CHEMISTRY FOR JEE

Exercise-1

OBJECTIVE QUESTIONS

Section (B) : Application of Electrochemical Series

- **B-4.** Sol. E°_{OP} of $K > E^{\circ}_{OP}$ of Al.
- **B-5.** Sol. E°_{OP} of Mg > E°_{OP} of Al.
- **B-7.** Sol. M is more reactive than carbon and B is more reaitive than A. Also both B and A are less reactive than C.

Section (D) : Application Nernst Equation in Different type of Electrodes and Cells

D-7. Sol. Net redox change is zero.

Section (E) : Electrolysis and Applications of Electrolysis (Faraday's law)

- **E-5.** Sol. $\frac{W}{2 \times 2} = \frac{W'}{4 \times 1}$
- **E-8.** Sol. Faraday's laws are independent of all other external factors and $W \propto Q$.
- **E-9. Sol.** 6×10^{23} electron = 1eq.

E-10. Sol.
$$\frac{0.55}{M} \times 3 = \frac{0.55 \times 100 \times 60}{96500}$$

 $\Rightarrow M = 48.25 \text{ g/mol}$

E-12. Sol.
$$\frac{W}{M} \underset{x n =}{\overset{x n = 96500}{96500}}; \frac{0.838}{184} \underset{x n}{x n} \underset{=}{\overset{40 \times 60 \times 1.0}{96500}} \Rightarrow n = 6.$$

Section (F) : Faraday laws (Electrolysis)

- **F-6.** Sol. $Q = it = 100 \times 10^{-3} \times 30 \times 60 = 180$
- **F-7.** Sol. Oxidation occurs at anode; $CI^- \rightarrow \frac{1}{2} CI_2 + e^-$
- F-8. Sol. The characteristics of fuel cell.

F-9. Sol.
$$\frac{(W)_{H_2}}{(W)_{Cu}} = \frac{(Ew)_{H_2}}{(Ew)_{Cu}}$$



Section (G) : Electrical Conductance (Basic Definitions and Calculation of Conductance of Different Mixtures)

G-1. Sol. $Ka = 25 \times 10^{-6} \stackrel{\wedge eq}{=} = 19.6 \text{ Scm}^2 \text{ eq}^{-1}$, C = 0.01 $Ka = 0.01 \times \alpha^2 \qquad \Rightarrow \qquad \alpha = \sqrt{\frac{25 \times 10^{-6}}{10^{-2}}} = 5 \times 10^{-2}$ $\alpha = 5 \times 10^{-2} = \frac{\frac{19.6}{\sqrt{eq}}}{\sqrt{eq}} \qquad \Rightarrow \qquad \frac{19.6}{\sqrt{eq}} = \frac{19.6}{5 \times 10^{-2}} = 392 \text{ Scm}^2 \text{ eq}^{-1}.$ **G-6.** Sol. Conductance (G) $= \frac{1}{R} \Rightarrow \frac{1}{300}$ $\therefore \qquad \kappa = G^{\left(\frac{\ell}{A}\right)}$ Cell constant $\left(\frac{\ell}{A}\right) = \frac{0.013}{1} \times 300 = 3.9 \text{ cm}^{-1}$

Section (H) : Kohlrausch Law and Its Applications

H-1. Sol. $\lambda_{Ag^+} = 62.3 \text{ Scm}^2 \text{ mol}^{-1}$, $\lambda_{cl^-} = 67.7 \text{ Scm}^2 \text{ mol}^{-1}$ $K_{Agcl} = 3.4 \times 10^{-6} \text{ Scm}^{-1}$ $\Lambda_{Agcl}^{\infty} = (62.3 + 67.5) = \frac{1000 \times 3.4 \times 10^{-6}}{\text{S}}$ $S = \frac{3.4 \times 10^{-3}}{(62.3 + 67.5)} = 2.6 \times 10^{-5} \text{ M}$

Exercise-2

PART - I : OBJECTIVE QUESTIONS

1. Ans. As $E^{0}_{Cu2+} \longrightarrow Cu = 0.337 \text{ V} > \overset{E^{0}_{H^{+}/H_{2}}}{\therefore Cu^{2+}}$ can be reduced by H_{2} .

2. Sol.
$$H^+ + e^- \longrightarrow \frac{1}{2} H_2$$
. $E = 0 - \frac{.0591}{1} \log_{10} \frac{1}{[H^+]} = + 0.591 \log_{10}[H^+]$.
 $E_1 = 0 \{pH = 0\}$.

 $E_2 = + 0.0591 \log_{10}[10^{-7}] = -.0591 \times 7 \{at \ pH = 7\} = -0.41 \ V.$

- 6. Sol. Number of moles of Cu^{2+} discharged from anode = number of moles of Cu^{2+} deposited at cathode.
- 9. Sol. $2Fe + \overline{2} \underset{\text{Brown}}{O_2 \to Fe_2O_3}$

$$Ag + H_2S \rightarrow Ag_2S$$

- **10. Sol.** Follow theory of corrosion.
- **11.** Sol. $Cl_2 + 2KI \rightarrow 2KCI + l_2$; iodine will be first to impart violet colour to CHCl₃ layer.

12. Sol.
$$E_1 = \frac{-0.059}{1} \log [H^+]$$

or $pH_1 = E_1 / 0.059 = pK_a + \log \frac{x}{y}$
 $pH_2 = E_2 / 0.059 = pK_a + \log \frac{y}{x}$
or $\frac{E_1 + E_2}{0.059} = 2 pK_a$ or $pK_a = \frac{E_1 + E_2}{0.118}$

13. Sol.
$$E_{Fe^{2+}/Fe}^{\circ} = -0.441 \text{ V}$$

 $E_{Fe^{3+}/Fe}^{\circ} = -0.771 \text{ V}$
 $E_{cell}^{\circ} = E_{OP_{Fe}/Fe^{2+}}^{\circ} + E_{RP_{Fe^{3+}/Fe^{2+}}}^{\circ} \text{ (see redox change)}$
 $= + 0.441 + 0.771 = 1.212 \text{ V}$

14. Sol. Salt bridge is used to remove or eliminate liquid junction potential arised due to different relative speed of ions of electrolytes at the junction of two electrolytes in an electrochemical cell. Thus, A salt used for this purpose should have almost same speeds of its cation and anion.

15. Sol.
$$E_{cell} = \frac{E_{cell}^{0} - \frac{0.0591}{2} \log_{10} \frac{1}{[Cu^{2+}]}}{\log_{10} \frac{1}{[Cu^{2+}]}}$$
.
16. Sol. Eq. of AI = Eq. of Ag
 $\therefore \qquad \frac{W_{AI}}{9} = \frac{W_{Ag}}{108} \text{ or } \qquad \frac{W_{AI}}{W_{Ag}} = \frac{9}{108}$
18. Sol. $\frac{W}{7} = \frac{1930 \times 0.75}{96500}$; $W = 0.14 \text{ g}$

23. Sol.
$$\frac{1000 \times 2}{(55+32)} = \frac{27 \times 24 \times 3600 \times \eta}{96500}$$
 or $\eta = 0.951 = 95.1\%$

24. Sol. After removing cathode no net charge will flow but ions move randomly.

Exercise-3

PART - I : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS) OFFLINE JEE(MAIN)

1.	Sol.	The E° of cell will be zero.
••	00	

2. Sol. Here Cr^{3+} is oxidised to $C_2O_7^{2-}$

3.	Sol.	At LHS (oxidation) 2 × (Ag \rightarrow Ag	$g^+ + e^-$) $E^{0}_{ox} = -x$
	At RH	S (reduction) $Cu^{2+} + 2e^{-} \rightarrow Cu$	$E^{o}_{red} = + y$
	2Ag +	$Cu^{2+} \rightarrow Cu + 2Ag^{+}$	$E^{o}_{red} = (y - x)$

- $K = \frac{1}{\rho} = \frac{1}{R} \frac{\ell}{A}$
- 4. Sol.

5. Sol. $0 = 0.295 - 2 \log K$; $\log K = 10$; $K = 10^{10}$.

6.

Sol.		A	В	С
	E ^o red	+0.5 V	–3.0 V	–1.2 V
	The reduc	ing power follows	the following or	der : $B > C > A$.

0.059

- **7. Sol.** $E^{o}_{cell} = 0.77 + 0.14 = 0.91$ volt.
- 8. Sol. $^{0}_{\text{NaBr}} = 12$

 $^{\tilde{\wedge}}_{NaBr}$ = 126 + 152 – 150 = **128 S cm² mol⁻¹**.

9. Sol. $Zn + 2H^{+}_{(aq)} \longrightarrow Zn^{2+}(aq) + H_2(g)$ 0.0591 $[Zn^{2+}]pH_2$

$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{[L^{-1} - 19^{-1}]^2}{[H^+]^2}$$

Adding H_2SO_4 means increasing H_+ and therefore E_{cell} will increase and reaction will shift to forward direction.

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

- **11. Sol.** Difluoroacetic acid will be strongest acid due to electron withdrawing effect of two fluoring atoms so as it will show maximum electrical conductivity.
- **12.** Sol. $Al^{3+} + 3e^{-} \longrightarrow Al$.

 5.12×10^{3}

14.

Sol.

27 =189.62 mol.

Charge = $189.62 \times 3 \times 96500 = 5.489 \times 10^7$ coulomb.

13. Sol. $CH_3COONa + HCI \rightarrow CH_3COOH + NaCI$

 $\Lambda^{0}_{CH_{3}COONa} + \Lambda^{o}_{HCI} = \Lambda^{0}_{CH_{3}COOH} + \Lambda^{o}_{NaCI}$

 $\Lambda^{0}_{CH_{3}COOH} = \Lambda^{0}_{CH_{3}COONa} + \Lambda^{0}_{HCI} - \Lambda^{0}_{NaCI}$

From the reaction,

Thus to calculate the value of $\Lambda^{0}_{CH_{3}COOH}$ one should know the value of Λ^{0}_{NaCl} along with $\Lambda^{0}_{CH_{3}COONa}$ and Λ^{0}_{HCl} .

or

0.059

 $0.152 = -0.8 - 1 \log K_{SP}$

- ; $\log K_{SP} = -16.11.$
- **15.** Sol. According to Kohlrausch's law the molar conductivity at infinite diluation (Λ°) for weak electrolyte CH₃COOH is

 $\Lambda^{o}_{CH3COOH} = \Lambda^{o}_{CH3COONa} + \Lambda^{o}_{HCI} - \Lambda^{o}_{NaCI}$

So for calculating the value of $\Lambda_{oCH3COOH}$, value of Λ_{oNaCl} should also be known.

16. Sol.
$$0 = +1.1 - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}; \log \frac{[Zn^{2+}]}{[Cu^{2+}]} = 37.3.$$
; $\frac{[Zn^{2+}]}{[Cu^{2+}]} = 10_{37.3}$ Ans.

17. Sol.
$$E_{cell} = E^{0}_{cell} - \frac{0.059}{6} \log \frac{[Cr^{+3}]^{2}}{[Fe^{+2}]^{3}}$$

= $0.3 - \frac{0.056}{6} \log \frac{(0.1)^{2}}{(0.01)^{3}} = 0.3 - 0.04 = 0.26 V$

18. Sol. $Fe^{3+} + 3e^{-} \longrightarrow Fe \quad \Delta G_1 = -3 \times F \times \frac{E_{Fe^{3+}/Fe}^0}{E_{Fe^{2+}/Fe}^0}$ $Fe^{2+} \longrightarrow Fe \quad \Delta G_2 = -2 \times F \times \frac{E_{Fe^{2+}/Fe}^0}{E_{Fe^{2+}/Fe}^0}$ $Fe^{3+} + e^{-} \longrightarrow Fe^{2+} \quad \Delta G = \Delta G_1 - \Delta G_2$ $\Delta G = 3 \times 0.036F - 2 \times 0.439 \times F = -1 \times E^0 (Fe^{3+}/Fe^{+2}) \times F$ $E^0 (Fe^{3+}/Fe^{+2}) = 2 \times 0.439 - 3 \times 0.036$ = 0.878 - 0.108 = 0.770 V

19. Sol. $2 \over 3 Al_2 O_3 \longrightarrow 4 \over 3 Al + O_2$ $\Delta_r G = +966 \text{ kJ mol}^{-1} = 966 \times 10^3 \text{ J mol}^{-1}$ $\Delta G = - \text{ nFE}_{cell}$ $966 \times 10^3 = -4 \times 96500 \times E_{cell}$ $E_{cell} = 2.5 \text{ V}$

- 20. Sol. $2H^+$ (aq) + $2e^- \longrightarrow H_2$ (g) $E_{red} = E^{o}_{red} - \frac{0.0591}{n} \log \frac{P_{H_2}}{(H^+)^2}; E_{red} = 0 - \frac{0.0591}{2} \log \frac{2}{(1)^2}; \qquad E_{red} = -\frac{0.0591}{2} \log 2$ Ered is forund to be negative for (3) option. (fodYi (3) esa Ered dk eku .kkRed gS½ ... $X + Y^{2+} \rightarrow X^{2+} + Y$ 21. Sol. For reaction to be spontaneous E^o must be positive. $E^{o}_{Zn/Zn+2} + E^{o}_{Ni2+/Ni} = 0.76 + (-0.23) = +0.53$ (positive) 22. Sol. Higher the SRP, better is oxidising agent Hence MnO₄- is strongest oxidising agent 23. Sol. x = 1.4 S/m. $R = 50 \Omega$ M = 0.2 $K = \frac{1}{R} \times \frac{\ell}{A}$ \Rightarrow A = 1.4 x 50 m⁻¹. Now, new soltuion has M = 0.5, R = 280Ω $\Rightarrow \mathbf{K} = \frac{1}{\mathsf{R}} \frac{\mathbf{\ell}}{\mathsf{x} \mathsf{A}} = \frac{1}{280} \times 1.4 \times 50 = \frac{1}{4}$ $\Rightarrow \Lambda_{M} = \frac{K}{1000 \times M} = \frac{\frac{1}{4}}{1000 \times 0.5} = \frac{1}{2000} = 5 \times 10^{-4}$ $\lambda_c = \lambda_{\infty} - B\sqrt{C}$ (Debye Huckel onsagn equation) Sol. 24. 25. Sol. Reason : Higher the position of element in the electrochemical series, more difficult is the reduction of its cations. If Ca²⁺ (aq) is electrolysed, water is reduced in preference to it. Hence it cannot be reduced electrolytically from an aqueous solutions. $Mn^{2+} \xrightarrow{E_1^0 = 1.51V} Mn^{2+} \xrightarrow{E_2^0 = -1.18V} Mn$ Sol. 26.
 - 5. Sol. With $\longrightarrow Mn^{2+} \longrightarrow Mn$ \therefore for Mn²⁺ disproportionation, E⁰ = -1.51 V -1.18 V = -2.69 V < 0 Reaction is non-spontaneous. $Mn^{2+} \xrightarrow{E_1^0 = 1.51V} Mn^{2+} \xrightarrow{E_2^0 = -1.18V} Mn$
 - **27.** Sol. $Cu^{2+} + 2e^{-} \longrightarrow Cu$ 2F 1 mole

= 63.5 g.

- **28. Sol.** Galvanization is applying a coating of Zn.
- **29.** Sol. For strongest reducing agent E_{OP}° should be maximum.

$$\begin{split} E^{\circ}_{OP\ Cr/Cr^{+3}} &= 0.74\ V\\ Whereas\\ E^{\circ}_{OP\ Mn^{2^{+}}/MnO_{4}^{-}} &= -1.51\ V\\ E^{\circ}_{OP\ Cr^{3^{+}}/Cr_{2}O_{7}^{-2}} &= -1.33\ V\\ E^{\circ}_{OP\ Cl^{-}/Cl_{2}} &= -1.36\ V \end{split}$$

ONLINE JEE(MAIN)

5. Sol. Electrons flow from anode to cathode always.

6. Sol. $MnO_{4}^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_{2}O$ $E = 1.51 - \frac{0.059}{5} \log \frac{[MnO_{4}^{-}][H^{+}]^{8}}{[MnO_{4}^{-}][H^{+}]^{8}}$

Taking Mn^{2+} and MnO_4^- in standard state i.e. 1 M,

 $E = 1.51 - \frac{0.059}{5} \times 8 \log \frac{1}{[H^+]} = 1.51 - \frac{0.059}{5} \times 8 \times 3 = 1.2268 V$

Hence at this pH, $^{MnO_4^-}$ will oxidise only Br⁻ and I⁻ as SRP of Cl₂/Cl⁻ is 1.36 V which is greater than that for $^{MnO_4^-}$ /Mn²⁺.

7. Sol. If a block of copper metal is dropped into a beaker containing solution of 1 M ZnSO₄, no reaction will occur because $E_{Zn^{2+}/Zn}^{o} = -0.76 \text{ V}$

 $E^{o}_{Cu^{2+}/Cu} = +0.34 \text{ V}$

Hence Cu can't displace Zn from ZnSO₄ solution.

8. Sol. Fact

9.

Sol. $Fe^{2+} + 2e^{-} \longrightarrow Fe + \stackrel{E_1^o}{=} -0.47 \text{ V}$ $\underbrace{Fe^{3+} + e^{-} \longrightarrow Fe^{2+} + \stackrel{E_2^o}{=} +0.77 \text{ V}}_{Fe^{2+} + e^{-}}$

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

$$E_{3}^{o} = \frac{n_{1}E_{1}^{o} + n_{2}E_{2}^{o}}{n_{1} + n_{2}}$$

$$= \frac{2 \times (-0.47) + 2 \times (0.77)}{2 + 1}$$

$$= -0.057V$$

10.

 $\mathsf{E}^{\mathsf{o}}_{\mathsf{T}\ell/\mathsf{T}\ell^+} = + 0.34\mathsf{V}$ Sol. $= E^{o}_{A\ell/A\ell^{+}} = + 0.55V$ Therefore $T\ell^+$ more stable

 $E^{o}_{Mn^{2^+}/Mn^{3^+}} = 1.57V \ E^{o}_{H^+/H_2} = OV$ Sol. 11. Mn²⁺ cannot reduce H⁺ to H₂ 12. Sol. Cell reaction : $M_{(s)} + 3Ag^+ (aq) \longrightarrow M^{3+} (aq) + 3Ag_{(s)}$ Applying Nernst equation : $\mathsf{E}^o_{cell} - \frac{0.059}{}$

E_{cell} = I ^{con} n log₁₀ Q
∴ 0.421 = (0.8 ×
$$E^{o}_{M^{3+}/M}$$
) - $\frac{0.059}{3}$ log₁₀ $\frac{0.001}{(0.01)^{3}}$

:
$$E_{M^{3+}/M}^{o} = 0.32V$$

PART - II : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

001

* Marked Questions may have more than one correct option.

Zn | Zn²⁺ (0.01 M) | | Fe²⁺ (0.001 M) | Fe, 1. Sol. E = 0.2905. cell reaction, $Zn + Fe^{2+} = Zn^{2+} + Fe$. 0.0591 0.01 $0.2905 = E^{\circ} 2^{-1} \log 0.001$ $E^{0} = 0.32$ Volt. At equilibrium, (IkE; ij) $E_{cell} = 0$. 0.0591 $0 = 0.32 - 2 \log K_{eq}$ $K_{eq} = 10^{0.32/0.0295}$.

Sol. Fe \longrightarrow Fe²⁺ + 2e⁻, 2. 0.44 V.

1 $2H^+ + 2O_2 + 2e^- \longrightarrow H_2O$, 1.23 V. 1 $Fe + 2H^+ + 2 O_2 \longrightarrow Fe^{2+} + H_2O_1$, $E^0 = 0.44 + 1.23 = 1.67$ volt. $\Delta G^{\circ} = -2 \times 1.67 \times 96500 = -322.3 \text{ kJ}.$ 3. Sol. Mol of NaCl = $4 \times 0.5 = 2$ mol. 1 1 No. of mole of Cl₂ evolved = $\overline{2} \times \text{mol}$ of NaCl = $\overline{2} \times 2 = 1$ mol. Sol. 4. Taking the 1:1 molar combination of Na-Hg amalgam. weight = $2 \times 23 + 2 \times 200 = 446$ g. $2Na_{+} + 2e_{-} \longrightarrow 2Na.$ 5. Sol. No. of Faraday required = 2. total charge = 2 × 96500 = **193000 coulomb.** *:*. 6. Sol. $Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$. $E^{\circ} = 1.36 + (-0.54) = 0.82 V (+ ve)$. Spontaneous. 7. $Mn^{3+} + e^{-} \longrightarrow Mn^{2+}$ Sol. 1.50 volt. $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$, 1.23 volt. $4Mn^{3+} + 2H_2O \longrightarrow 4Mn^{2+} + O_2 + 4H^+$ $E_{cell} = 1.5 - 1.23 = 0.27$ volt. (+ ve). Mn³⁺ will oxidise H₂O. I x t (sec) 96500 Faraday law equivalents of H₂ produced = 8. Sol. $10 \times 10^{-3} \text{ xt}$ 96500 $0.01 \times 2 =$ = 96500 x 2 = t 19.3 x 10⁴ sec = t 9. Sol. M (s) | M⁺ (aq, 0.05 M) || M⁺ (aq, 1 M) | M(s) Anode : M (s) $\in \in \rightarrow M^+$ (aq) + e⁻ Cathode : M^+ (aq) + $e^- \rightarrow M$ (s) M+ (aq) |c = M+ (aq) |a M⁺(aq)|_a 0.0591 $E_{cell} = E^{\circ}_{cell} - \frac{1}{\log} M^{+}(aq)|_{c}$ 0.05 0.0591 $= 0 - 1 \log \left(-\frac{1}{1} \right)$ = + ve = 70 mV and hence $\Delta G = - nFE_{cell} = - ve$.



$$\begin{split} & E_{cell} = 0 - \frac{0.059}{2} log \Biggl\{ \frac{M^{2+}(aq)_a}{10^{-3}} \Biggr\} \\ & E_{cell} = 0 - \frac{0.059}{2} log \Biggl\{ \frac{M^{2+}(aq)_a}{10^{-3}} \Biggr\} \\ & 0.059 = \frac{log \Biggl\{ \frac{M^{2+}(aq)_a}{10^{-3}} \Biggr\} \\ & -2 = \frac{log \Biggl\{ \frac{M^{2+}(aq)_a}{10^{-3}} \Biggr\} \\ & 10^{-2} \times 10^{-3} = M^{2+} (aq)_a = solubility = s \\ & K_{sp} = 4s^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15} \end{split}$$

14. Sol. $\Delta G = -nFE_{cell} = -2 \times 96500 \times 0.059 \times 10^{-3} \text{ kJ/mole} = -11.4 \text{ kJ/mole}.$

$$F_{e^{3+}}^{e^{3+}} \xrightarrow{+0.77V}{n=1} Fe^{2+} \xrightarrow{-0.44V}{n=2} Fe$$
15. Sol. (P) $E^{0}F_{e3+}, Fe$ XV n = 3
 $\Rightarrow 1 \times 0.77 + 2 \times (-0.44) = 3 \times x$
 $\frac{0.11}{3}$ $\forall \sim -0.04 V.$
(Q) $4H_{2}O \xrightarrow{-0.14} 4H^{+} + 4OH^{-}$
 $2H_{2}O \longrightarrow O_{2} + 4H^{+} + 4e^{-} - 1.23 V$
 $+ O_{2} + 2H_{2}O + 4e^{-} \longrightarrow 4OH^{-} + 0.4 V$
 $4H_{2}O \xrightarrow{-0.52V} Cu$
(R) $E^{0}(Cu2++Cu \rightarrow 2Cu+)$ $+ 0.34V, n = 2$
 $\times \times 1 + 0.52 \times 1 = 0.34 \times 2$
 $\times = 0.16 V.$
 $\Rightarrow Cu^{2+} + e^{-} \longrightarrow Cu^{+} - 0.16 V$
 $+ Cu \longrightarrow Cu^{+} + e^{-} - 0.52 V$
 $Cu^{2+} + Cu \longrightarrow 2Cu^{+} - 0.36 V$
However, in the given option, $-0.18 V$ is printed.
 $Cr^{3+} - \frac{x}{n=1} + Cr^{2+} - \frac{-0.91V}{n=2} + Cr$
(s) $E^{0}(Cr3+, Cr2+) - 0.74V, n = 3$
 $\times \times 1 + 2 \times (-0.91) = 3 \times (-0.74)$
 $\times -1.82 = -2.22$

 $\begin{array}{ll} \Rightarrow & x = - \ 0.4 \ V \\ & \mbox{Hence, most appropriate is (D).} \\ & (P) - (3) \ ; \ (Q) - (4) \ ; \ (R) - (1) \ ; \ (S) - 2. \end{array}$

16. Sol. Salt bridge is introduced to keep the solutions of two electrodes separate, such that the ions in electrode do not mix freely with each other. But it cannot stop the process of diffusion. It does not participate in the chemical reaction. However, it is not necessary for occurence of cell reaction, as we know that designs like lead accumulator, there was no salt bridge, but still reactions takes place.

 $E_{cell} = E_{cell}^{\circ} - \frac{0.059}{2} \frac{[M^{2+}][H^{+}]^{2}}{Iog_{10}} \frac{[M^{2+}][H^{+}]^{2}}{[M^{4+}]pH_{2}}$ 17. Sol. 0.059 $0.092 = 0.151 = 2 \log_{10} 10^{x}$ $\therefore x = 2$ 18. Ans. 6 C = 0.0015MSol. ℓ = 120 cm $G = 5 \times 10^{-7} s$ $a = 1 \text{ cm}^2$ а G = κ× ^α/ℓ $5 \times 10^{-7} = \kappa \times \frac{1}{120}$ $\kappa = 6 \times 10^{-5} \text{ s cm}^{-1}$ $\frac{\kappa \times 1000}{6 \times 10^{-5} \times 1000}$ $\Lambda_{\rm m}^{\rm c} = \frac{\kappa \times 1000}{\rm M} = \frac{6 \times 1000}{\rm M}$ 0.0015 pH = 4 $[H^+] = 10^{-4} = c \alpha = 0.0015 \alpha$ 10^{-4} $\alpha = 0.0015$ $6\!\times\!10^{-5}\!\times\!1000$ $\alpha = \frac{\Lambda_{\rm m}^{\rm c}}{\Lambda_{\rm m}^{\rm o}} \Rightarrow \frac{10^{-4}}{0.0015} = \frac{\frac{0.0015}{0.0015}}{\Lambda_{\rm m}^{\rm o}}$ $\Lambda_{\rm m}^{\rm o}$ = 6 × 10² s cm² mole⁻¹ 19. Sol.

Additional Problems For Self Practice (APSP)

Marked Questions may have for Revision Questions.

PART - I : PRACTICE TEST PAPER

1. Sol.
$$E_{coll} \Rightarrow \frac{E_{SR}^{0} + J_{SR}^{0} + E_{FR}^{0} + J_{FR}^{0}}{2} \Rightarrow 0.15 - 0.77 = -0.62 V$$

2. Sol. $EMF = E_{contractor} - E_{Parrota}^{0} = 0.76 - 0.41 = 0.35.$
3. Sol. $2Cu^{+1} \longrightarrow Cu + Cu^{+2}$
 $2Cu^{+1} + 2e \longrightarrow 2Cu$
 $Cu - 2e \longrightarrow Cu^{+2}$
 $2Cu^{+1} \longrightarrow Cu^{+2} + Cu$
 $\frac{2 \times 0.521 + 2(-0.337)}{2} = 0.184$
Section- B
4. Sol. $CIO_{3^{-}} + 2H_{2}O + 4e \longrightarrow CIO^{-} + 4OH^{--}$; ΔG_{1}°
 $CIO^{-} + H_{2}O + e \longrightarrow \frac{1}{2}Cl_{2} + 2OH^{--}$; ΔG_{2}°
 $\frac{1}{2}Cl_{2} + e \longrightarrow CI^{-}$; ΔG_{3}°
 $\frac{CIO_{3^{-}} + 3H_{2}O + 3e \longrightarrow CI^{-} + 6OH^{--}$; ΔG_{3}°
 $CIO_{3^{-}} + 3H_{2}O + 3e \longrightarrow CI^{-} + 6OH^{--}$; ΔG_{3}°
 $CIO_{3^{-}} + 3H_{2}O + 3e \longrightarrow CI^{-} + 6OH^{--}$; ΔG_{3}°
 $Sol. E^{\circ} = -4F \approx 0.54 - 1F \times 0.45 - 1F \times 1.07$
 $Sol. E^{\circ} = + \frac{6}{6} = + 0.61 V$
5. Sol. $\frac{W_{1}}{E_{1}} = \frac{W_{2}}{E_{2}}; \frac{4}{12} = \frac{W_{A_{0}}}{108}; W_{A_{0}} = 36$
6. Sol. $Zn + Ni^{+2} \rightarrow Zn^{+2} + Ni$
 $E^{\circ} = \frac{E_{NI}^{0} + N_{1}}{P_{0}} = \frac{E_{2}^{0} + 0.53 V}{Positive value shows that the process is spontaneous. Rest of all (I) (III) (IIII) combination have negative E^{\circ} value.$

- (I) $E^{\circ} = -0.44 (-0.23) = -0.21 V$
- (II) $E^{\circ} = -0.76 (-0.23) = -0.53 V$
- (III) $E^{\circ} = -0.76 (-0.44) = -0.32 V$

Section-C

7.

Sol.
$$Cu_{2+} + 1e_{-} \rightarrow Cu_{+}$$

 $E_{1}^{0} = 0.15 \text{ v} \ \Delta G_{1}^{0} = -n_{1} \ E_{1}^{0} \text{ F}$
 $Cu_{+} + 1e_{-} \rightarrow Cu$
 $Cu_{2+} + 2e_{-} \rightarrow$

Sol. $\Delta G = - nFE; \text{ if } E > 0; \Delta G < 0 \Rightarrow$ Spontaneous reaction.

Note: If E^ocell > 0, then the reaction will be spontaneous at standard conditions, not necessarily at all condition or given condition.

Section-D

 $H^+ + e^- \longrightarrow \frac{1}{2} H_2$, $E = 0 - \frac{.0591}{1} \log_{10} \frac{1}{[H^+]} = + 0.0591 \log_{10}[H^+]$. 9. Sol. $E_1 = 0 \{ pH = 0 \}.$ $E_2 = + 0.0591 \log_{10}[10^{-7}] = -.0591 \times 7 \{at pH = 7\} = -0.41 V.$

 $E_{cell} = E_{cell}^{0} - \frac{0.0591}{1} \log_{10}[H^{+}] [CI^{-}] \qquad \text{and} \qquad E_{cell}^{'} = E_{cell}^{0} - \frac{0.0591}{1} \log_{10} 100[H^{+}] [CI^{-}].$ Sol. 10. $E'_{cell} - E_{cell} = -2 \times 0.0591 = -0.1182.$

11. Sol.
$$E_{cell} = \frac{E_{cell}^{0} - \frac{0.0591}{2}}{I_{cell} - \frac{1}{2}} \log_{10} \frac{\frac{P_{Cl_{2(anode)}}}{P_{Cl_{2(cathode)}}}}{\frac{1}{2} - \frac{1}{2}} = 0 - \frac{0.0591}{2} \log_{10} \frac{P_{1}}{P_{2}}}{\log_{10} \frac{1}{P_{2}}}$$

13.

Sol. Cell representation is correct, however working of cell will depend upon SRP values of both electrodes as well as concentration/partial pressure of species involved in cell reaction.

For $E_{cell} = E_{cell}^{o}$, $[Fe^{3+}] = [Fe^{2+}] = [I^{-}] = 1 \text{ M } \& P_{I_2} = 1 \text{ bar}.$ Cell reaction : $2Fe^{3+}$ (aq) + $2I^{-}$ (aq) $\rightarrow 2Fe^{2+}$ (aq) + $I_2(g)$ [I^{-} oxidized & Fe^{3+} reduced].

Section-E

14. Sol. Cell notation is anode || cathode.

Section-F

0.06

15. Sol. $0.34 = 2 \log K_{eq}$ log K_{eq} = 11.3 or K_{eq} = 2 × 10¹¹

Section-G

16. Sol. $Zn_{2+} + 2e_{-} \rightarrow Zn$ Q = it $= 5 \times 40 \times 60$ = 12000amount of $Zn = \frac{12000 \times 65}{2 \times 96500} = 4.065 \text{ g}$

17. Sol. For same charge passed mole of H_2 produced = 2 x moles of O_2 produced.

Section-H

19. Sol. $\frac{\frac{m_X}{m_Y}}{m_Y} = \frac{\frac{A_X}{2} \times Q}{1} \implies \frac{m_X}{m_Y} = 1 \qquad \because \qquad A_X = 2A_Y$

20. Sol.
$$\frac{W}{E} = \frac{it}{96500} \Rightarrow \frac{3}{E} = \frac{9.95 \times 10 \times 60}{96500} \Rightarrow E = 48.5$$

21. Sol. Let wt of metal deposited for x, y, z is 3a, 2a, a respectively & let moles of e⁻ passing for x, y, z be 1, 2 and 3 respectively then the wt of x, y, z deposited is E_x, 2E_y, 3E_z (where E_x, E_y, E_z are equivalent wt. of x, y, z)

$$\therefore E_{x} = 3a$$

$$2E_{y} = 2a \Rightarrow E_{y} = a$$

$$3E_{z} = a \Rightarrow E_{z} = \frac{a}{3}$$

$$\therefore E_{x} : E_{y} : E_{z}$$

$$= 3a : a : \frac{a}{3} = 9 : 3 : 1$$

Section-I

22.

Sol.

 $C_{4}H_{10} + \frac{13}{2}O_{2} \longrightarrow 4CO_{2} + 5H_{2}O$ 2 mol 13mol O₂ \bigcup 52mol electron transfer

Section-J

23. Sol. $R = \frac{1}{k} \frac{\ell}{A}$

Dilution upto twice of initial volume just complete submerge of electrodes, k becomes half and A becomes double. Hence R remains 50 Ω .

24. Sol.
$$K = \frac{1}{R} \left(\frac{\ell}{a} \right) \Rightarrow 0.0112 = \frac{1}{55} \left(\frac{\ell}{a} \right) \Rightarrow \frac{\ell}{a} = 0.616$$

25. Sol.
$$\lambda_{eq} = \frac{\left(\frac{1}{R} \times G^*\right) \times 10^{-3}}{N}$$
 $\therefore 10^{-2} = \frac{\left(\frac{1}{50} \times G^*\right) \times 10^{-3}}{1/10}$ $\therefore G^* = 50 \text{ m}^{-1}$

26. Sol. $\Lambda_m(\text{NaCl})$, $\lambda_m(\text{Na}^+)$, $\lambda_m(\text{Cl})$ keep on increasing as concentration decreases but κ keeps on decreasing with dilution.

Section- K

27. Sol. (i) K₂SO₄. Al₂(SO₄) . 24 H₂O $\Rightarrow 2^{K_{aq}^{+}} + 2^{Al_{aq}^{+3}} + 4^{SO_{aq}^{-2}}$. $\lambda_{m(Potashalum)}^{\alpha} = 2^{\lambda_{m}^{\alpha}(K^{+})} + 2^{\lambda_{m}^{\alpha}(Al^{+3})} + 4^{\lambda_{m}^{\alpha}(SO_{4}^{-2})}$ $= 2 \times 73.5 + 2 \times 189 + 4 \times 160 = 1165 \text{ r-.cm}^2.\text{mol}^{-1}$ V.F. for Potash alum = 8 . (total Positive charge) $\lambda_{eq}^{\alpha}(\text{Potashalum}) = \frac{\lambda_{eq}^{\alpha}(\text{Potashalum})}{8} = \frac{1165}{8} = 145.6 \,\Omega - \text{cm}^2 \text{ eq}^{-1}$ $\frac{\lambda_{eq}^{\alpha}(\text{Potashalume})}{\lambda_{eq}^{\alpha}(\text{Potashalume})} = \frac{1165}{145.6} = 8 : 1$ λ_{m}^{α}

(ii) $\overline{\lambda_{eq}^{\alpha}} = V.F.$ of Compound, V.F. of Potash alume = 8.

28. Sol.
$$(SA)^{\oplus} + CI^{-}$$
 $(SAB)^{\oplus} + CI^{-}$ $(SABB)^{\oplus} + CI^{-}$

H⁺ have highest mobility in comparison with Na^{\oplus} , both compound 100% dissociate. because Molar mass of H⁺ is less than Na^{\oplus} ion and NH₄OH is weak basic.

29. Sol. Equivalent conductance in different cell is equal : $\lambda_{eq} = \frac{K \times 1000}{N}$ K and N are constant

Section-L

30. Sol. $CH_3COOH + NaOH \longrightarrow Na^+ + CH_3COO^- + H_2O$ Conductance Ist increases slowly since no. of ions increases. After end point it increases sharply due to OH⁻ ions.

PART - II : PRACTICE QUESTIONS

- 2. Sol. The metal placed below in electrochemical series does not react with that metal salt solution which metal is placed above in series.
- **5.** Sol. At Anode : $2H_2O(\ell) \longrightarrow 4H^+(aq) + O_2(g) + 4e^-$

At Cathode : Ag⁺ (aq) + e⁻ \longrightarrow Ag (s) Eq. of O₂ evolved = Eq. of Ag formed \Rightarrow 0.1 Total loss in wt. $\frac{0.1 \times 32}{4}$ + 0.1 × 108 \Rightarrow 0.8 + 10.8 \Rightarrow 11.6 wt. of final solution = 108 - 11.6 \Rightarrow 96.4 g

- 8. Sol. Ionic compounds in molten state are conductor of electricity because of free ions.
- 9. Sol. $Zn = \frac{Zn_{(C_1)}^{2+}}{Zn_{(C_2)}^{2+}} + 2e^{-}$ $Zn_{(C_2)}^{2+} + 2e^{-} = Zn$ $Zn_{(C_2)}^{2+} = \frac{Zn_{(C_1)}^{2+}}{Zn_{(C_1)}^{2+}}$ $E = 0 - \frac{0.0591}{2} \log \frac{C_1}{C_2}$ $E \Rightarrow +ve \text{ When } C_1 < C_2$
- **10. Sol.** The e.m.f. of cell decreases gradually and finally to zero due to liquid junction potential arised in cell after removal of salt bridge.
- **11. Sol.** Metal with $\text{ ve } E^{\circ} P \text{ or } + \text{ ve } E^{\circ} O P$ possesses the tendency to get itself oxidised.

12. Sol.
$$AI \rightarrow AI_{3+} + 3e_{-}$$

$$\frac{x \times 9.65 \times 27}{3 \times 96500} = 10_{-3} \times 27$$
 (here, x is time in second)
By solving
x = 30 s

13. Sol. Au+ + e- → Au(s); E⁰ = 1.69 V(1); ΔG⁰1 Au₃₊ + 3e- → Au(s); E⁰ = 1.40 V(2); ΔG⁰2 From (2) - (1) Au₃₊ + 2e- → Au₊(s); ΔG⁰3 = ΔG⁰2 - ΔG⁰1 -2 × F × E⁰ = -3 × F × 1.40 + 1 × 1.69 × F; E⁰ = 1.255 V ∴ $E^{0}_{Au^{+}|Au^{3+}} = -1.255 V$

 $E_{H_2/H^+} = \frac{0.0591}{1} - \log_{10} \frac{[H^+]}{\sqrt{pH_2}}$ 14. Sol. 15. n = 2 for given reaction so $\Delta G^{\circ} = -nFE^{\circ}$ Sol. *:*. $-210 \times 1000 = -2 \times 96500 \times E^{\circ}$ E = 1.09 V ⇒ $\frac{\kappa \times 1000}{M} \Rightarrow \frac{1}{\rho} \times \frac{1}{M} \times 1000; \Lambda m =$ 1000 ху 17. Sol. Λm = 18. Sol. $\Lambda \sim m$ (NaBr) = $\Lambda \sim m$ (NaCl) + $\Lambda \sim m$ (KBr) - $\Lambda \sim m$ (KCl) ∧∞m (Na+) + ∧∞m (Br–) = 126.5 + 151.5 – 150 ∧∞m (Na+) = 50 $\Lambda m = \frac{\kappa}{M} \times 1000 \ ; \ (x + y) = \frac{\kappa}{M} \times 1000$ 19. Sol. $1000 \times \kappa$ M = (x + y)⇒ Solubility (in gL-1) = $\frac{\kappa \times 1000 \times 188}{x + y}$ Ka = Ca2 = $0.1 \times \left(\frac{7}{380.8}\right)^2$ = 3.38 × 10-5 Sol. 20. $\frac{\Lambda_{\infty}^{\mathsf{C}}}{\Lambda_{\mathsf{m}}^{\infty}}$ 21. Sol.