TOPIC : ELECTROCHEMISTRY

EXERCISE # 1

Section (A)

1.✍ In galvanic cell/electro chemical cell electrical energy is produced due to some chemical reaction.

6.✍ KCl can make precipitate with $AgNO_3$, $Pb(NO_3)_2$ so can't be used along these electrolyte.

Section (B)

1. E^o_{OP} of Mg > E^o_{OP} of Al.

2. E^o_{OP} for Cr^{2+} / Cr^{3+} is maximum +0.41 V and this Cr^{2+} will be easily oxidised to Cr^{3+}.

4. More –ve value of E^o means larger reducing power.

5. As $E^o_{Cu2+} \longrightarrow Cu = 0.337\ V > E^0_{H^+/H_2}$

$\therefore$ Cu^{2+} can be reduced by H_2 .

8.✍ E^o_{OP} of K > E^o_{OP} of Al.

Section (C)

1.✍ E^0 is intensive property and it does not depend on mass of F_2 taking part.

5. $E^o_{Fe^{2+}/Fe} = -\ 0.441\ V$

$E^o_{Fe^{3+}/Fe} = -\ 0.771\ V$

$E^o_{cell} = E^o_{OP_{Fe/Fe^{2+}}} + E^o_{RP_{Fe^{3+}/Fe^{2+}}}$ (see redox change)

$= +\ 0.441 + 0.771 = 1.212\ V$

Section (D)

5. $$E^o_{cell} = E^o_{cell} - \frac{2.303\quad RT}{F}\ \log\left[\frac{[Ni]}{[Ni^{2+}]}\right] = -\ 0.25 - \frac{0.06}{2}\ \log\left(\frac{1}{0.1}\right) (\because\ n = 2) = -\ 0.25 - 0.03 \times 1$$

$E_{cell} = -\ 0.28\ V$

6.✍ $E_{cell} = E^0_{Pb^{2+}/Pb} - E^0_{Zn^{2+}/Zn} = -\ 0.12 - (-0.76) = +0.64\ V$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\ \log\ \frac{[Zn^{2+}]}{[Pb^{2=}]} = 0.64 - \frac{0.0591}{n} \log 0.1 = 0.64 + 0.02955 = 0.667\ V$$

7. $$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log Q$$

$$\underset{0.1\ M}{Cu^{2+}} + Zn(s) \rightarrow \underset{1M}{Zn^{2+}} + Cu$$

$$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1}{0.1} = 10 \Rightarrow \qquad E_{cell} = 1.10 - \frac{0.591}{2}\ \log 10 = 1.10 - 0.0295 = 1.0705\ V$$

9.✍ $$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log_{10} \frac{1}{[Cu^{2+}]}.$$

10. Net redox change is zero.

11. $Zn \longrightarrow Zn^{2+}_{(C_1)} + 2e^-$

$Zn^{2+}_{(C_2)} + 2e^- \longrightarrow Zn$

$Zn^{2+}_{(C_2)} \rightleftharpoons Zn^{2+}_{(C_1)}$

$E = 0 - \frac{0.0591}{2} \log \frac{C_1}{C_2}$

$E \rightarrow$ +ve When $C_1 < C_2$

Section (E)

4.✍ Oxidation occurs at anode;

$Cl^- \longrightarrow \frac{1}{2} Cl_2 + e^-$

5. Pure water does not conduct electricity. But when small amount of acid say H_2SO_4 is added to it, water ionises. On passing electricity, it decomposes, H_2SO_4 being a strong electrolyte ionise completely whereas water is feebly ionised.

$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$

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

During electrolysis, the hydrogen ions migrate towards the cathode and discharge here in the form of hydrogen gas.

$2H^+ + 2e^-\ \ H_2\uparrow$

The overall reactions are :

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

$4H^+ + 4e^- \longrightarrow 2H_2$

At cathode

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

$4H^+ + 2H_2O \longrightarrow 2H_2$

At anode

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Overall cell reaction :

$4H^+ + 2H_2O \rightleftharpoons 2H_2 + O_2 + 4H^+$ as we see that acid used is regenerated at the end. Therefore, the whole electrolysis reaction is the dissociation of water to give oxygen at anode and hydrogen at cathode catalysed by H_2SO_4.

6. After decomposition of Cu^{2+} ions. H^+ ion will be discharged at cathode as its SRP is higher than of Fe^{2+} and Zn^{2+}.

Section (F)

5. Faraday`s laws are independent of all other external factors and $W \propto Q$.

6. 6×10^{23} electron = 1eq.

8.✍ $8H^+ + 5e^- + MnO_4^- \longrightarrow Mn^{+2} + 4H_2O$

(1 mole)

5 mole e^- = 5 Faraday.

9. $Ag^+ + e^- \longrightarrow Ag$

mole = $\frac{108}{108}$

= 1 mole

i.e. 1 faraday required

12. $\frac{W}{2 \times 2} = \frac{W'}{4 \times 1}$

15.✍ $\frac{W}{M} \times n = \frac{I \times t}{96500}$; $\frac{0.838}{184} \times n = \frac{40 \times 60 \times 1.0}{96500}$ $\Rightarrow$ n = 6.

18.✍ Eq. of Al = Eq. of Ag

$\therefore$ $\frac{W_{Al}}{9} = \frac{W_{Ag}}{108}$ or $\frac{W_{Al}}{W_{Ag}} = \frac{9}{108}$

19. $\frac{W}{7} = \frac{1930 \times 0.75}{96500}$; W = 0.14 gm

Section (G)

4. $2Fe + \frac{3}{2} O_2 \longrightarrow \underset{\text{Brown}}{Fe_2O_3}$

$Cu + CO_2 + H_2O \longrightarrow \underset{\text{Green}}{CuCO_3 . Cu(OH)_2}$

$Ag + H_2S \longrightarrow \underset{\text{Black}}{Ag_2S}$

Section (H)

1.✍ Conductivity = Conductance × Cell constant
Hence, units of conductivity = $ohm^{-1} \times cm^{-1}$

Section (I)

1. $\Lambda^{\infty}_{CH3COOH} = \lambda^{\infty}_{H+} + \lambda^{0}_{CH3COO-}$ = (35 + 315) mho cm^2 equ^{-1} = 350 mho cm^2 equ^{-1}.

7.✍ $Ka = 25 \times 10^{-6}$ $\wedge_{eq} = 19.6\ Scm^2\ eq^{-1}$, C = 0.01

$Ka = 0.01 \times \alpha^2 \quad \Rightarrow \quad \alpha = \sqrt{\frac{25 \times 10^{-6}}{10^{-2}}} = 5 \times 10^{-2}$

$\alpha = 5 \times 10^{-2} = \frac{19.6}{\overset{\circ}{\wedge}_{eq}} \quad \Rightarrow \quad \overset{\circ}{\wedge}_{eq} = \frac{19.6}{5 \times 10^{-2}} = 392\ Scm^2\ eq^{-1}$.

EXERCISE # 2

1.✍ Salt bridge complete the electrical circuit and minimises the liquid - liquid junction potential.

6.✍ The metal placed below in electrochemical series does not react with that metal salt solution which metal is placed above in series.

7. M is more reactive than carbon and B is more reaitive than A. Also both B and A are less reactive than C.

9.✍ Lowest S.R.P., highest reducing power.
10. Lower S.R.P. containing ion can displace higher S.R.P. containing ion.

11.✍ Lowest S.R.P., highest reducing power.

12. Ionic compounds in molten state are conductor of electricity because of free ions.

14.✍ $Fe^{3+} + 3e^- \longrightarrow Fe$, – 0.036 volt

$Fe \longrightarrow Fe^{2+} + 2e^-$, 0.44 volt

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$

$+ 3 \times 0.036f - 2 \times 0.44 \times f = -1 \times E^{\circ} \times f$

$E^\circ = 0.772$ Volt

15. $Cu+ + e– \longrightarrow Cu$, $E^\circ = x_1$ Volt

$Cu^{2+} + 2e^- \longrightarrow Cu$, x_2 Volt

$Cu \longrightarrow Cu^+ + e^-$ $-x_1$Volt

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

$$-2 \times x_2 \times f + 1 \times x_1 \times f = -1 \times E^o \times f$$

$E^o = 2x_2 - x_1$

16.✍ For spontaneous reaction in every condition

$E_{cell} > 0$, $\Delta G < 0$ and Q (reaction quotient) < K (equilibrium constant).

23.✍ $H_{2(p_1)} \longrightarrow 2H^+ + 2e^-$

$2H^+ + 2e^- \longrightarrow H_{2(p_2)}$

$X_{2(p_1)} \longrightarrow X_{2(p_2)}$

$$E = 0 - \frac{0.0591}{2} \log \frac{p_2}{p_1}$$

$P_2 < P_1$ for $E \rightarrow +ve$

24.✍ $E = 0 - \frac{0.0591}{2} \log \frac{16}{4} = -\frac{0.0591}{2} \times 2 \log 2 = -0.0591 \times 0.301$ **$= -0.0178$ Volt.**

If connected in reverse direction,E = 0.0178 volt.

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

29.✍ At anode $Ag \longrightarrow Ag^+ + e^-$

At cathode $Ag^+ + e^- \longrightarrow Ag$

So conc. of Ag^+ will remain same .

30. Mole of Fe deposited = $\frac{1}{2} \times 3 = 1.5$ mole

$W_{Fe} = 1.5 \times 56 =$ **84 g.**

31.✍ $W = \frac{63.5}{2 \times 96500} \times 2 \times 60 \times 60 = 2.37$ g

% of efficiency = ×100.

32. $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

No. of Faraday passed = $\frac{9.65 \times 1000}{96500} = 0.1$ F

n_{OH^-} formed = 0.1 mol

nNaOH = 0.1 mol $\equiv$ **4 g.**

33. Equivalence of H_2 = equivalence of O_2

$$\frac{0.224}{22.4} \times 2 = \frac{\text{volume of } O_2}{22.4} \times 4$$

0.112 litre = volume of O_2.

34. $\frac{0.55}{M} \times 3 = \frac{0.55 \times 100 \times 60}{96500}$ $\Rightarrow$ M = 48.25 g/mol

35. $Ag^+ + e^- \longrightarrow Ag$

$Mg \longrightarrow Mg^{2+} + 2\,e^-$

Number of atoms of Mg = $= \frac{4}{24} \times 2N_a = \frac{1}{3}N_a$

Number of moles of Ag = $\frac{\frac{1}{3}N_a}{N_a} = \frac{1}{3}$

wt. of Ag (in g) = $\frac{1}{3} \times 108 = 36$ g

37. The discharged acid cell (lead storage battery or cell) can be recharged by passing a direct current through it in opposite direction. During recharging of cell, the electrode material are restored in their original forms. Due to formation of H^+ and SO_4^{2-} ions the specific gravity of sulphuric acid increases and it attains the original value (1.3 g/cm^3) and also its EMF (voltage) increases.

During charging

At negative electrode :

$$PbSO_4(s) + 2e^- \xrightarrow[\text{current}]{\text{direct}} Pb(s) + SO_4^{2-}(aq)$$

At positive electrode :

$$PbSO_4(s) + 2H_2O \xrightarrow[\text{current}]{\text{direct}}$$

overall charging reaction :

$$\underbrace{2PbSO_4(s) + 2H_2O}_{\text{present on electrodes}} \xrightarrow{\text{Charging}} \underbrace{Pb(s) + PbO_2(s)}_{\text{electrode materials recovered}} + \underbrace{4\overset{+}{H}(aq) + SO_4^{2-}(aq)}_{H_2SO_4 \text{ reformed}}$$

overall reaction during charging :

$Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$

38. During the charging of a lead storage battery, the reaction at the anode and cathode are

Anode : $PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$

Cathode : $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + e^-$

In both the reactions H_2SO_4 is regenerated.

40.✍ For strong electrolyte

$\Lambda_M^C = \Lambda_M^\infty - b\sqrt{C}$

41.✍ Molar conductivity α no. of ions per mole of electrolyte.

43.✍ $\wedge_{m,BaSO_4} = (x_1 + x_2\,x - 2x_3) \quad \Rightarrow \quad \wedge_{eq.,BaSO_4} = \frac{\wedge_{eq.,BaSO_4}}{n - \text{factor}}$

$\wedge_{eq.,BaSO_4} = \frac{(x_1 + x_2 - 2x_3)}{2}$

44.✍ $Ka = 25 \times 10^{-6}$ $\wedge_{eq} = 19.6$ $Scm^2\,eq^{-1}$, C = 0.01

$Ka = 0.01 \times \alpha^2 \quad \Rightarrow \quad \alpha = \sqrt{\frac{25 \times 10^{-6}}{10^{-2}}} = 5 \times 10^{-2}$

$\alpha = 5 \times 10^{-2} = \frac{19.6}{\overset{\circ}{\wedge}_{eq}} \quad \Rightarrow \quad \overset{\circ}{\wedge}_{eq} = \frac{19.6}{5 \times 10^{-2}} = 392$ $Scm^2\,eq^{-1}$.

45. $Ka = C\alpha^2 = 0.1 \times \left(\frac{7}{380.8}\right)^2$ $\mathbf{= 3.38 \times 10^{-5}}$

EXERCISE # 3

PART - I

12. At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated.

Hence $\overset{\circ}{\Lambda}_{Al2(SO4)3} = \overset{\circ}{\Lambda}_{Al3+} + \overset{\circ}{\Lambda}_{SO_4^{2-}}$

13. EMF of a cell = Reduction potential of cathode – Reduction potential of anode
= Reduction potential of cathode + Oxidation potential of anode
= Oxidation potential of anode – Oxidation potential of cathode.

14. $\lambda_{eq} = \kappa \times V = \frac{\kappa \times 1000}{\text{normality}}$

On dilution, the number of current carrying particles per cm³ decreases but the volume of solution increases. Consequently, the ionic mobility increases, which in turn increases the equivalent conductance of strong electrolyte.

15. $2(e^- + Fe^{+3} \longrightarrow Fe^{+2})$ $E^o = 0.77$ V

$2I^- \longrightarrow I_2 + 2e^-$ $E^o = 0.536$ V

$2Fe^{+3} + 2I^- \longrightarrow 2Fe^{+2} + I_2$ $E^o = E^o_{ox} + E^o_{red}$

$= 0.77 - 0.536$

$= 0.164$ V

So, Reaction will taken place.

16. x = –1.2 V
y = + 0.5 V
z = –3.0 V
z > X > y
as $E°_{RP}\downarrow$, Reducing Power $\uparrow$

17. $Cu^{2+} + 1e^- \rightarrow Cu^+$ $E_1^0 = 0.15$ v $\Delta G_1^0 = - n_1 E_1^0 F$

$Cu^+ + 1e^- \rightarrow Cu$ $E_2^0 = 0.50$ v $\Delta G_2^0 = -n_2 E_2^0 F$

$Cu^{2+} + 2e^- \rightarrow Cu$ $\Delta G^o = \Delta G^o_1 + \Delta G^o_2$

$(-1)\, n\, E^0 F = (-1)\, n_1 E_1^0 F + (-1)\, n_2 E_2^0 F$

$E^0 = \frac{n_1E_1^0 + n_2E_2^0}{n} = \frac{0.15 \times 1 + 0.50 \times 1}{2}$ $\Rightarrow$ 0.325

18. $E^o_{Sn^{4+}/Sn^{2+}} = +0.15$ V

$E^o_{Cr^{3+}/Cr} = -0.74$ V

$E°_{cell} = E°_C - E°_A = 0.15 - (-0.74)$

$= 0.89$ V

19. $\Delta G^o = -nE^oF$

$E^o_{cell} > 0$

$\Delta G^o = -RT\ell nK_{eq}$

$\Delta G^o > 0$; $K_{eq} < 1$

20. $\Lambda^o_{m(NH_4OH)} = \Lambda^o_{m(NH_4Cl)} + \Lambda^o_{m(NaOH)} - \Lambda^o_{m(NaCl)}$.

21. E^o more positive, reducing agent will be greater.

22. $\lambda^0_M = \lambda^0_{CH3COONa} + \lambda^0_{HCl} - \lambda^0_{NaCl}$

$= 91 + 425.9 - 126.4$

= 390.5

23. $H_2 \longrightarrow 2H^+ + 2e^-$

1 atm 10^{-10}

$$E_{H_2/H^+} = 0 - \frac{0.059}{2}\log\frac{\left(10^{-10}\right)^2}{1}$$

$$E_{H_2/H^+} = +0.59 \quad V$$

24. $\alpha = \frac{\Lambda_M}{\Lambda_M^\infty} = \frac{9.54}{238}$ = 0.04008 = 4.008 %

25. $E°_{Cell} = E°_{OP} + E°_{RP}$

$= 0.76 + 0.34 = 1.10$ V

26. $MnO_4^{2-} \longrightarrow MnO_4^-$

0.1 mole

v.f. = 1

So, 0.1 mole = 96500 × 0.1

= 9650 C charge is required

27. $n_{O_2} = \frac{5600}{22400} = \frac{1}{4}$

$\frac{w_{Ag}}{108} \times 1 = \frac{w_{O_2}}{M_{O_2}} \times 4$ $(2H_2O \; O_2 + 4H^+ + 4e^-)$

$\frac{w_{Ag}}{108} = \frac{1}{4} \times 4$

$w_{Ag} = 108$ g

28. Fuel cell convert chemical energy of fuel like H_2, CH_4 into electrical energy

29. $2H^+_{(aq.)} + 2e^- \longrightarrow H_2$ (reduction reaction)

$$E = E^o - \frac{0.059}{2}\log\frac{P_{H_2}}{\left[H^+_{(aq.)}\right]^2}$$

$$0 = 0 - \frac{0.059}{2}\log\frac{P_{H_2}}{\left[10^{-7}\right]^2}$$

(In order to make log1 = 0)

$P_{H_2} = (10^{-7})^2 = 10^{-14}$ atm

30. $\lambda^o_M = \frac{k \times 1000}{M} = \frac{5.76 \times 10^{-3} \times 1000}{0.5}$ = 11.52 S cm^2 mol^{-1}.

31. $\frac{W}{E} = \frac{1 \times 60}{96500} = \frac{6}{9650}$ = no. of mole e^-

no. of e^- = $\frac{6}{9650} \times 6.02 \times 10^{23}$ = 3.75×10^{20}

32. $E°_{Zn^{+2}/Zn} = -0.76$ V

$E°_{Fe^{+2}/Fe} = -0.44$ V

Zn has higher negative SRP (Standard reduction potential) so it work as anode and protect iron to make iron as cathode.

33. Nernst equation for the given cell representation is given as

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

Value of EMF will be greater if $\left[Cu^{2+}\right] > \left[Zn^{2+}\right]$.

34. $BrO_4^- \xrightarrow{1.82V} BrO_3^- \xrightarrow{1.5V} HBrO \xrightarrow{1.595V} Br_2 \xrightarrow{1.0652V} Br^-$

For HBrO :

$HBrO \longrightarrow BrO_3^- + Br_2$

(+1) (+5) (0)

E^0_{cell} = (SRP)$_C$ – (SRP)$_A$ = $E^0_{HBrO/Br_2} - E^0_{BrO_3^-/HBrO}$

= 1.595 – 1.5 > 0 (Positive)

So reaction is spontaneous.

35. The standard Gibb's energy (Δ, G^o) = $-nFE^{\ominus}_{cell}$

Value of n = 2

$\Delta G^o = -2 \times 96500 \times 0.24 = -46320J = -46.32$ kJ

36. Nernst equation :

$$E^{\ominus}_{cell} = E^{\ominus}_{cell} \frac{-0.059}{n}\log Q_C$$

at equilibrium Ecell = 0, $Q_C = K_C$

$$E^{\ominus}_{cell} = \frac{-0.059}{n}\log K_C$$

Value of $E^{\ominus}_{cell}$ = 0.59 V

$$0.59 = \frac{0.059}{1}\log K_C$$

Value of n = 1

K_C = antilog 10

$K_C = 1 \times 10^{10}$

37. More –ve reducing potential, the more reducing power :

$E^0_{Al^{3+}/Al}$ = - 1.66 V

$E^0_{Ag^+/Ag}$ = 0.80 volt

$E_{K^+/K}$ = -2.93 volt

$E_{Cr^{3+}/Cr}$ = 0.74 volt

The decreasing order of reducing power

K > Al > Cr > Ag

38. $\lambda^{\infty}_{M(CH_3COOH)} \rightleftharpoons \vec{\lambda}^{\infty}_{CH_3COO^-} + \lambda^{\infty}_{H^+}$ ……(1)

$x = \lambda^{\infty}_M\left(H_2SO_4\right) \rightleftharpoons \lambda^{\infty}_{SO_4^{2-}} + 2\lambda^{\infty}_{H^+}$ ……(2)

$y = \lambda^{\infty}_M\left(K_2SO_4\right) \rightleftharpoons \lambda^{\infty}_{SO_4^{2-}} + 2\lambda^{\infty}_{H^+}$ ……(3)

$Z = \lambda^{\infty}_M\left(CH_3COOH\right) \rightleftharpoons \lambda^{\infty}_{CH_3COO^-} + \lambda^{\infty}_{K^+}$ ……(4)

eq^n (1) = eq^n (4) + $\frac{1}{2}$ eq^n (2) – $\frac{1}{2}$ eq^n (3)

$$= Z + \frac{1}{2}(x) - \frac{1}{2}y = \frac{x-y}{2} + z$$

PART - II

1. $2AgCl(s) + H_2(g)\ (1\ bar) \longrightarrow 2HCl(aq) + 2Ag(s)$

The cell with this cell reaction can be represented as :

$Pt(s)\ |\ H_2(g)\ (1\ bar)\ |\ 1M HCl(aq),\ ||\ Ag^+(aq)\ ||\ Ag(s)$

(anode) (cathode)

silver is undergoing reduction ($Ag^+ \longrightarrow Ag$) in this reaction, hence it will act as cathode in the cell. Option (1) has KCl which is not present in the cell, so it is incorrect. (3) has AgCl(s) and AgCl do not ionise, it is also incorrect. (4) at cathode Ag is being oxidised to Ag^+ and at cathode oxidation does not take place hence it is also incorrect.

Note : Remember LEO ⟶ loss of electrons is oxidation.

2. We know that,

standard Gibbs energy, $\Delta G^o = -nEF^o_{cell}$

For the cell reaction,

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

$\Delta G^o = -2 \times 96500 \times 0.46 = -88780\ J = -88.7\ kJ - 89.0\ kJ$

3. Galvanised iron i.e. iron coated with zinc does not rust easily as zinc has more negative electrode potential (–0.7V) than iron.

(–0.41V) i.e., zine is lesser reactive than iron.

4. $NaBr \rightleftharpoons Na^+ + Br^-$

$$\left.\begin{array}{l} 2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \\ Na^+ + OH^- \longrightarrow NaOH \end{array}\right] \text{at cathode}$$

$Br^- - e^- \longrightarrow Br$

$Br + Br \longrightarrow Br_2$ (at anode)

So, the products are H_2, Br_2 and NaOH. H_2 at cathode, Br_2 at anode and NaOH in solution.

5. In a Daniel cell $Zn\ |\ Zn^{2+}\ ||\ Cu^{2+}\ |\ Cu$

$E_{cell} = 1.1\ V$

The reaction of oxidation half cell

$Zn \longrightarrow Zn^{2+} + 2e^-$

The reaction of reduction half cell

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

So, $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

Because Zn is oxidised, it is deposited at anode and Cu is reduced so, it is deposited at cathode. If the opposite potential is greater than 1.1 V, then the electrons flow from cathode to anode. So both the statements are true and correct explanation.

7. The correct reason is the currect carried by cation and anion is equal to their transport number.

8. $Zn(l) + Hg(g) \longrightarrow ZnO(s) + Hg(l)$

The cell potential remains constant during its life as the overall reaction does not involve any ion ini solution whose concentration changes during its life time.

9. Given, pH = 14; $\therefore$ pOH = 0 and $[OH^-] = 1\ M$

$[Cu^{2+}][OH^-]^2 = k_{sp} = 1.0 \times 10^{-19}$

$\therefore \quad [Cu^{2+}] = 1.0 \times 10^{-19}\ M$

For the half-reaction,

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

$$E_{Cu^{2+}/Cu} = E^o_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]} = 0.34 - \frac{0.0591}{2}\log 10^{19} = -0.22\ V$$

10. In Hall-Heroult process, the following reactions occur

$3C + 2Al_2O_3 \longrightarrow 4Al + 3CO_2$

$4Al^{3+} + 12e^- \longrightarrow 4\ Al$

$\therefore \quad \Delta G^o = 3\Delta G_f^o(CO_2) - 2\ \Delta G_f^o(Al_2O_3)$

$= 3(-394) - 2(-1520)$

$= 1858$ kJ

$\Delta G^o = nFE^\circ_{cell}$

$$-E^\circ_{cell} = \frac{1858 \times 1000}{12 \times 96500} = 1.60\ V$$

11. $2NaCl + 2H_2O \xrightarrow{\text{electrolysis}} H_2 + Cl_2 + 2NaOH$

Weight of NaCl present in 0.5 L = 0.5 mol

charge = 965 × 5 = 4825 C

$\therefore$ Number of moles decomposed = $\dfrac{1 \times 4825}{96500} = 0.05$ mol

$\therefore$ Number of moles of NaOH formed is also 0.05.

$\therefore$ Molarity = $\dfrac{0.05 \times 1000}{500} = 0.1$

pOH = 1, pH = 13

12. $$E = E^\circ - \frac{0.05}{n} \log \frac{1}{[M^{n+}]}$$

$$= 0 - \frac{0.059}{1} \log \frac{1}{[10^{-4}]} = -0.236\ V$$

13. For a redox reaction to be spontaneous, the EMF of the cell must be positive.

As, $-\Delta G = nFE_{cell}$

Therefore, for E_{cell} = +ve, ΔG is always negative.

14. $$k = \frac{1}{R} \times \text{Cell constant} = \frac{0.47}{31.6} = 0.01487$$

24. $$E^0_{cell} = \frac{0.059}{2} \log k$$

$$E^0_{B^+/B} - E^0_{A^{+2}/A} = \frac{0.059}{2} \log$$

$$E^0_{B^+/B} - 0.34 = \frac{0.059}{2} \times 15.6$$

$$E^0_{B^+/B} = 0.80$$

25. Molar conductivity $\Lambda_m = \dfrac{\kappa \times 1000}{M}$

$$\frac{2 \times 10^{-6} \times 1000}{0.1}$$

$= \dfrac{2}{100}$ cm^2 mole^{-1}

M = Molarity

κ = specific conductivity

$\kappa = \dfrac{1}{R}$ x cell constant

$= \dfrac{1}{R}$ x $\dfrac{\ell}{A}$

$= \dfrac{1}{5 \times 10^3 \Omega}$ x $\dfrac{1\,cm}{100\ cm^2}$

$= 2 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$

26. $E_{Cell} = E^0_{Cell} - \frac{RT}{nF}\ell nQ$

$= 3.17 - \frac{0.059}{2}\ \log\frac{\left(Mg^{2+}\right)}{\left(Ag^{+}\right)^2} = 3.01\ V$

PART - III

1. $E^o_{cell} = 0.77 + 0.14 = 0.91$ volt.

2. $\overset{0}{\wedge}_{NaBr} = 126 + 152 - 150 =$ **$128\ S\ cm^2\ mol^{-1}$.**

3. $Zn + 2H^+_{(aq)} \longrightarrow Zn^{2+}\ (aq) + H_2\ (g)$

$E = E^o\ \frac{0.0591}{2} - \log\frac{[Zn^{2+}]\ \ pH_2}{[H^+]^2}$

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

4. $Cr^{2+} \mid Cr^{3+} = +0.41V$ $Mn^{2+} \mid Mn^{3+} = -1.57V$

$Fe^{2+} \mid Fe^{3+} = -0.77V$ $Co^{2+} \mid Co^{3+} = -1.97V$

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

5. Difluoroacetic acid will be strongest acid due to electron withdrawing effect of two fluoring atoms so as it will show maximum electrical conductivity.

6. $Al^{3+} + 3e^- \longrightarrow Al$.

$\frac{5.12\times10^3}{27} = 189.62$ mol.

Charge = 189.62 × 3 × 96500 = 5.489×10^7 coulomb.

7. $CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$ From the reaction,

$\Lambda^0_{CH_3COONa} + \Lambda^o_{HCl}\ \Lambda^0_{CH_3COOH} = +\ \Lambda^o_{NaCl}$ or $\Lambda^0_{CH_3COOH} = \Lambda^0_{CH_3COONa} + \Lambda^o_{HCl} - \Lambda^o_{NaCl}$

Thus to calculate the value of $\Lambda^0_{CH_3COOH}$ one should know the value of Λ^o_{NaCl} along with $\Lambda^0_{CH_3COONa}$ and Λ^o_{HCl}.

8. $0.152 = -0.8 - \frac{0.059}{1}\log K_{SP}$; **$\log K_{SP} = -16.11$.**

9. C = 0.1 M, R = 100 Ω

$K = 1.29\ Sm^{-1} = \frac{1}{100} \times \frac{\ell}{A}$.

C = 0.02 M, R = 520 Ω.

$K = \frac{1}{520} \times 129$

$\mathring{A}_M = \frac{\frac{1}{520}\times129}{1000\times0.02}$ **$= 124 \times 10^{-4}\ Sm^2mol^{-1}$.**

10. According to Kohlrausch's law the molar conductivity at infinite diluation (Λ^o) for weak electrolyte CH_3COOH is

$\Lambda^o_{CH3COOH} = \Lambda^o_{CH3COONa} + \Lambda^o_{HCl} - \Lambda^o_{NaCl}$

So for calculating the value of $\Lambda^o_{CH3COOH}$, value of Λ^o_{NaCl} should also be known.

11. $0 = +1.1 - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$; $\log \frac{[Zn^{2+}]}{[Cu^{2+}]} = 37.3.$; $\frac{[Zn^{2+}]}{[Cu^{2+}]}$ **$= 10^{37.3}$ Ans.**

12. $E_{cell} = E^0_{cell} - \frac{0.059}{6} \log \frac{[Cr^{+3}]^2}{[Fe^{+2}]^3} = 0.3 - \frac{0.056}{6} \log \frac{(0.1)^2}{(0.01)^3} = 0.3 - 0.04 = 0.26$ V

13. $Fe^{3+} + 3e^- \longrightarrow Fe$ $\Delta G_1 = -3 \times F \times E^0_{Fe^{3+}/Fe}$

$Fe^{2+} \longrightarrow Fe$ $\Delta G_2 = -2 \times F \times E^0_{Fe^{2+}/Fe}$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $\Delta G = \Delta G_1 - \Delta G_2$

$\Delta G = 3 \times 0.036F - 2 \times 0.439 \times F = -1 \times E^0 (Fe^{3+}/Fe^{+2}) \times F$

$E^0 (Fe^{3+}/Fe^{+2}) = 2 \times 0.439 - 3 \times 0.036 = 0.878 - 0.108 = 0.770$ V

14. $\frac{2}{3} Al_2O_3 \longrightarrow \frac{4}{3} Al + O_2$

$\Delta_r G = +966$ kJ mol^{-1} $= 966 \times 10^3$ J mol^{-1}

$\Delta G = -nFE_{cell}$

$966 \times 10^3 = -4 \times 96500 \times E_{cell}$

$E_{cell} = 2.5$ V

15. $2H^+ (aq) + 2e^- \longrightarrow H_2 (g)$

$E_{red} = E^o_{red} - \frac{0.0591}{n} \log \frac{P_{H_2}}{(H^+)^2}$; $E_{red} = 0 - \frac{0.0591}{2} \log \frac{2}{(1)^2}$; $E_{red} = -\frac{0.0591}{2} \log 2$

$\therefore$ E_{red} is forund to be negative for (3) option.

16. $X + Y^{2+} \longrightarrow X^{2+} + Y$

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)

17. Higher the SRP, better is oxidising agent. Hence MnO_4^- is strongest oxidising agent

18. x = 1.4 S/m.

R = 50 Ω

M = 0.2

$K = \frac{1}{R} \times \frac{\ell}{A} \Rightarrow \frac{\ell}{A} = 1.4 \times 50$ m^{-1} Now, new soltuion has M = 0.5, R = 280 Ω

$\Rightarrow K = \frac{1}{R} \times \frac{\ell}{A} = \frac{1}{280} \times 1.4 \times 50 = \frac{1}{4}$

$\Rightarrow \Lambda_M = \frac{K}{1000 \times M} = \frac{\frac{1}{4}}{1000 \times 0.5} = \frac{1}{2000} = 5 \times 10^{-4}$

19. $\lambda_c = \lambda_\infty - B\sqrt{C}$ (Debye Huckel onsagn equation)

20. Reason : Higher the position of element in the electrochemical series, more difficult is the reduction of its cations.

If Ca^{2+} (aq) is electrolysed, water is reduced in preference to it. Hence it cannot be reduced electrolytically from an aqueous solutions.

21. $Mn^{2+} \xrightarrow{E_1^0 = 1.51V} Mn^{2+} \xrightarrow{E_2^0 = -1.18V} Mn$

$\therefore$ for Mn^{2+} disproportionation, $E^0 = -1.51$ V -1.18 V $= -2.69$ V < 0. Reaction is non-spontaneous.

22. $Cu^{2+} + 2e^- \longrightarrow Cu$

2F 1 mole

= 63.5 g.

23. Galvanization is applying a coating of Zn.

24. For strongest reducing agent E°_{OP} should be maximum.

$E^\circ_{OP\,Cr/Cr^{+3}}$ = 0.74 V

Whereas

$E^\circ_{OP\,Mn^{2+}/MnO_4^-}$ = –1.51 V

$E^\circ_{OP\,Cr^{3+}/Cr_2O_7^{-2}}$ = –1.33 V

$E^\circ_{OP\,Cl^-/Cl_2}$ = –1.36 V

25. $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$

1 mol 3mol

3 mol O_2 is required for Burning 1 mol B_2H_6

$H_2O \xrightarrow{\text{Electrolysis}} H_2 + \frac{1}{2}O_2$ (V.F. of O_2 = 4)

$$\frac{\text{Equivalent of } O_2}{\text{V.F. of } O_2} = \text{mol of } O_2 = 3$$

$$\left[\frac{(100A)\times t\,\text{sec.}}{96500}\right]\times\frac{1}{4} = 3 \qquad \therefore\ t = \frac{3\times96500\times4}{100\times3600}\text{hr.} = 3.22\text{hrs.}$$

26. $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}$

For 2F current passed, $PbSO_4$ electrolyzed = 303g/mol

For 0.05F; $PbSO_4$ electrolyzed = $\frac{0.05\times303}{2}$ = 7.6g

27. Higher the SOP, higher will be reducing power.

28. A : $\frac{1}{2}H_2(g) \rightarrow H^+(aq.) + e^-$ $E^\circ = 0.0$ V

C : $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$ $E^\circ = x$ V

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{1}\log\{[H^+][Cl^-]\}$

$0.92 = x - \frac{0.06}{1}\log(10^{-12})$

$0.92 = x + 0.72$

$x = 0.92 - 0.72 = 0.2$ Volts

29. Fact

30. $E^\circ_{cell} = E^\circ_{Zn(s)|Zn^{+2}} + E^\circ_{Au^{+3}/Au(s)}$

= $SOP_{anode} + SRP_{cathode}$

= 0.76 V + 1.4 V = 2.16V

E°_{cell} is maximum with $E^\circ_{Au^{+3}|Au(s)}$ and E°_{cell} is intensive property so does not depend on number of electron transferred in cell reaction.

31. $\lambda^\circ_m(HA) = \lambda^\circ_m(HCl) + \lambda^\circ_m(NaA) - \lambda^\circ(NaCl)$

$= 425.9 + 100.5 - 126.4$

$= 400$

$$\lambda^\circ_m = \frac{K \times 1000}{M} \Rightarrow \frac{5 \times 10^{-5} \times 10^{3}}{10^{-3}}$$

$= 50$

$$\alpha = \frac{50}{400} = 0.125$$