J-ADVANCED

1. $2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq.)} \longrightarrow 2Fe^{+2}_{(aq.)} + 2H_2O_{(\ell)}$

$$E = E^\circ - \frac{.0591}{4} \log \frac{[Fe^{+2}]^2}{P_{O_2} \cdot [H^+]^4}$$

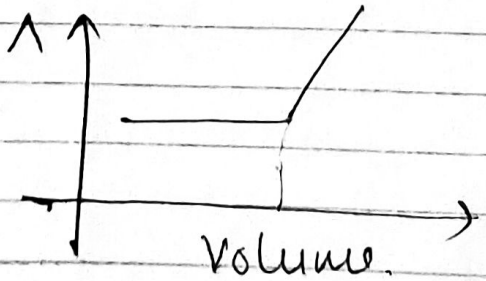
$$E = 1.67 - \frac{.0591}{4} \log \frac{(10^{-3})^2}{(10^{-1})(10^{-3})^4}$$

$$E = 1.67 - \frac{.0591}{4} \log 10^7$$

$$E = 1.67 - \frac{.0591}{4} \times 7$$

$$E = 1.566 \text{ Volt}$$

(2) Initially on adition of $AgNO_{3(aq.)}$ in aqueous KCl, KCl will convert in $KNO_{3(aq.)}$ and AgCl becomes p.p.t. so ultimately KCl will be replaced by KNO_3 so conductance ($\wedge$) will remain constant.
After Equivalence point on addition of $AgNO_3$ it will increase number of ions so conductance will increase



Q.3. $\Delta G = -nFE$

$= \frac{-2 \times 96500 \times .059}{1000} = -11.38$ KJ/mol

Q.4

$M \longrightarrow M^{+2}$

$M^{+2} \longrightarrow M$

$E = 0 - \frac{.059}{2} \log \frac{[M^{+2}]_{anode}}{10^{-3}}$

$.059 = -\frac{.059}{2} \log \frac{[M^{+}]_{anode}}{10^{-3}}$

$[M^{+}]_{anode} = 10^{-5}$ Molar

$MX_2 \rightleftharpoons M^{+2} + 2X^{\ominus}$

$\quad\quad\quad\quad s \quad\quad 2s$

$K_{sp} = (s)(2s)^2$

$K_{sp} = 4s^3$

$s = [M^{+2}] = 10^{-5}$

$K_{sp} = 4 \times 10^{-15}$

JEE (ADVANCED)

Q.5 (P) $\mathcal{E}^{\circ}_{Fe^{+3},Fe}$

$e^{\ominus} + Fe^{+3} \longrightarrow Fe^{+2}$ $\quad \mathcal{E}^{\circ}_1 = .77$

$2e^{\ominus} + Fe^{+2} \longrightarrow Fe$ $\quad \mathcal{E}^{\circ}_2 = -0.44$

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

$$3(\mathcal{E}^{\circ}_{Fe^{+3},Fe}) = 1\times(.77) - 2(.44)$$

$$\mathcal{E}^{\circ}_{Fe^{+3}/Fe} = -.0366 \simeq -0.04$$

Q. $2H_2O \longrightarrow O_2 + 4H^{+} + 4e^{\ominus}$ $\quad \mathcal{E}^{\circ}_1 = -1.23$

$O_2 + 2H_2O + 4e^{\ominus} \longrightarrow 4OH^{\ominus}$ $\quad \mathcal{E}^{\circ}_2 = +0.40$

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

$$4(\mathcal{E}^{\circ}) = -1.23\times4 + 0.4\times4$$

$$\mathcal{E}^{\circ} = -.83$$

R. $\mathcal{E}^{\circ}(Cu^{+2} + Cu \longrightarrow 2Cu^{+})$

$= \cancel{\mathcal{E}^{\circ}_{Cu^{+2}/Cu^{+}} + \mathcal{E}^{\circ}_{Cu^{+}/Cu}}$

$=$

$2e^{\ominus} + Cu^{+2} \longrightarrow Cu \qquad \mathcal{E}^{\circ}_1 = +0.34$

$2Cu \longrightarrow 2Cu^{+} + 2e^{\ominus} \qquad \mathcal{E}^{\circ}_2 = -.52$

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

(1) $\mathcal{E}^{\circ} = 0.34 \times 2 - .52 \times 2$

$\mathcal{E}^{\circ} = -0.36 \simeq -0.4$

(5) $3e^{-} + Cr^{+3} \longrightarrow Cr \qquad \mathcal{E}^{\circ} = -0.74$

$Cu \longrightarrow Cr^{+2} + 2e^{-} \qquad \mathcal{E}^{\circ} = +0.91$

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

(1) $\mathcal{E}^{\circ}_{Cr^{+3}, Cr^{+2}} = 3(-.74) + 2(0.91)$

$= -0.4$

Q.6 (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

Q.7 (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 rxn

(D) after applying salt bridge, it stop mixing of two electrolyte

8.

$$\lambda^{\circ}_{X^{\ominus}} \simeq \lambda^{\circ}_{Y^{\ominus}}$$

$$\lambda^{\circ}_{H^+} + \lambda^{\circ}_{X^{\ominus}} \simeq \lambda^{\circ}_{H^+} + \lambda^{\circ}_{Y^{\ominus}}$$

$$\lambda^{\circ}_{HX} \simeq \lambda^{\circ}_{HY}$$

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

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

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

$$\frac{\sqrt{\frac{K_{a(HX)}}{.01}}}{\sqrt{\frac{K_{a(HY)}}{0.1}}} = \frac{1}{10}$$

$$\frac{K_{a(HX)} / .01}{K_{a(HY)} / 0.1} = \frac{1}{100}$$

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

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

9. Let x mol of M^+ oxidised so

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

$$x = 4 \text{ mol}$$

10.

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

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

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

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{[H^+]^2 [M^{+2}]}{P_{H_2} [M^{+4}]}$$

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

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

$$x = 2$$

(11)

$$\Lambda_m = \frac{\frac{1}{R} \cdot \frac{l}{A} \times 1000}{M}$$

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

$$\Lambda_m = 40 \text{ S cm}^2 \text{ mol}^{-1}$$

$HX \rightleftharpoons H^+ + X^\ominus$

$C-C\alpha \quad C\alpha \quad C\alpha$

$[H^+] = C\alpha$

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

$\alpha = 1/15$

$\alpha = \frac{\lambda_m}{\lambda_m^\circ}$

$\frac{1}{15} = \frac{40}{\lambda_m^\circ}$

$\lambda_m^\circ = 600$

$\lambda_m^\circ = 6 \times 10^2 \ S\,cm^2\,mol^{-1}$

$Z = 6$

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

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

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

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

13. $A \longrightarrow A^{+n} + ne^{\ominus}$] $\times 2$

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

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

$$\Delta G = \Delta G^{\circ} + RT \ln \frac{[A^{+n}]^2}{[B^{+2n}]}$$

$$0 = \Delta G^{\circ} + (8.3 \times 300) \ln 4$$

$$\Delta G^{\circ} = -3486 \text{ Joule/mn.}$$

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

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$\Delta G^{\circ} = 2\Delta G^{\circ} - T\Delta S^{\circ}$$

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

14. $Mg + Cu^{+2} \longrightarrow Mg^{+2} + Cu$

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

$$2.67 = 2.7 - \frac{R}{F} \times \frac{300 \times 2.303}{2} \log \frac{x}{1}$$

$$-.03 = -\frac{300 \times 2.3}{2} \times \frac{1}{11500} \log x$$

$\log x = 1$

$\therefore$

$x = 10$