Level-II

Chapter 3

Electrochemistry

Solutions

SECTION - A

Objective Type Questions (One option is correct)

1. H_2(1 atm) | 2.26 M HCOOH || 0.222 M CH_3COOH| (1 atm) H_2

   $K_a(HCOOH) = 1.77 \times 10^{-4}$,

   $K_a(CH_3COOH) = 1.8 \times 10^{-5}$

   Emf of the cell is (Neglect the liquid-liquid junction potential)

   (1) 0.0591 V (2) –0.0591 V (3) 0.02955 V (4) –0.02955 V

Sol. Answer (2)

$$HCOOH \rightleftharpoons HCOO^- + H^+$$

$$C_1(1-\alpha) \qquad C_1\alpha \qquad C_1\alpha$$

$$[H^+]_L = C_1\alpha = \sqrt{(K_a)_1 \times C_1}$$

$$CH_3\,COOH \rightleftharpoons CH_3COO^- + H^+$$

$$c_2(1-\alpha) \qquad c_2\alpha \qquad c_2\,\alpha$$

$$\therefore \quad [H^+]_R = \sqrt{(Ka)_2 \times C_2}$$

$$E = E^o - \frac{0.0591}{1}\log\frac{[H^+]_L}{[H^+]_R}$$

$$E = 0 - \frac{0.0591}{1}\log\frac{\sqrt{K_1 \times C_1}}{\sqrt{K_2 \times C_2}}$$

$$\text{or} \quad E = -\frac{0.0591}{2}\log\frac{1.77\times10^{-4}\times2.26}{1.8\times10^{-5}\times0.222}$$

$$E = -\frac{0.0591}{2}\log 100 = -\,0.0591$$

2. Given that

$NiO_2 + 4H^+ + 2e^- \rightarrow Ni^{2+} + 2H_2O$, E° = 1.678 V

$NiO_2 + 2H_2O + 2e^- \rightarrow Ni(OH)_2 + 2OH^-$, E° = –0.49 V

For the following reaction

$Ni(OH)_2 + 2H^+ \rightleftharpoons Ni^{2+} + 2H_2O$

Gibb's free energy change (in kJ mol^{-1}) is

(1) 418.424 (2) –229.284 (3) –418.424 (4) 229.284

Sol. Answer (3)

$$\begin{array}{lll} NiO_2 + 4H^+ + 2e^- & \longrightarrow Ni^{2+} + 2H_2O & , E_1^o = 1.678\text{ V} \\ Ni(OH)_2 + 2OH^- + 2e^- & \longrightarrow NiO_2 + 2H_2O + 2e^-, & E_2^o = +0.49\text{ V} \\ \hline Ni(OH)_2 + 2H^+ & \longrightarrow Ni^{2+} + 2H_2O & , E^o = x\text{ V} \\ \hline \end{array}$$

$$\Delta G^o = \Delta G_1^o + \Delta G_2^o = -nF(E_1^o + E_2^o)$$

$= -2 \times 96500 \times (1.678 + 0.49)$ J mol^{-1}

$= -418.424$ kJ mol^{-1}

3. Emf of cell given, Ag(s), AgCl(s)||KCl(aq)|Hg_2Cl_2(s)|Hg(s) is 0.05 V at 300 K and temperature coefficient of the cell is 3.34×10^{-4} VK^{-1}. Calculate the change in enthalpy of the cell.

(1) 965 (2) 9650 (3) 96500 (4) 96.5

Sol. Answer (2)

$2Ag \rightarrow 2Ag^+ + 2e^-$: (anode)

$Hg_2^{2+} + 2e^- \rightarrow 2Hg$: (cathode)

$\because$ n = 2

$$\Delta H = -nFE_{cell} + nFT\left(\frac{\partial E_{cell}}{\partial T}\right)_P$$

$= 2 \times 96500(300 \times 3.34 \times 10^{-4} - 0.05)$

$= 9650$ J mol^{-1}

4. Given : $Ag^+ + e^- \rightarrow Ag$; $E°_{red} = 0.799$ V

Dissociation constant for $[Ag(NH_3)_2]^+$ into Ag^+ and NH_3 is 6×10^{-14}. Then for the following half-cell reaction:

$[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$, calculate E° at 298 K.

(1) 0.019 V (2) 0.03 V (3) 0.014 V (4) 0.19 V

Sol. Answer (1)

$$\begin{array}{lll} Ag & \longrightarrow Ag^+ + e^- \; ; & E_{OP}^o = -0.799\text{ V} \\ Ag(NH_3)_2^+ + e^- & \longrightarrow Ag + NH_3 ; & E_{RP}^o = ? \\ \hline Ag(NH_3)_2^+ & \rightleftharpoons Ag^+ + 2NH_3 & \\ \hline \end{array}$$

$$E_{cell} = E_{cell}^o + \frac{0.0591}{1}\log_{10}\frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} = 0 \text{ at equilibrium}$$

$\Rightarrow \quad E^{o}_{cell} = 0.0591 \times \log_{10} K_C = 0.0591 \times \log_{10}(6 \times 10^{-14})$

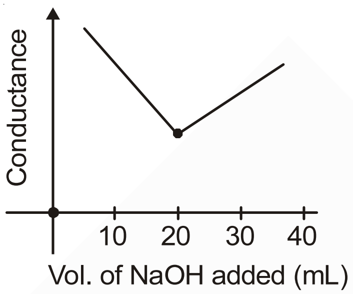
$= -0.780 \text{ V}$

$= E^{o}_{OP(Ag/Ag^{+})} + E^{o}_{RP(Ag(NH_3)_2^{+}/Ag)}$

$\Rightarrow \quad E^{o}_{Ag(NH_3)_2^{+}/Ag} = -0.780 + 0.799$

$= +0.019 \text{ V}$

5. 25 mL of HCl solution is titrated with 0.10 mole.L^{-1} NaOH solution in a conductivity cell. The data obtained were plotted to give the graph shown below.



The concentration of HCl solution is

(1) 0.040 M (2) 0.060 M (3) 0.080 M (4) 0.01 M

Sol. Answer (3)

$(HCl)_{moles} = (NaOH)_{moles}$ at the end point

$$\frac{25}{1000} \times M = 0.10 \times \frac{20}{1000}$$

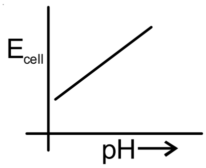
$$M = \frac{0.40}{5} = 0.080 \text{ M}$$

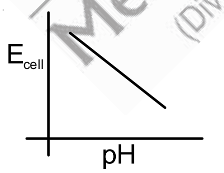
$M_{HCl} = 0.080$ M

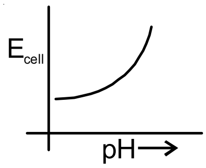
6. The graph that represents the dependence of cell voltage (E_{cell}) on the pH for the reaction at constant temperature is

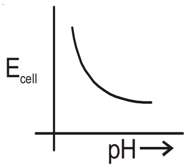
$$2Au^{3+}_{(aq)} + 3H_{2(g)} \longrightarrow 2\,Au_{(s)} + 6H^{+}_{(aq)}$$

(Assume $[Au^{3+}]$ = 1.0 M, it remains constant and constant H_2 gas pressure is maintained)

(1)


(2)


(3)


(4)


Sol. Answer (1)

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{6} \log_{10}[H^{+}]^{6}$$

$$= E^{\circ}_{cell} + \frac{0.0591}{6} \times 6 \times \left(-\log_{10}(H^{+})\right)$$

$$E_{cell} = E^{\circ}_{cell} + 0.0591\,pH$$

$y = c + mx$

7. Electrolytes having same value of constant A in Debye-Huckel-Onsager equation is/are

$$\lambda_m = \lambda_m^o - A\sqrt{c}$$

$MgCl_2$	$CaCl_2$	$MgSO_4$	NaCl
(I)	(II)	(III)	(IV)

(1) (I), (II) & (III) (2) (II), (III) & (IV) (3) (I) & (III) (4) (I) & (II)

Sol. Answer (4)

8. Correct statements from the below is/are

(I) Cell potential of Ni-Cd cell remains constant during its lifetime.

(II) The output of fuel cell is lower than the theoretically expected.

(III) Concentration of H_2SO_4 in Pb-storage battery decreases during charging of the battery.

(IV) The cell potential remains constant in Hg-cell as the overall reaction does not involve ions concentration.

(1) (I), (II) & (III) (2) (I), (II) & (IV) (3) (II), (III) & (IV) (4) (III) & (IV)

Sol. Answer (2)

Facts

9. Methods effective in preventing corrosion is/are

(1) Surface treatment (coating) (2) Anodizing

(3) Galvanisation (4) All of these

Sol. Answer (4)

Fact

10. What happens to pH of an aqueous solution of $CuSO_4$ when it is treated with external source of electricity using inert electrodes? [Assume no change in volume due to electrolysis]

(1) Decreases

(2) Increases

(3) Remains same

(4) First increases and then decreases

Sol. Answer (1)

OH^- ion concentration decreases due to oxidation at anode. Hence H^+ concentration relatively increases and pH will decrease.

11. If A^{3+}, B^{2+} and C^+ reduce at cathode in different experiments. If equal charge is given to each ion and charge to mass ratio of each ion is same, select the correct statement.

[Efficiency is 100% in each experiment and A^{3+}, B^{2+} and C^+ reduce to A, B and C respectively]

(1) Mass deposit of A is maximum among all three ions

(2) Mass deposit of B is maximum among all three ions

(3) Mass deposit of C is maximum among all three ions

(4) Same mass of A, B and C deposit

Sol. Answer (4)

If equal charge is given then equal number of equivalent deposit

[eq. of A = eq. of B = eq. of C]

$$\Rightarrow \left(\frac{\text{Mass of A deposit}\times 3}{\text{Molar mass of A}}\right) = \frac{\text{Mass of B deposit}\times 2}{\text{Molar mass of B}} = \frac{\text{Mass of C deposit}\times 1}{\text{Molar mass of C}}$$

12. The value of ΔG°_{cell} at 298 K for $M(s)/M^{+3} \,||\, A^+/A(s)$ is

$E^\circ_{M^{+3}/M} = x$ $E^\circ_{A^+/A} = y$

(1) $-3F(x + y)$ (2) $3F(x - y)$ (3) $3F(x - 3y)$ (4) $3F(x + y)$

Sol. Answer (2)

$\Delta G^\circ_{cell} = -nF\,E^\circ_{cell}$

$n \Rightarrow 3$

$E^\circ_{cell} = y - x$

$\therefore \quad \Delta G^\circ_{cell} = -3F(y - x) = 3F(x - y)$

13. 965 A current is passed for 5 minute in molten solution and 27 g of metal is deposit at cathode. The possible molten solution is [Assume electrode are inert and 1 Faraday = 96500 C. Current efficiency of process is 100%]

(1) NaCl (2) $MgCl_2$ (3) $AlCl_3$ (4) All of these

Sol. Answer (3)

Number of faraday given $\Rightarrow 965 \times 5 \times 60 = 3$ F

So number of equivalent of metal deposit = 3

14. 0.1 M aqueous solution of KCl having molar conductance x S $cm^2\,mol^{-1}$. If resistance offered by solution is 1000 ohm, then value of cell constant is

(1) $10^{-2}x\ cm^{-1}$ (2) $0.1x\ cm^{-1}$ (3) $x\ cm^{-1}$ (4) $10^2\ cm^{-1}$

Sol. Answer (2)

$$\Lambda_m = \frac{K \times 1000}{M}$$

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

$$\frac{\ell}{A} = KR$$

$$\frac{\Lambda_M \times M}{1000} = K$$

$$\Rightarrow \quad \frac{x \times 0.1}{1000} = K$$

$$\text{cell constant } \left(\frac{\ell}{A}\right) = \frac{x(0.1)}{1000} \times 1000 = 0.1x\ cm^{-1}$$

15. Which of the following is correct reaction for anode in fuel cell?

(1) $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ (2) $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$

(3) $H_2O \rightarrow H^+ + OH^-$ (4) $2O^{2-} \rightarrow O_2 + 4e$

Sol. Answer (2)

16. $\Lambda^{\circ}_{m}AlCl_3$ (in S cm^2 mol^{-1}) is equal to

[Given,

$\Lambda^{\circ}_{m(Al(OH)_3)} = x\ S cm^2\ mol^{-1}$

$\Lambda^{\circ}_{m(HCl)} = y\ S cm^2\ mol^{-1}$

$\Lambda^{\circ}_{m(H_2O)} = z\ S cm^2\ mol^{-1}$

Here $\Lambda^{\circ}_{m} \rightarrow$ limiting molar conductivity]

(1) x + 3y – z (2) x + 3y – 3z (3) x + y – 3z (4) x – 3y + 3z

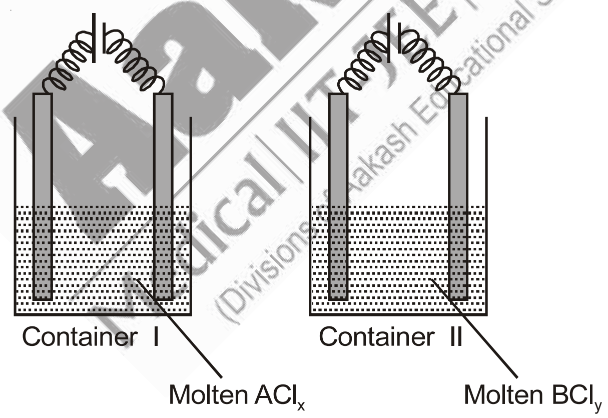
Sol. Answer (2)

$$\Lambda^{\circ}_{m}(AlCl_3) = \Lambda^{\circ}_{m}Al^{3+} + 3\Lambda^{\circ}_{m}Cl^{-}$$

$$\Lambda^{\circ}_{m}(AlCl_3) = \Lambda^{\circ}_{m}Al^{3+} + 3\Lambda^{\circ}_{m}OH^{-1} + 3\Lambda^{\circ}_{m}H^{+} + 3\Lambda^{\circ}_{m}Cl^{-1} - 3\Lambda^{\circ}_{m}H^{+} - 3\Lambda^{\circ}_{m}OH^{-1}$$

$$= x + 3y - 3z$$

17. If equal charge is given in both container and it was found that mass of metal A deposit is same as of mass of metal B deposit. If $\frac{M_B}{M_A} = \frac{3}{2}$. (Given electrodes are inert, M_B and M_A are molar mass of B and A). Then $\left(\frac{x}{y}\right)$ is



(1) 2 (2) $\frac{2}{3}$ (3) $\frac{3}{2}$ (4) 3

Sol. Answer (2)

Equal charge given so

No. of equivalent of A deposit = No. of equivalent of B deposit

$\Rightarrow$ (moles × n-factor)$_A$ = (moles × n-factor)$_B$

$$\Rightarrow \frac{\text{Mass of A deposited}}{M_A} \times x = \frac{\text{Mass of B deposited}}{M_B} \times y \Rightarrow \frac{x}{y} = \frac{M_A}{M_B} = \left(\frac{2}{3}\right)$$

18. $\underset{}{Zn(s)}|\underset{(0.1M)}{ZnSO_4}||\underset{(0.1M)}{CuSO_4}|Cu(s)$ Cell-I

$Zn(s)|\underset{(0.1M)}{ZnSO_4}||\underset{(0.05M)}{Ag_2SO_4}|Ag(s)$ Cell-II

$Cu(s)|\underset{0.1M}{CuSO_4}||\underset{(0.05M)}{Ag_2SO_4}|Ag(s)$ Cell-III

$E^\circ_{Zn^{+2}/Zn} = -x\,V \quad E^\circ_{Cu^{+2}/Cu} = y\,V \quad E^\circ_{Ag^+/Ag} = z\,V$

If x, y and z all have positive values and z > x > y then which cell have highest E°_{cell} at 298 K?

(1) Cell-I (2) Cell-II

(3) Cell-III (4) Cannot be determined

Sol. Answer (2)

E°_{cell} for Cell-I = y + x

E°_{cell} for Cell-II = z + x

E°_{cell} for Cell-III = z – y

19. Which of the following cell have highest E_{cell} at 298K?

(1) $Cu(s)|\underset{0.1M}{CuSO_4}||\underset{0.1M}{CuSO_4}|Cu(s)$

(2) $Cu(s)|\underset{0.01M}{CuSO_4}||\underset{0.1M}{CuSO_4}|Cu(s)$

(3) $Cu(s)|\underset{0.1M}{CuSO_4}||\underset{0.01M}{CuSO_4}|Cu(s)$

(4) $Cu(s)|\underset{1M}{CuSO_4}||\underset{1M}{CuSO_4}|Cu(s)$

Sol. Answer (2)

20. The molar conductivity (in S cm^2mol^{-1}) of aqueous solution of CH_3COOH that have pH = 3 is (Given limiting molar conductivity of CH_3COOH solution is 3900 Scm^2mol^{-1} and dissociation constant of CH_3COOH is 10^{-5}).

(1) 39 (2) 39×10^4 (3) 39×10^{-4} (4) 39×10^{-6}

Sol. Answer (1)

pH = 3, $[H^+] = 10^{-3} = \sqrt{10^{-5} \times C}$

$c = 10^{-1}$

$C\alpha = 10^{-3}$

$\alpha = 10^{-2}$

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} \Rightarrow \Lambda_m = \alpha\Lambda^\circ_m = 39\ Scm^2\,mol^{-1}$$

21. The E°(in V) at 298 K of the given cell is

$A_{(s)} | \underset{(C_1)}{A^{3+}} || \underset{(C_2)}{B^{2+}} | B_{(s)}$

Given

$2A(s) \longrightarrow 2A^{3+} + 6e^-$ $E° = 2x$ V

$3B^{2+} + 6e^- \longrightarrow 3B(s)$ $E° = 3y$ V

(1) y – x (2) y + x (3) 3y + 2x (4) 3y – 2x

Sol. Answer (3)

$E° (A^{3+}/A) = -2x$

$E° (B^{2+}/B) = 3y$

So $E°_{cell} = 3y - (-2x) = 3y + 2x$

22. Equilibrium constant for the given cell at 25°C $A(s)|A^{+3}(aq)||B^{+2}(aq)|B(s)$ is

(Given that $E^{\circ}_{cell} = 0.04$ V and $\frac{2.303RT}{F} = 0.06$ at 25°C)

(1) 10^2 (2) 10^4 (3) 10^{-2} (4) 10^{-4}

Sol. Answer (2)

$2A + 3B^{+2} \longrightarrow 2A^{+3} + 3B$

$$E^{\circ}_{cell} = \frac{0.06}{6} \log K_c$$

$$\log K_c = \frac{0.04 \times 6}{0.06} = 4$$

$$K_c = 10^4$$

23. Which of the following reaction occur at anode in lead-storage battery when battery is in use?

(1) $PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO_{4\,(aq)}^{2-}$

(2) $PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow PbO_{2(s)} + SO_{4\,(aq)}^{-2} + 4H^+ + 2e^-$

(3) $Pb_{(s)} + SO_{4\,(aq)}^{-2} \rightarrow PbSO_{4(s)} + 2e^-$

(4) $PbO_2 + SO_4^{-2} + 4H^+ + 2e \rightarrow PbSO_4 + 2H_2O$

Sol. Answer (3)

Fact

24. For which of the following cell, $E_{cell} = E^{\circ}_{cell}$ at 298 K?

(1) $\underset{(s)}{Zn} \left| \underset{0.1M}{ZnSO_4} \right|\left| \underset{0.1M}{CuSO_4} \right| Cu(s)$ (2) $\underset{(s)}{Zn} \left| \underset{0.1M}{ZnSO_4} \right|\left| \underset{0.1M}{AgNO_3} \right| Ag(s)$

(3) $Cu \left| \underset{0.1M}{CuSO_4} \right|\left| \underset{0.1M}{AgNO_3} \right| Ag(s)$ (4) $\underset{(s)}{Al} \left| \underset{0.1M}{Al^{+3}} \right|\left| \underset{0.1M}{Cu^{+2}} \right| Cu(s)$

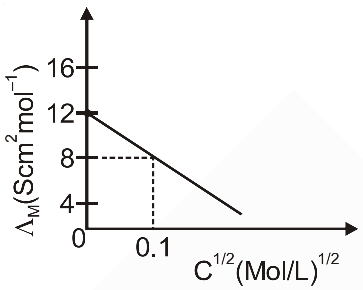
Sol. Answer (1)

$Zn + Cu^{+2} \rightarrow Cu(s) + Zn^{+2}$

Q = 1

$E_{cell} = E^{\circ}_{cell}$

25. A graph is given between molar conductivity and $\sqrt{C}$ (C→concentration) for a strong electrolytic solution. The conductivity (k) of the solution is



(1) 8×10^{-4} S cm^{-1} (2) 8×10^{-5} S cm^{-1} (3) 8×10^{6} S cm^{-1} (4) 8×10^{-6} S cm^{-1}

Sol. Answer (2)

When $\sqrt{C}$ is 0.1, $\Lambda_M = 8$

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

$M = 10^{-2}$ $k = 8 \times 10^{-5}$ S cm^{-1}

SECTION - B

Objective Type Questions (More than one options are correct)

1. Which of following is/are correct?

(1) The metallic conduction is due to the movement of electrons in the metal

(2) The electrolytic conduction is due to the movement of ions in the solution

(3) The metallic conduction increases with increase in temperature whereas electrolytic conduction decreases with increase in temperature

(4) None of these

Sol. Answer (1, 2)

The metallic conduction is due to the presence of electrons in the metal and electrolytic conduction is due to the movement of ions in the solution.

2. Molar conductance of 2 M H_2A acid is 10 S cm^2 mol^{-1}. Molar conductance of H_2A at infinite dilution is 400 S cm^2 mol^{-1}. Which statement is/are correct?

(1) Degree of dissociation is 2.5% and pH of solution is 1.0

(2) Degree of dissociation is 4 and pH of solution is 1.4

(3) Dissociation constant of H_2A is 6.24×10^{-5}

(4) Dissociation constant of H_2A as per $H_2A \rightleftharpoons 2H^+ + A^{2-}$ is 2.56×10^{-4}

Sol. Answer (1, 4)

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} - \frac{10}{400} = \frac{1}{40} = 2.5\%$$

At equation, $H_2A \rightleftharpoons 2H^+ + A^{2-}$

$C(1-\alpha) \quad 2C\alpha \quad C\alpha$

$$K_{eq} = \frac{(2C\alpha)^2 \times C\alpha}{C(1-\alpha)}$$

Putting C = 2 M, α = 0.025

$K_{eq} = 2.56 \times 10^{-4}$

$[H^+] = 2C\alpha = 0.1 = 10^{-1}$

$pH = -\log 10^{-1} = 1$

3. Which compounds have maximum conductivity?

(1) 0.2 M $[Cr(NH_3)_3Cl_3]$ (2) 0.15 M $[Cr(NH_3)_4Cl_2]Cl$

(3) 0.1 M $[Cr(NH_3)_5Cl]Cl_2$ (4) 0.07 M $[Cr(NH_3)_6]Cl_3$

Sol. Answer (2, 3)

$[Cr(NH_3)_4Cl_2]Cl \rightarrow [Cr(NH_3)_4Cl_2]^{2+} + Cl^-$

$\Rightarrow$ 0.15 × 2 = 0.30

and for

$[Cr(NH_3)_5Cl]Cl_2 \rightarrow [Cr(NH_3)_5Cl]^{2+} + 2Cl^-$

$\Rightarrow$ 0.1 × 3 = 0.30

4. For electrolyte A_xB_y which is/are not correct relation between molar conductivity (Λ_M) and equivalent conductivity (Λ_{eq})

(1) $\Lambda_M = xy\ \Lambda_{eq}$ (2) $\Lambda_{eq} = xy\ \Lambda_M$ (3) $x\Lambda_M = y\ \Lambda_{eq}$ (4) $y\Lambda_M = x\ \Lambda_{eq}$

Sol. Answer (2, 3, 4)

For the electrolyte $A_x B_y$

n-factor = xy

$\Lambda_M = (xy)\Lambda_{eq}$

Only 1st option is correct & others are incorrect option.

5. The cell constant of a conductivity cell is defined as (σ = cell constant, l = length between the electrode, A = area, R = resistance, G = conductance, K = conductivity, ρ = specific resistance)

(1) $\sigma = \frac{l}{A}$ (2) $\sigma = \frac{\rho}{R}$ (3) $\sigma = (G\rho)^{-1}$ (4) $\sigma = \frac{G}{K}$

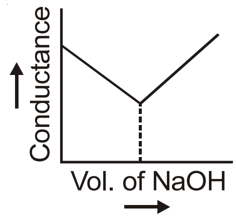
Sol. Answer (1, 3)

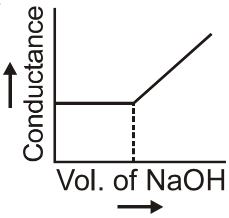
$$R = \rho\frac{l}{A} \Rightarrow \frac{1}{\rho} = \frac{1}{R}\frac{l}{A}$$

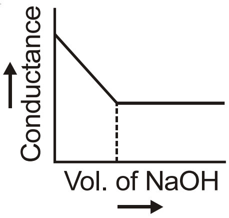
$$K = C \times \frac{l}{A}$$

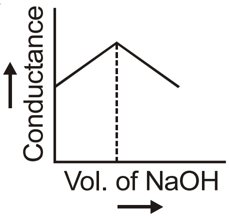
$$\rho = \frac{RA}{l};\ \sigma = \frac{l}{A} \text{ and } \sigma = (G\rho)^{-1}$$

6. Which of following plots will not be obtained for a conductometric titration of HCl and NaOH?

(1) 

(2) 

(3) 

(4) 

Sol. Answer (2, 3, 4)

In the conductometric titration of HCl and NaOH conductance first decreases, reaches a minimum value and then increases.

7. 1.0 L of 0.1 M aqueous solution of KCl is electrolysed. A current of 96.50 mA is passed through the solution for 10 hours. Which is/are correct? (Assume volume of solution remains constant during electrolysis)

(1) After electrolysis molarity of K^+ is 0.064 and molarity of Cl^- is 0.064

(2) After electrolysis molarity of K^+ is 0.1 and molarity of Cl^- is 0.064

(3) At S.T.P. 202 ml of Cl_2 produced when current efficiency is 50%

(4) At S.T.P. 606 ml of total gases produced when current efficiency is 50%

Sol. Answer (2, 3)

i = 96.50 A, t = 10 × 60 × 60 s

Solution is 1.0 L and 0.1 M

Moles present = 1 × 0.1 = 0.1 moles

Reactions :

$2H^+ + 2e \rightarrow H_2 : 2Cl^- \rightarrow Cl_2 + 2e^-$

$$\frac{w}{M} = \frac{it}{nF} = \frac{w}{M} = \frac{96.50 \times 10 \times 60 \times 60 \times 10^{-3}}{2 \times 96500} = 0.018$$

For Cl^- = 0.036; Molarity = 0.1 – 0.036 = 0.064

$$V_{Cl_2} = \frac{0.018 \times 22.4}{2} = 0.202 \text{ L or 202 ml.}$$

K^+ will not discharge.

8. 1000 ml 2 M $CuSO_4$ is electrolysed by a current of 9.65 amp for 2 hours. Which is/are correct?

(1) After electrolysis remaining concentration of Cu^{+2} is 1.64 M using Cu electrode

(2) After electrolysis remaining concentration of Cu^{+2} is 1.64 M using Pt-electrode

(3) When remaining concentration of Cu^{+2} is 1.822 then volume of solution is reduced by 10% using Pt-electrode

(4) 17.15 g copper deposit when current efficiency is 75% using copper electrode

Sol. Answer (2, 3, 4)

No. of moles of $CuSO_4$

= 1000 × 2 = 2000 millimoles = 2 moles

i = 9.65 A; t = 2 hrs = 2 × 60 × 60 s

Cu deposited is $w = \frac{E \times it}{F}$

$\Rightarrow$ $w = \frac{63.5}{\alpha} \times \frac{9.65\times2\times60\times60}{96500} = 22.86$

$n = \frac{W}{M} = 0.36$

$\Rightarrow$ $2 - 0.36 = 1.64$

Hence, molarity = 1.64 M using Pt electrode

$w = \frac{63.5}{2} \times \frac{75}{100} \frac{(9.65)\times2\times60\times60}{96500} = 17.15$ g

9. Which statement is correct about electrolysis of $CuSO_4$?

(1) At cathode Cu will deposit and at anode O_2 will be produced using Pt-electrode

(2) At cathode Cu will not deposit but Cu dissolve at anode using Cu-electrode

(3) At cathode Cu will deposit and at anode O_2 will be produced using Cu-electrode

(4) At cathode Cu will deposit and at anode Cu will dissolve using Cu-electrode

Sol. Answer (1, 4)

Using Pt electrodes

$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$

$H_2O \rightarrow H^+ + HO^-$

At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

Anode : $4HO^- \rightarrow 2H_2O + O_2 + 4e^-$

Products are Cu and O_2

Using Cu electrodes

Anode : $Cu \rightarrow Cu^{2+} + 2\,e^-$

Cathode : $Cu^{2+} + 2\,e^- \rightarrow Cu$

10. Aqueous solution of which electrolyte produces H_2 gas at cathode, when electrolysed among inert electrodes?

(1) NaCl (2) $MgCl_2$ (3) $CuCl_2$ (4) AgCl

Sol. Answer (1, 2)

H^+ has lower discharge potential as compared to Na^+ and Mg^{2+}

Hence, in case of NaCl and $MgCl_2$ reaction is $2H^+ + 2e^- \rightarrow H_2$.

11. For the electrolysis of $CuSO_4$ solution which is/are correct?

(1) Cathode reaction : $2H^+ + 2e \longrightarrow H_2$ using Pt electrode

(2) Cathode reaction : $Cu^{+2} + 2e^- \longrightarrow Cu$ using Cu electrode

(3) Anode reaction : $Cu \longrightarrow Cu^{+2} + 2e^-$ using Cu electrode

(4) Anode reaction : $Cu \longrightarrow Cu^{+2} + 2e^-$ using Pt electrode

Sol. Answer (2, 3)

$CuSO_4$(aq) forms the ions

Cu^{2+}, H^+, HO^- and SO_4^{2-}

Using Pt electrode

At cathode; $Cu^{2+} + 2e \rightarrow Cu$

Using Cu electrodes

At anode : $Cu \rightarrow Cu^{2+} + 2e^-$

12. Which solution(s) become(s) more acidic after the electrolysis using inert electrodes?

(1) NaCl solution (2) $CuSO_4$ solution (3) $AgNO_3$ solution (4) Na_2SO_4 solution

Sol. Answer (2, 3)

In the electrolysis of $CuSO_4$ solution and $AgNO_3$ solution, H_2SO_4 and HNO_3 are formed respectively.

13. $Zn \mid Zn^{+2}(1M) \parallel Ni^{+2}(1\ M) \mid Ni$, Antilog (0.7411) = 5.5

$E^\circ_{Zn^{+2}/Zn} = -0.75\ V,\ E^\circ_{Ni^{+2}/Ni} = -0.24\ V$

Which statement is/are correct for above cell?

(1) Emf of cell is 0.51 V and cell reaction is spontaneous

(2) Emf of cell is –0.51 V and cell reaction is non-spontaneous

(3) Emf of cell is zero when concentration of Ni^{+2} is 5.5×10^{-18} M

(4) Cell reaction is non-spontaneous when concentration of Ni^{+2} is less than 5.5×10^{-18} M

Sol. Answer (1, 3, 4)

The given cell is

$Zn|Zn^{2+}(1M)||Ni^{2+}(1M)|Ni$

$E^o = (0.75) + (-0.24) = 0.51V$

and cell reaction is spontaneous.

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

$\Rightarrow$ E = 0; $[Ni^{2+}] = 5.5 \times 10^{-18}$ M

The cell reaction is

Non-spontaneous when concentration of M^{2+} is less than 5.5×10^{-18} M.

14. Which is/are correct statements about salt bridge?

(1) Velocity of ions of salt bridge are almost equal

(2) Salt bridge completes the electric circuit

(3) Ions of salt bridge discharge at electrode

(4) Ions of salt bridge do not discharge at electrode

Sol. Answer (1, 2, 4)

Salt Bridge contains electrolyte which do not participate in the electrochemical change, completes the cell circuit and it is also necessary that velocity of ions of salt bridge are almost equal.

15. K_{sp} for AgBr = 8×10^{-13}

Ag, $AgNO_3$ (1.0 M) || KBr (1.0 M), AgBr, Ag

For above cell which is/are correct?

(1) $E_{cell} = 0.715$ V (2) $E_{cell} = -0.715$ V

(3) $\Delta G = -1 \times 96500 \times 0.715$ (4) $\Delta G = 1 \times 96500 \times 0.715$

Sol. Answer (2, 4)

For the 1st Half cell

Anode : $Ag \rightarrow Ag^+ + e^-$

Cathode : $Ag^+ + e^- \rightarrow Ag$

$$E = -\frac{0.0591}{1} \log \frac{[Ag^+]_L}{[Ag^+]_R}$$

$$E = -0.0591 \log \frac{1}{[Ag^+]}$$

K_{sp} (AgBr) = $[Ag^+][Br^-]$

$$[Ag^+]_R = \frac{8\times10^{-13}}{1} = 8 \times 10^{-13} \text{ M}$$

$$E = -0.0591 \log \frac{1}{8\times10^{-13}} = -0.0591 \log \frac{10^{13}}{8}$$

$\Rightarrow$ $0.0591 \log 8 \times 10^{-13}$.

$0.0591 (0.6 - 13) = -0.715$ V

and $\Delta G = -nFE = +1 \times 96500 \times 0.715$

16. Which statement is/are correct?

(1) In voltaic cell electrons flow from anode to cathode

(2) In voltaic cell, anode is negative electrode and cathode is positive electrode

(3) Oxidation take place at anode and reduction take place at cathode in electrochemical cell

(4) In electrolytic cell oxidation take place at cathode and reduction take place at anode

Sol. Answer (1, 2, 3)

At cathode always reduction takes place and at anode always oxidation takes place.

Hence (4) will not the correct statement.

17. $E^\circ_{Zn^{+2}/Zn} = -0.76$ V, $E^\circ_{Ni^{+2}/Ni} = -0.24$ V

$E^\circ_{Fe^{+3}/Fe} = -0.04$ V, $E^\circ_{Cd^{+2}/Cd} = -0.40$ V

Which is/are correct statements?

(1) $Zn^{+2} + Cd \longrightarrow Cd^{+2} + Zn$, spontaneous

(2) $Ni^{+2} + Cd \longrightarrow Ni + Cd^{+2}$, spontaneous

(3) $Fe^{+3} + Ni \longrightarrow Ni^{+2} + Fe$, spontaneous

(4) $Cd^{+2} + Zn \longrightarrow Zn^{+2} + Cd$, spontaneous

Sol. Answer (2, 3, 4)

For (1)

$Zn^{2+} + Cd \rightarrow Cd^{2+} + Zn$

$$E^o = E^o_{Cd/Cd^{2+}} + E^o_{Zn^{2+}/Zn} = (0.40) + (-0.76) = -0.36 < 0$$

Non-spontaneous

For $Ni^{2+} + Cd \rightarrow Cd^{2+} + Ni$

$$E^o = E^o_{Cd/Cd^{2+}} + E^o_{Ni^{2+}/Ni} = (0.40) + (-0.24) > 0 \text{ is spontaneous}$$

for $Fe^{3+} + Ni \rightarrow Ni^{2+} + Fe$

$E^o = E^o_{Ni/Ni^{2+}} + E^o_{Fe^{3+}/Fe} = (0.24) + (-0.04) > 0$ i.e. spontaneous

and for reaction

$Cd^{2+} + Zn \rightarrow Zn^{2+} + Cd$

$E^o = E^o_{Zn/Zn^{2+}} + E^o_{Cd^{2+}/Cd} = (0.76) + (-0.40) > 0$ is spontaneous.

18. In which of the following cells, reaction quotient is equal to one?

(1) $Pb|PbC_2O_4, CaC_2O_4, CaCl_2(0.1\ M)||CuSO_4(0.1\ M)\ |\ Cu$

(2) $Zn|ZnSO_4(0.1\ M)||CuSO_4(0.1\ M)|Cu$

(3) $Zn|ZnSO_4(0.1\ M)||Hg_2Cl_2, KCl(0.1\ M)|Hg, Pt$

(4) $Cu|CuSO_4(0.1\ M)||SnCl_2(0.1\ M)|SnCl_4(0.1M), Pt$

Sol. Answer (1, 2)

In (3), Q = 10

In (4), Q = 0.1

19. Which of the following cells give the cell potential to their standard values?

(1) $Zn|Zn^{2+}(0.01\ M)||H_3O^+(0.1\ M)|H_2(1\ atm), Pt$

(2) $Cu|Cu^{2+}(0.25\ M)||Ag^+(0.5\ M)|Ag$

(3) $Cd|Cd^{2+}(0.01\ M)||pH = 1|H_2(1\ atm), Pt$

(4) $Zn|Zn^{2+}(0.1\ M)||pH = 1|H_2(1\ atm), Pt$

Sol. Answer (1, 2, 3)

For $E_{cell} = E^o_{cell}, K_C = 1$.

20. Daniell cell : $\underset{(50\ ml\ 1M)}{Zn|Zn^{+2}(aq)}||\underset{(50\ ml\ 1M)}{Cu^{+2}(aq)|Cu}$ operates as electrolysis cell for 60 min and a current of 0.965 A is passed. Which is/are correct?

$(E^\circ_{Cu^{+2}/Cu} = 0.34\ V,\ E^\circ_{Zn^{+2}/Zn} = -0.76\ V)$

(1) After electrolysis Zn^{+2} concentration is 1.36 M

(2) After electrolysis Cu^{+2} concentration is 0.64 M

(3) After electrolysis Zn^{+2} concentration is 0.82 M

(4) After electrolysis Cu^{+2} concentration is 1.18 M

Sol. Answer (1, 2)

W_{Cu} (deposited) = $\frac{31.75}{96500} \times 0.965 \times 60 \times 60 = 1.143$ g

Total weight of copper = $50 \times 10^{-3} \times 1 \times 63.5 = 3.175$ g

Left weight of copper = 3.175 – 1.143 = 2.032 g

Molarity of Cu^{2+} solution = $\frac{2.032}{63.5} \times \frac{1000}{50} = 0.64$ M

Molarity of Zn^{2+} solution = 1 + 0.36 = 1.36 M

21. Saturated solution of KNO_3 is used to make 'salt-bridge'. Then incorrect option(s) is/are

(1) Velocity of K^+ is zero

(2) Velocity of NO_3^- is zero

(3) Velocity of both K^+ and NO_3^- are nearly the same

(4) KNO_3 is highly soluble in water

Sol. Answer (1, 2)

Fact.

22. Which of following statement(s) is/are correct?

(1) If temperature coefficient is greater than zero, cell reaction is endothermic

(2) If temperature coefficient is less than zero, cell reaction is endothermic

(3) If temperature coefficient is less than zero, cell reaction is exothermic

(4) If E_{cell} is negative then ΔG is negative and cell reaction is spontaneous

Sol. Answer (1, 3)

It is known fact that ΔH and temperature coefficient are related as,

$$\Delta H > 0 \text{ for } \left(\frac{\partial E}{\partial T}\right) > 0$$

$$\text{and } \Delta H < 0 \text{ for } \left(\frac{\partial E}{\partial T}\right) < 0$$

23. The standard emf of the cell

$Fe \mid Fe^{+2}(aq) \mid\mid Cd^{+2} \mid Cd$ is 0.0372 V and temperature coefficient of emf is –0.125 VK^{-1}. Which is/are correct about the cell (at room temperature)?

(1) $\Delta G° = 7.18$ kJ, $\Delta H° = –7196.43$ kJ

(2) $\Delta G° = –7.18$ kJ, $\Delta H° = 7196.43$ kJ

(3) $\Delta G° = –7.18$ kJ, $\Delta H° = –7196.43$ kJ

(4) $\Delta S° = –24.125$ kJ K^{-1}, reaction is spontaneous

Sol. Answer (3, 4)

The emf of cell

$Fe|Fe^{2+}||Cd^{2+}|Cd$, $E^o = 0.0372$

$\therefore \Delta G^o = –nFE^o = – 2 \times 96500 \times 0.0372$

$\therefore \Delta G^o = – 7179.6 \text{ J} = – 7.18 \text{ kJ}$

$$(\Delta S) = nF\left(\frac{\partial E_{cell}}{\partial T}\right)_P$$

$\therefore (\Delta S^o) = 2 \times F \times (–0.125)$

$\Rightarrow – 7180 = – \Delta H^o + 298 \{2 \times 96500 \times 0.125\}$

$\therefore \Delta H^o = – 7196.43$ kJ

24. When a lead-storage battery is discharged, then incorrect option(s) is/are

(1) H_2SO_4 is consumed

(2) Pb is formed

(3) SO_2 is evolved

(4) $PbSO_4$ is consumed

Sol. Answer (2, 3, 4)

Pb is consumed and $PbSO_4$ is formed. SO_2 is not evolved.

25. Which is/are correct about corrosion?

(1) Due to corrosion $FeO.xH_2O$ formed

(2) Due to corrosion $Fe_2O_3.xH_2O$ formed

(3) Presence of air and moisture increases the rate of corrosion

(4) Magnesium is used as sacrificial anode

Sol. Answer (2, 3, 4)

In corrosion

$Fe \rightarrow Fe^{2+} + 2e$ is formed and the formation of oxide i.e., $Fe_2O_3.xH_2O$ takes place and presence of air and moisture is must.

Mg can be used as sacrificial anode.

SECTION - C

Linked Comprehension Type Questions

Comprehension-I

An electrochemical cell is constructed by immersing a piece of copper wire in 50 ml of 0.1 M $CuSO_4$ solution and zinc strip in 50 ml of 0.1 M $ZnSO_4$ solution

$$[E^\circ_{Cu^{+2}/Cu} = 0.34 \text{ V}, \ E^\circ_{Zn^{+2}/Zn} = -0.76 \text{ V}]$$

1. The emf of cell is

(1) 1.07 V (2) 1.1 V (3) 1.3 V (4) 1.13 V

Sol. Answer (2)

$E^o_{Cu^{2+}/Cu} = 0.34$ V and $E^o_{Zn^{2+}/Zn} = -0.76$ V

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

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

$\therefore \quad E = E^o = E^o_{Zn/Zn^{2+}} + E^o_{Cu^{2+}/Cu}$

$\therefore \quad E = (0.76) + (0.34)$

$\therefore \quad E = E^o = 1.1$ V

2. The emf of cell increases when small amount of concentrated NH_3 is added to

(1) $ZnSO_4$ solution (2) $CuSO_4$ solution (3) Both (1) & (2) (4) Can't say

Sol. Answer (1)

When NH_3 is added to $ZnSO_4$ solution, NH_3 reacts with Zn^{2+} in the following manner :

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

i.e., $[Zn^{2+}]$ decreases.

In the equation

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

If $[Zn^{2+}]$ decreases then $\log \frac{[Zn^{2+}]}{[Cu^{2+}]}$ decreases hence, EMF of cell increases.

3. In a separate experiment, 50 ml of 1.5 M NH_3 is added to $CuSO_4$ solution. Emf of the cell is

$$[K_f\,([Cu(NH_3)_4]^{+2}) = 5.88 \times 10^{13}]$$

(1) 0.933 V (2) 1.327 V (3) 1.467 V (4) 0.696 V

Sol. Answer (4)

Due to the complex formation, $[Cu^{2+}]$ decreases & it can be calculated by the reaction,

$$\underset{50\times0.1}{Cu^{2+}} + \underset{50\times1.5}{4HN_3} \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

$$[Cu^{2+}] = \frac{[Cu(NH_3)_4]^{2+}}{[NH_3]^4 \times k_f} = \frac{\frac{50\times0.1}{100}}{(0.55)^4 \times 5.88\times10^{13}} = 9.3 \times 10^{-15}\ M$$

$$E_{cell} = 1.1 - \frac{0.0591}{2}\log\left(\frac{0.1}{9.3\times10^{-15}}\right) = 0.715\ V$$

Thus, the e.m.f. of cell decreases.

Comprehension-II

Molar conductivity of ions are given as product of charge on ions to their ionic mobilities and Faraday constant $\lambda_{A^{n+}} = n\mu_{A^{n+}}F$ (here μ is the ionic mobility of A^{n+}). For electrolytes say A_xB_y, molar conductivity is given by $\lambda_{m(A_xB_y)} = xn\mu_{A^{n+}}F + ym\lambda_{A^{m-}}F$.

ions	ionic mobility
K^+	7.616×10^{-4}
Ca^{+2}	12.33×10^{-4}
Br^-	8.09×10^{-4}
SO_4^{-2}	16.58×10^{-4}

1. The equivalent conductance of $CaSO_4$ at infinite dilution is

(1) 279 (2) 28.51×10^{-4} (3) 31.82×10^{-4} (4) 306

Sol. Answer (1)

Equivalent conductance of $CaSO_4$ is the sum of ionic conductance of Ca^{2+} & SO_4^{2-} .

$$\Lambda^\infty_{CaSO_4} = \Lambda^\infty_{Ca^{2+}} + \lambda^\infty_{SO_4^{2-}}$$

$$\Lambda^\infty_{Ca^{2+}} = \left(\mu_{Ca^{2+}}\right) F$$

$$\Lambda^\infty_{SO_4^{2-}} = \left(\mu_{SO_4^{2-}}\right) F$$

$\mu_{Ca^{2+}}$ & $\mu_{SO_4^{2+}}$ are ionic mobilities

$$\Lambda^\infty_{CaSO_4} = F\ \{12.33 + 16.58\} \times 10^{-4}$$

$$\Lambda^\infty_{CaSO_4} = 96500 \times 10^{-4} \times 28.91 = 278.98 \approx 279$$

$\therefore$ Equivalent conductance of $CaSO_4$ is 279.

2. If degree of dissociation of $CaSO_4$ solution is 10% then equivalent conductance of $CaSO_4$ is

(1) 27.9 (2) 2.851×10^{-4} (3) 3.182×10^{-4} (4) 30.6

Sol. Answer (1)

We know that

$$\alpha = \frac{\Lambda_C}{\Lambda^\infty}$$

$\Rightarrow$ $(0.1) = \dfrac{\Lambda_C}{(279)}$

$\Lambda_C = 279 \times (0.1) = 27.9$

$\Rightarrow$ Equivalent conductance = 27.9

Comprehension-III

Given below are a set of half-cell reactions (in acidic medium) alongwith their E° (in volt) values.

$I_2 + 2e^- \longrightarrow 2I^-$ $E^\circ = 0.54$

$Cl_2 + 2e^- \longrightarrow 2Cl^-$ $E^\circ = 1.36$

$Mn^{+3} + e^- \longrightarrow Mn^{+2}$ $E^\circ = 1.50$

$Fe^{+3} + e^- \longrightarrow Fe^{+2}$ $E^\circ = 0.77$

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ $E^\circ = 1.23$

1. Among the following, identify the correct statement

(1) Cl^- is oxidised by O_2 (2) Fe^{+2} is oxidised by iodine

(3) I^- is oxidised by chlorine (4) Mn^{+2} is oxidised by chlorine

Sol. Answer (3)

2. While Fe^{+3} is stable, Mn^{+3} is not stable in acid solution because

(1) O_2 oxidises Mn^{+2} to Mn^{+3} (2) O_2 oxidises both Mn^{+2} to Mn^{+3} and Fe^{+2} to Fe^{+3}

(3) Fe^{+3} oxidises H_2O to O_2 (4) Mn^{+3} oxidises H_2O to O_2

Sol. Answer (4)

3. The strongest reducing agent in aqueous solution is

(1) I^- (2) Cl^- (3) Mn^{+2} (4) Fe^{+2}

Sol. Answer (1)

SECTION - D

Matrix-Match Type Questions

1. Match the following.

Column-I **Complex (with coordination number of Co^{3+} as equal to six)**	**Column-II** **Maximum molar conductivity (S cm^2 mol^{-1})**
(A) $CoCl_3.6NH_3$	(p) 97
(B) $CoCl_3.5NH_3$	(q) 0
(C) $CoCl_3.4NH_3$	(r) 404
(D) $CoCl_3.3NH_3$	(s) 229

Sol. Answer A(r), B(s), C(p), D(q)

$[Co(NH_3)_6]\ Cl_3$ will give maximum number of ions(4) because of which conductivity is maximum *i.e.* 404.

In $[Co(NH_3)_3Cl_3]$ no ions are given.

Hence molar conductivity is zero.

$[Co(NH_3)_5Cl]Cl_2$ & $[Co(NH_3)_4Cl_2]\ Cl$ forms 3 & 2 ions.

2. Match the following.

Column-I	Column-II (Amount of charge used for diposition/liberation)
(A) 1 mol Al^{+3}	(p) F
(B) 2.3 gm of Na^+	(q) 3 F
(C) 3.6 gm of Mg^{+2}	(r) 0.1 F
(D) 11.2 L H_2 at S.T.P.	(s) 0.3 F

Sol. Answer A(q), B(r), C(s), D(p)

(A) 1 mole Al^{3+}

$$\frac{w}{E} = \frac{it}{F} \Rightarrow it = \frac{wF}{E}$$

$$it = 3\left(\frac{wF}{M}\right) = \frac{wF}{E} = 3F$$

(B) 2.3 g Na^+

$$it = \frac{w}{E}F = \frac{2.3}{23}F = 0.1\ F$$

(C) 3.6 g of Mg^{2+}

$$it = \frac{3.6}{12}F = 0.3\ F$$

(D) $\frac{11.2}{22.4} = \frac{1}{2}\ (n_{H_2})$

$$\frac{w}{E} = \frac{it}{F} \Rightarrow it = \frac{w}{E}F$$

$$= 2\left(\frac{w}{M}\right)F$$

$$= 2\times\frac{1}{2}F = F$$

3. Match the following.

Column-I	Column-II
(A) κ, specific conductance	(p) $\frac{\wedge_m^c}{\wedge_m^\infty}$
(B) $\wedge_m$, molar conductance	(q) $\wedge_m^\infty$
(C) α, degree of dissociation	(r) Decreases with dilution
(D) Kohlrausch law	(s) Decreases with increase in concentration of strong electrolytes

Sol. Answer A(r), B(s), C(p), D(q)

(A) Specific conductance decreases with dilution

(B) Molar conductance decreases with increase in concentration of electrolyte

(C) $\propto = \frac{\wedge_m}{\wedge_m^\infty}$ and decreases with dilution

(D) Resistance $\propto \frac{l}{A}$ and decreases with dilution

4. Match the following.

	Column-I		Column-II
(A)	Calomel electrode	(p)	Electrolyte concentration cell
(B)	$Zn\text{-}Cd(C_1)\,|CdCl_2|\,Zn\text{-}Cd(C_2)$	(q)	Metal-insoluble anion half cell
(C)	Quinhydrone electrode	(r)	Electrode concentration cell
(D)	$Pt|H_2(1\ atm)|H^+(C_1)||H^+(C_2)|H_2(1\ atm)|Pt$	(s)	Redox half cell

Sol. Answer A(q), B(r), C(s), D(p)

5. Match the following.

	Column-I (Electrolysis)		Column-II (Observation)
(A)	Aqueous solution of NaCl using inert electrodes	(p)	Metal loss at anode
(B)	Very dilute aqueous solution of NaCl using mercury cathode	(q)	Chlorine gas evolved at anode
(C)	$CuSO_4$ using copper electrodes	(r)	Oxygen gas evolved at anode
(D)	50% H_2SO_4 solution	(s)	A compound with peroxide bond is formed

Sol. Answer A(q), B(r), C(p), D(s)

SECTION - E

Assertion-Reason Type Questions

1. STATEMENT-1 : The molar conductivity of strong electrolyte decreases with increase in concentration.

and

STATEMENT-2 : At high concentration, migration of ion is slow.

Sol. Answer (1)

Molar conductance is given by the following expression

$$\mu = (K \times V) = \frac{K \times 1000}{c}$$

Here 'c' is the concentration

More is the concentration lesser is the molar conductance

Hence, both statements are correct and statement-2 is the correct explanation of statement-1.

2. STATEMENT-1 : Electrolysis of molten $PbBr_2$ using platinum electrodes produces Br_2 at anode.

and

STATEMENT-2 : Br_2 is obtained in gaseous state at room temperature.

Sol. Answer (3)

$PbBr_2 \rightarrow Pb^{2+} + 2Br^-$

At cathode :

$Pb^{2+} + 2e^- \rightarrow Pb$

At anode :

$2Br^- \rightarrow Br_2 + 2e^-$

Br_2 obtained in liquid state at room temperature.

$\therefore$ Statement-1 is correct and statement-2 is false.

3. STATEMENT-1 : For the concentration cell, $Zn(s)\left|\underset{C_1}{Zn^{+2}(aq)}\right|\left|\underset{C_2}{Zn^{+2}(aq)}\right|Zn$ for spontaneous cell reaction $C_1 < C_2$.

and

STATEMENT-2 : For concentration cell, $E_{cell} = \frac{RT}{nF}\log_e\frac{C_2}{C_1}$ for spontaneous reaction $E_{cell} = +ve \Rightarrow C_2 > C_1$.

Sol. Answer (1)

The given cell is

$Zn|Zn^{2+}(C_1)||Zn^{2+}(C_2)|Zn$

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

$$E_{Zn/Zn^{2+}} = E^o_{Zn/Zn^{2+}} - \frac{0.0591}{2}\log(C_1)$$

$$E_{Zn^{2+}/Zn} = E_{Zn^{2+}/Zn} - \frac{0.0591}{2}\log\left(\frac{1}{C_2}\right)$$

$$\therefore \quad E = (E^o_{Zn/Zn^{2+}} + E^o_{Zn^{2+}/Zn}) - \frac{0.0591}{2}\log\left(\frac{C_1}{C_2}\right)$$

$\therefore$ EMF of cell

$$E = \frac{-0.0591}{2}\log\left(\frac{C_1}{C_2}\right)$$

$$\log\left(\frac{C_1}{C_2}\right) < 0 \text{ for spontaneity}$$

$$\log\left(\frac{C_1}{C_2}\right) < \log 1$$

$\therefore$ $C_1 < C_2$.

$\therefore$ Statement-1 and statements-2 is correct and it is also the correct explanation.

4. STATEMENT-1 : A saturated solution of KCl is used to make salt bridge in concentration cells.

and

STATEMENT-2 : Mobility of K^+ and Cl^- are nearly same.

Sol. Answer (1)

Mobilities of ions involved in salt bridge is same which is used in concentration cells.

5. STATEMENT-1 : The molar conductance of weak electrolyte at infinite dilution is equal to sum of molar conductances of cations and anions.

and

STATEMENT-2 : Kohlrausch's law is applicable for strong electrolytes.

Sol. Answer (2)

$$\mu_{AB}^{\infty} = \mu_{A^+}^{\infty} + \mu_{B^-}^{\infty}$$

Kohlraush law is applicable for weak electrolyte and not for strong electrolyte.

6. STATEMENT-1 : When a copper wire is placed in a solution of $AgNO_3$, the solution acquires blue colour.

and

STATEMENT-2 : E^o_{RP} of Cu^{+2}/Cu is lesser than $E^o_{Ag^+/Ag}$.

Sol. Answer (1)

$Cu + AgNO_3 \rightarrow Cu^{2+} + Ag$

E^o for reaction is positive because $E^o_{Cu^{2+}/Cu} < E^o_{Ag^+/Ag}$

7. STATEMENT-1 : $\Delta G° = -nFE°$.

and

STATEMENT-2 : E° should be positive for a spontaneous reaction.

Sol. Answer (2)

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

But ΔG^o does not decide the spontaneity only ΔG decides the spontaneity of reaction.

$\therefore$ Both statements are correct but statement-2 is not the correct explanation.

8. STATEMENT-1 : One coulomb of electric charge deposits the weight that is equal to electrochemical equivalent of substance.

and

STATEMENT-2 : One faraday deposits one mole of substance.

Sol. Answer (3)

One faraday deposits one equivalent of substance.

9. STATEMENT-1 : If an aqueous solution of NaCl is electrolysed, the product obtained at the cathode is H_2 gas and not Na.

and

STATEMENT-2 : Gases are liberated faster than metals.

Sol. Answer (3)

$NaCl \rightleftharpoons Na^+ + Cl^-$

$H_2O \rightleftharpoons H^+ + OH^-$

Among cations, hydrogen has higher standard electrode potential and among anions chlorine has low standard electrode potential. Thus, at cathode preferentially H_2 gas is evolved, and at anode Cl_2 gas is evolved.

10. STATEMENT-1 : $H_2 + O_2$ fuel cell gives a constant voltage throughout its life.

and

STATEMENT-2 : In this fuel cell, H_2 reacts with OH^- ions, yet the overall concentration of OH^- ions does not change.

Sol. Answer (1)

In $H_2 + O_2$ fuel cell,

Anode : $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(\ell) + 4e^-$

Cathode : $O_2(g) + 2H_2O(\ell) + 4e^- \rightarrow 4OH^-(aq)$

OH^- consumed is reformed, so $[OH^-]$ does not change.

Hence, fuel-cell gives constant voltage throughout its life.

SECTION - F

Integer Answer Type Questions

1. The half cell potentials of a half cell $| A^{(x+n)+}, A^{x+} | Pt$ were found to be as follows:

% of reduced form	24.4	48.8
Half cell potential (V)	0.101	0.115

Determine the value of '*n*'.

Sol. Answer (2)

$$A^{(x+n)+} + ne^- \rightarrow A^{x+}$$

$$0.101 = E^o_{RP} + \frac{0.059}{n}\log\left(\frac{75.6}{24.4}\right)$$

$$0.115 = E^o_{RP} + \frac{0.059}{n}\log\left(\frac{51.2}{48.8}\right) \quad \Rightarrow n \simeq 2$$

2. The standard reduction potential of $E^o_{Bi^{3+}/Bi}$ and $E^o_{Cu^{2+}/Cu}$ are 0.226 V and 0.344 V respectively. A mixture of salts of Bi and Cu at unit concentration each is electrolysed at 25°C. At what value of $-\log[Cu^{2+}]$ does Bismuth starts to deposit during electrolysis?

Sol. Answer (4)

The passage of current would initially deposit Cu^{2+} till $E_{Cu^{2+}/Cu}$ becomes 0.266 V because then only Bi^{3+} will be deposited.

$$\text{Thus, } E_{Cu^{2+}/Cu} = E^o_{cu^{2+}/Cu} + \frac{0.059}{2}\log[Cu^{2+}]$$

$$0.266 = 0.344 + \frac{0.059}{2}\log(Cu^{2+}) \Rightarrow -\log[Cu^{2+}] = 4$$

3. A cell is containing two H electrodes. The negative electrode is in contact with a solution of pH = 6. EMF of the cell is 0.118 V at 25°C. Calculate pH at positive electrode.

Sol. Answer (4)

$$E_{cell} = 0.059\log\frac{[H^+]\text{cathode}}{[H^+]\text{anode}} = 0.059\ [\text{pH anode} - \text{pH cathode}]$$

0.118 = 0.059 [6 – pH]

pH = 4

4. How many faradays of electricity is required to deposit 2 mol copper from $CuSO_4$ solution?

Sol. Answer (4)

Equivalent weight of copper = 63.5/2

Hence, 2 mol require 4 F electricity.

5. A current of 3 ampere has to be passed through a solution of $AgNO_3$ solution to coat a metal surface of 80 cm^2 with 0.005 mm thick layer for a duration of approximately $(y)^3$ seconds. What is the value of y?

(Density of Ag is 10.5 g/cm^3)

Sol. Answer (5)

Volume of surface = 80 × 0.0005

= 0.04 cm^2

W_{Ag} = 0.04 × 10.5 = 0.42 gram

$$= \frac{Eit}{96500}$$

$$\Rightarrow \quad 0.42 = \frac{108 \times 3 \times t}{96500} \Rightarrow t = 125.09 \text{ s} = y^3$$

$\Rightarrow$ $y \approx 5$

6. The cost at 5 paise per kWh of operating an electric motor for 8 hours, which takes 15 ampere at 110 V, is 11y paise. Calculate y.

Sol. Answer (6)

Total energy consumed for 8 hours = iVt

$= 15 \times 110 \times 8 \times 10^{-3}$ kWh = 13.2 kWh

Total cost = 5 × 13.2 = 66 paise

11y = 66

$\Rightarrow$ y = 6

7. Water is reduced to H_2 at 298 K according to the given reaction

$$H_2O(\ell) + e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-(aq)$$

The reduction potential of cell at standard state is –x V, then value of [100x] is, where [ ] represents greatest integer function $\left[\text{Use, } \frac{2.303RT}{F} = 0.059 \text{ and } K_w = 10^{-14} \text{ at } 298\text{ K}\right]$

Sol. Answer (82)

1. $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$, $\Delta G_1^o = -RT\ln K_w$

2. $H^+ + e^- \longrightarrow \frac{1}{2}H_2(g)$, $\Delta G_2^o = 0$

3. $H_2O(l) \longrightarrow \frac{1}{2}H_2(g) + OH^-(aq)$, $\Delta G_3^o = -nFE^o_{H_2O/H_2}$

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

$-nFE^o_{H_2O/H_2} = -RT\ln K_w$

$$E^o_{H_2O/H_2} = \frac{0.059}{1}\log(10^{-14}) = -0.826$$

$\therefore$ $100x \simeq 82.6$, $[100x] = 82$

8. Consider the following standard reduction potentials

Electrode	Potential E^o
(a) $AgCl(s) + e^- \longrightarrow Ag + Cl^-$	0.222 V
(b) $AgBr(s) + e^- \longrightarrow Ag + Br^-$	0.03 V
(c) $AgI(s) + e^- \longrightarrow Ag + I^-$	–0.15 V
(d) $Ag_2S(s) + 2e^- \longrightarrow 2Ag + S^{2-}$	–0.69 V
(e) $AgNO_3(aq) + e^- \longrightarrow Ag + NO_3^-$	+0.8 V

On the basis of this information, how many acids from the following can produce $H_2(g)$ on reaction with Ag(s)?

HCl, HBr, HI, H_2S, HNO_3

[Assume H_2S completely dissociates into $2H^+$ and S^{2-}]

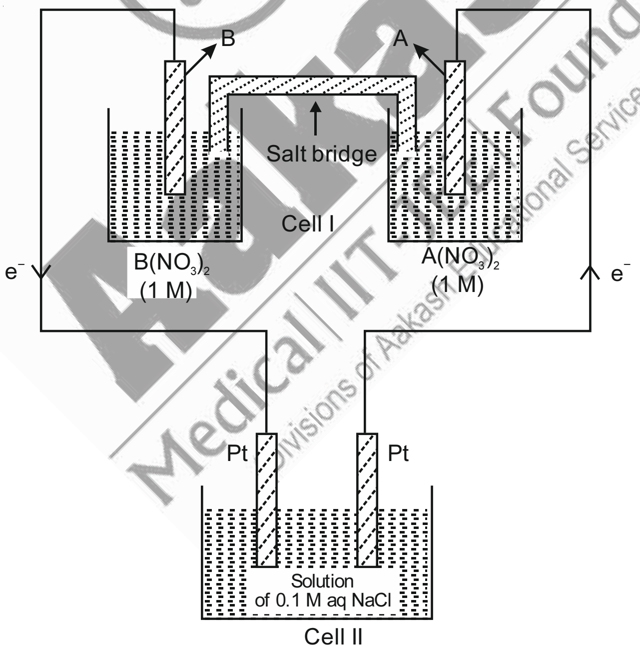
Sol. Answer (2)

If E^o_{cell} is positive then H_2 is produced.

$Ag + H^+ + I^- \longrightarrow AgI + \frac{1}{2}H_2 \qquad E^o = 0.151\ V$

$Ag + H_2S \longrightarrow Ag_2S + H_2(g) \qquad E^o = 0.692\ V$

9. Consider the data and diagram given below



$E^o_{A^{2+}/A} = 1\ V$

$E^o_{B^{2+}/B} = -0.93\ V$

$1\ F = 96500\ C\ mol^{-1} \qquad T = 298\ K$

Molar conductivity of 0.1 M aq. NaCl solution is found $1\ S\ cm^2\ mol^{-1}$ when measured in a conductivity cell that has cell constant $0.1\ cm^{-1}$. A constant current from cell I (electrochemical cell) flows to cell II (electrolytic cell) for 10^5 second. (Assume that potential of cell I is maintained constant during the operation).

If the mass of H_2 liberated at cathode in cell II is $a \times 10^{-b}$ kg (scientific notation), then the value of $a^2 + b^2$ is

Sol. Answer (40)

V = E.M.F of electrochemical cell

E.M.F = E^o = 1.93 V

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

$$1 = \frac{1000 \times K}{0.1}, \ K = 10^{-4}\,S\ cm^{-1}$$

$$R = \frac{1}{10^{-4}} \times 0.1 = 1000\ \Omega$$

$$i = \frac{1.93}{1000}$$

$$Q = i \times t = \frac{1.93 \times 10^5}{1000} = 193\ C$$

$$Q(\text{in Farad}) = \frac{193}{96500} = 0.002$$

Mol of H_2 = 0.001

Mass of H_2 = 0.002 g = 2 × 10^{-3} g = 2 × 10^{-6} kg

a = 2, b = 6 ⇒ $a^2 + b^2 = 40$

10. Consider the concentration cell Pt | $H_2(1\,atm), H^+(a_{H^+} = x) || H^+(a_{H^+} = 0.1), H_2(1\,atm)$ | Pt

E at 298 K is 0.118 V. Calculate the pH of the unknown solution

Sol. Answer (3)

$$E = -\frac{0.059}{1}\log\frac{x}{0.1}$$

$$0.118 = 0.059\log\frac{0.1}{x}$$

$$\log\left(\frac{0.1}{x}\right) = 2 \ \Rightarrow \ \frac{0.1}{x} = 10^2$$

x = 10^{-3}

pH = 3

11. How many statements are correct?

(i) At equilibrium, E_{cell} = zero is always satisfied.

(ii) Electrical conductance of metal depends on valence electrons per atom.

(iii) Electrical conductivity of graphite is more than diamond.

(iv) In conductivity cell, alternating current is used.

(v) Product of electrolysis is also dependant on the metal used as electrode.

(vi) As concentration increases, molar conductivity of weak electrolyte decreases more sharply than strong electrolyte.

Sol. Answer (6)

At equilibrium, $E_{cell} = 0$

$$E^o = \frac{0.059}{n}\log k$$

12. Experiment I : Molten solution of LiH is electrolysed by using inert electrode. If 1 F charge is given then x and y g of metal or gas is deposited / liberated at respective electrode.

Experiment II : Aqueous solution of $NaNO_3$ is electrolysed by using inert electrodes. If 1 F charge is given then p and z g of metal or gas is deposited / liberated at respective electrode. Find the value of x + y + p + z if molar mass of Li, H_2, O_2, Na and N_2 are 7 g/mol, 2 g/mol, 32 g/mol, 23 g/mol and 28 g/mol respectively.

Sol. Answer (17)

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

Mass of H_2 = 1 g

Cathode $Li^+ + 1e^- \longrightarrow Li(s)$

Mass of Li = 7 g

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

Mass of $O_2 = \frac{1}{4} \times 32 = 8$ g

Cathode $H_2O \longrightarrow \frac{1}{2}H_2 + OH^- + 1e^-$

Mass of $H_2 = \frac{1}{2} \times 2 = 1$ g

13. A saturated solution in PQ(s) and PR(s) has conductivity of 290×10^{-10} Scm^{-1}. If K_{SP} of PQ(s) and PR(s) are 3×10^{-14} and 1×10^{-14} respectively. The limiting molar conductivity of P^+, Q^- and R^- are 50 $Scm^2\ mol^{-1}$, x $Scm^2\ mol^{-1}$ and 200 $Scm^2\ mol^{-1}$ respectively. The value of x is

Sol. Answer (60)

$$PQ(s) \rightleftharpoons \underset{S_1+S_2}{P^+(aq)} + \underset{S_1}{Q^+(aq)}$$

$$PR \rightleftharpoons \underset{S_1+S_2}{P^+(aq)} + \underset{S_2}{R^+(aq)}$$

$$\frac{S_1}{S_2} = 3$$

$S_1 = 3[S_2]$

$$S_2 = \sqrt{\frac{10^{-14}}{4}} = 5\times10^{-8}\ M$$

$S_1 = 15 \times 10^{-8}$ M $\qquad (S_1 + S_2) = 20 \times 10^{-8}$ M

$$K = \sum c_i\lambda_i$$

$$10\times10^{-10} = \frac{20\times10^{-8}\times50}{1000} + \frac{x\times15\times10^{-8}}{1000} + \frac{200\times5\times10^{-8}}{1000}$$

290 = 100 + 1.5x + 100

90 = 1.5x

x = 60 S cm^2 mol^{-1}

14. Consider the following cell

Ag(s) | AgCl(s) | KCl(1M) | H^+(1M) | H_2(g) (1 atm) | Pt(s)

e.m.f of cell is decreased by how many of the factors given below?

(i) On increasing concentration of H^+ in cathodic compartment

(ii) On decreasing concentration of H^+ in cathodic compartment

(iii) On increasing concentration of Cl^- in anodic compartment

(iv) On decreasing concentration of (Cl^-) in anodic compartment

(v) On increasing Ag(s) in anodic compartment

(vi) On increasing pressure of H_2 in cathodic compartment

Sol. Answer (3)

Factor (ii), (iv) and (vi)

$$E_{cell} = E^o_{Ag^+/Ag} + 0.059\log\left(\frac{Cl^- \times H^+}{K_{sp}\times pH_2}\right)$$

❑ ❑ ❑