis

Moles of Cu^{2+} = $\frac{0.25 \times C}{2}$

Eq. of Cu^{2+} = $\frac{0.25 \times C}{2} \times 2$ = faraday of electricity.

$0.25 \times C = 2 \times 10^{-3} \times 16 \times 60/69500$

$C = \frac{2 \times 10^{-3} \times 16 \times 60}{0.25 \times 96500} = 7.95 \times 10^{-5}$ M

47. Cell reaction :

$Fe^{2+} + Ce^{4+} \longrightarrow Ce^{3+} + Fe^{3+}$

Q = 1

E = E° = 1.61 – 0.77 = 0.84 V

$\therefore$ Direction of flow of current is cathode to anode which will decrease with time.

48. The specie having higher reduction potential oxidizes the specie having lower reduction potential.

49. $E° = 0.77 - 0.54 = 0.23 = \frac{0.06}{2}\log K$

$K = 6.26 \times 10^{7}$

50. $Ag^{+}_{(cathode)} \dashrightarrow Ag^{+}_{(anode)}$

0.1 M 2 S

$Q = \frac{2S}{0.1}$

$E = 0.164 = -\frac{0.06}{2}\log\left(\frac{2S}{0.1}\right)$

$S = 9.23 \times 10^{-3}$

$Ksp = 4S^{3} = 2.287 \times 10^{-12}$