Chapter 3

Electrochemistry

Solutions

SECTION - A

Objective Type Questions

(Metallic/Electrolytic Conductors, Conductivity, Kohlrausch's Law)

- 1. The resistance of 0.0025 M solution of K_2SO_4 is 326 ohm. The specific conductance of the solution, if cell constant is 4.
 - (1) 4.997×10^{-4} (2) 5.997×10^{-7} (3) 6.997×10^{-4} (4) 1.20×10^{-2}
- **Sol.** Answer (4)

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \left(\frac{I}{a} \right) \qquad \Rightarrow \quad \frac{1}{326} \times 4 = 1.20 \times 10^{-2}$$

- 2. The conductivity of four electrolytes P, Q, R, S in ohm⁻¹ cm⁻¹ are as follows P(5×10^{-5}), Q(1×10^{-10}), R(7×10^{-8}); S(9.2×10^{-3}). The one which offers highest resistance to the passage of electric current is
 - (1) P (2) S (3) R (4) Q
- Sol. Answer (4)

Conductivity (κ), $\kappa = \frac{1}{R} \times \text{Cell constant}$ $\begin{bmatrix} \kappa \propto \frac{1}{R} \end{bmatrix} \longrightarrow \text{Resistance}$

$$\left. \stackrel{\sim}{=} \frac{1}{R} \right| \longrightarrow \text{Resistance}$$

(Q) has minimum conductivity so, maximum resistance

(Electrolysis, Quantitative aspects of Electrolysis and Faraday's laws)

3. The coulombic charge on one mole electron is

(1) 1.6×10^{-19} C (2) 96500 C (3) 6.02×10^{-23} C (4) 1.6×10^{-23} C

Sol. Answer (2)

Charge on *i.e.*, = -1.6×10^{-19} C On 1 mole e⁻ \Rightarrow |1.6 × 10⁻¹⁹ × N_A| 96500 C \longrightarrow known as 1 faraday

- Zn rod is placed in 100 mL of 1M CuSO₄ solution so that molarity of Cu²⁺ changes to 0.7 M. The molarity of SO₄²⁻ at this stage will be
 - (1) 0.8 M (2) 1 M (3) 0.7 M (4) 1.8 M

Sol. Answer (2)

 $CuSO_4 \longrightarrow Cu^{+2} + SO_4^{-2}$ 1m 1m 1m

after reaction SO_{4}^{-2} becomes spectator ion so, their concentration will not change.

- The time taken by the galvanic cell which operates almost ideally under reversible conditions at a current of 5. 10⁻¹⁶A to deliver 1 mole of electron is
 - (1) 19.30×10^{20} s (2) 4.825×10^{20} s (3) 9.65×10^{20} s (4) 3.4×10^{11} s

Sol. Answer (3)

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Q = it, charge on 1 mole of electrons = 1 Faraday = 96500 C $96500 = 10^{-16} \times t$

 $t = \frac{96500}{10^{-16}} = 96500 \times 10^{16} \implies 9.65 \times 10^{20} \text{ sec}$

6. A direct current deposits 54 g of silver (atomic mass = 108) during the electrolysis. The same quantity of electricity would deposit aluminium (atomic mass = 27) from aluminium chloride in molten state equal to

(A) ==

(1) 4.5 g (2) 5.4 g (3) 54 g (4) 27 g
Sol. Answer (1)

$$\frac{w_1}{w_2} = \frac{E_1}{E_2} \implies \frac{54}{w_2} = \frac{\frac{108}{\frac{27}{3}}}{\frac{27}{3}}$$

$$\therefore w_2 = \frac{54 \times 9}{108} = 4.5 g$$

During the electrolysis of water 4 mol of electrons were transferred from anode to cathode. The total volume 7. of gases produced at STP will be approximately

(2) 22.4 L (3) 44.8 L (1) 67.2 L (4) 89.4 L

Sol. Answer (1)

By electrolysis of H_2O \longrightarrow H_2 (cathode) \longrightarrow 11.2 L 16.8 L (Total) for 1 faraday O_2 (anode) \longrightarrow 5.6 L

So, for 4 mole of electrons = 4 faraday

⇒ 4 × 16.8 L = 67.2 L

8. The quantity of electricity required to reduce 12.3 g of nitro benzene to aniline assuming 50% current effeciency is

(1) 115800 C (2) 57900 C (3) 231600 C (4) 28950 C

Sol. Answer (1)



Current efficiency =
$$\frac{\text{Given wt.}}{\text{Deposited wt. (Theoritical)}} \times 100$$
$$\frac{50}{100} = \frac{12.3}{\text{w}}$$
$$w = \frac{12.3 \times 100}{50} = 24.6$$
$$w = \frac{\text{E}}{96500} \times \text{Q}$$
$$24.6 = \frac{\text{Mol.wt. of nitrobenzene}}{96500 \times 6(\text{n-factor of nitrobenzene})} \times \text{Q}$$
$$24.6 = \frac{123}{96500} \times \frac{1}{6} \times \text{Q}$$
$$Q = \frac{24.6 \times 96500 \times 6}{123} = 115,800 \text{ C}$$

9. A 100 watt, 110 volt lamp is connected in series with an electrolytic cell containing CdSO₄ solution, the weight of Cd deposited by the current for 10 hrs is (At. wt. of zCd = 112.4)

(1) 19.06 g (2) 38.12 g (3) 1.906 g (4) 3.812 g
Sol. Answer (1)

$$P = I.V$$

 $I = \frac{P}{V} = \frac{100}{110}$
 $w = \frac{E}{96500} \times it$
 $\Rightarrow \frac{112.4}{2} \times \frac{100}{110} \times 10 \times 60 \times 60 = 19.06 g$

- 10. The two platinum electrodes fitted in a conductance cell are 1.5 cm apart while the cross sectional area of each electrode is 0.75 cm². What is the cell constant?
 - (1) 1.25 cm (2) 0.5 cm (3) 2.0 cm^{-1} (4) 0.2 cm^{-1}
- Sol. Answer (3)

Cell constant
$$=\frac{l}{a}=\frac{1.5}{0.75}=2 \text{ cm}^{-1}$$

11. A current of 2.0 A is passed for 5 hours through a molten metal salt deposits 22.2 g of metal (At. mass: 177). The oxidation state of the metal in metal salt is

$$w = \frac{E}{96500} \times it$$

$$w = \frac{Atomic mass}{n - factor} \times it$$

n-factor (oxidation-state)

 $\Rightarrow \quad \frac{\text{Atomic mass} \times i \times t}{96500 \times w} = \frac{177 \times 2 \times 5 \times 60 \times 60}{96500 \times 22.2} = 2.97 \simeq 3$

- 12. A current of 0.965 ampere is passed through 500 ml of 0.2 M solution of ZnSO₄ for 10 minutes. The molarity of Zn²⁺ after deposition of zinc is
 - (1) 0.1 M (2) 0.5 M (3) 0.8 M (4) 0.194 M
- Sol. Answer (4)

 $M = \frac{W_1}{M \times V(L)}$ $0.2 = \frac{W_1 \times 1000}{65 \times 500}$

 $w_1 = 6.5g$

Deposited mass after passing electricity,

$$w_2 = \frac{\frac{65}{2}}{96500} \times 0.965 \times 10 \times 60 = 0.195 \text{ g}$$

left mass of $(Zn^{+2}) \rightarrow w_1 - w_2 = 6.5 - 0.195 = 6.305$

So,
$$M = \frac{6.305 \times 1000}{65 \times 500} = 0.194 M$$

13. Electrolysis of H₂SO₄ (conc.) gives the following at anode

(1) H_2 (2) O_2 (3) $H_2S_2O_3$ (4) $H_2S_2O_8$

At Anode

Sol. Answer (4)

Electrolysis of concentration $H_2SO_4 \rightarrow H^+ + HSO_4^-$

At Cathode

 $2H^{+} + 2e^{-} \rightarrow H_{2}$ $2H^{+} + 2e^{-} \rightarrow H_{2}$ $H_{2}S_{2}O_{8} + 2e^{-}$ \downarrow Marshall acid

(Electrochemical Cell, Commercial Cells or Batteries, Corrosion of Metals)

14. In SHE, the pH of the acid solution should be

Sol. Answer (3)

In SHE \rightarrow concentration of solution is 1 MHCI \rightarrow H⁺ + Cl⁻ pH = -log(H⁺) = -log(1) = 0

15. E.M.F. of Ni(s)|Ni²⁺ (aq) || Cu²⁺ (aq)|Cu(s) cell can be increased by

- (1) Adding NH₃ in the right half-cell
- (2) Increasing the conc. of Ni²⁺ ions
- (3) Adding dimethyl glyoxime into the left half-cell
- (4) Changing the electrolyte present in salt bridge

Sol. Answer (3)

$$\begin{split} \mathsf{N}\mathsf{i} + \mathsf{Cu}^{+2} & \longrightarrow \mathsf{Cu} + \mathsf{N}\mathsf{i}^{+2} \\ \mathsf{E} = \mathsf{E}^\circ + \frac{0.059}{2} \log \frac{[\mathsf{N}\mathsf{i}][\mathsf{Cu}]\mathsf{N}^{+2}]}{[\mathsf{Cu}][\mathsf{N}\mathsf{i}^{+2}]} \\ (1) \quad \mathsf{Cu}^{+2} + 4 \quad \mathsf{NH}_3 \longrightarrow [\mathsf{Cu}(\mathsf{NH}_3)_3]^{+2} \\ \textit{i.e., Concentration of } \mathsf{Cu}^{+2} \text{ decreases which decreases (E)} \\ (2) \quad (\mathsf{N}\mathsf{i}^{+2}) \text{ increases} \rightarrow \mathsf{E} \text{ decreases} \\ (3) \quad \mathsf{CH}_3 - \mathsf{C} - \mathsf{N} - \mathsf{OH} \\ & \qquad \mathsf{II} \\ & \qquad \mathsf{Ch}_3 - \mathsf{C} - \mathsf{N} - \mathsf{OH} \\ & \qquad \mathsf{II} \\ & \qquad \mathsf{Complex} \\ & \qquad \mathsf{(dimethyl glyoxime)} \\ & \qquad \mathsf{or dmg} \\ \textit{i.e., concentration of } \mathsf{N}\mathsf{i}^{+2} \text{ decreases} \rightarrow \mathsf{E}_{\mathsf{cell}} \text{ increases} \\ \mathbf{16. For given cell; } \mathsf{Zn} \mid \mathsf{Zn}^{+2} (\mathsf{C}_1) \mid \mid \mathsf{Zn}^{+2} (\mathsf{C}_2) \mid \mathsf{Zn}; \Delta\mathsf{G} \text{ is negative if} \\ & \qquad \mathsf{(1)} \quad \mathsf{C}_1 = \mathsf{C}_2 \\ & \qquad \mathsf{(2)} \quad \mathsf{C}_1 > \mathsf{C}_2 \\ \mathbf{20. C}_1 = \mathsf{C}_1 \\ \mathbf{20. Answer (3)} \\ \\ \mathsf{Zn} \mid \mathsf{Zn}^{+2} \mid \mathsf{Zn}^{+2} \mid \mathsf{Zn} \\ & \qquad \mathsf{(C_2)} \quad \longrightarrow \text{ This is concentration cell} \\ \\ \mathsf{E} = \mathsf{E}^\circ + \frac{0.059}{2} \log \frac{(\mathsf{Zn}^{+2}) \operatorname{ cathode}}{(\mathsf{Zn}^{+2}) \operatorname{ ande}} \\ & \qquad \mathsf{E}_{\mathsf{cell}} = \mathsf{O} + \frac{0.059}{2} \log \frac{\mathsf{C}_2}{\mathsf{C}_1} \\ & \qquad \mathsf{If} \quad \mathsf{C}_2 > \mathsf{C}_1 \rightarrow \mathsf{E}_{\mathsf{cell}} = \mathsf{positive then } \Delta\mathsf{G} \Rightarrow (-)\mathsf{n}\mathsf{FE}_{\mathsf{cell}}^{+\mathsf{ve}} \Rightarrow \mathsf{ negative} \\ \\ \mathbf{17. The emf of the cell, Zn} \mathsf{Zn} \mathsf{Zn}^{2/4} \mathsf{Ag} \mathsf{is independent of} \\ \end{array}$$

(1) The volume of Zn²⁺ and Ag⁺ solution

- (2) The molarity of Zn^{2+} ions in solution
- (3) The molarity of Ag⁺ions in solution
- (4) Temperature

Sol. Answer (1)

$$E = E^{\circ} + \frac{0.059}{2} \log \frac{[Ag^+]}{[Zn^{+2}]}$$

Volume of both $\rm Ag^{+}$ and $\rm Zn^{+2}$ remain same so, it does not effect $\rm E_{cell}$

18. Standard cell voltage for the cell Pb/Pb²⁺||Sn²⁺/Sn is -0.01V. If the cell is to exhibit $E_{cell} = 0$, the value of log [Sn²⁺] /[Pb²⁺] should be

(1) 0.33 (2) 0.5 (3) 1.5 (4) -0.5

Sol. Answer (1)

$$E = E^{\circ} + \frac{0.059}{2} \log \frac{[Sn^{+2}]}{[Pb^{+2}]}$$
$$0 = -0.01 + \frac{0.059}{2} \log \frac{(Sn^{+2})}{(Pb^{+2})}$$

$$\begin{array}{ll} 0.01 = \frac{0.059}{2} \log \frac{(\text{Sn}^{+2})}{(\text{Pb}^{+2})} \\ \\ \log \frac{(\text{Sn}^{+2})}{(\text{Pb}^{+2})} & \Rightarrow & \frac{0.01 \times 2}{0.059} & \Rightarrow & 0.33 \end{array}$$

19. The voltage of a cell whose half cell reactions are given below is

$$Mg^{2+} + 2e^{-} \longrightarrow Mg(s); E = -2.37 V$$

$$Cu^{2+} + 2e^{-} \longrightarrow Cu(s); E = +0.34 V$$
(1) -2.03 V
(2) 1.36 V
(3) 2.71 V
(4) 2.03 V

Sol. Answer (3)

 $E^{\circ} = E^{\circ}_{Cathode} - E^{\circ}_{Anode}$ The higher value of S.R.P shows cathodic reaction and lower value shows anodic reaction = 0.34 - (-2.37) = 2.71 V

- 20.The hydrogen electrode is dipped in a solution of pH = 3 at 25°C. The reduction potential of the electrode would be
(1) 0.177 V(2) 0.087 V(3) -0.177 V(4) 0.059 V
- **Sol.** Answer (3)

 $pH = 3, pH = -log_{10}(H^{+}) \qquad (H^{+}) = 10^{-3}, 2H^{+} + 2e^{-} \rightarrow H^{2}$ $3 = -log_{10}(H^{+}) \qquad E^{\circ}_{S.H.E} = 0, P_{H_{2}} = 1, log10 = 1$

$$E = E^{\circ} + \frac{0.059}{2} \log \frac{(H^{+})^{2}}{P_{H_{2}}}$$

$$\Rightarrow 0 + \frac{0.059}{2} \log \frac{(10^{-3})^{2}}{1}$$

$$\Rightarrow \frac{0.059}{2} (-6) \times \log 10 \Rightarrow (-)0.059 \times 3 = -0.177 \text{ V}$$

21. Zn | Zn²⁺_(ag) || Cu²⁺_(ag) | Cu E° for the cell is 1.10 V at 25°C. The equilibrium constant for the cell reaction is of the order of

(1) 10^{-37} (2) 10^{37} (3) 10^{-17} (4) 10^{17}

Sol. Answer(2)

$$E^{\circ} = \frac{0.059}{2} \log K_{C}$$

$$1.10 = \frac{0.059}{2} \log_{10} K_{C}$$

$$\log_{10} K_{C} = \frac{1.10 \times 2}{0.059}$$

$$\log_{10} K_{C} = 37.2 \approx 37$$

$$K_{C} = 10^{37}$$

22. What will be the emf of the given cell?

 $Pt | H_{2(P1)} | H_{(aq)}^+ | H_{2(P2)} | Pt$

(1)
$$\frac{RT}{F} \ln \frac{P_1}{P_2}$$
 (2) $\frac{RT}{2F} \ln \frac{P_1}{P_2}$ (3) $\frac{RT}{F} \ln \frac{P_2}{P_1}$ (4) $\frac{RT}{2F} \ln \frac{P_2}{P_1}$

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Sol. Answer (2)

$$E = E^{\circ} - \frac{0.059}{2} \log \frac{(P_{H_2}) \text{ Cathode}}{(P_{H_2}) \text{ Anode}}$$

$$\Rightarrow \quad 0 - \frac{0.059}{2} \log \frac{p_2}{p_1}$$

$$\Rightarrow \quad 0 - \frac{0.059}{2} \log \frac{p_2}{p_1}$$

$$E^{\circ}_{S.H.E.} = 0$$
or
$$E = \frac{0.059}{2} \log \frac{p_1}{p_2}$$
or
$$E = \frac{2.303 \text{ RT}}{2 \text{ F}} \log \frac{p_1}{p_2} = \frac{\text{RT}}{2 \text{ F}} \ln \frac{p_1}{p_2}$$
Which of the following can evide function function (2.5)

23. Which of the following can oxidise fluoride ions?

(1) O_3 (2) CI_2 (3) Br_2 (4) No chemical substance

Sol. Answer (4)

 F^- can never oxidised by other oxidising agent because F_2 itself is strong oxidising agent due to maximum standard reduction potential.

Reactivity↓]

- 24. If the standard reduction potential E° for four divalent elements X, Y, Z, W are -1.46 V, -0.36V, 0.15 V and -1.24 V respectively then
 - (1) X will replace Z²⁺ from aqueous solution
 - (2) Y will replace Z²⁺ from aqueous solution
 - (3) W will replace Z²⁺ from aqueous solution
 - (4) All statements are correct.

Sol. Answer (4)

S.R.P or oxidising power
$$\begin{array}{c} Z > Y > W > X \\ Reactivity \downarrow \end{array} \qquad [S.R.P^{\uparrow} = \\ so, \begin{bmatrix} X \rightarrow will \text{ replace, } (Z, Y, W) \\ Y \rightarrow will \text{ replace} \rightarrow Z \\ W \rightarrow will \text{ replace} \rightarrow Z \text{ and } Y \end{bmatrix} all \text{ are correct}$$

more reactive metal replace less reactive metal.

- 25. The following facts are available
 - $2A^{-} + B_{2} \longrightarrow 2B^{-} + A_{2}$ $2C^{-} + B_{2} \longrightarrow \text{No reaction}$ $2D^{-} + A_{2} \longrightarrow 2A^{-} + D_{2}$

Which of the following statement is correct?

(1)
$$E^{o}_{C^{-}/C_{2}} > E^{o}_{B^{-}/B_{2}} > E^{o}_{A^{-}/A_{2}} > E^{o}_{D^{-}/D_{2}}$$

(2) $E^{o}_{C^{-}/C_{2}} < E^{o}_{B^{-}/B_{2}} < E^{o}_{A^{-}/A_{2}} < E^{o}_{D^{-}/D_{2}}$
(3) $E^{o}_{C^{-}/C_{2}} < E^{o}_{B^{-}/B_{2}} > E^{o}_{A^{-}/A_{2}} > E^{o}_{D^{-}/D_{2}}$

(4) Can't predict

Sol. Answer (2)

According to given reactions

- B₂ can oxidise A⁻, and cannot oxidise C⁻
- A₂ can oxidise D⁻

So, reduction potential
$$\rightarrow$$
 $\begin{array}{ccc} C_2 & > B_2 & > & A_2 & > & D_2 \\ \hline & & & & & \\ (C) \text{ can reduced but not oxidised by } D^- \end{array}$ (A) reduced by D^-

So, oxidation potential \rightarrow C_2 < B_2 < A_2 < D_2

SECTION - B

Previous Years Questions

Consider the change in oxidation state of Bromine corresponding to different emf values as shown in the diagram 1. below :

$$BrO_{4}^{-} \xrightarrow{1.82 \text{ V}} BrO_{3}^{-} \xrightarrow{1.5 \text{ V}} HBrO$$
$$Br^{-} \xrightarrow{1.0652 \text{ V}} Br_{2} \xleftarrow{1.595 \text{ V}}$$

Then the species undergoing disproportionation is

(1)
$$BrO_3^-$$
 (2) Bi

Sol. Answer (3)

$$HBrO \longrightarrow Br_{2}^{+1}, E_{HBrO/Br_{2}}^{0} = 1.595 V$$
$$HBrO \longrightarrow BrO_{3}^{-}, E_{BrO_{3}^{-}/HBrO}^{0} = 1.5 V$$

 E^{o}_{cell} for the disproportionation of HBrO,

$$E_{cell}^{o} = E_{HBrO/Br_{2}}^{o} - E_{BrO_{3}}^{o}/HBrO}$$

= 1.595 - 1.5
= 0.095 V = + ve

Hence, option (3) is correct answer.

[NEET-2018]

2

In the electrochemical cell, Zn|ZnSO₄(0.01M)||CuSO₄(1.0 M)|Cu, the emf of this Daniel cell is E₁. When the concentration of ZnSO₄ is changed to 1.0 M and that of CuSO₄ changed to 0.01 M, the emf changes to E₂.

From the following, which one is the relationship between E_1 and E_2 ? (Given, $\frac{RT}{F} = 0.059$) [NEET-2017]

(1) $E_1 = E_2$ (2) $E_1 < E_2$ (3) $E_1 > E_2$ (4) $E_2 = 0 \neq E_1$

Sol. Answer (3)

Zn|ZnSO₄(0.01 M)||CuSO₄(1.0 M)|Cu

$$\therefore \quad \mathsf{E}_1 = \mathsf{E}_{\mathsf{cell}}^{\mathsf{o}} - \frac{2.303\mathsf{RT}}{2\times\mathsf{F}} \times \log\frac{(0.01)}{1}$$

When concentrations are changed

- $\therefore \quad \mathsf{E}_2 = \mathsf{E}_{\mathsf{cell}}^{\mathsf{o}} \frac{2.303\mathsf{RT}}{2\mathsf{F}} \times \mathsf{log}\frac{1}{0.01}$ *i.e.*, $\mathsf{E}_1 > \mathsf{E}_2$
- If the E^o_{cell} for a given reaction has a negative value, which of the following gives the correct relationships for the values of ΔG° and K_{eq}? [NEET (Phase-2) 2016]

(1) $\Delta G^{\circ} > 0; K_{eq} < 1$ (2) $\Delta G^{\circ} > 0; K_{eq} > 1$ (3) $\Delta G^{\circ} < 0; K_{eq} > 1$ (4) $\Delta G^{\circ} < 0; K_{eq} < 1$

Sol. Answer (1)

 $\begin{array}{ll} \because & \mathsf{E}^{\circ}_{\mathsf{cell}} = -\mathsf{ve} \\ \\ \therefore & \Delta \mathbf{G}^{\circ} = +\mathsf{ve} \And \mathsf{K}_{\mathsf{eq}} = -\mathsf{ve} \ \textit{i.e., } \Delta \mathbf{G}^{\circ} > 0 \And \mathsf{K}_{\mathsf{eq}} < 1 \end{array}$

- 4. The molar conductivity of a 0.5 mol/dm³ solution of AgNO₃ with electrolytic conductivity of 5.76 × 10⁻³ S cm⁻¹ at 298 K [NEET-Phase-2-2016]
 - (1) $2.88 \text{ S cm}^2/\text{mol}$ (2) $11.52 \text{ S cm}^2/\text{mol}$ (3) $0.086 \text{ S cm}^2/\text{mol}$ (4) $28.8 \text{ S cm}^2/\text{mol}$

Sol. Answer (2)

$$n_{\rm m} = \frac{\kappa \times 1000}{M} = \frac{5.76 \times 10^{-3} \times 1000}{0.5} = 11.52 \text{ S cm}^2/\text{mol}$$

- During the electrolysis of molten sodium chloride, the time required to produce 0.10 mol of chlorine gas using a current of 3 amperes is [NEET-Phase-2-2016]
 - (1) 55 minutes (2) 110 minutes (3) 220 minutes (4) 330 minutes

Sol. Answer (2)

For 1 mole Cl₂, 2 F electricity is required

.:. For 0.1 mole Cl₂, 0.2 F electricity will be required

∴ Q = I × t

or,
$$t = \frac{Q}{I} = \frac{0.2 \times 96500}{3 \times 60} \approx 110$$
 min.

6. The number of electrons delivered at the cathode during electrolysis by a current of 1 ampere in 60 seconds is (charge on electron = 1.60 × 10⁻¹⁹ C) [NEET-Phase-2-2016]

(1)
$$6 \times 10^{23}$$
 (2) 6×10^{20} (3) 3.75×10^{20} (4) 7.48×10^{23}

Sol. Answer (3)

Q = I × t
= 1 A × 60 s = 60 C
∴ No. of electrons =
$$\frac{60}{1.602 \times 10^{-19}}$$
 = 3.75 × 10²⁰

7. Zinc can be coated on iron to produce galvanized iron but the reverse is not possible. It is because

- (1) Zinc is lighter than iron
- (2) Zinc has lower melting point than iron
- (3) Zinc has lower negative electrode potential than iron
- (4) Zinc has higher negative electrode potential than iron

Sol. Answer (4)

$$E^{\circ}_{Zn^{2(+)}/Zn} = -0.76 V$$

 $E^{\circ}_{Fe^{2(+)}/Fe} = -0.44 V$

8. The pressure of H_2 required to make the potential of H_2 – electrode zero in pure water at 298 K is

[NEET-2016]

[NEET-Phase-2-2016]

(1) 10 ⁻⁴ atm	(2) 10 ⁻¹⁴ atm	(3) 10 ⁻¹² atm	(4) 10 ⁻¹⁰ atm
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Sol. Answer (2)

2H⁺ + 2e⁻ → H₂(g)

$$E = E^{\circ} - \frac{0.0591}{2} \times \log \frac{P_{H_2}}{[H^+]^2} = 0 - \frac{0.0591}{2} \times \log \frac{P_{H_2}}{(10^{-7})^2}$$
∴ For potential of H₂ electrode to be zero, P_{H2} should be 10^{-14} i.e., $\log \frac{10^{-14}}{10^{-14}} = 0$
9. Aqueous solution of which of the following compounds is the best conductor of electric current?
[Re-AIPMT-2015]
(1) Ammonia, NH₃ (2) Fructose, C₆H₁₂O₆ (3) Acetic acid, C₂H₄O₂ (4) Hydrochloric acid, HCl
Sol. Answer (4)
In aqueous medium, HCl easily ionises to H[⊕] and Cl⁽⁻⁾, thus the HCl solution would be the best conductor of all the given options.
10. A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as **[AIPMT-2015]**
(1) Ni-Cd cell (2) Fuel cell (3) Electrolytic cell (4) Dynamo
Sol. Answer (2)
Fact
11. When 0.1 mol MnO₄²⁻ is oxidised the quantity of electricity required to completely oxidise MnO₄²⁻ to MnO₄ is **[AIPMT-2014]**
(1) 96500 C (2) 2 × 96500 C (3) 9650 C (4) 96.50 C
Sol. Answer (3)
 $\frac{q}{96500} = n-factor × 0.1$

q = 1 × 0.1, ∴ q = 9650 C

- 12. The weight of silver (At. Wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of O₂ at STP will be [AIPMT-2014]
 - (1) 5.4 g (2) 10.8 g (3) 54.0 g (4) 108.0 g
- Sol. Answer (4)

$$\frac{Wt(Ag)}{108} \times 1 = \frac{V_{O_2}}{22.4} \times 4$$
$$\frac{Wt(Ag)}{108} = \frac{6500}{22400} \times 4$$
$$Wt(Ag) = \frac{108 \times 4}{4}$$
$$Wt(Ag) = 108 \text{ g}$$

13. A button cell used in watches functions as following

4

Sol. Answer (4)

$$E^{\circ} = E^{\circ}_{Cathode} - E^{\circ}_{Anode} \implies 0.34 - (-0.76) = 1.10 V$$

- At 25°C molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is 9.54 ohm⁻¹ cm² mol⁻¹ and at infinite dilution its molar conductance is 238 ohm⁻¹ cm² mol⁻¹. The degree of ionisation of ammonium hydroxide at the same concentration and temperature is [NEET-2013]
 - (1) 20.800% (2) 4.008% (3) 40.800% (4) 2.080%

Sol. Answer (2)

$$\begin{array}{c} \wedge_{\rm m}^{\rm C} = 9.54\,\Omega^{-1}\,{\rm cm}^2\,{\rm mol}^{-1} \\ \wedge_{\rm m}^{\infty} = 238\,\Omega^{-1}\,{\rm cm}^2\,{\rm mol}^{-1} \end{array} \right| \qquad \qquad \alpha = \frac{\wedge_{\rm m}^{\rm C}}{\wedge_{\rm m}^{\infty}} = \frac{9.54}{238} = 0.04008 = 0.04008 = 4.008\%$$

15. A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of pH = 10 and by passing hydrogen gas around the platinum wire at one atm pressure. The oxidation potential of electrode would be?

[NEET-2013]

(1) 0.59 V (2) 0.118 V (3) 1.18 V (4) 0.059 V

Sol. Answer (1)

 \therefore pH = 10 \therefore $\left[H^{\oplus}\right] = 10^{-10}$ M

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

 $E_{reduction} = E^\circ - \frac{0.059}{2} \log \frac{P_{H_2}}{(H^+)^2}$, \therefore $E_{S,H,E}^\circ = 0$
 $= 0 - \frac{0.059}{2} \log \frac{1}{(10^{-10})^2} = \frac{0.059}{2} \log 10^{20}$
 $E_{reduction} = \frac{-0.059}{2} \times 20 \times \log 10 = -0.059 \times 10 = -0.59 \text{ V}$ so, $E_{oxidation} = +0.59 \text{ V}$

16. Limiting molar conductivity of NH₄OH $\left(i.e.\mathring{\Lambda}_{m}(NH_{4}OH)\right)$ is equal to [AIPMT (Prelims)-2012] (2) $\Lambda_{m}^{\circ}(NH_{4}CI) + \Lambda_{m}^{\circ}(NaOH) - \Lambda_{m}^{\circ}(NaCI)$ (1) $\Lambda_{m}^{o}(NH_{4}OH) + \Lambda_{m}^{o}(NH_{4}CI) - \Lambda_{m}^{o}(HCI)$ (3) $\Lambda_m^{\circ}(NH_4CI) + \Lambda_m^{\circ}(NaCI) - \Lambda_m^{\circ}(NaOH)$ (4) $\Lambda_m^{\circ}(NaOH) + \Lambda_m^{\circ}(NaCI) - \Lambda_m^{\circ}(NH_4CI)$ Sol. Answer (2) $\stackrel{\circ}{\wedge_{m(NH_{4}OH)}} = \stackrel{\circ}{\wedge_{m(NH_{4}^{\oplus})}} + \stackrel{\circ}{\wedge_{m(OH^{(-)})}}$ $= \stackrel{\circ}{\overset{\circ}{_{\mathsf{m}}}} (\mathsf{NH}_{\mathtt{4}}^{\oplus}) + \stackrel{\circ}{\overset{\circ}{_{\mathsf{m}}}} (\mathsf{CI}^{(-)}) + \stackrel{\circ}{\overset{\circ}{_{\mathsf{m}}}} (\mathsf{Na}^{\oplus}) + \stackrel{\circ}{\overset{\circ}{_{\mathsf{m}}}} (\mathsf{OH}^{(-)}) - \stackrel{\wedge}{\overset{\mathsf{m}}{_{\mathsf{m}}}} (\mathsf{Na}^{\oplus}) - \stackrel{\circ}{\overset{\circ}{_{\mathsf{m}}}} (\mathsf{CI}^{(-)})$ *i.e.*, $\bigwedge_{m(NH_{4}CI)}^{\circ} + \bigwedge_{m(NaOH)}^{\circ} - \bigwedge_{m(NaCI)}^{\circ} = \bigwedge_{m(NH_{4}OH)}^{\circ}$ 17. Standard reduction potentials of the half reactions are given below $F_{2(g)} + 2e^- \rightarrow 2F_{(ag)}^-; \qquad E^\circ = +2.85 \text{ V}$ $Cl_{2(q)} + 2e^- \rightarrow 2Cl^-_{(aq)}; \qquad E^\circ = +1.36 \text{ V}$ $\operatorname{Br}_{_{2(I)}}$ + 2e⁻ \rightarrow 2Br⁻_(aq); E^o = +1.06 V $I_{2(s)}$ + 2e⁻ \rightarrow 2I⁻_(ac); E^o = +0.53 V The strongest oxidising and reducing agents respectively are [AIPMT (Mains)-2012] (1) F₂ and I⁻ (2) Br₂ and Cl⁻ (3) Cl₂ and Br⁻ (4) Cl₂ and I₂ Sol. Answer (1) S.R.P/oxidising power \longrightarrow F₂ (Strongest oxidising) > Cl₂ > Br₂ > l₂ Reducing power \longrightarrow F₂ < Cl₂ < Br₂ < I₂ (Strongest reducing 18. Molar conductivities (Λ_m°) at infinite dilution of NaCl, HCl and CH₃COONa are 126.4, 425.9 and 91.0 S cm² mol^-1 respectively, Λ_m^{o} for CH_3COOH will be [AIPMT (Mains)-2012] (1) 425.5 S cm² mol⁻¹ (2) 180.5 S cm² mol⁻¹ (3) 290.8 S cm² mol⁻¹ (4) 390.5 S cm² mol⁻¹ Sol. Answer (4) $\begin{array}{ccc} CH_{3}COONa \ + \ HCI \longrightarrow CH_{3}COOH \ + \ NaCl & & \downarrow \\ & \downarrow & \downarrow & \downarrow & \downarrow \\ \wedge \stackrel{\circ}{m} \longrightarrow 91 \ + \ 425.9 \ = \ \stackrel{\circ}{x} \ + \ 126.4 \end{array}$ $^{\circ}_{\text{m}} = x = (91 + 425.9) - 126.4 = 390.5 \,\text{S}\,\text{cm}^2 \,\text{mol}^{-1}$ (CH₃COOH) 19. The Gibb's energy for the decomposition of Al₂O₃ at 500°C is as follows $\frac{2}{2}$ Al₂O₃ \longrightarrow $\frac{4}{2}$ Al+O₂; Δ_r G = +960 kJ mol⁻¹

The potential difference needed for the electrolytic reduction of aluminium oxide (Al₂O₃) at 500°C is at least

[AIPMT (Mains)-2012]

(1) 4.5 V (2) 3.0 V	(3) 2.5 V	(4) 5.0 V
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Sol. Answer (3)

$$\mathsf{E}_{\mathsf{cell}} = -\frac{\Delta G}{\mathsf{nF}} = -\frac{960 \times 1000}{4 \times 96500} \mathsf{V} = 2.487 \,\mathsf{V} \approx 2.5 \,\mathsf{V}$$

- 20. The electrode potentials for $Cu_{(aq)}^{2+} + e^- \rightarrow Cu_{(aq)}^+$ and $Cu_{(aq)}^+ + e^- \rightarrow Cu_{(s)}$ are +0.15 V and +0.50 V respectively. The value of $E^{0}_{Cu^{2+}/Cu}$ will be [AIPMT (Prelims)-2011] (1) 0.150 V (2) 0.500 V (3) 0.325 V (4) 0.650 V Sol. Answer (3) $Cu^{+2} + e^{-} \longrightarrow Cu^{+}; \qquad \qquad E^{\circ} = 0.15 \ V, \ \Delta G_{1}^{\circ} = -nFE^{\circ} = -1 \times F \times (0.15)$ $Cu^+ + e^- \longrightarrow Cu$; $E^\circ = 0.50 \text{ V}, \ \Delta G_2^\circ = -1 \times F \times (0.50)$ On adding $Cu^{+2} + 2e^{-} \longrightarrow Cu$ $\Delta G_3^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ}$ $-2FE_{2}^{\circ} = -F(0.15) - F(0.50)$ $-2FE_{2}^{\circ} = -0.65F$ $E_3^{\circ} = \frac{-0.65}{-2} = 0.325 V$
- Standard electrode potential for Sn⁴⁺ / Sn²⁺ couple is +0.15 V and that for the Cr³⁺/Cr couple is -0.74 V. These two couples in their standard state are connected to make a cell. The cell potential will be

[AIPMT (Prelims)-2011]

(1) + 1.83 V (2) + 1.19 V (3) + 0.89 V (4) + 0.18 V

Sol. Answer (3)

$$\begin{split} \mathsf{E}^\circ &= \mathsf{E}^\circ_\mathsf{c} - \mathsf{E}^\circ_\mathsf{a} & \text{higher value of S.R.P} \longrightarrow \mathsf{Cathodic reaction} \\ &= 0.15 - (-0.74) \\ &= 0.89 \ \mathsf{V} \end{split}$$

- 22. If the E_{cell}^{o} for a given reaction has a negative value, then which of the following gives the correct relationships for the values of ΔG° and K_{eq} ? [AIPMT (Prelims)-2011]
 - $(1) \quad \Delta G^{\circ} > 0; \ {\rm K}_{eq} < 1 \\ (2) \quad \Delta G^{\circ} > 0; \ {\rm K}_{eq} > 1 \\ (3) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} > 1 \\ (4) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 1 \\ (5) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 1 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 1 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 1 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 1 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 1 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 1 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 1 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0; \ {\rm K}_{eq} < 1 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0; \ {\rm K}_{eq} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} < 0 \\ (6) \quad \Delta G^{\circ} < 0; \ {\rm K}_{eq} <$
- Sol. Answer (1)
 - $\Delta G^{\circ} = -nF \ E_{Cell}^{\circ} = -nF \left(-E_{Cell}^{\circ}\right)$ *i.e.*, $\Delta G^{\circ} > 0 \rightarrow \text{positive}$ $\Delta G^{\circ} = -2.303 \ \text{RT} \ \log_{10} \text{K}_{C}$ If $\Delta G^{\circ} = \text{positive}$ then K_{C} must be negative, so $\text{K}_{C} < 1$.

23. An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to

[AIPMT (Prelims)-2010]

- (1) Increase in ionic mobility of ions
- (2) 100% ionisation of electrolyte at normal dilution
- (3) Increase in both i.e. number of ions and ionic mobility of ions
- (4) Increase in number of ions

Sol. Answer (1)

On increasing dilution mobility of ions of strong electrolyte increases.

- 24. For the reduction of silver ions with copper metal, the standard cell potential was found to be +0.46V at 25°C. The value of standard Gibbs energy, ΔG° will be (F = 96500 C mol⁻¹) [AIPMT (Prelims)-2010]
- (1) -89.0 kJ (2) -89.0 J (3) -44.5 kJ (4) -98.0 kJSol. Answer (1) $2 \text{ Ag}^+ + \text{Cu} \rightarrow 2 \text{ Ag} + \text{Cu}^{+2}$ $\Delta \text{G}^\circ = -\text{nFE}^\circ_{\text{Cell}}$

$$= \frac{-2 \times 96500 \times 0.46}{1000} \text{ kJ}$$
$$= -88.78 \text{ kJ} \simeq -89 \text{ kJ}$$

25. Which of the following expressions correctly represents the equivalent conductance at infinite dilution of $AI_2(SO_4)_3$. Given that $\Lambda^o_{AI^{3+}_4}$ and $\Lambda^o_{SO^{2-}_4}$ are the equivalent conductances at infinite dilution of the respective ions?

[AIPMT (Mains)-2010]

[AIPMT (Mains)-2010]

(1)
$$2\Lambda_{Al^{3+}}^{\circ} + 3\Lambda_{SO_4^{2-}}^{\circ}$$
 (2) $\Lambda_{Al^{3+}}^{\circ} + \Lambda_{SO_4^{2-}}^{\circ}$ (3) $(\Lambda_{Al^{3+}}^{\circ} + \Lambda_{SO_4^{2-}}^{\circ}) \times 6$ (4) $\frac{1}{3}\Lambda_{Al^{3+}}^{\circ} + \frac{1}{2}\Lambda_{SO_4^{2-}}^{\circ}$

Sol. Answer (2)

Equivalent conductance $\wedge_{eq[Al_2(SO_4)_3]}^{\circ} = \wedge_{Al^{3(+)}}^{\circ} + \wedge_{SO_4^{2^-}}^{\circ}$

- 26. Consider the following relations for emf of an electrochemical cell
 - (a) emf of cell = (Oxidation potential of anode) (Reduction potential of cathode)
 - (b) emf of cell = (Oxidation potential of anode) + (Reduction potential of cathode)
 - (c) emf of cell = (Reductional potential of anode) + (Reduction potential of cathode)
 - (d) emf of cell = (Oxidation potential of anode) (Oxidation potential of cathode)

Which of the above relations are correct?

Options:

((1)	(c) and (a) ((2)	(a)) and (b)	(3) ((c)	and (c) (4	4)	(b) and (d)	
•	• •	(0) 0	~ /	<u> </u>	(~)	/	~ /	(0) (ν - <i>ν</i>			• /	` ~	/	~ /	

Sol. Answer (4)

$$E_{Cell}^{\circ} = E_{Cathode}^{\circ} - E_{Anode}^{\circ}$$
or
$$E_{Cell}^{\circ} = E_{Oxidation}^{\circ} + E_{Reduction}^{\circ}$$
or
$$E_{Cell}^{\circ} = E_{Oxidation}^{\circ} - E_{Oxidation}^{\circ}$$
(Anode)

27. Given (i) $Cu^{2+} + 2e^- \rightarrow Cu$. $E^{\circ} = 0.337$ V (ii) $Cu^{2+} + e^{-} \rightarrow Cu^{+}$. $E^{\circ} = 0.153 V$ Electrode potential, E° for the reaction, $Cu^+ + e^- \rightarrow Cu$, will be [AIPMT (Prelims)-2009] (1) 0.90 V (2) 0.30 V (3) 0.38 V (4) 0.52 V Sol. Answer (4) $Cu^{2+} + 2 e^{-} \longrightarrow Cu$; $E^{\circ} = 0.337 V$...(i) $Cu^{2*} + e^- \longrightarrow Cu^+ \ ; \qquad \qquad E^\circ = 0.153 \ V$...(ii) (i) - (ii). $Cu^{2+} + 2 e^{-} \longrightarrow Cu ; \qquad \Delta G_1^{\circ} = -2 F(0.337)$ $Cu^{2+} + e^- \longrightarrow Cu^+$; $\Delta G_2^\circ = -F[0.153]$ $\label{eq:constraint} \begin{array}{ccc} - & - & \\ \hline Cu^+ + e^- & \longrightarrow Cu \ ; \ \Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ \end{array}$ $\Rightarrow -1 \times F \times E_{Cell}^{\circ} = -2F(0.337) - (-F \times 0.153)$ \Rightarrow -FE[°]_{Cell} = -2F×0.337 + 0.153F $\Rightarrow -FE_{Cell}^{\circ} = -0.52F$ $\therefore E_{Cell}^{\circ} = 0.52 \text{ V}$

Al₂O₃ is reduced by electrolysis at low potentials and high currents. If 4.0 × 10⁴ amperes of current is passed through molten Al₂O₃ for 6 hours, what mass of aluminium is produced? (Assume 100% current efficiency, At. mass of Al = 27 g mol⁻¹)

(1) 8.1×10^4 g (2) 2.4×10^5 g (3) 1.3×10^4 g (4) 9.0×10^3 g

Sol. Answer (1)

$$W = \frac{E_{AI}}{96500} \times I \times t = \frac{\frac{27}{3}}{96500} \times 4 \times 10^4 \times 6 \times 60 \times 60 = 8.05 \times 10^4 \text{ g}$$

29. The equivalent conductance of $\frac{M}{32}$ solution of a weak monobasic acid is 8.0 mho cm² and at infinite dilution is 400 mho cm². The dissociation constant of this acid is [AIPMT (Prelims)-2009]

(1) 1.25×10^{-6} (2) 6.25×10^{-4} (3) 1.25×10^{-4} (4) 1.25×10^{-5}

Sol. Answer (4)

$$K = \frac{C\alpha^2}{1-\alpha} \text{ for weak electrolyte } 1-\alpha \approx 1; ((\alpha) << 1)$$
$$K = C\alpha^2$$
$$\therefore \quad \alpha = \frac{\wedge_m^C}{\wedge_m^\infty} = \frac{8}{400}$$
Now
$$K = \frac{1}{32} \times \left(\frac{8}{400}\right)^2 = 1.25 \times 10^{-5}$$

30. Kohlrausch's law states that at

[AIPMT (Prelims)-2008]

- (1) Infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte
- (2) Finite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the naure of the other ion of the electrolyte
- (3) Infinite dilution each ion makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte
- (4) Infinite dilution, each ion makes definite contribution to conductance of an electrolyte whatever be the nature of the other ion of the electrolyte

Sol. Answer (1)

Kohlrauschs law

31. Standard free energies of formation (in kJ/mol) at 298 K are -237.2, -394.4 and -8.2 for H₂O (I), CO₂ (g) and [AIPMT (Prelims)-2008] pentane (g) respectively. The value of $\mathsf{E}_{\mathsf{cell}}^\circ$ for the pentane-oxygen fuel cell is

(4) 1.0968 V (1) 0.0968 V (2) 1.968 V (3) 2.0968 V

Sol. Answer (4)

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 $C_5H_{12} + 8O_2 \longrightarrow 5CO_2 + H_2O$ [change in oxidation state(n) = 32]

$$\Delta G_{\text{reaction}} = \Sigma G_{\text{products}} - \Sigma G_{\text{reactants}}$$

$$\Delta G_{\text{reaction}} = \left[5 \times G_{(CO_2)} + 6 \times G_{(H_2O)} \right] - \left[G_{(C_5H_{12})} \right]$$

$$= \left[(5 \times -394.4) + 6 \times (-237.2) \right] - \left[-8.2 \right]$$

$$= (-1972 - 1423.2) + 8.2$$

$$\therefore -nFE^{\circ}_{\text{Cell}} = -3387 \text{ kJ}$$

$$E_{Cell}^{\circ} = \frac{-3387 \times 10^3}{-32 \times 96500} = 1.09 \text{ V}$$

32. On the basis of the following E° values, the strongest oxidizing agent is

 $[Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + e^{-1}; \quad E^\circ = -0.35 \text{ V}$ $Fe^{2+} \rightarrow Fe^{3+} + e^{-1}$; E° = - 0.77 V [AIPMT (Prelims)-2008] (1) [Fe(CN)₆]³⁻ (2) [Fe(CN)₆]⁴⁻ (3) Fe²⁺ (4) Fe³⁺

Sol. Answer (4)

$$\begin{array}{c|c} E^{\circ}_{\text{oxidation}} \\ [Fe(CN)_{6}]^{-4} \\ -0.35 \text{ V} \end{array} \xrightarrow{} \begin{array}{c} E^{\circ}_{\text{oxidation}} \\ (Fe^{*2}) \\ -0.77 \text{ V} \end{array} \end{array} \xrightarrow{} \begin{array}{c} \text{Oxidation potential } \uparrow = \text{Reducing nature } \uparrow, \text{ so oxidising nature } \downarrow \\ i.e., \begin{array}{c} E^{\circ}_{\text{Reduction}} \\ [Fe(CN)_{6}]^{-3} \end{array} \xrightarrow{} \begin{array}{c} E^{\circ}_{\text{Reduction}} \\ (Fe^{*3}) \end{array} \xrightarrow{} \begin{array}{c} \text{Strongest oxidising agent} \end{array}$$

33. The equilibrium constant of the reaction $Cu(s) + 2Aq^+ (aq) \rightarrow Cu^{2+}(aq) + 2Aq(s)$; $E^{\circ} = 0.46V$ at 298 K is [AIPMT (Prelims)-2007] (1) 4.0×10^{15} (2) 2.4×10^{10} (3) 2.0×10^{10} (4) 4.0×10^{10} Sol. Answer (1) Cu + 2 Ag⁺ \longrightarrow Cu⁺² + 2 Ag ; E° = 0.46 V $\Delta G = -nFE_{Cell} = -2.303 RTlogK_{c}$ -2 × FE_{Cell} = -2.303 × 8.314 × 298 logK_c $-2 \times 96500 \times (0.46) = -2.303 \times 8.314 \times 298 \log K_{a}$ $\log_{10}K_{c} = 15.55$ $K_c = (10^{15.55})$ antilog = 4 × 10¹⁵ 34. The efficiency of a fuel cell is given by [AIPMT (Prelims)-2007] (3) $\frac{\Delta G}{\Delta S}$ (1) $\frac{\Delta S}{\Delta G}$ (2) $\frac{\Delta H}{\Delta G}$ (4) $\frac{\Delta G}{\Delta H}$ **Sol.** Answer (4) Efficiency of fuel cell = $\frac{\Delta G}{\Delta H}$ 35. If $E^{\circ}_{Fe^{2^+}/Fe} = -0.441 \text{ V}$ and $E^{\circ}_{Fe^{3^+}/Fe^{2^+}} = 0.771 \text{ V}$, the standard EMF of the reaction Fe + 2Fe³⁺ \rightarrow 3Fe²⁺ [AIPMT (Prelims)-2006] will be (1) 0.330 V (2) 1.653 V (3) 1.212 V (4) 0.111 V Sol. Answer (3) $Fe^{2+} + 2 e^{-} \longrightarrow Fe$ $\frac{\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{+2}}{\text{Fe}^{+} 2\text{Fe}^{3+} \longrightarrow 3 \text{Fe}^{2+}}$ Cell representation Fe | Fe²⁺ || Fe³⁺ | Fe²⁺ $E_{Cell}^{\circ} = E_{Fe^{3+}|Fe^{2+}}^{\circ} - E_{Fe^{2+}|Fe}^{\circ}$ = 0.771 - (-0.441)= 1.212 V A hypothetical electrochemical cell is shown belowA|A⁺(xM)||B⁺(yM)|B, the emf measured is +0.20 V. The cell reaction is [AIPMT (Prelims)-2006] (1) $A^+ + B \rightarrow A + B^+$ (2) $A^+ + e^- \rightarrow A : B^+ + e^- \rightarrow B$ (4) $A + B^+ \rightarrow A^+ + B$ (3) The cell reaction cannot be predicted Sol. Answer (4) $E = E_c^{\circ} - E_a^{\circ}$

 E_{Cell} = positive \longrightarrow so ΔG = negative \longrightarrow *i.e.*, given reaction is feasible reaction

i.e,
$$A + A^+ + e^-$$
 (Oxidation)

 $B^+ + e^- \longrightarrow B$ (Reduction)

net reaction A + B⁺ \longrightarrow A⁺ + B

- 37. 4.5g of aluminium (at. mass 27 amu) is deposited at cathode from Al³⁺ solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from H⁺ ions in solution by the same quantity of electric [AIPMT (Prelims)-2005] charge will be
 - (1) 22.4 L (2) 44.8 L (3) 5.6 L (4) 11.2 L
- Sol. Answer (3)

 $AI^{+3} + 3 e^{-} \longrightarrow AI [4.5 g] = w_{1}$ $2H^+ + 2e^- \longrightarrow H_2$ (Volume = ?) $(G.E)_{AI} = (G.E)_{H_2}$ $\Rightarrow \frac{W}{F} = \frac{22.4}{V}$ $\Rightarrow \quad \frac{4.5}{\frac{27}{2}} = \frac{22.4}{V} = \frac{W_2}{E_2}$ $\Rightarrow \frac{4.5}{9} = \frac{W_2}{\frac{2}{2}}$ $\therefore w_2 = 0.5 g$ for 2g $H_2 \longrightarrow 22.4$ L \Rightarrow 1g $\longrightarrow \frac{22.4}{2}$ $\therefore 0.5 \text{ g} \longrightarrow \frac{22.4}{2} \times 0.5 = 5.6 \text{ L}$

- 38. A solution contains Fe²⁺, Fe³⁺ and I⁻ ions. This solution was treated with iodine at 35°C. E° for Fe³⁺/Fe²⁺ is +0.77 V and E° for $I_2/2I^-$ = 0.536 V. The favourable redox reaction is
 - (1) I^- will be oxidised to I_2
 - (3) I_2 will be reduced to I^-

(2) Fe²⁺ will be oxidised to Fe³⁺

(4) There will be no redox reaction

Sol. Answer (1)

S.R.P or oxidising power

(Fe) can oxidise (I) or Fe⁺³ reduced and I⁻ will be oxidised

39. Standard reduction potentials at 25°C of Li⁺/Li, Ba²⁺/Ba, Na⁺/Na and Mg²⁺/Mg are -3.05, -2.90, -2.71 and -2.37 volt respectively. Which one of the following is the strongest oxidizing agent?

(1) Ba²⁺ (2) Ma²⁺ (3) Na⁺ (4) Li⁺

Sol. Answer (2)

- 40. To protect iron against corrosion, the most durable metal plating on it, is
 - (1) Copper plating (2) Zinc plating (3) Nickel plating (4) Tin plating
- Sol. Answer (2)

Most durable metal for iron is zinc [Fact].

Fe > I

41. An electrochemical cell is set up as :

Pt; H₂ (1 atm) |HCl (0.1 M) || CH₃COOH (0.1M) |

- H₂ (1 atm) ; Pt. The e.m.f. of this cell will not be zero, because
- (1) Acids used in two compartments are different
- (2) e.m.f. depends on molarities of acids used
- (3) The temperature is constant
- (4) pH of 0.1 M HCl & 0.1 M CH₃COOH is not same

Sol. Answer (4)

 $\begin{array}{c} \mathsf{HCI} \longrightarrow \mathsf{H}^* + \mathsf{CI}^- & \mathsf{CH_3COOH} \rightleftharpoons \mathsf{CH_3COO^-} + \mathsf{H}^* \\ \text{Strong acid} & & \mathsf{Weak acid} \\ \text{more pH} & & & \mathsf{less pH} \\ \\ & & & \\ & &$

42. Electrode potential for the following half-cell reactions are

$$\label{eq:angle} \begin{split} Zn &\rightarrow Zn^{2+} + 2e^-; \ E^\circ = + \ 0.76 \ V; \\ Fe &\rightarrow Fe^{2+} + 2e^-; \ E^\circ = + \ 0.44 \ V \end{split}$$

The EMF for the cell reaction Fe^{2^+} + $Zn \rightarrow Zn^{2^+}$ + Fe will be

- (1) -0.32 V (2) + 1.20 V
- (3) 1.20 V (4) + 0.32 V

Sol. Answer (4)

$Zn \longrightarrow Zn^{+2} + 2e^{-}$	$E_{oxidation}^{\circ} = +0.76 V$	$\longrightarrow E_{\text{reduction}}^{\circ} = -0.76 \text{ V}$
$Fe \longrightarrow Fe^{+2} + 2e^{-}$	$E_{oxidation}^{\circ} = 0.44 V -$	$\longrightarrow E_{reduction}^{\circ} = -0.44 V$
$E^{\circ} = E_{c}^{\circ} - E_{a}^{\circ}$	at cathode	at anode
= -0.44 - (-0.76)	Fe ⁺² <u>→</u> Fe	$Zn \longrightarrow Zn^{+2} + 2e^{-}$
= +0.32 V		

43. How many grams of cobalt metal will be deposited when a solution of cobalt(II) chloride is electrolyzed with a current of 10 amperes for 109 minutes (1 Faraday = 96,500 C; Atomic mass of Co = 59 u)

(1) 0.66 (2) 4.0 (3) 20.0 (4) 40.0

Sol. Answer (3)

$$CO^{+2} \longrightarrow Co$$

$$w = \frac{E}{96500} \times it = \frac{\frac{59}{2}}{96500} \times 10 \times 109 \times 60 = 19.9 \simeq 20 \text{ g}$$

- 44. A 5 ampere current is passed through a solution of zinc sulphate for 40 minutes. The amount of zinc deposited at the cathode is
 - (1) 0.4065 gm (2) 65.04 gm (3) 40.65 gm (4) 4.065 gm

Sol. Answer (4)

w =
$$\frac{E}{96500}$$
 × it = $\frac{\frac{65}{2}}{96500}$ × 40 × 60 × 5 = 4.065 g
[Zn⁺² + 2e⁻ ----> Zn]

- 45. The molar conductances of NaCl, HCl and CH₃COONa at infinite dilution are 126.45, 426.16 and 91 ohm⁻¹ cm² mol⁻¹ respectively. The molar conductance of CH₃COOH at infinite dilution is
 - (1) 698.28 ohm⁻¹ cm² mol⁻¹
 - (2) 540.48 ohm⁻¹ cm² mol⁻¹
 - (3) 201.28 ohm⁻¹ cm² mol⁻¹
 - (4) 390.71 ohm⁻¹ cm² mol⁻¹

Sol. Answer (4)

$$CH_{3}COONa + HCI \longrightarrow CH_{3}COOH + NaCl$$

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

$$\wedge_{m}^{\circ} = 91 + 426.16 = x + 126.45$$

$$x = 390.71$$

$$\wedge_{m}^{\circ}(CH_{3}COOH)$$

- 46. E° for the cell, Zn|Zn²⁺(aq)||Cu²⁺(aq)|Cu is 1.10 V at 25°C, the equilibrium constant for the reaction Zn + Cu²⁺ (aq) → Cu + Zn²⁺ (aq) is the order of
 - (1) 10^{+18} (2) 10^{+37} (3) 10^{-28} (4) 10^{-37}

Sol. Answer (2)

$$E = E^{\circ} = \frac{0.059}{n} \log K_{c}$$

At equilibrium

$$E^{\circ} = \frac{0.059}{2} \log_{10} K_{c}$$
$$1.10 = \frac{0.059}{2} \log_{10} K_{c}$$
$$K_{c} = 10^{+37}$$

- 47. For the cell reaction, Cu²⁺ (C₁ · aq) + Zn(s) = Zn²⁺ (C₂ · aq) + Cu(s) of an electrochemical cell, the change in Free Energy ΔG at a given temperature is a function of
 - (1) $\ln(C_2)$ (2) $\ln(C_2/C_1)$ (3) $\ln(C_1)$ (4) $\ln(C_1 + C_2)$
- Sol. Answer (2)

$$Cu^{+2}_{C_1} + Zn = Zn^{+2}_{C_2} + Cu$$

$$\Rightarrow \Delta G = -2.303 \text{RT} \log \frac{(\text{Zn}^{+2})}{(\text{Cu}^{+2})}$$
$$\Rightarrow \Delta G = -2.303 \text{RT} \log \frac{\text{C}_2}{\text{C}_1} \text{ or } \Delta G = -\text{RT} \ln \frac{\text{C}_2}{\text{C}_1}$$

- 48. The specific conductance of a 0.1 N KCl solution at 23°C is 0.012 ohm⁻¹ cm⁻¹. The resistance of cell containing the solution at the same temperature was found to be 55 ohm. The cell constant will be
 - (1) 0.918 cm^{-1} (2) 0.66 cm^{-1} (3) 1.142 cm^{-1} (4) 1.12 cm^{-1}

Sol. Answer (2)

$$\kappa = \frac{1}{R} \times \left(\frac{l}{a}\right) \rightarrow \text{Cell constant}$$
$$0.012 = \frac{1}{55} \times \left(\frac{l}{a}\right)$$
$$\left(\frac{l}{a}\right) = 0.012 \times 55 = 0.66 \text{ cm}^{-1}$$

- 49. For the disproportionation of copper $2Cu^+ \rightarrow Cu^{2+}$ Cu, E° is (Given E° for Cu^{2+}/Cu is 0.34 V and E° for Cu^{2+}/Cu^+ is 0.15 V)
 - (1) 0.49 V (2) -0.19 V (3) 0.38 V (4) -0.38 V
- Sol. Answer (3)

$$2Cu^{+} \longrightarrow Cu^{+2} + Cu \qquad E^{\circ} = ?$$
1.
$$Cu^{+2} + 2e^{-} \longrightarrow Cu \qquad E^{\circ} = 0.34 \text{ V}; \qquad \Delta G_{1}^{\circ} = -2F(0.34)$$
2.
$$Cu^{+2} + e^{-} \longrightarrow Cu^{+} \qquad E^{\circ} = 0.15 \text{ V}; \qquad \Delta G_{2}^{\circ} = -F(0.15)$$

Reaction (2) is multiplied by (2)

So,
$$2 Cu^{+2} + 2e^{-} \longrightarrow 2 Cu^{+} (E^{\circ} = 0.15 V) \dots (3) \dots \Delta G_{3}^{\circ} = -2F[0.15]$$

Now reaction [(1) - (3)] then we get required reaction.

$$Cu^{*2} + 2 e^{-} \longrightarrow Cu \longrightarrow \Delta G_{1}^{\circ}$$

$$-2Cu^{*2} + 2 e^{-} \longrightarrow 2 Cu^{*} \longrightarrow \Delta G_{3}^{\circ}$$

$$-Cu^{*2} \longrightarrow Cu - 2 Cu^{*}$$
or
$$2 Cu^{*} \longrightarrow Cu + 2 Cu^{*2} \longrightarrow \Delta G_{4}^{\circ}$$

So,
$$\Delta G_4^{\circ} = \Delta G_1^{\circ} - \Delta G_3^{\circ}$$

 $-nFE_4^{\circ} = -2F(0.34) - (-2F \times 0.15)$
 $-1 \times FE_4^{\circ} = -2F(0.34) + 2F \times 0.15$
 $E^{\circ} \quad 0.38 \text{ V}$

- 50. Cell reaction is spontaneous when
 - (1) ΔG° is negative (2) ΔG° is positive (3) ΔE°_{Red} is positive (4) ΔE°_{Red} is negative

Sol. Answer (1)

For spontaneous reaction ΔG° = negative.

- 51. Equivalent conductances of Ba²⁺ and Cl⁻ ions are 127 and 76 ohm⁻¹ cm² eq⁻¹ respectively. Equivalent conductance of BaCl₂ at infinite dilution is (in the unit ohm⁻¹ cm² eq⁻¹)
 - (1) 139.5 (2) 101.5 (3) 203 (4) 279

Sol. Answer (3)

$$\wedge_{eq}^{\infty} = \wedge_{eq}^{+} + \wedge_{eq}^{-} = 127 + 76 = 203$$

$$(Ba^{+2}) \quad (C|^{-})$$

52. Standard electrode potentials are

 Fe^{2+}/Fe ; $E^{\circ} = -0.44$ volts

 Fe^{3+}/Fe^{2+} ; E° = 0.77 volts

Fe²⁺, Fe³⁺ and Fe blocks are kept together, then

(1) Fe³⁺ increases

(3) Fe²⁺/Fe³⁺ remains unchanged

(2) Fe³⁺ decreases
(4) Fe²⁺ decreases

Sol. Answer (2)

 $Fe^{+2} \xrightarrow{2 e^{-}} Fe$; $E^{\circ} = -0.44$

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

 Fe^{+3} have more S.R.P than Fe^{+2} so, Fe^{+3} reduces more than Fe^{+2} . *i.e.*, Fe^{+3} is converted into Fe^{+2} which means Fe^{+3} decreases $\longrightarrow Fe^{+2}$ increases

53. $PbO_2 \rightarrow PbO, \Delta G_{298} < 0$

 $SnO_2 \rightarrow SnO, \Delta G_{298} > 0$

Most probable oxidation state of Pb and Sn will be

(1) Pb⁴⁺, Sn⁴⁺ (2) Pb⁴⁺, Sn²⁺ (3) Pb²⁺, Sn²⁺ (4) Pb²⁺, Sn⁴⁺

Sol. Answer (4)

 $Pb^{+4}O_2 \longrightarrow Pb^{+2}O, \Delta G < 0$, negative

Spontaneous

i.e., $Pb^{+4} \longrightarrow Converted into Pb^{+2}$, so Pb^{+4} decreases, Pb^{+2} increases

Formation of Pb^{+2} increases \longrightarrow stability increases

 $Sn^{+4}O_2 \longrightarrow Sn^{+2}O$ $\Delta G > 0$, positive

Non-spontaneous

i.e., Sn⁺⁴ cannot easily converted into Sn⁺² i.e., formation of Sn⁺² decreases

 \longrightarrow Stability of Sn⁺² decreases

 \longrightarrow Stability of Sn⁺⁴ increases

- 54. The most convenient method to protect the bottom of ship made of iron is
 - (1) Coating it with red lead oxide
 - (2) White tin plating
 - (3) Connecting it with Mg block
 - (4) Connecting it with Pb block
- Sol. Answer (3)
- 55. In electrolysis of NaCl when Pt electrode is taken then H₂ is liberated at cathode while with Hg cathode it forms sodium amalgam
 - (1) Hg is more inert than Pt
 - (2) More voltage is required to reduce H⁺ at Hg than at Pt
 - (3) Na is dissolved in Hg while it does not dissolve in Pt
 - (4) Conc. of H⁺ ions is larger when Pt electrode is taken
- Sol. Answer (2)

During electrolysis of NaCl using Pt electrode then H⁺ is higher discharge potential than Na⁺

So, H⁺ get reduced and form H₂ at cathode but using Hg cathode H⁺ is lower discharge potential than Na⁺ so Na⁺ get reduced and form amalgam

- i.e., H⁺ required more voltage at Hg
- 56. On the basis of the information available from the reaction of O_{2} ,

$$\frac{4}{3}AI + O_2 \rightarrow \frac{2}{3}AI_2O_3, \ \ \Delta G = -827 \ kJmol^{-1}, \label{eq:gamma}$$

the minimum e.m.f. required to carry out electrolysis of Al_2O_3 is (F = 96500 C mol⁻¹)

(1) 2.14 V (2) 4.28 V (3) 6.42 V (4) 8.56 V

Sol. Answer (1)

$$\begin{array}{l} \underbrace{4}{3} \operatorname{Al} + \operatorname{O}_2 \rightarrow \underbrace{2}{3} \operatorname{Al}_2 \operatorname{O}_3^{} ; \quad \Delta G = -827 \text{ kJ/mole} \\ \\ \text{Total change} = \underbrace{2}{3} \times 6 = 4 \qquad \text{one } [\operatorname{Al} \rightarrow (+3)], \text{ so } (2) \text{ Al} \rightarrow +6, \\ \\ \Delta G = -n \mathsf{FE}_{\mathsf{Cell}} = -4 \times 96500 \times \mathsf{E}_{\mathsf{Cell}} \\ -827 \times 10^3 = -4 \times 96500 \times \mathsf{E}_{\mathsf{Cell}} \\ \\ \\ \mathsf{E}_{\mathsf{Cell}} = \underbrace{-827 \times 10^3}_{-4 \times 96500} = 2.14 \text{ V} \end{array}$$

57. The e.m.f. of a Daniel cell at 298 K is ${\rm E_1}$

When the concentration of $ZnSO_4$ is 1.0 M and that of $CuSO_4$ is 0.01 M, the e.m.f. changed to E_2 . What is the relationship between E_1 and E_2 ?

(1) $E_1 > E_2$ (2) $E_1 < E_2$ (3) $E_1 = E_2$ (4) $E_2 = 0 \neq E_1$

Sol. Answer (1)

$$\begin{split} \mathsf{E}_{1} &= \mathsf{E}^{\circ} - \frac{0.059}{2} \log \frac{(\mathsf{Zn}^{+2})}{(\mathsf{Cu}^{+2})} \\ \mathsf{E}_{0} &= \mathsf{E}^{\circ} - \frac{0.059}{2} \log \frac{0.01}{1.0} \qquad \dots (1) \\ &\Rightarrow \qquad \mathsf{E}^{\circ} - \frac{0.059}{2} \log 10^{-2} = \mathsf{E}^{\circ} - \frac{0.059}{2} (-2) \\ \mathsf{E}_{1} &= \mathsf{E}^{\circ} + 0.059 \\ &\qquad \mathsf{E}_{2} &= \mathsf{E}^{\circ} - \frac{0.059}{2} \log \frac{1}{0.01} \\ &\qquad \mathsf{E}_{2} &= \mathsf{E}^{\circ} - \frac{0.059}{2} \log 10^{2} \\ &\Rightarrow \qquad \mathsf{E}^{\circ} - \frac{0.059 \times 2}{2} \\ &\Rightarrow \qquad \mathsf{E}^{\circ} - 0.059 \\ &\qquad \mathsf{E}_{1} &= \mathsf{E}^{\circ} + 0.059 \qquad \qquad [\mathsf{E}_{2} &= \mathsf{E}^{\circ} - 0.059] \\ &\qquad i.e., \qquad \mathsf{E}_{1} &> \mathsf{E}_{2} \end{split}$$

58. The standard e.m.f. of a galvanic cell involving cell reaction with n = 2 is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be (Given $F = 96500 \text{ C mol}^{-1}$, R = 8.314 J K⁻¹ mol⁻¹)

(1) 2.0 × 10 ¹¹	(2) 4.0 × 10 ¹²	(3) 1.0×10^2	(4) 1.0 × 10 ¹⁰
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$$E^{\circ} = \frac{0.059}{n} \log K_{c}$$

$$0.295 = \frac{0.059}{2} \log_{10} K_{c}$$

$$\log_{10} K_{c} = \frac{0.295 \times 2}{0.059}$$

$$\log_{10} K_{c} = 10$$

$$K_{c} = 10^{10}$$

59. The mass of carbon anode consumed (giving only carbon dioxide) in the production of 270 kg of aluminium metal from bauxite by the Hall process is (Atomic Mass: AI = 27)

(1) 270 kg	(2) 540 kg	(3) 90 kg	(4) 180 kg
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Sol. Answer (3)

change = 4

$$O + 4$$

 $C + O_2 \rightarrow CO_2$
 $(w_1) = ?$
 $(n-factor = 4)$

$$\begin{pmatrix} \frac{w_1}{E_0} \end{pmatrix}_c = \begin{pmatrix} \frac{w_2}{E_2} \end{pmatrix}_{AI}$$

$$AI_2O_3 : 2H_2O + Na_2CO_3 \longrightarrow NaAIO_2$$

$$\downarrow H_2O$$

$$NaOH + AI(OH)_3$$

$$\begin{pmatrix} \frac{w_1}{w_2} \end{pmatrix} = \frac{E_1}{E_2}$$

$$AI \stackrel{\text{reduction}}{AI_2O_3} AI_2O_3$$

$$w_2 = 270 \text{ kg}$$

$$n-factor = 3 (AI^{*3})$$

$$w_1 = \frac{3}{9} \times 270 = 90 \text{ kg}$$

60. Consider the half-cell reduction reaction :

$$\label{eq:Mn2+} \begin{split} &\mathsf{Mn}^{2+} + 2e^- \to \mathsf{Mn}, \ \mathsf{E}^\circ = -1.18 \ \mathsf{V} \\ &\mathsf{Mn}^{2+} \to \mathsf{Mn}^{3+} + e^-, \ \mathsf{E}^\circ = -1.51 \ \mathsf{V} \\ &\mathsf{The} \ \mathsf{E}^\circ \ \mathsf{for} \ \mathsf{the} \ \mathsf{reaction} \ 3 \ \mathsf{Mn}^{2+} \to \mathsf{Mn}^0 + 2 \ \mathsf{Mn}^{3+}, \ \mathsf{and} \ \mathsf{possibility} \ \mathsf{of} \ \mathsf{the} \ \mathsf{forward} \ \mathsf{reaction} \ \mathsf{are}, \ \mathsf{respectively} \\ &(1) \ -2.69 \ \mathsf{V} \ \mathsf{and} \ \mathsf{no} \qquad (2) \ -4.18 \ \mathsf{V} \ \mathsf{and} \ \mathsf{yes} \qquad (3) \ +0.33 \ \mathsf{V} \ \mathsf{and} \ \mathsf{yes} \qquad (4) \ +2.69 \ \mathsf{V} \ \mathsf{and} \ \mathsf{no} \\ \\ &\mathsf{Sol.} \ \mathsf{Answer} \ (1) \end{split}$$

$$\begin{split} Mn^{+2} + 2e^{-} &\to Mn &; \quad \Delta G_{1}^{\circ} = -2F(-1.18)V \\ Mn^{+2} &\to Mn^{+3} + e^{-}] \times 2 &; \quad \Delta G_{2}^{\circ} = -2F(-1.51) \end{split}$$

On addition

$$3 \text{ Mn}^{+2} \longrightarrow 2 \text{ Mn}^{+3} + \text{Mn} \quad ; \quad \Delta G_3^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ}$$
$$-2FE_{Cell}^{\circ} = -2F(-1.18) - 2F(-1.51)$$
$$-2FE_{Cell}^{\circ} = 5.38F$$
$$E_{Cell}^{\circ} = (-)\frac{5.38}{2} = -2.69 \text{ V}$$

SECTION - C

Assertion-Reason Type Questions

1. A: Molar conductivity of solution increases with dilution for weak electrolyte.

R: Degree of ionization increases with dilution.

$$\Lambda_{\rm m} = \frac{\mathbf{x} \times 1000}{({\rm M} = {\rm n} \, / \, {\rm V})} = {\rm V} \left(\frac{\mathbf{x} \times 1000}{{\rm n}}\right)$$
$$\Lambda_{\rm m} \propto {\rm V}.$$

and according to Ostwald's law

 $\alpha \propto \sqrt{V}$

- 2. A: H₂ and O₂ is obtained if dil. solution of Na₂SO₄ is electrolysed using Pt electrodes.
 - R: Platinum electrode is inert electrode.
- Sol. Answer (2)

In case of dil solution, H₂ at cathode and O₂ at anode are obtained.

- 3. A: Anode is positive electrode and cathode is negative electrode in electrolytic cell.
 - R : Anode is negative electrode and cathode is positive electrode in electrochemical cell.
- Sol. Answer (2)

In electrolytic cell : (+)ve end of battery is connected to anode while (–)ve end to cathode. Electrochemical cell : Oxidation takes place at anode while reduction takes place at cathode.

- 4. A: Lithium is the strongest reducing agent in the periodic table.
 - R: Fluorine is the strongest oxidising agent in the periodic table.

Sol. Answer (2)

Li = highest oxidation potential.

 F_2 = highest reduction potential.

- 5. A: Electrode potential of hydrogen is pH dependent.
 - R: Electrode potential of hydrogen electrode is always zero.

Sol. Answer (3)

$$\mathsf{E}_{\mathsf{cell}} = \mathsf{E}_{\mathsf{cell}}^{\mathsf{o}} - \frac{\mathsf{RT}}{\mathsf{nF}}\mathsf{log}[\mathsf{H}^+]$$

$$E_{\text{cell}}^{o} = 0$$

$$[\mathsf{E}_{\mathsf{cell}} \neq 0]$$

- 6. A: Sodium ions are discharged when aqueous solution of NaCl electrolysed using mercury electrode.
 - R: The nature of electrode can affect the order of discharge of ions.

Sol. Answer (2)

 $Na^+ + e^- \rightarrow Na$

Fact

- e.g., In case Pt electrode, H₂ is released while in case of Hg electrode, Na⁺ ion are discharged.
- 7. A: Copper rod turns colourless solution of zinc sulphate to blue.

R: Zinc reduces Cu²⁺ ions to Cu⁺.

Sol. Answer (4)

Zn replace Cu^{+2} ion from its solution and turn blue colour to colourless solution. $Cu^{+2} + Zn \rightarrow Cu + Zn^{+2}$.

- 8. A : At equilibrium E_{cell} becomes zero.
 - R: At equilibrium reduction potential of both the electrodes becomes equal.

Sol. Answer (1)

$$E_{cell} = 0 = \Delta G$$

$$E_{cell} = E_{oxi}^{o} + E_{red} = 0$$

$$\begin{bmatrix} E_{red(C)}^{o} = E_{red(A)}^{o} \\ E_{oxi(A)}^{o} = E_{oxi(C)}^{o} \end{bmatrix}$$

- A : Molten aluminium chloride when electrolysed using 0.1 F, deposits o.1 g equivalent of aluminium.
 R : Mass of substance deposited ∝ quantity of electricity.
- Sol. Answer (2)

 $\rm AI^{+3} + 3e^- \rightarrow \rm AI$

3 mole charge = 1 g equivalent electron = 1 F charge is required to deposit 1 mole of Al.

 $\therefore~$ 0.1 F \rightarrow 0.1 mole AI is deposited.

 \Rightarrow [W = ZQ] (Independent statement)

10. A: Lead storage battery does not require salt bridge.

R: The solid nature of each oxidising agent and reducing agent prevent direct cantact.

Sol. Answer (1)

Fact.

11. A: Electrolysis of molten calcium hydride produces hydrogen gas at the cathode.

R: Hydrogen in calcium hydride is present as H⁺ ion.

Sol. Answer (4)

 CaH_2 $2H^- \rightarrow H_2 + 2e^-$ (anode)

12. A : Molar conductivity of 0.1 M NH_4OH solution is less than that of 0.001 M NH_4OH solution.

R : Dilution increases the degree of ionisation of NH_4OH .

Sol. Answer (1)

$$\Lambda_{\rm m} = \frac{{\rm K} \times 1000}{{\rm M}}$$
$$\Rightarrow \quad \Lambda_{\rm m} \propto \frac{1}{{\rm M}}, \, \pi_{\rm m}$$
$$\Rightarrow \quad [\Lambda_{\rm m} \propto {\rm V}] \quad \left[\because {\rm M} = \right]$$

13. A: Block of magnesium are often stapped to steel hulls of ocean going ships.

R: Magnesium causes cathodic protection of iron.

 $\frac{n}{V}$

Sol. Answer (1)

Mg is more reactive than iron or oxidation potential of Mg > oxidation potential of Fe.

14. A: Salt bridge is used generally in the electrochemical cell.

R: The ions of the electrolyte used in the salt bridge should have the nearly same transport numbers.

Sol. Answer (2)

Salt bridge is used to maintain electrical neutrality of solution.

Velocity of ions is nearly same.

15. A: When $CuSO_4$ is electrolysed using Cu electrodes then O_2 gas is evolved at anode.

R : The discharge potential of OH^- is more than SO_4^{-2-} .

Sol. Answer (4)

At anode,

 $\rm Cu \rightarrow \rm Cu^{+2} + 2e^-$

16. A: One faraday electricity deposite 1 mole of Na & 2 mole of Cu in NaCl & CuSO₄ solution respectively.

R: One faraday electricity always deposite 1 mole of any substance.

Sol. Answer (4)

One, faraday

- = 1 mole of electron
- :. 1 mole of electron \Rightarrow 1 mole of Na deposit and $\frac{1}{2}$ mole of Cu deposit.
- $\label{eq:cut} \mathsf{Cu}^{\text{+}2} \texttt{+} \texttt{2e}^{\text{-}} \rightarrow \mathsf{Cu} \text{, } \mathsf{Na}^{\text{+}} \texttt{+} \texttt{e}^{\text{-}} \rightarrow \mathsf{Na} \text{.}$

