Electrochemistry

SOLUTIONS

Exercise-I (Conceptual Questions)

1. Ans. (3)

Strong electrolytes are those for which degree of dissociation (α) is 100% at any concentration.

2. Ans. (2)

When a salt like NaCl is molten, in molten state its ions becomes mobile and those mobile ions are charge carrier which are responsible for conduction of electricity.

3. Ans. (3)

In electrolytic conduction charge carrier are mobile ions due to which conduction occurs.

4. Ans. (1)

Equivalent conductance $\left(\lambda_{eq.}\right)=\dfrac{\kappa\times1000}{N}$

For KCl v.f. = 1, So N = M

$$\lambda_{eq}\propto\frac{1}{N}$$

$N\uparrow\Rightarrow\lambda_{eq}\downarrow$ or $M\uparrow\Rightarrow\lambda_{eq}\downarrow$

5. Ans. (3)

Given : Specific resistance (ρ) = R

Concentration (N) = C g-eq L^{-1}

Now, Specific conductance (κ) = $\dfrac{1}{\rho}=\dfrac{1}{R}$

Equivalent conductance $(\lambda_{eq})=\dfrac{\kappa\times1000}{N}$

$$=\frac{\frac{1}{R}\times1000}{C}$$

$$=\frac{1000}{R.C}$$

6. Ans. (3)

Specific conductance $(\kappa)=\dfrac{1}{\rho}$

$\kappa\downarrow\Rightarrow\ \rho\uparrow$

$R=\rho.\dfrac{\ell}{A}$

$\kappa\downarrow\Rightarrow\rho\uparrow\Rightarrow R\uparrow$

7. Ans. (3)

Given :

Specific conductance (κ) = 1.061×10^{-4}5cm^{-1}

Now Molar conductance $(\lambda_m)=\dfrac{\kappa\times1000}{M}$

$$=\frac{1.061\times10^{-4}\times10^{3}}{0.01}$$

= 10.61 S cm^{2}mol^{-1}

8. Ans. (2)

With dilution, inter ionic interaction decreases so conductance increase.

9. Ans. (1)

Given : Concentration (N) = 0.01 N

Resistance (R) = 210 Ω

Cell constant (G*) = $\dfrac{\ell}{A}=0.66\text{cm}^{-1}$

Now $\quad G=\dfrac{1}{R}=\dfrac{1}{120}$

$$\kappa=G*G^{*}=\frac{1}{210}\times0.66$$

$$\lambda_{eq}=\frac{\kappa\times10^{3}}{N}=\frac{\left(\frac{1}{210}\times0.66\right)\times10^{3}}{0.01}$$

= 314.28 mho cm^{2}eq^{-1}

10. Ans. (2)

In case of electrolytic conduction charge carrier are mobile ions while in case of metallic conduction change carrier ore Kernels, so increasing temp. mobility of ion increases hence resistance decreases.

11. Ans. (1)

Given : specific conductance

$$(\kappa)=0.0014\Omega^{-1}\text{cm}^{-1}$$

Conc. (M) = 0.01M

Now

$$\lambda_{eq}=\frac{\kappa\times1000}{N}$$

n-factor for KCl = 1

So N = M = 0.01

$$=\frac{0.0014\times1000}{0.01}$$

$$\lambda_{eq}=140$$

12. Ans. (1)

Specific conductance is conductance due to 1 ml electrolytic solution on dilution no of ions per ml decreases hence specific conductance decreases.

13. Ans. (1)

Given: $\lambda^{\infty}_{e\ CH_3COONa} = 91\text{ mho cm}^2\text{eq}^{-1}$

$\lambda^{\infty}_{e\ HCl} = 426\text{ mho cm}^2\text{eq}^{-1}$

$\lambda^{\infty}_{e\ CH_3COOH} = 391\text{ mho cm}^2\text{eq}^{-1}$

$\lambda^{\infty}_{e\ NaCl} = \lambda^{\infty}_{e\ Na^+} + \lambda^{\infty}_{e\ Cl^-}$

$= \lambda^{\infty}_{e\ CH_3COONa} + \lambda^{\infty}_{e\ HCl} - \lambda^{\infty}_{e\ CH_3COOH}$

= 91 + 426 – 391

= 126

14. Ans. (3)

Given : α = 90% = 0.9

$\lambda^{\infty}_{e} = 425\Omega^{-1}\text{cm}^2\text{eq}^{-1}$

$\kappa = 3.825\Omega^{-1}\text{cm}^{-1}$

Now, $\alpha = \dfrac{\lambda^{c}_{e}}{\lambda^{\infty}_{e}}$

$\lambda^{c}_{e} = \lambda^{\infty}_{e} \times \alpha$

$\lambda^{c}_{e} = 425 \times \dfrac{90}{100}$ ... (1)

Also, $\lambda^{c}_{e} = \dfrac{\kappa \times 1000}{N}$ ... (2)

Equation (1) & (2)

$425 \times \dfrac{90}{100} = \dfrac{\kappa \times 1000}{N}$

$425 \times \dfrac{90}{100} = \dfrac{3.825 \times 1000}{N}$

N = 10N

15. Ans. (1)

$\wedge^{o}_{HOAc} = \wedge^{o}_{H^+} + \wedge^{o}_{OAc^-}$

$= \wedge^{o}_{NaOAc} + \wedge^{o}_{HCl} - \wedge^{o}_{NaCl}$

To substract molar conductance of Na^+ and Cl^- We required $\wedge^{0}_{NaCl}$.

16. Ans. (2)

$\wedge^{o}_{M\ NaNO_3} = \wedge^{o}_{M\ Na^+} + \wedge^{o}_{M\ NO_3^-}$

$= \wedge^{o}_{M\ NaCl} + \wedge^{o}_{M\ AgNO_3} - \wedge^{o}_{M\ AgCl}$

= 110.3 + 116.5 – 121.6

= 105.2 $Scm^2\ mol^{-1}$

17. Ans. (4)

Given : $\kappa = 3.06 \times 10^{-6}\Omega^{-1}\text{cm}^{-1}$

$\lambda_M = 1.53\ \Omega^{-1}\text{cm}^{-1}\text{mol}^{-1}$

At saturation,

$\lambda_M = \dfrac{\kappa \times 1000}{S}$

$S = \dfrac{3.06 \times 10^{-6} \times 1000}{1.53} = 2 \times 10^{-3}\text{ mol / L}$

$BaSO_4$ is AB type of salt

$K_{sp} = S^2$

$= (2 \times 10^{-3})^2 = 4 \times 10^{-6}$

18. Ans. (2)

Acc. To KOHLRAUSCH'S LAW,

At infinite dilution, each ion make definite contribution to equivalent conductance of an electrolyte whatever be the nature of other ion of the electrolyte.

19. Ans. (2)

In galvanic cell, electron move from anode to cathode in external circuit so current flows from cathode to anode. From representation Cu to Ag.

20. Ans. (2)

In Daniel cell current flows from cathode to anode. So copper to zinc in external circuit.

21. Ans. (4)

Reaction representing standard reduction potential of zinc.

$Zn^{+2}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$

22. Ans. (2)

Zero electrode potential of standard hydrogen electrode is assumed to be zero.

23. Ans. (4)

In construction of S.H.E. a platinum block is used with conducting wire at $1M[H^+]$, 1 bar pressure and 25°C temp. The use of platinum block is adsorb H_2 gas at surface.

24. Ans. (2)

$\underbrace{Zn\,|\,Zn^{+2}(1M)}_{\text{Anode}}\,||\,\underbrace{H^+(1M)\,|\,H_2(1atm)}_{\text{Cathode}}$

$E^{o}_{cell} = \left(E^{o}_{RP}\right)_{Cathode} - \left(E^{o}_{RP}\right)_{Anode}$

$\downarrow$

$= E^{o}_{H^+/H_2} - E^{o}_{Zn^{+2}/Zn}$

= 0–(–0.76)

= +0.76 V

25. Ans. (2)

Acc. to representation, it is reverse of Daniel cell so non spontaneous

So $E_{cell} = -ive$

26. Ans. (3)

$$\overset{\text{Cathode}}{2Fe^{+3} + 2I^- \longrightarrow 2Fe^{+2} + I_2}$$

Anode

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

$= 0.771-0.536$

$= 0.235$ V

27. Ans. (1)

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

On rearranging

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

That is reduction reaction.

28. Ans. (1)

At anode always oxidation occurs At cathode always reduction occurs.

29. Ans. (4)

In Daniel cell, Anode is zinc and cathode is copper.

Zinc is consumed and copper is deposited

30. Ans. (4)

Acc. to E.C.S.; $SRP_{Na^+} < SRP_{Zn^{+2}}$

So Na being more reactive, Zn cannot displace Na^+ ion.

31. Ans. (1)

Strong reducing agent will have more standard oxidation potential.

$$E^o_{Zn/Zn^{+2}} > E^o_{Cr/Cr^{+3}} > E^o_{H_2/H^+} > E^o_{Fe^{+2}/Fe^{+3}}$$

32. Ans. (3)

More SOP $\Rightarrow$ more reactive metal displaces less reactive.

$$E^o_{Fe/Fe^{+2}} > E^o_{Cu/Cu^{+2}} > E^o_{Ag/Ag^+}$$

33. Ans. (4)

More SOP $\Rightarrow$ more Reducing power

SOP A < C < B

34. Ans. (2)

Check by option $E_{cell} = (E_{RP})_{Cathode} - (E_{RP})_{Anode}$

1. $\Rightarrow E_{Cu^{+2}/Cu} - E_{Zn^{+2}/Zn}$

   $= +0.34 - (-0.76) = 1.1$ V

2. $\Rightarrow E_{Ag^+/Ag} - E_{Zn^{+2}/Zn}$

   $= +0.80-(-0.76) = +1.56$ V

3. $\Rightarrow E_{Cu^{+2}/Cu} - E_{H^+/H_2}$

   $= 0.34-0 = +0.34$ V

4. $\Rightarrow E_{Ni^{+2}/Ni} - E_{H^+/H_2}$

   $= -0.55-0 = -0.55$ V

35. Ans. (2)

SRP $Mg^{+2} > Na^+ > Ba^{+2} > Li^+$

More SRP $\Rightarrow$ strong oxidising Agent

36. Ans. (1)

For non-metal, substance having more SRP have greater tendency to reduce itself and oxidise other, while less SRP substance have greater tendency to oxidise itself and reduce other.

37. Ans. (3)

Lesser SRP substance will oxidise itself and reduce other.

Like Zn will oxidise itself but reduce Ag^+ and Cu^{+2} ions.

38. Ans. (3)

SRP C > B > A > D

Lesser SRP $\Rightarrow$ more reactive metal more reactive metal displace less reactive from its aqueous solution.

39. Ans. (4)

For solution to turn blue copper must get oxidise and convert into Cu^{+2}.

Acc. to E.C.S

SRP of Cu < SRP of Ag

So, copper will displace Ag^+ ions from its solutions.

40. Ans. (3)

Acc. to E.C.S., metals having lesser SRP are more reactive and displacer less reactive metal ion in their aqueous solutions.

41. Ans. (1)

Strong oxidizing agent will have lesser SOP. Oxidising agent ion will reduce itself and oxidise other.

42. Ans. (3)

Cell is at standard condition.

So $E^{o}_{cell} = (E^{o}_{RP})_{cathode} - (E^{o}_{RP})_{Anode}$

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

$= 1.5-(-0.25)$

$= 1.75$ V

43. Ans. (4)

Cell reaction :

$$\underbrace{2T\ell_{(s)} + \overbrace{Cu^{+}_{(aq)} \longrightarrow 2T\ell^{+}_{(aq.)}}^{\text{Anode}} + Cu_{(s)}}_{\text{Cathode}}$$

$$\text{Ecell} = E_{cell} = E^{0}_{cell} - \left\{\frac{0.0591}{n}\log\frac{[T\ell^{+}]^2}{[Cu^{+2}]}\right\}$$

From relation $[Cu^{+2}]\uparrow$ or $[T\ell^{+}]\downarrow \Rightarrow E_{cell}\uparrow$

44. Ans. (4)

$Ag^{+}_{(aq.)} + e^{-} \rightarrow Ag_{(s)}$

$$E_{cell} = E^{o}_{red} - \frac{0.0591}{n}\log\frac{1}{[Ag^{+}]}$$

$$= E^{o}_{red} - \frac{0.0591}{1}\log\frac{1}{10^{-1}} \quad \because |Ag^{+}| = 10^{-1}$$

$= E^{o}_{red} - 0.0591$

45. Ans. (3)

pH = 1; $[H^{+}] = 10^{-1}$M

$2H^{+}_{(aq.)} + 2e^{-} \longrightarrow H_{2(g)}$

Nernst equation

$$E_{cell} = E^{o}_{red} - \frac{0.0591}{2}\log\frac{p_{H_2}}{[H^{+}]^2}$$

$\because p_{H_2} = 1; [H^{+}] = 1M; E^{0}_{red} = 0$

$$E_{cell} = 0 - \frac{0.0591}{2}\log\frac{1}{(10^{-1})^2}$$

$E_{cell} = -0.0591$ V

46. Ans. (2)

Reaction :

$$\overbrace{Cl_{2(g)} + \underbrace{2Br^{-}_{(aq)} \longrightarrow 2Cl^{-}_{(aq.)}}^{\text{Gain of } e^- = 2e^-} + Br_{2(\ell)}}_{\text{Loss of } e^- = 2e^-}$$

Nernst equation

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log\frac{[Cl^{-}]^2}{P_{Cl_2}\times[Br^{-}]^2}$$

$E^{o}_{cell} = 0.29V; n = 2; P_{Cl_2} = 0.25;$

$[Cl^{-}] = [Br^{-}] = 0.01M$

$$E_{cell} = 0.29 - \frac{0.0591}{2}\log\frac{(0.01)^2}{(0.25)(0.01)^2}$$

$= 0.272$ V

47. Ans. (1)

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

no. of e^- transferred = $2e^-$

Nernst equation

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

$$= 1.1 - \frac{0.0591}{2}\log\frac{(0.1)}{(0.1)}$$

$= 1.1$ V

48. Ans. (1)

EMF of cell is intensive property does not depend on stochiometric coefficient.

49. Ans. (1)

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

Let $[Zn^{+2}]_i = 1M$

After 10 times dilution $[Zn^{+2}]_f = \frac{1}{10}M$

Nernst equation

$$E_i = E^{o} - \frac{0.0591}{2}\log[Zn^{+2}]^1_i = E^0$$

$$E_f = E^{o} - \frac{0.0591}{2}\log[Zn^{+2}]^1_f$$

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

$= E^{o} + 0.0295$

$= \approx E^{0} + 0.03$

50. Ans. (4)

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

$pH_i = 0$; $[H^+]_i = 10^0 = 1$ M

$pH_f = 7$; $[H^+]_f = 10^{-7}$ M

Nernst equation

$$E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{P_{H_2}}{[H^+]^2}$$

$$(\because P_{H_2} = 1atm);\ E^0_{cell} = 0$$

$$E_i = 0 - \frac{0.0591}{2}\log\frac{1}{1} = 0$$

$$E_f = 0 - \frac{0.591}{2}\log\frac{1}{(10^{-7})^2} = \frac{-0.0591}{2}\times\log 10^{14}$$

$$= -\frac{0.0591}{2}\times 14$$

$= -0.0591 \times 7$

$= -0.41$ V

51. Ans. (3)

$$Sn_{(s)} + 2Ag^+_{(aq.)} \rightarrow Sn^{+2}_{(aq.)} + 2Ag_{(s)}$$

no. of e^- transferred = $2e^-$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{\left[Sn^{+2}\right]}{\left[Ag^+\right]^2}$$

$[Ag^+]\uparrow \Rightarrow E_{cell}\uparrow$

52. Ans. (2)

$$E^o_{cell} = -0.35V$$

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

= +ve

non-spontaneous

53. Ans. (1)

$$E^o_{cell} = +\frac{0.0591}{n}\log(K_c)$$

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

= 0.354 V

54. Ans. (3)

$$\Delta G^o = -nFE^o_{cell}$$

(i) $OCl^- + 2e^- \rightarrow Cl^-$; $\Delta G^o_1 = -2\times F\times 0.94$

(ii) $Cl^- \rightarrow \frac{1}{2}Cl_2 + 1e^-$; $\Delta G^o_2 = -1\times F\times(-1.36)$

(iii) $OCl^- + 1e^- \rightarrow \frac{1}{2}Cl_2$; $\Delta G^o_3 = -1\times F\times E^0_3$

(iii) = (i) + (ii)

$$\Delta G^o_3 = \Delta G^o_1 + \Delta G^o_2$$

$$-1\times F\times E^o_3 = [-2\times F\times 0.94] + [-1\times F\times(-1.36)]$$

$$E^o_3 = 0.52V$$

55. Ans. (2)

$$2H^+_{(aq.)} + 2e^- \rightarrow H_{2(g)}$$

pH = 3; $[H^+] = 10^{-3}$M

Nernst equation

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{P_{H_2}}{[H^+]^2}$$

n = 2; $pH_2 = 1atm$; $[H^+] = 10^{-3}$M ; $E^o_{cell} = 0$

$$E_{cell} = 0 - \frac{0.0591}{2}\log\frac{1}{(10^{-3})^2}$$

= −0.177V

56. Ans. (3)

Reaction : $H_{2(g)} + \underset{(0.001M)}{2H^+} \longrightarrow \underset{(10^{-8}M)}{2H^+} + H_{2(g)}$

no. of e^- transferred = $2e^-$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{(10^{-8})^2}{(10^{-3})^2}$$

$E^o_{cell} = 0$; n = 2

$$E_{cell} = 0 - \frac{0.0591}{2}\log\frac{10^{-16}}{10^{-6}}$$

= + 0.295 V

57. Ans. (3)

Cell reaction : $Cu + 2Ag^+ \longrightarrow Cu^{+2} + Ag$

No. of e^- transferred = 2

Initial : $[Cu^{+2}]_i = 1M = [Ag^+]_i$

Final : $[Cu^{+2}]_f = 10M = [Ag^+]_f$

Initial : $E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{[Cu^{+2}]^1_i}{[Ag^+]^2_i} = E^o_{cell}$

Final :

$$E_{cell} = E^o_{cell} - \frac{0.0591}{2}\log\frac{(10)^1}{(10)^2} = E^o + 0.0295V$$

58. Ans. (4)

Cell Reaction :

Cathode

$$3Ni_{(s)} + 2Au^{+3} \longrightarrow 3Ni^{+2} + 2Au_{(s)}$$

(0.1M) (1M)

Anode

n = 6e⁻

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{6}\log\frac{\left[Ni^{+2}\right]^{3}}{\left[Au^{+3}\right]^{2}}$$

$$= \left[E^{o}_{Au^{+3}/Au} - E^{o}_{Ni^{+2}/Ni}\right] - \frac{0.0591}{6}\log\frac{1^{3}}{(10^{-1})^{2}}$$

$$= \left[1.5-(-0.25)\right] - \frac{0.0591}{6}\log 10^{2}$$

= 1.73 V

59. Ans. (3)

At 298K for reaction n = 2

$$\text{So, } E^{o}_{cell} = \frac{0.0591}{n}\log K_{C}$$

$$\log K_{C} = \frac{E^{o}_{cell}\times n}{0.0591}$$

$$= \frac{0.465\times 2}{0.0591}$$

$\log K_C = 15.73$

Taking antilog

$K_C = 3.16\times10^{15}$

60. Ans. (2)

For reaction n = 2

$E_{cell} = 0.5105$ V

Nernst equation

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{2}\log\frac{\left[Zn^{+2}\right]^{1}}{\left[Ni^{+2}\right]^{1}}$$

$$E^{o}_{cell} = E_{cell} + \frac{0.0591}{2}\log\frac{[Zn^{+2}]}{[Ni^{+2}]}$$

$$= 0.5105 + \frac{0.0591}{2}\log\frac{(1)}{(0.1)}$$

= 0.54 V

61. Ans. (3)

Cell reaction :

Anode

$$Fe + 2Fe^{+3} \longrightarrow 3Fe^{+2}$$

Cathode

$$E^{o}_{cell} = \left(E^{o}_{RP}\right)_{cathode} - \left(E^{o}_{RP}\right)_{Anode}$$

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

= 0.771–(–0.441)

= 1.212V

62. Ans. (1)

$$n_{H_2} = \frac{V_{ml}\text{ at STP}}{22400} = \frac{112}{22400} = \frac{1}{200}$$

$$w_{H_2} = n_{H_2}\times(M_w)_{H_2} = \frac{1}{200}\times 2 = \frac{1}{100}\text{g}$$

Faraday I[st] law

$$w_{H_2} = \frac{E_{H_2}}{96500}\times i\times t \qquad \because E_{H_2} = 1$$

$$\frac{1}{100} = \frac{1}{96500}\times i\times 965$$

i = 1 A

63. Ans. (4)

Acc to Faraday II[nd] law :-

For $FeCl_2$ and $FeCl_3$

$$\frac{w_{Fe^{+2}}}{w_{Fe^{+3}}} = \frac{E_{Fe^{+2}}}{E_{Fe^{+3}}}$$

$$\because E_{W} = \frac{M_{w}}{\text{v.f.}}$$

$$= \frac{\frac{56}{2}}{\frac{56}{3}}$$

$$= \frac{3}{2}$$

64. Ans. (3)

Farady I[st] law :-

$$w = \frac{E_{W}}{96500}\times i\times t$$

$$3 = \frac{E_{W}}{96500}\times 9.65\times(10\times 60)$$

$E_W = 50$

65. Ans. (3)

$$1\text{mol} \rightarrow \overset{-2}{H_2O} \longrightarrow \overset{0}{O_2} + 2e^-$$

Loss of e^- = 2mol

Charge transfer = 2F $\quad (\because 1 \text{ mol } e^- = 1F)$

$= 2\times96500C$

$= 1.93\times10^5C$

66. Ans. (1)

Faraday Ist law

$$w = \frac{\frac{\text{At wt}}{\text{v.f.}}}{96500}\times Q \qquad (\because Q = i\times t)$$

$$2.977\,g = \frac{\frac{106.4}{\text{v.f.}}}{96500}\times10800$$

v.f. = +4

67. Ans. (1)

For dil. H_2SO_4

At Cathode : H_2 gas is liberated

At Anode : O_2 gas is liberated

Faraday IInd law :

$$\frac{w_{\text{Cathode}}}{w_{\text{Anode}}} = \frac{E_{H_2}}{E_{O_2}} = \frac{1}{8}$$

68. Ans. (2)

Fused $CaH_2 \longrightarrow Ca^{+2} + 2H^-$

At Cathode : Ca is deposited

At Anode : H_2 is liberated

69. Ans. (3)

Faraday Ist law :

$$w = \frac{E_{Ag}}{96500}\times i\times t$$

$$= \frac{\frac{107.87}{1}}{96500}\times965\times1$$

= 1.0787 g

70. Ans. (3)

Acc. to reaction

1 mol Al deposite an transfer of 3 mol e^- (3 F charge)

1 mol Al ——— 3F charge

$13.5\text{ g} \Rightarrow \frac{1}{2}$ mol Al ——— $\frac{3}{2}$ = 1.5 F charge

71. Ans. (4)

For aq. Na_2SO_4

$SOP_{SO_4^{-2}} < SOP_{H_2O}$

So at anode : O_2 will liberate

$SRP_{Na^+} < SRP_{H_2O}$

Cathode : H_2 will liberate

72. Ans. (2)

$1\text{ F} \Rightarrow 1$ mol e^-

So, $AgNO_3$

$$\downarrow$$

$$Ag^+ + \underset{1\text{mol } e^-}{1e^-} \longrightarrow \underset{1\text{mol Ag}}{Ag}$$

73. Ans. (1)

$BaCl_2 \rightarrow Ba^{+2} + 2Cl^-$

$96500C \Rightarrow 1$ Faraday $\Rightarrow 1$ mol e^-

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

$\qquad\quad\downarrow \qquad\quad \downarrow$

(2F) $\quad$ 2 mol $e^- \rightarrow$ 1 mole barium

$1F \longrightarrow \frac{1}{2}$ mole barium

74. Ans. (2)

Faraday IInd law

$$\frac{w_{Ca}}{w_{Ac}} = \frac{(E_w)_{Ca}}{(E_w)_{Al}}$$

$$\frac{40\times10^3}{w_{Al(g)}} = \frac{\frac{40}{2}}{\frac{27}{3}}$$

w_{Al} = 18000 g

= 18 Kg

75. Ans. (2)

Acc. to Faraday IInd law :

$$w_{Ag} : w_{Cu} : w_{Fe} = E_{w_{Ag}} : E_{w_{Cu}} : E_{w_{Fe}}$$

$$= \frac{108}{1} : \frac{63.5}{2} : \frac{56}{3}$$

Now convert mass in mole = $\frac{w}{\text{At.wt}}$

$$n_{Ag} : n_{Cu} : n_{Fe} = \frac{w_{Ag}}{(\text{At. wt})_{Ag}} : \frac{w_{Cu}}{(\text{At. wt})_{Cu}} : \frac{w_{Fe}}{(\text{At. wt})_{Fe}}$$

$$= \frac{\frac{108}{1}}{108} : \frac{\frac{63.5}{2}}{63.5} : \frac{\frac{56}{3}}{56}$$

$$= \frac{1}{1} : \frac{1}{2} : \frac{1}{3}$$

76. Ans. (2)

For aq. $CuSO_4$

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

At Anode : $2H_2O_{(\ell)} \longrightarrow O_{2(g)} + 4H^+ + 4e^-$

$[H^+]\uparrow \Rightarrow pH\downarrow$

77. Ans. (3)

For aq. NaCl

At cathode : H_2 gas is liberated

At anode : Cl_2 gas is liberated

78. Ans. (1)

On charging lead accumulator, reverse of galvanic cell happen i.e. becomes electrolytic cell.

79. Ans. (3)

Thermodynamic efficiency of cell :

$= \frac{\Delta G}{\Delta H} \times 100$

$= \frac{-nFE}{\Delta H} \times 100$

Exercise-II (Previous Year Questions)

1. Ans. (3)

Balancing $\qquad$ Charge

$MnO_4^{-2} \longrightarrow MnO_4^- + 1e^-$

$\downarrow$

$1\text{mol} \longrightarrow 1\text{mol } e^-$

$0.1\text{mol } MnO_4^{-2} \longrightarrow 0.1 \text{ mol } e^-$

$\Downarrow$

0.1 F

$\Downarrow$

0.1×96500

$= 9650 \text{ C}$

2. Ans. (4)

$n_{O_2} = \frac{V_{ml}}{22400} = \frac{5600}{22400} = \frac{1}{4}$

$w_{O_2} = n_{O_2} \times (M_w)_{O_2}$

$= \frac{1}{4} \times 32 = 8g$

Faraday II[nd] law

$\frac{w_{Ag}}{w_{O_2}} = \frac{E_{Ag}}{E_{O_2}} = \frac{\frac{108}{1}}{8}$

$\frac{w_{Ag}}{8} = \frac{108}{8}$

$w_{Ag} = 108$

3. Ans. (4)

Fuel cell converts combustion energy of fuels like H_2 & CH_4 directly into electrical energy.

4. Ans. (1)

In pure water pH = 7 ; $[H^+] = 10^{-7}$

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

$E_{Cell} = E^o_{Cell} - \frac{0.0591}{2} \log \frac{P_{H_2}}{[H^+]^2}$

$0 = 0 - \frac{0.0591}{2} \log \frac{P_{H_2}}{(10^{-7})^2}$

$0 = \log P_{H_2} - \log 10^{-14}$

$\text{Log } P_{H_2} = \log 10^{-14}$

$P_{H_2} = 10^{-14} \text{ atm}$

5. Ans. (4)

$\lambda_M = \frac{\kappa \times 1000}{M}$

$= \frac{5.76 \times 1000}{0.5}$

$= 11.52 \text{ S cm}^2/\text{mol}$

6. Ans. (4)

Faraday I[st] law :

$w_{Cl_2} = \frac{E_{Cl}}{96500} \times i \times t \qquad \because \quad w_{Cl_2} = n_{Cl_2} \times (M_w)_{Cl_2}$

$7.1 = \frac{\frac{35.5}{1}}{96500} \times 3 \times t \qquad = 0.1 \times 71$

$t = 6600 \text{ Sec} \qquad = 7.1g$

$t = 110\text{min.}$

7. Ans. (3)

Given :- $\quad E^o_{Cell} = -ve$

$\Delta G° = -nF E^o_{Cell}$

$\Rightarrow +ve \text{ or } > 1$

$E^o_{Cell} = \frac{0.0591}{n} \log K$

$\log K < 0$

$K < 1$

8. Ans. (1)

Charge (Q) = i × t

= 1 × 60

= 60 C

no. of e^- $= \dfrac{Q}{\text{Charge on } 1e^-} = \dfrac{60}{1.6\times10^{-19}}$

$= 3.75 \times 10^{20}$

9. Ans. (2)

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

(1M) $(10^{-2}M)$

$$E_1 = E° - \frac{0.00591}{2}\log\frac{|Zn^{+2}|^1}{|Cu^{+2}|^1}$$

$$= E° - \frac{0.0591}{2}\log\frac{10^{-2}}{1} = E° + 0.0591$$

$$E_2 = E° - \frac{0.0591}{2}\log\frac{1}{10^{-2}} = E° - 0.0591$$

$E_1 > E_2$

10. Ans. (4)

$HBrO \xrightarrow{1.5V} BrO_3^-$ ...(i)

$HBrO \xrightarrow{1.595V} Br_2$ ...(ii)

$2HBrO \longrightarrow BrO_3^- + Br_2$

$E^o_{Cell} = \left(E^o_{RP}\right)_C - \left(E^o_{RP}\right)_A$

Spontaneous reaction

$= -1.5 - (-1.595)$

$= +0.095V \Rightarrow$ + ve Value

So HBrO disproportionates to BrO_3^- & Br_2

11. Ans. (3)

$$E^o_{Cell} = \frac{0.0591}{n}\log K_C$$

$$\log K_C = \frac{E^o_{Cell}\times n}{0.0591} = \frac{0.59\times1}{0.0591}$$

$\log K_C = 10$

$K_C = 10^{10}$

12. Ans. (1)

$\Delta G° = -nF E^o_{Cell}$

$= -2 \times 96500 \times 0.24$

$= -46320$ J/mol

$= -46.32$ KJ/mol

13. Ans. (4)

$$\lambda^o_{M_{CH_3COOH}} = \lambda^o_{M_{CH_3COO^-}} + \lambda^o_{M_{H^+}}$$

$$= \lambda^o_{M_{CH_3COO^-K^+}} + \frac{1}{2}\lambda^o_{M_{H_2SO_4}} - \frac{1}{2}\lambda^o_{M_{K_2SO_4}}$$

$$= z + \frac{x}{2} - \frac{y}{2}$$

14. Ans. (2)

More Reducing Power $\Rightarrow$ SRP min

K > Al > Cr > Ag

15. Ans. (2)

$CaCl_2 \longrightarrow Ca^{+2} + 2Cl^-$

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

(2F) 2 mol $e^- \longrightarrow$ 1mol Calcium (40g)

40g Ca $\longrightarrow$ 2 F Charge

20g Ca $\longrightarrow$ 1 F charge

16. Ans. (3)

For dil. H_2SO_4

at Anode H_2O get discharge

So product at anode will be O_2 (gas).

17. Ans. (3)

According to ECS ; max SRP will be of

$Au^{+3} + 3e^- \longrightarrow Au(s)$

18. Ans. (2)

Fuel cell :-

Reactant $\Rightarrow H_{2(g)}$; $O_{2(g)}$

$\downarrow$

Product $\Rightarrow H_2O_{(g)}$

19. Ans. (2)

$$\lambda^\infty_{M_{CH_3COOH}} = \lambda^\infty_{M_{CH_3COO^-}} + \lambda^\infty_{M_{H^+}}$$

$$= \lambda^\infty_{M_{CH_3COO^-Na^+}} + \lambda^\infty_{M_{H^+Cl^-}} - \lambda^\infty_{M_{Na^+Cl^-}}$$

= 91 + 426.16 −126.45

= 390.71

20. Ans. (3)

$$\lambda^o_{M_{CH_3COOH}} = \lambda^o_{M_{CH_3COO^-}} + \lambda^o_{M_{H^+}}$$

= 50 + 350 = 400

$$\alpha = \frac{\lambda^C_M}{\lambda^o_M} = \frac{20}{400} = \frac{1}{20}$$

$\alpha = 5\%$

$K_c = C\alpha^2$

$$= 0.007 \times \left(\frac{1}{20}\right)^2$$

$= 1.75\times10^{-5}$ mol/L

21. Ans. (3)

For non spontaneous $\Rightarrow$ E^o_{Cell} = –ve

$$E^o_{Cell} = \left(E^o_{RP}\right)_C - \left(E^o_{RP}\right)_A$$

$$= E^o_{Cu^{+2}/Cu} - E^o_{Ag^+/Ag}$$

= 0.34 – (0.8)

= –0.46 V

22. Ans. (4)

Acc. to question for O_2 to liberate possible reaction at Cathode & Anode will be :

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

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

So $E^o_{Cell} = \left(E^o_{RP}\right)_C - \left(E^o_{RP}\right)_A$

= 1.51 – (1.223)

= +0.287V

= the sport.

So O_2 gas will liberate

23. Ans. (3)

$$E^o_{Co^{+3}/Co^{+2}} > E^o_{Al^{+3}/Al}$$

So reaction at cathode & Anode will be:-

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

Anode : $Al \longrightarrow Al^{+3} + 3e^-$

$E^o_{Cell} = \left(E^o_{RP}\right)_C - \left(E^o_{RP}\right)_A = 1.81 - (-1.66)$

= + 3.47V

24. Ans. (2)

$\Delta G° = -nF\,E^o_{Cell}$

= –2 × 96500 × 1.1

= –21227 J/mol

= –212.27 kJ/mol

25. Ans. (2)

Centimolar solution = $\frac{1}{100} M = 0.01M$

Conductivity (k) = 0.0210 $ohm^{-1}\ cm^{-1}$

Resistance (R) = 60 ohm

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

$$\Rightarrow 0.0210 = \frac{1}{60}\left(\frac{\ell}{A}\right) \Rightarrow \frac{\ell}{A} = 1.26 cm^{-1}$$

26. Ans. (4)

$\Delta_rG = -nFE_{cell}$

E_{cell} is an intensive property and Δ_rG is an extensive property as it depends on number of $e^{\ominus}$ transferred in cell reaction.

27. Ans. (1)

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

1 mol H_2O will req. 2F charge

(B) $8H^+ + MnO_4^- + 5e^- \to Mn^{+2} + 4H_2O$

1 mole MnO_4^- will req. 5F charge.

(C) $CaCl_2 + 2e^- \to Ca + 2Cl^{-1}$

1.5 mole Ca will req. 3F charge.

(D) $2FeO + H_2O \to Fe_2O_3 + 2H^+ + 2e^-$

1 mole FeO will req. 1 F charge.

(A)-(II), (B)-(IV), (C)-(I), (D)-(III)

28. Ans. (2)

$$W = \frac{Eit}{96487}$$

$$W = \frac{\frac{63}{2} \times 9.6487 \times 100}{96487}$$

W = 0.315 g of Cu

29. Ans. (2)

Production of hydrogen by electrolysis of water is not an example of corrosion.

30. Ans. (1)

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

$\Delta G° = -nF\,E^0_{cell}$

$\Delta G°$ = – 2 × 96487 × 0.32 J

$\Delta G°$ = –61.75 kJ/mol

Exercise-III (Analytical Questions)

1. Ans. (4)

Statement-I : $W_{NonPV} = -\Delta G = W_{electrical}$

Statement-II : $\Delta G = -nFE_{Cell}$

n $\Rightarrow$ no. of e^- transfer depends on & stoichiometry

E_{Cell} $\Rightarrow$ EMF of Cell $\to$ intensive

F $\Rightarrow$ 96500 C

G $\Rightarrow$ extensive property

2. Ans. (3)

Statement-I : For electrolysis of aq. NaCl Product obtained are

Anode :- $2Cl^- \rightarrow Cl_{2(g)} + 2e^-$

Cathode :- $2H_2O_{(\ell)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq.)}$

Statement-II : $E^o_{Cu^{+2}/Cu} > E^o_{Fe^{+2}/Fe}$

Copper is more reactive than iron

3. Ans. (1)

Statement-I : EMF of cell is intensive property

Statement-II : EMF of cell = cell voltage which is intensive

4. Ans. (2)

Statement-I : In electrolytic cell

Cathode is negative

Anode is positive

In galvanic cell

Cathode is positive

Anode is negative

Statement-II : In Daniel cell

Oxidation of Zinc occurs $\Rightarrow$ loss of e^-

Reduction of Copper occurs $\Rightarrow$ gain of e^-

5. Ans. (3)

Statement-I : molten NaH $\Rightarrow Na^+$; H^-

Cathode :- $Na^+ + e^- \rightarrow Na_{(s)}$

Anode :- $2H^+ \rightarrow H_{2(g)} + 2e^-$

Statement-II : In electrolytic refining

Impure metal $\Rightarrow$ Anode

Pure metal $\Rightarrow$ Cathode

6. Ans. (2)

On dilution of weak electrolyte

1.dod $\alpha\% \uparrow \Rightarrow$ no. of ions $\uparrow$

2.Inter ionic attraction forces $\downarrow$

Hence molar conductance increases rapidly.

7. Ans. (1)

Daniel Cell

$Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$

Nernst equation:

$$E_{cell} \quad E^o_{cell} - \frac{0.0591}{2}\log\frac{|Zn^{+2}|^1}{|Cu^{+2}|^1}$$

$$E_{cell} = E^o_{cell} + \frac{0.0591}{2}\log\frac{|Cu^{+2}|^1}{|Zn^{+2}|^1}$$

$[Cu^{+2}]\uparrow \Rightarrow E_{cell} \uparrow$

8. Ans. (4)

Statement-I :

Cell const. $G^* = \frac{\ell}{A}$

depends on Construction of cell.

Statement-II : Conductance is due to charge corries (ions):-

(i) mobility

(ii) no. of charge carrie (ions)

9. Ans. (2)

Min

Mg^{+2}/Mg

Cu^{+2}/Cu

Hg^{+2}/Hg

Ag^+/Ag

max $\downarrow$

SRP

SRP min $\Rightarrow$ metal reactivity $\uparrow$

* Mg^{+2} can not be displaced by Cu.

* Ag can not displace Cu^{+2}

10. Ans. (3)

Spontaneous Condition :-

$\rightarrow$ ΔG = negative

also $\Delta G = -nFE_{cell}$

$\rightarrow$ So E_{cell} = positive

11. Ans. (3)

(a) λ_m - with temp. - because in increase in K.E. of Ions.

(c) increase in concentration, increases inter ionic attraction forces hence λ_M decreases.

(d) Increases in polarity will increase d.o.d (X) Which will increases ions no. so increase in molar conductivity.