Electrochemistry

SOLUTIONS

Exercise – I (JEE-Main Pattern)

SECTION–A

1. **Ans. (3)**

$$E = E^0 - \frac{0.0591}{n}\log\frac{[Sn^{2\oplus}]}{[Ag^{\oplus}]^2}$$

Cell potential E will increase if $[Sn^{2\oplus}]$ decrease or $[Ag^{\oplus}]$ increase.

2. **Ans. (1)**

$$E = E^0 - \frac{0.059}{2}\log\frac{[Zn^{2\oplus}]}{[Cu^{2\oplus}]}$$

$$E = 1.10 - \frac{0.059}{2}\log\frac{0.1}{0.1}$$

E = 1.10 volt

3. **Ans. (1)**

$$E_{cell} = E^0 - \frac{0.059}{2}\log\frac{[Zn^{2\oplus}]P_{H_2}}{[H^{\oplus}]^2}$$

As $[H^{\oplus}]$ increases, E_{cell} will also increase and equilibrium will shift in forward direction.

4. **Ans. (4)**

$\Delta G = +966 \times 1000 = 96000$ J mol^{-1}

$\Delta G = -nFE$

$966000 = -4 \times 96500 \times E$

E = –2.5 volt

So, minimum 2.5 volt battery will be required.

5. **Ans. (1)**

W = ZQ

W = ZIt

So, amount of ion discharge will be not proportional to it's resistance.

6. **Ans. (3)**

Eq.(Cu) = mole of $e^{\ominus}$

$\frac{63.5}{63.5}\times 2$ = mole of $e^{\ominus}$

Mole of $e^{\ominus}$ = 2 mol

Number of $e^{\ominus} = 2 \times 6.02 \times 10^{23}$

$= 12.04 \times 10^{23}$

7. **Ans. (3)**

W = ZQ

Q = 1 coulomb

Then W = Z

Here Z is electrochemical equivalent.

8. **Ans. (3)**

$Sn^{n\oplus}(aq) \longrightarrow Sn(s)$

$W = \frac{M \times i \times t}{n \times 96500}$

$\frac{5.95}{119} \times n = \frac{9.65 \times 1000}{96500}$

n = 2

9. **Ans. (1)**

Eq. (H_2O) = no. of faraday

$\frac{18}{18} \times 2 = \frac{3 \times t}{96500}$

t = 64333.33 second

t = 17.87 hour

10. **Ans. (3)**

gm equivalents = number of faradays

gm equivalents = $\frac{6 \times 10^{20}}{6 \times 10^{23}}$

gm equivalents = 0.001

11. **Ans. (3)**

Eq. (H_2O) = no. of faraday

1 × 2 = no. of faraday

So, charge in coulomb = 2 × 96500

= 193000

= 1.93 × 10^5 coloumb

12. **Ans. (2)**

Volume of silver plate = 5 × 10^{-3} × 80

= 0.4 cm^3

Mass of silver plate = (0.4 × 1.08) gm

Eq. (Ag) = $\frac{It}{96500}$

$\frac{0.4 \times 1.08}{108} \times 1 = \frac{9.65 \times t}{96500}$

t = 40 sec

13. **Ans. (3)**

More concentrated the solution, more will be the resistance of electrolyte and consequently less will be the conductance. Here, 2N NaCl is the most concentrated solution, hence, its resistance will be the highest.

14. **Ans. (1)**

Increases with increase of temperature.

15. **Ans. (3)**

Liquid HCl does not dissociate into ions.

16. Ans. (1)

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} = \frac{2.6 \times 10^{-1} \times 1000}{(1 \times 2)} = 1.3 \times 10^2 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$$

17. Ans. (2)

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{16.30}{(349.8 + 40.9)} = 0.04172 \text{ or } 4.172\%$$

18. Ans. (4)

$$\text{Cell constant } C = \frac{\ell}{A} = \frac{2.5}{5} = 0.5 \text{ cm}^{-1} = 50 \text{ m}^{-1}$$

19. Ans. (4)

$$\Lambda^0_{m(H_2O)} = \lambda^0_{m(H^{\oplus})} + \lambda^0_{m(OH^{\ominus})} = 0.035 + 0.020$$

$$= 0.055 \text{ mho m}^2 \text{ mol}^{-1}$$

$$\text{Now, } \Lambda_m = \frac{\kappa}{C \times 1000} \Rightarrow 0.055 = \frac{5.5 \times 10^{-6}}{C \times 1000}$$

$$\therefore C = 10^{-7} \text{ M} \Rightarrow K_W = C^2 = 10^{-14} \text{ M}^2$$

20. Ans. (1)

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{7.814 \times 10^{-4}}{3.907 \times 10^{-2}} = 0.02$$

$$\text{Now, } K_a = \frac{\alpha^2 . C}{1 - \alpha} \simeq \alpha^2 . C = (0.02)^2 \times 0.05$$

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

SECTION-B

1. Ans. (2)

$$E^0_{cell} = E^0_{Ce^{4\oplus}|Ce^{3\oplus}} + E^0_{Co|Co^{2\oplus}}$$

$$1.89 = E^0_{Ce^{4\oplus}|Ce^{3\oplus}} + 0.28$$

$$E^0_{Ce^{4\oplus}|Ce^{3\oplus}} = 1.61 \text{ volt}$$

2. Ans. (1)

$$E^0_{cell} = E^0_{Cl^{\ominus}/Cl_2} + E^0_{Pt^{2\oplus}/Pt}$$

$$-0.15 = -E^0_{Cl_2/Cl^{\ominus}} + 1.20$$

$$E^0_{Cl_2|Cl^{\ominus}} = 1.35 \text{ V}$$

3. Ans. (0)

$2e^{\ominus} + Fe^{2\oplus}(aq) \longrightarrow Fe(s)$ $\quad E^0_1 = -0.44$

$e^{\ominus} + Fe^{3\oplus}(aq) \longrightarrow Fe^{2\oplus}(aq)$ $\quad E^0_2 = 0.77$

$3e^{\ominus} + Fe^{3\oplus}(aq) \longrightarrow Fe(s)$

$$E^0_{Fe^{3\oplus}|Fe} = \frac{n_1E^0_1 + n_2E^0_2}{n}$$

$$= \frac{2\times(-0.44)+1\times(0.77)}{3} = \frac{-0.11}{3}$$

4. Ans. (7)

$$e^{\ominus} + H^{\oplus}_{(aq)} \longrightarrow \frac{1}{2}H_{2(g)}$$

$$E = 0 - \frac{0.059}{1}\log\frac{P^{1/2}_{H_2}}{[H^{\oplus}]}$$

$$E = 0 - 0.059\log\frac{1}{[H^{\oplus}]}$$

$$-0.413 = -0.059pH$$

pH = 7

5. Ans. (0)

$$Zn\,(s) \longrightarrow Zn^{2\oplus}\,(aq) + 2e^{\ominus}$$

$$2e^{\ominus} + Zn^{2\oplus}\,(aq) \longrightarrow Zn\,(s)$$

$$E = 0 - \frac{0.059}{2}\log\frac{0.01}{0.1}$$

$$E = \frac{0.059}{2} = 0.0295$$

6. Ans. (4)

$$\tfrac{1}{2}\,H_2(g) \longrightarrow H^{\oplus}(aq) + e^{\ominus}$$

$$e^{\ominus} + H^{\oplus}(aq) \longrightarrow \tfrac{1}{2}\,H_2(g)$$

$$E = 0 - \frac{0.059}{1}\log\frac{x}{1}$$

$0.2364 = -0.059\log x$

$x = 10^{-4}$

$pH = -\log[H^{\oplus}] = -\log 10^{-4} = 4$

7. Ans. (0)

Eq. H_2 = Eq. O_2

$$\frac{P(0.224)}{RT}\times 2 = \frac{P}{RT}(V_{O_2})\times 4$$

$$V_{O_2} = 0.112 \text{ litre}$$

8. Ans. (2)

$$\text{Equivalent of Ni} = \frac{It}{96500}$$

$$n_{Ni}\times 2 = \frac{5\times 20\times 60}{96500}$$

$n_{Ni} = 0.03108$ mol

Mass of Ni = 0.03108×58.7

≈ 1.82 gm

9. **Ans. (6)**

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

$$8\times10^{-7} = \frac{1}{R}.\left(\frac{2}{4}\right)$$

$$R = \frac{10^7}{16} = 6.25\times10^5\,\Omega$$

$$I = \frac{V}{R} = \frac{1}{10^7/16} = 1.6\times10^{-6}\,\text{amp}$$

10. **Ans. (12)**

$$\Lambda_m^\infty(CH_3COOH) = \Lambda_m^\infty(CH_3COONa) + \Lambda_m^\infty(HCl) - \Lambda_m^\infty(NaCl)$$

$$= 100 + 425 - 125$$

$$= 400\ Scm^2mol^{-1}$$

$$\Lambda_{eq}\times n_{factor} = \Lambda_m$$

$$48 \times 1 = \Lambda_m$$

$$\alpha = \frac{48}{400} = 12\times10^{-2} = 0.12$$

Dissociation percentage is 12.

Exercise – II (JEE-Main PYQs)

1. **Ans. (3)**

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

$$1.4 = \frac{1}{50}.\frac{\ell}{A} \Rightarrow \frac{\ell}{A} = 70\,m^{-1}$$

$$\kappa = \frac{1}{R}.\frac{\ell}{A} \Rightarrow \kappa = \frac{1}{280}\times70 = \frac{1}{4}\,Sm^{-1}$$

$$\lambda_m = \frac{1/4}{1000\times0.5} = 5 \times 10^{-4}\ Sm^2\ mol^{-1}$$

2. **Ans. (3)**

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

$$E_{MnO_4^\ominus/Mn^{2\oplus}} = E^0_{MnO_4^\ominus/Mn^{2\oplus}} - \frac{0.059}{5}\log\frac{1}{[H^\oplus]^8}$$

$$E_{MnO_4^\ominus/Mn^{2\oplus}} = 1.51 - \frac{0.059}{5}\log\frac{1}{(10^{-3})^8}$$

$$E_{MnO_4^\ominus/Mn^{2\oplus}} = 1.22\ volt$$

Now $MnO_4^\ominus$ can oxidise ion $X^\ominus$ then

$$\Rightarrow E_{MnO_4^\ominus/Mn^{2\oplus}} + E_{X^\ominus/X_2} > 0$$

$$\Rightarrow E_{MnO_4^\ominus/Mn^{2\oplus}} > E_{X_2/X^\ominus}$$

This condition is satisfied by $I^\ominus$ & $Br^\ominus$.

3. Ans. (2)

Copper cannot displace $Zn^{2\oplus}$ as Zn is present above in electrochemical series with respect to copper.

4. Ans. (1)

$$\begin{array}{l}CH_2—COOK\\ |\\ CH_2—COOK\end{array} + 2H_2O \longrightarrow H_{2(g)} + C_2H_{4(g)} + 2CO_{2(g)} + 2KOH$$

Potassium succinate

Eq. H_2 = Eq. C_2H_4 = Eq. CO_2 = 0.2

$$n_{H_2} \times 2 = n_{C_2H_4} \times 2 = n_{CO_2} \times 1 = 0.2$$

$$n_{H_2} = 0.1 mol.$$

$$n_{C_2H_4} = 0.1 \text{ mol}$$

$$n_{CO_2} = 0.2 \text{ mol}$$

Total volume = 0.4 × 22.4 = 8.96 lit

5. Ans. (3)

$Fe^{2\oplus}(aq) + 2e^{\ominus} \longrightarrow Fe(s)$ $\qquad E_1^0 = -0.47$

$Fe^{3\oplus}(aq) + e^{\ominus} \longrightarrow Fe^{2\oplus}(aq)$ $\qquad E_2^0 = +0.77$

$Fe^{3\oplus}(aq) + 3e^{\ominus} \rightarrow Fe(s)$

$$E^0 = \frac{n_1E_1^0 + n_2E_2^0}{n} = \frac{2(-0.47) + 0.77}{3}$$

$$E^0 = -0.057 \text{ V}$$

6. Ans. (1)

$M(s) + 3Ag^{\oplus}(aq) \longrightarrow M^{3\oplus}(aq) + 3Ag(s)$

$$0.421 = \left(E^0_{M/M^{3\oplus}} + 0.8\right) - \frac{0.0591}{3}\log\frac{10^{-3}}{(10^{-2})^3}$$

$$0.421 = E^0_{M/M^{3\oplus}} + 0.8 - 0.0591$$

$$E_{M/M^{3\oplus}} = -0.32 \text{ V}$$

$$E_{M^{3\oplus}/M} = +0.32 \text{ V}$$

7. Ans. (2)

$B_2H_6(g) + 3O_2 \longrightarrow B_2O_3(s) + 3H_2O$

Moles of $B_2H_6 = \frac{27.6}{27.6} = 1$

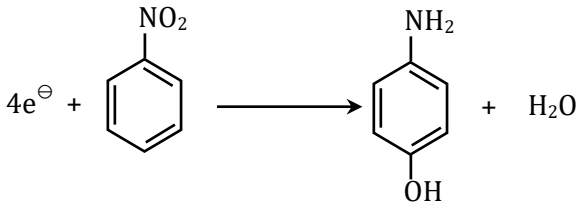
$\therefore$ Moles of O_2 required = 3 × 1 = 3

Equivalent of $O_2 = \frac{It}{96500}$

$3 \times 4 = \frac{100 \times t}{96500} \Rightarrow t = 11580$ sec (n_f of O_2 in this reaction is 4)

t = 3.2 hours.

8. Ans. (4)



$$\text{Eq. (p-aminophenol)} = \frac{It}{96500}$$

$$\frac{m}{109} \times 4 = \frac{9.65 \times 3600}{96500}$$

M = 9.81 g

9. Ans. (3)

$$E^0_{cell} = E^0_{Zn/Zn^{2\oplus}} + E^0_{M^{\oplus}/M}$$

$$= 0.76 + E^0_{Au^{3\oplus}/Au}$$

$$= 0.76 + 1.4 = 2.16V$$

10. Ans. (1)

$\Delta G° = -RT \ln K$

$-2 \times 96000 \times 2 = -8 \times 300 \ln K$

$\ln K = 160$

$K = e^{160}$

11. Ans. (1)

$$\frac{dE^0}{dT} = \frac{\Delta S^0}{nF} = -5 \times 10^{-4}$$

$$\frac{\Delta S^0}{2 \times 96000} = -5 \times 10^{-4}$$

$\Delta S^0 = -96$ J/Kmol

$\Delta G° = \Delta H° - T\Delta S°$

$$\frac{-2 \times 96000 \times 2}{1000} = \Delta H° + 300 \times \frac{96}{1000}$$

$-384 - 28.8 = \Delta H°$

$\Delta H° = -412.8$ KJ/mol

12. Ans. (2)

$$\Lambda^0_{HA} = 100.5 + 425.9 - 126.4$$

$$\Lambda^0_{HA} = 400$$

$$\Lambda^{0.001}_{HA} = \frac{5 \times 10^{-5} \times 1000}{10^{-3}} = 50 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\alpha_{HA} = \frac{\Lambda^{0.001}_{HA}}{\Lambda^0_{HA}} = \frac{50}{400} = 0.125$$

13. Ans. (1)

$\frac{1}{2}H_{2(g)} \longrightarrow H^{\oplus}_{(aq)} + e^{\ominus}$

$e^{\ominus} + AgCl_{(s)} \longrightarrow Ag_{(s)} + Cl^{\ominus}_{(aq)}$

$$\frac{1}{2}H_{2_{(g)}} + AgCl_{(s)} \rightarrow Ag_{(s)} + Cl^{\ominus}_{(aq)} + H^{\ominus}_{(aq.)}$$

$$E = E^{\circ} - \frac{0.06}{n}\log\frac{[H^{\oplus}][Cl^{\ominus}]}{(P_{H_2})^{1/2}}$$

$$0.92 = \left(E^0_{H_2/H^{\oplus}} + E^0_{Cl^{\ominus}/AgCl/Ag}\right) - \frac{0.06}{1}\log\frac{\left(10^{-6}\right)\left(10^{-6}\right)}{1}$$

$$0.92 = 0 + E^0_{Cl^{\ominus}/AgCl/Ag} + 0.72$$

$$E^0_{Cl^{\ominus}|AgCl|Ag} = 0.2\ V$$

14. Ans. (3)

Eq. ($PbSO_4$) = no. of faraday

$$\frac{m_{PbSO_4}}{303} \times 2 = 0.05$$

$$m_{PbSO_4} = 7.575\ gm$$

$$\approx 7.6\ gm$$

15. Ans. (1)

$2e^{\ominus} + Cu^{2\oplus}(aq) \longrightarrow Cu\ (s)$ $\qquad E^0_1 = 0.34$

$Cu\ (s) \longrightarrow Cu^{\oplus}(aq) + e^{\ominus}$ $\qquad E^0_2 = -0.522$

$e^{\ominus} + Cu^{2\oplus}(aq) \longrightarrow Cu^{\oplus}(aq)$

$E^0 \times 1 = 0.34 \times 2 - 0.522 \times 1$

$E^0 = 0.158\ V$

16. Ans. (2.15)

$$\overset{0}{\cancel{E}} = E^0 - \frac{0.06}{2}\log\frac{[Sn^{2\oplus}]}{[Pb^{2\oplus}]}$$

At equilibrium

$$0 = \left(+0.14 - 0.13\right) - 0.03\log\frac{[Sn^{2\oplus}]}{[Pb^{2\oplus}]}$$

$$0.01 = 0.03\log\frac{[Sn^{2\oplus}]}{[Pb^{2\oplus}]}$$

$$10^{1/3} = \frac{[Sn^{2\oplus}]}{[Pb^{2\oplus}]}$$

$$\frac{[Sn^{2\oplus}]}{[Pb^{2\oplus}]} = 2.15$$

17. Ans. (3776)

Eq. is-

$MnO_4^{\ominus} + H^{\oplus} + 5e^{\ominus} \rightarrow Mn^{2\oplus} + 4H_2O$

Nernst equation:

$$E_{cell} = E^0_{Cell} - \frac{0.059}{5}\log\frac{[Mn^{2\oplus}]}{[MnO_4^{\ominus}]}\left[\frac{1}{H^{\oplus}}\right]^8$$

(I) Given $[H^{\oplus}] = 1M$

$$E_1 = E^0 - \frac{0.059}{5}\log\frac{[Mn^{2\oplus}]}{[MnO_4^{\ominus}]}$$

(II) Now : $[H^{\oplus}] = 10^{-4}M$

$$E_2 = E^0 - \frac{0.059}{5}\log\frac{[Mn^{2\oplus}]}{[MnO_4^{\ominus}]} \times \frac{1}{(10^{-4})^8}$$

$$= E^0 - \frac{0.059}{5}\log\frac{Mn^{2\oplus}}{[MnO_4^{\ominus}]} + \frac{0.059}{5}\log 10^{-32}$$

therefore : $|E_1 - E_2| = \frac{0.059}{5} \times 32$

= 0.3776 V = 3776 × 10^{-4}

x = 3776

18. Ans. (266)

$$K = \frac{1}{R} \times \text{constant}$$

$0.152 \times 10^{-3} = \frac{1}{1750}$ cell constant

cell constant = 266 × 10^{-3}

19. Ans. (917)

$Cr_2O_7^{2\ominus} + 14H^{\oplus} + 6e^{\ominus} \rightarrow 2Cr^{3\oplus} + 7H_2O$

$$E = 1.33 - \frac{0.059}{6}\log\frac{(0.1)^2}{(10^{-2})(10^{-3})^{14}}$$

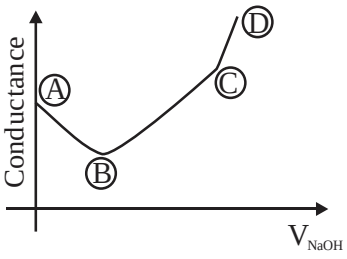
$$E = 1.33 - \frac{0.059}{6} \times 42 = 0.917$$

E = 917 × 10^{-3}

x = 917

20. Ans. (2)

$\underset{(WA)}{C_6H_5COOH} + \underset{(SB)}{NaOH} \longrightarrow \underset{(Salt)}{C_6H_5COONa} + H_2O$



(A) $\rightarrow$ (B) Free $H^{\oplus}$ ions are replaced by $Na^{\oplus}$ which decreases conductance.

(B) $\rightarrow$ (C) Un-dissociated benzoic acid reacts with NaOH and forms salt which increases ions & conductance increases.

(C) $\rightarrow$ (D) After equivalence point at (3), NaOH added further increases $Na^{\oplus}$ & $OH^{\ominus}$ ions which further increases the conductance.

Exercise - III (JEE Advanced Pattern)

SECTION–I

1. Ans. (B)

$G^* = \frac{\ell}{A} = \frac{10}{100} = 0.1$; G= 0.0001 S; V = 100 × 10 = 1000 cm^3 = 1 litre

κ = G, G* = 0.1 × 0.0001 = 10^{-5} S cm^{-1}

$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{(0.1 \times 0.0001) \times 1000}{0.5} = 0.02$ S cm^2 mol^{-1}

2. Ans. (A)

$\Lambda_{eq} = \kappa \times \frac{1000}{N}$; 1.50 × 10^{-4} × 10^4 = 9 × 10^{-6} × 10^{-2} × $\frac{1000}{N}$; N = 6 × 10^{-5}

$S = M = \frac{N}{nf} = \frac{6 \times 10^{-5}}{3} = 2 \times 10^{-5}$ mol / L

$Ag_3PO_{4(s)} \rightleftharpoons 3\,Ag^{\oplus} + PO_4^{3\ominus}$

K_{sp} 3 S S

$K_{sp} = (3S)^3 . S = 27.S^4$

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

3. Ans. (A)

$Al^{3\oplus}(aq) + 3e^{\ominus} \rightarrow Al(s)$

$\frac{X}{96500} = 3$

X = 3 × 96500

$Ag^{\oplus}(aq) + e^{\ominus} \rightarrow Ag(s)$

$\frac{X}{96500}$ moles of Ag will be deposited

$\frac{3 \times 96500}{96500}$ = 3 mol Ag

4. Ans. (B)

Mass of silver = (80 × 5 × 10^{-3}) × 1.05 gm

Moles of Ag = 0.42/108 = 3.8 × 10^{-3}

No. of Faraday = $\frac{3 \times t}{96500}$

$\frac{3t}{96500} = 3.8 \times 10^{-3}$

t = 122.23 sec

5. Ans. (C)

ΔG should be negative for a spontaneous process

$\Delta G = -nFE_{cell} < 0$

$\Delta G = \Delta G° + RT\,\ell nQ$

For equilibrium $\Delta G = 0$

$\Delta G° = -RT\ell nK_{eq}$

For spontaneous reaction, it should be forward in direction so, K_{eq} must be > 1

Then, $E^0_{cell} > 0$

SECTION-II

6. Ans. (C,D)

Discharging reaction

$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_{4(s)} + 2H_2O$

H_2SO_4 will be consumed and density of solution decreases.

7. Ans. (B,C,D)

(A) Dilute H_2SO_4 by Cu electrode

Anode $\Rightarrow Cu \rightarrow Cu^{2\oplus}$

(B) Dilute H_2SO_4 by inert electrode

Anode $\Rightarrow H_2O \rightarrow O_2$

(C) Fused NaOH with inert electrode

Anode $\Rightarrow OH^{\ominus} \rightarrow O_2$

(D) Dilute NaCl with inert electrode

Anode $\Rightarrow H_2O \rightarrow O_2$

8. Ans. (ABC)

$2H_2O \longrightarrow$	$2H_2$ +	O_2
$\frac{270}{18} = 15mol$	0	0
0	15 mol	7.5 mol

$V_{O_2} = 168$ lit

$V_{H_2} = 336$ lit

Total produced volume = 504 lit

Equivalent of H_2O = no. of faraday $\times \frac{75}{100}$

15×2 = no. of faraday $\times \frac{3}{4}$

No. of faraday = 40 F

So, option A, B & C are correct.

9. Ans. (B,C)

(A) $\Rightarrow Cl_2 + SO_4^{2\ominus} \longrightarrow Cl^{\ominus} + S_2O_8^{2\ominus}$

E = 1.36 – 2 = –0.64 volt

So, Cl_2 cannot oxidise $SO_4^{2\ominus}$

(B) $Cl_2 + Br^{\ominus} \longrightarrow Cl^{\ominus} + Br_2$ E= 1.36 – 1.09 = 0.27

$Cl_2 + I^{\ominus} \longrightarrow Cl^{\ominus} + I_2$ E = 1.36 – 0.54 = 0.82

So, option B is correct Cl_2 can oxidise both $I^{\ominus}$ and $Br^{\ominus}$

(C) $S_2O_8^{2\ominus} + Cl^{\ominus} \longrightarrow SO_4^{2\ominus} + Cl_2$ E = 2 – 13.6 = 0.64

$S_2O_8^{2\ominus} + I^{\ominus} \longrightarrow SO_4^{2\ominus} + Br_2$ E = 2 – 0.54 = 1.46

So $S_2O_8^{2\ominus}$ will oxidise $Cl^{\ominus}$, $I^{\ominus}$, $Br^{\ominus}$

(D) $Br^{\ominus}$ cannot be reduced further.

10. Ans. (A,D)

$Cl^{\ominus}_{(aq.)} + H^{\oplus}_{(aq.)} + Ag_{(s)} \longrightarrow AgCl_{(S)} + ½\ H_{2(g)}$

$$E = E^0 - \frac{0.0591}{1}\log\frac{P_{H_2}^{1/2}}{\left[Cl^{\ominus}\right]\left[H^{\oplus}\right]}$$

On increasing P_{H_2}, E.M.F. of cell decreases.

Decrease in $\left[Cl^{\ominus}\right]$ by KCl will decrease cell e.m.f.

SECTION–III

11. Ans. (C)

$$\begin{array}{ll} \text{At C,} & Ag^{\oplus}(aq) + e \longrightarrow Ag(s) \\ \text{At A,} & Ag(s) + Cl^{\ominus}(aq) \longrightarrow AgCl(s) + e \\ \hline \text{Overall} & Ag^{\oplus}(aq) + Cl^{\ominus}(aq) \longrightarrow AgCl(s) \end{array}$$

$$E_{cell} = E^o_{cell} - \frac{0.06}{1}\log\frac{1}{[Ag^{\oplus}]_C[Cl^{\ominus}]_A}$$

$$= E^o_{cell} - \frac{0.06}{1}\log\frac{1}{0.1\times 0.1}$$

or, $E_{cell} = E^o_{cell} - 0.06\times 2$

or, $E_{cell} = E^o_{cell} - 0.12$ ...(1)

Now, $E^o_{cell} = E^o_{Ag^{\oplus}/Ag} - E^o_{Cl^{\ominus}/AgCl/Ag}$

$$= E^o_{Ag^{\oplus}/Ag} - [E^o_{Ag^{\oplus}/Ag} + \frac{0.06}{1}\log K_{spAgCl}]$$

$= -0.06 \log K_{spAgCl}$

$= -0.06 \log 10^{-10}$

$= 0.6$ V

Clearly $E_{cell} = 0.6 - 0.12 = 0.48$ V > 0

$\therefore$ option(C) R – A – I is incorrect.

12. Ans. (A)

(Q) Pt, Cl_2(0.1 bar) | KCl(1M)

||NaCl(1M) Cl_2(1bar), Pt

$$\begin{array}{ll} \text{At A,} & 2Cl^{\ominus} \longrightarrow Cl_2 + 2e^{\ominus} \\ \text{At C,} & Cl_2 + 2e^{\ominus} \longrightarrow 2Cl^{\ominus} \\ \hline \text{Overall} & Cl_2(1\text{bar}) + 2Cl^{\ominus}(1M) \longrightarrow Cl_2(0.1\text{bar}) + 2Cl^{\ominus}(1M) \end{array}$$

$$E_{cell} = 0 - \frac{0.06}{2}\log\frac{P_{Cl_2,A} \times [Cl^{\ominus}]_C^2}{P_{Cl_2,C} \times [Cl^{\ominus}]_A^2}$$

when [KCl] is increases $\Rightarrow [Cl^{\ominus}]_A$ is increased

$\Rightarrow E_{cell}$ is increased.

13. Ans. (C)

$$E_{cell} = 0 - \frac{0.06}{1}\log\frac{[Ag^{\oplus}]_A}{[Ag^{\oplus}]_C}$$

when $[Ag^{\oplus}]_A$ is increased $\Rightarrow E_{cell}$ will decrease.

SECTION–IV

14. Ans. (A)

(A - Q, R; B - P, Q; C – Q, R; D - P, S)

	At C	At A	
(A) HCl(dilute)	H_2	Cl_2	$\rightarrow$ Q, R
(B) NaCl(dil, aq)	H_2	O_2	$\rightarrow$ P, Q
(C) NaCl(conc.)	H_2	Cl_2	$\rightarrow$ Q, R
(D) $AgNO_3$(aq)	Ag	O_2	$\rightarrow$ P, S

15. Ans. (C)

(A) $E^o_{cell} = E^o_{Cu^{2\oplus}/Cu} - E^o_{Mn^{2\oplus}/Mn}$

$= 0.34 - (-1.18) = 1.52V$

$$E_{cell} = E^o_{cell} - \frac{0.06}{2}\log\frac{[Mn^{2\oplus}]}{[Cu^{2\oplus}]}$$

or $E_{cell} = 1.52 - \frac{0.06}{2}\log\frac{0.1}{0.01}$

$= 1.52 - 0.03 = \boxed{1.49V}$

$\therefore$ P $\rightarrow$ 3, $\therefore$ (C) is correct.

(B) $Ag\left|AgBr\right|^{Br^{\ominus}}_{(0.1M)}\left\|{}^{Ag^{\oplus}}_{(0.01M)}\right|Ag$

$$E_{cell} = 0 - \frac{0.06}{1}\log\frac{[Ag^{\oplus}]_A}{[Ag^{\oplus}]_C}$$

or $E_{cell} = -\frac{0.06}{1}\log\frac{K_{spAgBr}}{[Br^{\ominus}][Ag^{\oplus}]}$

or $E_{cell} = \frac{-0.06}{1}\log\frac{10^{-13}}{0.1\times0.01}$

$= -0.06 \times (-10) = \boxed{0.6V}$

(C) $Pt, H_2(4\ atm)\left|\begin{matrix}H^{\oplus}\\(0.01M)\end{matrix}\right|\left|\begin{matrix}Cl^{\ominus}\\(0.2M)\end{matrix}\right|\left|\begin{matrix}Cl_2\\(1\ atm)\end{matrix}\right|Pt^{\ominus}$

$$\text{At C,}\quad \frac{1}{2}Cl_2(g)+e\longrightarrow Cl^{\ominus}(aq)$$

$$\text{At A,}\quad \frac{1}{2}H_2(g)\longrightarrow H^{\oplus}(aq)+e$$

$$\text{Overall}\quad \frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g)\longrightarrow H^{\oplus}(aq)+Cl^{\ominus}(aq)$$

$$E^{o}_{cell}=E^{o}_{Cl_2/Cl^{\ominus}}-E^{o}_{H^{\oplus}/H_2}=1.36-0=1.36\ V$$

$$E_{cell}=1.36-\frac{0.06}{1}\log\frac{[H^{\oplus}]_A[Cl^{\ominus}]_C}{P^{1/2}_{H_2(g)}P^{1/2}_{Cl_2(g)}}$$

$$\text{or, } E_{cell}=1.36-\frac{0.06}{1}\log\frac{0.01\times0.2}{(4)^{1/2}\times(1)^{1/2}}$$

$$=1.36-0.06\log10^{-3}$$

$$=1.36+0.18=1.54V$$

(D) $Pt,\left|\begin{matrix}Fe^{2\oplus} & Fe^{3\oplus}\\(0.2M) & (0.02M)\end{matrix}\right|\left|\begin{matrix}MnO_4^{\ominus} & Mn^{2\oplus} & H^{\oplus}\\(0.1M), & (0.1M), & pH=5\end{matrix}\right|Pt$

$$\text{At A:}\quad Fe^{2\oplus}\longrightarrow Fe^{3\oplus}+e]\times5$$

$$\text{At C:}\quad MnO_4^{\ominus}+8H^{\oplus}+5e\longrightarrow Mn^{2\oplus}+4H_2O$$

$$\text{Overall}\quad 5Fe^{2\oplus}+MnO_4^{\ominus}+8H^{\oplus}\longrightarrow5Fe^{3\oplus}+Mn^{2\oplus}+4H_2O$$

$$E^{o}_{cell}=E^{o}_{MnO_4^{\ominus}/Mn^{2\oplus}}-E^{o}_{Fe^{3\oplus}/Fe^{2\oplus}}$$

$$=1.52-0.77=0.75\ V$$

$$E_{cell}=E^{o}_{cell}-\frac{0.06}{5}\log\frac{[Fe^{3\oplus}]^5\times[Mn^{2\oplus}]}{[Fe^{2\oplus}]^5\times[MnO_4^{\ominus}]\times[H^{\oplus}]^8}$$

$$\text{or } E_{cell}=0.75-\frac{0.06}{5}\log\left(\frac{0.02}{0.2}\right)^5\times\frac{0.1}{(0.1)(10^{-5})^8}$$

$$=0.75-\frac{0.06}{5}\log10^{35}$$

$$=0.75-0.06\times7$$

$$=0.75-0.42=\boxed{0.33V}$$

SECTION–V

16. Ans. (10.00)

$$\kappa=\frac{1}{\rho}=\frac{1}{R}\left(\frac{\ell}{A}\right)=\frac{1}{50}\times\frac{2.1}{4.2}=\frac{1}{100}\text{ and }\Lambda_{eq.}=\frac{\kappa\times1000}{N}=\frac{1}{100}\times\frac{1000}{1}=10\ S\ cm^2\ eq^{-1}$$

17. Ans. (600.00)

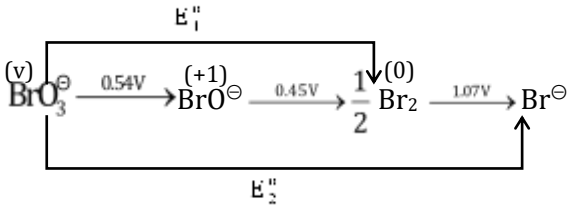
$\Lambda^{\infty}_{m}(H_2C_2O_4) = 700 + 800 - 900 = 600\Omega^{-1}\ cm^2\ mol^{-1}$

18. Ans. (12.00)

$Fe^{2\oplus} + Ce^{4\oplus} \rightleftharpoons Fe^{3\oplus} + Ce^{3\oplus}$

$E° = 1.44 - 0.68 = 0.76V = \frac{0.06}{1} \log K_C$; $K_C = 4.64 \times 10^{12}$

19. Ans. (0.55, 0.61)



$E_1^o = \frac{(5-1)(0.54)+(1-0)\times 0.45}{(5-0)} = \frac{2.16+0.45}{5} = 0.522V$

$E_2^o = \frac{(5-0)\times 0.522+(0-(-1))\times 1.07}{5-(-1)} = \frac{2.61+1.07}{6} = 0.613\ V$

20. Ans. (193.00)

$d = \frac{M}{V} \Rightarrow 10.8 = \frac{M}{80\times 5\times 10^{-4}} \Rightarrow M = 10.8 \times 400 \times 10^{-4}\ g$

$W = \frac{E\times I\times t}{96500} \Rightarrow 10.8\times 400\times 10^{-4} = \frac{108\times 2\times t}{96500} \Rightarrow t = 193\ sec$

Exercise - IV (JEE Advanced PYQs)

1. Ans. (D)

(P) $E^0_{Fe^{3\oplus},Fe}$

$e^{\ominus} + Fe^{3\oplus} \longrightarrow Fe^{2\oplus}$ $\quad E_1^0 = 0.77$

$2e^{\ominus} + Fe^{2\oplus} \longrightarrow Fe$ $\quad E_2^0 = -0.44$

$3e^{\ominus} + Fe^{3\oplus} \longrightarrow Fe$

$3\left(E^0_{Fe^{3\oplus},Fe}\right) = 1\times(0.77) - 2(0.44)$

$E^0_{Fe^{3\oplus}/Fe} = -0.0366 \approx -0.04\ V$

(Q) $2H_2O \longrightarrow O_2 + 4H^{\oplus} + 4e^{\ominus}$ $\quad E_1^0 = -1.23$

$O_2 + 2H_2O + 4e^{\ominus} \longrightarrow 4OH^{\ominus}$ $\quad E_2^0 = +0.40$

$4H_2O \longrightarrow 4H^{\oplus} + 4OH^{\ominus}$

$4\left(E^0\right) = -1.23\times 4 + 0.4\times 4$

$E^0 = -0.83\ V$

(R) $E^0\ (Cu^{2\oplus} + Cu \longrightarrow 2Cu^{\oplus})$

$2e^{\ominus} + Cu^{2\oplus} \longrightarrow Cu$ $\quad E_1^0 = +0.34$

$2Cu \longrightarrow 2Cu^{\oplus} + 2e^{\ominus}$ $\quad E_2^0 = -0.52$

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

$2 \times E^0 = 0.34 \times 2 - 0.52 \times 2$

$E^0 = \frac{-0.36}{2} = -0.18\,V$

(S) $3e^{\ominus} + Cr^{3\oplus} \longrightarrow Cr$ $\quad E^0 = -0.74$

$Cr \longrightarrow Cr^{2\oplus} + 2e^{\ominus}$ $\quad E^0 = +0.91$

$Cr^{3\oplus} \longrightarrow Cr^{2\oplus}$

$1 \times E^0_{Cr^{3\oplus}, Cr^{2\oplus}} = 3(-0.74) + 2(0.91)$

$= -0.4\ V$

2. Ans. (A)

(P) First increase then does not change much

(Q) First remain constant then increase

(R) First decrease then does not change much

(S) First decrease then increase

3. Ans. (A,B)

(A) Salt bridge does not actively participate in cell reaction.

(B) Stops diffusion of ion from one electrode to another.

(C) Salt bridge is not necessary for cell reaction to occur, it is necessary to carry out the cell reaction for long time.

(D) After applying salt bridge, it stops mixing of two electrolytes.

4. Ans. (3)

$\lambda^0_{X^{\ominus}} \approx \lambda^0_{Y^{\ominus}}$

$\lambda^0_{H^{\oplus}} + \lambda^0_{X^{\ominus}} \approx \lambda^0_{H^{\ominus}} + \lambda^0_{Y^{\ominus}}$

$\lambda^0_{HX} \approx \lambda^0_{HY}$

$\frac{\lambda_{HX}}{\lambda_{HY}} = \frac{1}{10}$

$\frac{\lambda_{HX}/\lambda^0_{HX}}{\lambda_{HY}/\lambda^0_{HY}} = \frac{1}{10}$

$\frac{\alpha_{HX}}{\alpha_{HY}} = \frac{1}{10}$

$\frac{\sqrt{\frac{(K_a)_{HX}}{0.01}}}{\sqrt{\frac{(K_a)_{HY}}{0.1}}} = \frac{1}{10}$

$\frac{K_a(HX)/0.01}{K_a(HY)/0.1} = \frac{1}{100}$

$\frac{K_a(HX)}{K_a(HY)} = \frac{1}{1000}$

$p^{K_a(HX)} - p^{K_a(HY)} = 3$

5. **Ans. (4)**

Let x mol of $M^{\oplus}$ oxidised so

$+193 \times 1000 = -2x \times 96500 \times (-0.25)$

$x = 4$ mol

6. **Ans. (D)**

$H_2 \longrightarrow 2H^{\oplus} + 2e^{\ominus}$

$2e^{\ominus} + M^{4\oplus} \longrightarrow M^{2\oplus}$

$H_2 + M^{4\oplus} \longrightarrow 2H^{\oplus} + M^{2\oplus}$

$$E_{cell} = E^0_{Cell} - \frac{0.059}{2}\log\frac{[H^{\oplus}]^2[M^{2\oplus}]}{P_{H_2}[M^{4\oplus}]}$$

$$0.092 = 0.151 - \frac{0.059}{2}\log 10^{x}$$

$$0.092 = 0.151 - \frac{0.059}{2}x$$

$x = 2$

7. **Ans. (6)**

$$\lambda_m = \frac{\frac{1}{R}.\frac{\ell}{A}\times 1000}{M}$$

$$\lambda_m = \frac{5\times 10^{-7}\times\frac{120}{1}\times 1000}{15\times 10^{-4}}$$

$\lambda_m = 40$ S c.m^2 mol^{-1}

$HX \rightleftharpoons H^{\oplus} + X^{\ominus}$

$c - c\alpha \quad c\alpha \quad c\alpha$

$[H^{\oplus}] = c\alpha$

$10^{-4} = 15 \times 10^{-4} \times \alpha$

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

$$\alpha = \frac{\lambda_m}{\lambda^0_m}$$

$$\frac{1}{15} = \frac{40}{\lambda^0_m}$$

$$\lambda^0_m = 600$$

$\lambda^0_m = 6 \times 10^2$ S cm^2 mol^{-1}

$Z = 6$

8. **Ans. (B)**

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

$$E = 1.1 - \frac{RT(2.303)}{2F}\log\frac{10}{1}$$

$\Delta G = -nFE = -2FE$

$\Delta G = -2.2F + RT(2.303)$

9. Ans. (–11.62)

$$A \longrightarrow A^{n\oplus} + ne^{\ominus} \times 2$$

$$2ne^{\ominus} + B^{2n\oplus} \longrightarrow B$$

$$2A + B^{2n\oplus} \longrightarrow 2A^{n\oplus} + B$$

$$\Delta G = \Delta G^\circ + RT\,\ell n\left(\frac{[A^{n\oplus}]^2}{[B^{2n\oplus}]}\right)$$

$O = \Delta G^\circ + (8.3 \times 300)\,\ell n4$

$\Delta G^\circ = -3486$ Joule/mol

$2\Delta G^\circ = \Delta H^\circ$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^0$

$\Delta G^\circ = 2\Delta G^\circ - T\Delta S^0$

$$\Delta S^0 = \frac{\Delta G^\circ}{T} = \frac{-3486}{300} = -11.62$$

10. Ans. (10)

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

$$E = E^0 - \frac{RT(2.303)}{nF}\log\frac{[Mg^{2\oplus}]}{[Cu^{2\oplus}]}$$

$$2.67 = 2.7 - \frac{R}{F}\times\frac{300\times2.3}{2}\log\frac{x}{1}$$

$$-0.03 = -\frac{300\times2.3}{2}\times\frac{1}{11500}\log x$$

$\log x = 1$

$x = 10$

11. Ans. (13.32)

$$\text{At A,}\quad H_2 \longrightarrow 2H^{\oplus} + 2e^{\ominus}]\times2$$

$$\text{At C,}\quad O_2 + 4H^{\oplus} + 4e^{\ominus} \longrightarrow 2H_2O$$

$$\text{Overall}\quad 2H_2(g) + O_2(g) \longrightarrow 2H_2O$$

$$E^o_{cell} = E^o_{O_2/H_2O} - E^o_{H^{\oplus}/H_2} = 1.23 - 0 = 1.23\ V$$

$\therefore\ \Delta G^\circ = -nFE^0_{cell} = -4 \times 96500 \times 1.23$ J

$= -474.78$ kJ.

$\therefore\ W_{max} = \Delta G^\circ = -474.78$ kJ

$\because\ \eta = 70\%$

$\therefore\ W = -474.78 \times 0.7$ kJ $= -323.346$ kJ

$2H_2(g) + O_2(g) \rightarrow 2H_2O$

10^{-3}mole

$\because$ 2 mole H_2 gives 323.346 kJ work

$\therefore$ 10^3 mole H_2 gives $\frac{323.346}{2}\times10^{-3}$kJ = 166.173 J.

ideal gas = 1 mole $\Rightarrow$ n = 1

monoatomic, q = 0,

$\because \Delta U = q + W$

$\therefore W = \Delta U = nC_{v_m}\Delta T$

or, $\Delta T = \frac{w}{nC_{V_m}} = \frac{166.173}{1\times\frac{3}{2}R}$

$= \frac{166.173\times2}{3\times8.314} = \boxed{13.32}$

12. Ans. (0.86)

$\Lambda_m^o = 4 \times 10^2$ Scm^2 mol^{-1}

$\Lambda_{m_1} = y \times 10^2$ Scm^2 mol^{-1}; $\Lambda_{m_2} = 3y \times 10^2$ Scm^2 mol^{-1}

$\alpha = \frac{\Lambda_{m_1}}{\Lambda_m^o} = \frac{y}{4}$ or, $\alpha = \frac{y}{4}$ ...(1)

$\alpha_2 = \frac{\Lambda_{m_2}}{\Lambda_m^o} = \frac{3y}{4}$.

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = \frac{C\alpha_2^2}{20(1-\alpha_2)} \Rightarrow \frac{C\times\left(\frac{y}{4}\right)^2}{\left(1-\frac{y}{4}\right)} = \frac{C\times\left(\frac{3y}{4}\right)^2}{20\left(1-\frac{3y}{4}\right)}$$

or, $\frac{1}{4-y} = \frac{9}{20(4-3y)}$

or, $80 - 60y = 36 - 9y$

or, $y = \frac{44}{51} = 0.862$ $\therefore$ $\boxed{Ans = 0.86}$

13. Ans. (0.21 or 0.22)

$\Lambda_m^o = 4 \times 10^2$ Scm^2 mol^{-1}

$\Lambda_{m_1} = y \times 10^2$ Scm^2 mol^{-1}; $\Lambda_{m_2} = 3y \times 10^2$ Scm^2 mol^{-1}

$\alpha = \frac{\Lambda_{m_1}}{\Lambda_m^o} = \frac{y}{4}$ or, $\alpha = \frac{y}{4}$ ...(1)

$\alpha_2 = \frac{\Lambda_{m_2}}{\Lambda_m^o} = \frac{3y}{4}$.

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = \frac{C\alpha_2^2}{20(1-\alpha_2)} \Rightarrow \frac{C\times\left(\frac{y}{4}\right)^2}{\left(1-\frac{y}{4}\right)} = \frac{C\times\left(\frac{3y}{4}\right)^2}{20\left(1-\frac{3y}{4}\right)}$$

or, $\frac{1}{4-y} = \frac{9}{20(4-3y)}$

or, 80 – 60y = 36 – 9y

or, $y = \frac{44}{51} = 0.862$ $\therefore$ $\boxed{Ans = 0.86}$

$\alpha = \frac{y}{4} = \frac{0.862}{4} = 0.215$ $\therefore \boxed{Ans = 0.21 \text{ or } 0.22}$

14. Ans. (A,B,C)

$X(s)|X^{2\oplus}(aq, 0.001M)||Y^{2\oplus}(aq, 0.1\ M)|\ Y(s)$

$E_{cell} = E° - \frac{0.059}{2}\log\frac{10^{-3}}{0.1}$

$= E° - \frac{0.059}{2} \times (-2)$

or, $E_{cell} = E° + 0.059$ ...(1)

(A) When X = Cd, Y = Ni, E° = – 0.24 – (– 0.40) = 0.16V

$\therefore E_{cell} = 0.16 + 0.059 > 0 \Rightarrow$ (A) is correct.

(B) When X = Cd, Y = Fe, E° = – 0.44 – (– 0.40) = – 0.04 V

$\therefore E_{cell} = -0.04 + 0.059 = 0.019 > 0 \Rightarrow$ (B) is correct

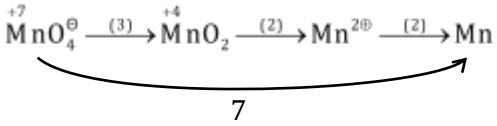
(C) when X = Ni and Y = Pb, E° = – 0.13 – (– 0.24) = 0.11 V

$\therefore E_{cell} = 0.11 + 0.059 > 0 \Rightarrow$ (C) is correct

(D) When X = Ni and Y = Fe, E° = – 0.44 – (– 0.24) = – 0.20 V

$\therefore E_{cell} = -0.20 + 0.059 < 0 \Rightarrow$ (D) is wrong

15. Ans. (0.77)



For the required reaction $\Delta G° = \Delta G°_1 + \Delta G°_2 + \Delta G°_3$

$\Rightarrow 7 \times E = 1.68 \times 3 + 1.21 \times 2 + (-1.03) \times 2$

$E = \frac{5.4}{7} = 0.7714$

Ans. = 0.77

16. Ans. (7)

$\Lambda°(U_mY_p) = m \times \lambda°_{U^{p\oplus}} + p \times \lambda°_{Y^{m\ominus}} = 250$

25m + 100p = 250

m + 4p = 10 ...(1)

$\Lambda°(V_mX_n) = m \times \lambda_{V^{n\oplus}} + n \times \lambda°_{X^{m\ominus}} = 440$

100m + 80n = 440

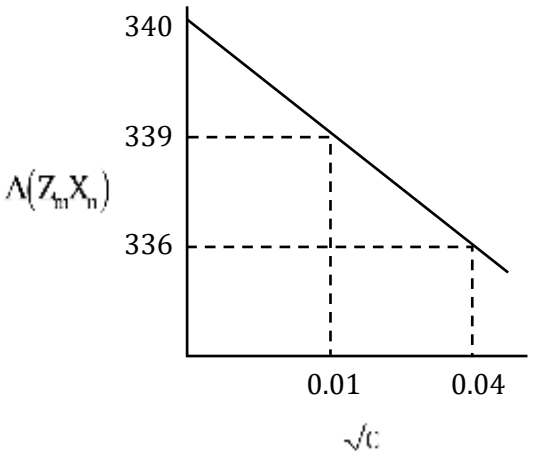
5m + 4n = 22 ...(2)

From the extrapolation of curve

$\Lambda°(Z_mX_n) = 340$

$m \times \lambda°_{Z^{n\oplus}} + n\lambda°_{X^{m\ominus}} = 340$

50m + 80n = 340



$5m + 8n = 34$ ...(3)

(3) — (2) $\Rightarrow$ $4n = 12 \Rightarrow n = 3$

Putting in (2) we get $m = 2$

Putting in (1) we get $p = 2$

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

17. Ans. (A)

For weak acid, $\alpha = \frac{\Lambda_m}{\Lambda_0}$

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow K_a(1-\alpha) = C\alpha^2$$

$$\Rightarrow K_a\left(1-\frac{\Lambda_m}{\Lambda_0}\right) = C\left(\frac{\Lambda_m}{\Lambda_0}\right)^2$$

$$\Rightarrow K_a - \frac{\Lambda_m K_a}{\Lambda_0} = \frac{C\Lambda_m^2}{(\Lambda_0)^2}$$

Divide by 'Λ_m'

$$\Rightarrow \frac{K_a}{\Lambda_m} = \frac{C\Lambda_m}{(\Lambda_0)^2} + \frac{K_a}{\Lambda_0}$$

$$\Rightarrow \frac{1}{\Lambda_m} = \frac{C\Lambda_m}{K_a(\Lambda_0)^2} + \frac{1}{\Lambda_0}$$

Plot $\frac{1}{\Lambda_m}$ vs $C\Lambda_m$ has

Slope = $\frac{1}{K_a(\Lambda_0)^2} = S$

y-intercept = $\frac{1}{\Lambda_0} = P$

Then, $\frac{P}{S} = \frac{\frac{1}{\Lambda_0}}{\frac{1}{K_a(\Lambda_0)^2}} = K_a\Lambda_0$