

## 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  $\text{AgNO}_3$ ,  $\text{Pb}(\text{NO}_3)_2$  so can't be used along these electrolyte.

#### Section (B)

1.  $E^\circ_{\text{OP}}$  of Mg >  $E^\circ_{\text{OP}}$  of Al.
2.  $E^\circ_{\text{OP}}$  for  $\text{Cr}^{2+} / \text{Cr}^{3+}$  is maximum +0.41 V and this  $\text{Cr}^{2+}$  will be easily oxidised to  $\text{Cr}^{3+}$ .
4. More -ve value of  $E^\circ$  means larger reducing power.
5. As  $E^\circ_{\text{Cu}^{2+}} \longrightarrow \text{Cu} = 0.337 \text{ V} > E^\circ_{\text{H}^+ / \text{H}_2}$   
 $\therefore \text{Cu}^{2+}$  can be reduced by  $\text{H}_2$ .
8.  $E^\circ_{\text{OP}}$  of K >  $E^\circ_{\text{OP}}$  of Al.

#### Section (C)

1.  $E^\circ$  is intensive property and it does not depend on mass of  $\text{F}_2$  taking part.

$$\begin{aligned}
 5. \quad E^\circ_{\text{Fe}^{2+} / \text{Fe}} &= -0.441 \text{ V} \\
 E^\circ_{\text{Fe}^{3+} / \text{Fe}} &= -0.771 \text{ V} \\
 E^\circ_{\text{cell}} &= E^\circ_{\text{OP}_{\text{Fe} / \text{Fe}^{2+}}} + E^\circ_{\text{RP}_{\text{Fe}^{3+} / \text{Fe}^{2+}}} \quad (\text{see redox change}) \\
 &= +0.441 + 0.771 = 1.212 \text{ V}
 \end{aligned}$$

#### Section (D)

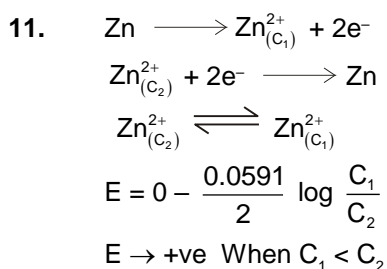
$$\begin{aligned}
 5. \quad E^\circ_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{2.303}{F} RT \log \left[ \frac{[\text{Ni}]}{[\text{Ni}^{2+}]} \right] = -0.25 - \frac{0.06}{2} \log \left( \frac{1}{0.1} \right) (\because n = 2) = -0.25 - 0.03 \times 1 \\
 E_{\text{cell}} &= -0.28 \text{ V}
 \end{aligned}$$

$$\begin{aligned}
 6. \quad E_{\text{cell}} &= E^\circ_{\text{Pb}^{2+} / \text{Pb}} - E^\circ_{\text{Zn}^{2+} / \text{Zn}} = -0.12 - (-0.76) = +0.64 \text{ V} \\
 E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]} = 0.64 - \frac{0.0591}{n} \log 0.1 = 0.64 + 0.02955 = 0.667 \text{ V}
 \end{aligned}$$

$$\begin{aligned}
 7. \quad E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0591}{n} \log Q \\
 \text{Cu}^{2+} + \text{Zn(s)} &\rightarrow \text{Zn}^{2+} + \text{Cu} \\
 0.1 \text{ M} \quad \quad \quad & \quad \quad 1 \text{ M} \\
 Q &= \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = \frac{1}{0.1} = 10 \Rightarrow E_{\text{cell}} = 1.10 - \frac{0.591}{2} \log 10 = 1.10 - 0.0295 = 1.0705 \text{ V}
 \end{aligned}$$

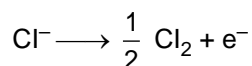
$$9. \quad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log_{10} \frac{1}{[\text{Cu}^{2+}]}$$

10. Net redox change is zero.

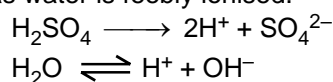


### Section (E)

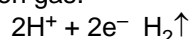
4. ✎ Oxidation occurs at anode;



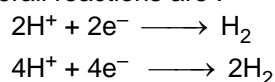
5. Pure water does not conduct electricity. But when small amount of acid say  $\text{H}_2\text{SO}_4$  is added to it, water ionises. On passing electricity, it decomposes,  $\text{H}_2\text{SO}_4$  being a strong electrolyte ionise completely whereas water is feebly ionised.



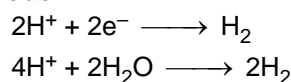
During electrolysis, the hydrogen ions migrate towards the cathode and discharge here in the form of hydrogen gas.



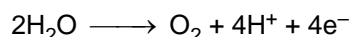
The overall reactions are :



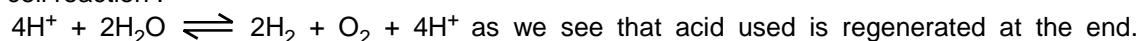
**At cathode**



**At anode**



Overall cell reaction :



Therefore, the whole electrolysis reaction is the dissociation of water to give oxygen at anode and hydrogen at cathode catalysed by  $\text{H}_2\text{SO}_4$ .

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

### Section (F)

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

6.  $6 \times 10^{23}$  electron = 1eq.

8. ✎  $8\text{H}^+ + 5\text{e}^- + \text{MnO}_4^- \longrightarrow \text{Mn}^{+2} + 4\text{H}_2\text{O}$   
 (1 mole)  
 5 mole  $\text{e}^-$  = 5 Faraday.

9.  $\text{Ag}^+ + \text{e}^- \longrightarrow \text{Ag}$   
 $\text{mole} = \frac{108}{108}$   
 $= 1 \text{ mole}$   
 i.e. 1 faraday required

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

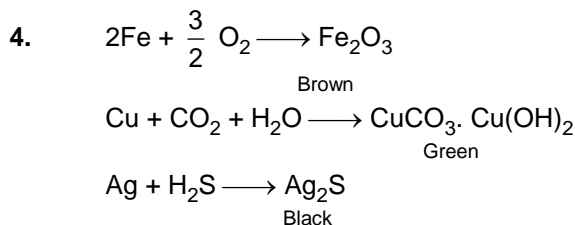
$$15. \frac{W}{M} \times n = \frac{I \times t}{96500}; \frac{0.838}{184} \times n = \frac{40 \times 60 \times 1.0}{96500} \Rightarrow n = 6.$$

$$18. \text{Eq. of Al} = \text{Eq. of Ag}$$

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

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

### Section (G)



### Section (H)

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

### Section (I)

$$1. \quad \Lambda^\infty_{\text{CH}_3\text{COOH}} = \lambda^\infty_{\text{H}^+} + \lambda^\infty_{\text{CH}_3\text{COO}^-} = (35 + 315) \text{ mho cm}^2 \text{ eq}^{-1} = 350 \text{ mho cm}^2 \text{ eq}^{-1}.$$

$$7. K_a = 25 \times 10^{-6} \quad \Lambda_{\text{eq}} = 19.6 \text{ Scm}^2 \text{ eq}^{-1}, C = 0.01$$

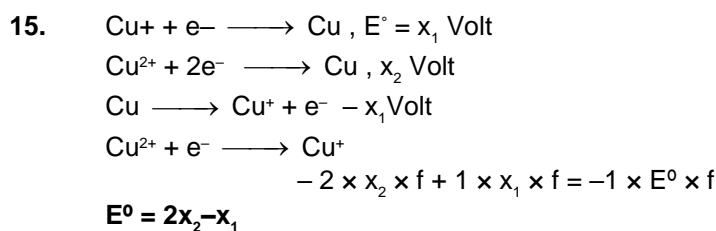
$$K_a = 0.01 \times \alpha^2 \Rightarrow \alpha = \sqrt{\frac{25 \times 10^{-6}}{10^{-2}}} = 5 \times 10^{-2}$$

$$\alpha = 5 \times 10^{-2} = \frac{19.6}{\Lambda_{\text{eq}}} \Rightarrow \Lambda_{\text{eq}}^\circ = \frac{19.6}{5 \times 10^{-2}} = 392 \text{ Scm}^2 \text{ eq}^{-1}.$$

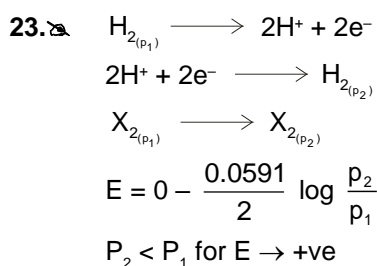
## EXERCISE # 2

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 reactive 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.  $\text{Fe}^{3+} + 3\text{e}^- \longrightarrow \text{Fe}, -0.036 \text{ volt}$   
 $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-, 0.44 \text{ volt}$   
 $\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+}$   
 $+ 3 \times 0.036 - 2 \times 0.44 \times f = -1 \times E^\circ \times f$

$$E^{\circ} = 0.772 \text{ Volt}$$

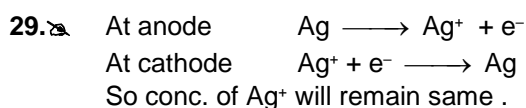


16. For spontaneous reaction in every condition  
 $E_{\text{cell}} > 0$ ,  $\Delta G < 0$  and  $Q$  (reaction quotient)  $< K$  (equilibrium constant).



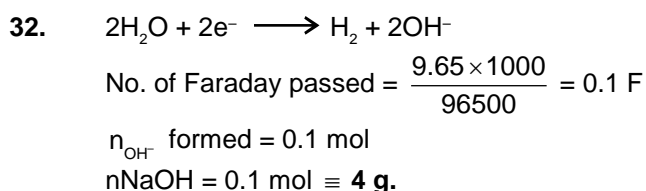
24.  $E = 0 - \frac{0.0591}{2} \log \frac{16}{4} = - \frac{0.0591}{2} \times 2 \log 2 = -0.0591 \times 0.301 = -0.0178 \text{ Volt.}$   
 If connected in reverse direction,  $E = 0.0178 \text{ volt.}$

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



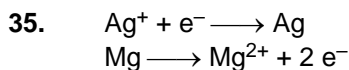
30. Mole of Fe deposited  $= \frac{1}{2} \times 3 = 1.5 \text{ mole}$   
 $W_{\text{Fe}} = 1.5 \times 56 = 84 \text{ g.}$

31.  $W = \frac{63.5}{2 \times 96500} \times 2 \times 60 \times 60 = 2.37 \text{ g}$   
 % of efficiency  $= \times 100.$



33. Equivalence of  $\text{H}_2$  = equivalence of  $\text{O}_2$   
 $\frac{0.224}{22.4} \times 2 = \frac{\text{volume of } \text{O}_2}{22.4} \times 4$   
 $0.112 \text{ litre} = \text{volume of } \text{O}_2.$

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



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

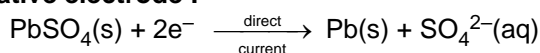
$$\text{Number of moles of Ag} = \frac{\frac{1}{3} N_a}{N_a} = \frac{1}{3}$$

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

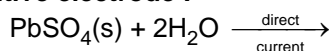
37. The discharged acid cell (lead storage battery or cell) can be recharged by passing a direct current through it in opposite direction. During recharging of cell, the electrode material are restored in their original forms. Due to formation of  $\text{H}^+$  and  $\text{SO}_4^{2-}$  ions the specific gravity of sulphuric acid increases and it attains the original value ( $1.3 \text{ g/cm}^3$ ) and also its EMF (voltage) increases.

**During charging**

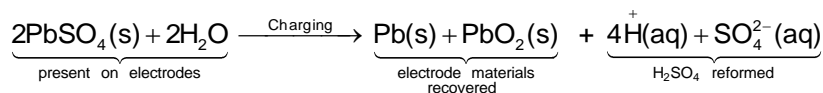
**At negative electrode :**



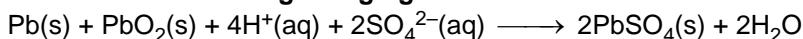
**At positive electrode :**



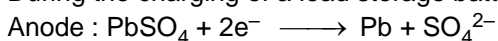
overall charging reaction :



**overall reaction during charging :**



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



In both the reactions  $\text{H}_2\text{SO}_4$  is regenerated.

40. For strong electrolyte

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

41. Molar conductivity  $\propto$  no. of ions per mole of electrolyte.

$$43. \Lambda_{m, \text{BaSO}_4} = (x_1 + x_2 - 2x_3) \Rightarrow \Lambda_{\text{eq}, \text{BaSO}_4} = \frac{\Lambda_{\text{eq}, \text{BaSO}_4}}{n - \text{factor}}$$

$$\Lambda_{\text{eq}, \text{BaSO}_4} = \frac{(x_1 + x_2 - 2x_3)}{2}$$

44.  $K_a = 25 \times 10^{-6}$   $\Lambda_{\text{eq}} = 19.6 \text{ Scm}^2 \text{ eq}^{-1}$ ,  $C = 0.01$

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

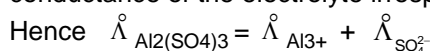
$$\alpha = 5 \times 10^{-2} = \frac{19.6}{\Lambda_{\text{eq}}^\circ} \Rightarrow \Lambda_{\text{eq}}^\circ = \frac{19.6}{5 \times 10^{-2}} = 392 \text{ Scm}^2 \text{ eq}^{-1}.$$

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

### 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.

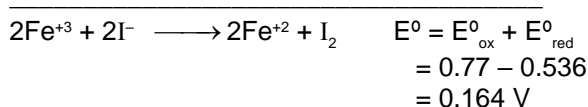


13. EMF of a cell = Reduction potential of cathode – Reduction potential of anode  
 = Reduction potential of cathode + Oxidation potential of anode  
 = Oxidation potential of anode – Oxidation potential of cathode.

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

On dilution, the number of current carrying particles per  $\text{cm}^3$  decreases but the volume of solution increases. Consequently, the ionic mobility increases, which in turn increases the equivalent conductance of strong electrolyte.

15.  $2(\text{e}^- + \text{Fe}^{+3} \longrightarrow \text{Fe}^{+2}) \quad E^\circ = 0.77 \text{ V}$   
 $2\text{I}^- \longrightarrow \text{I}_2 + 2\text{e}^- \quad E^\circ = 0.536 \text{ V}$



So, Reaction will take place.

16.  $x = -1.2 \text{ V}$   
 $y = +0.5 \text{ V}$   
 $z = -3.0 \text{ V}$   
 $z > x > y$   
 as  $E_{\text{RP}}^\circ \downarrow$ , Reducing Power  $\uparrow$

17.  $\text{Cu}^{2+} + 1\text{e}^- \rightarrow \text{Cu}^+ \quad E_1^\circ = 0.15 \text{ V} \quad \Delta G_1^\circ = -n_1 E_1^\circ F$   
 $\text{Cu}^+ + 1\text{e}^- \rightarrow \text{Cu} \quad E_2^\circ = 0.50 \text{ V} \quad \Delta G_2^\circ = -n_2 E_2^\circ F$   
 $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu} \quad \Delta G^\circ = \Delta G_1^\circ + \Delta G_2^\circ$   
 $(-1) n E^\circ F = (-1) n_1 E_1^\circ F + (-1) n_2 E_2^\circ F$   
 $E^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n} = \frac{0.15 \times 1 + 0.50 \times 1}{2} \Rightarrow 0.325$

18.  $E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^\circ = +0.15 \text{ V}$   
 $E_{\text{Cr}^{3+}/\text{Cr}}^\circ = -0.74 \text{ V}$   
 $E_{\text{cell}}^\circ = E_{\text{C}}^\circ - E_{\text{A}}^\circ = 0.15 - (-0.74)$   
 $= 0.89 \text{ V}$

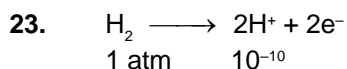
19.  $\Delta G^\circ = -nE^\circ F$   
 $E_{\text{cell}}^\circ > 0$   
 $\Delta G^\circ = -RT \ln K_{\text{eq}}$   
 $\Delta G^\circ > 0 \quad ; \quad K_{\text{eq}} < 1$

20.  $\Lambda_{\text{m}(\text{NH}_4\text{OH})}^\circ = \Lambda_{\text{m}(\text{NH}_4\text{Cl})}^\circ + \Lambda_{\text{m}(\text{NaOH})}^\circ - \Lambda_{\text{m}(\text{NaCl})}^\circ$

21.  $E^\circ$  more positive, reducing agent will be greater.

22.  $\lambda_{\text{M}}^\circ = \lambda_{\text{CH}_3\text{COONa}}^\circ + \lambda_{\text{HCl}}^\circ - \lambda_{\text{NaCl}}^\circ$   
 $= 91 + 425.9 - 126.4$

$$= 390.5$$

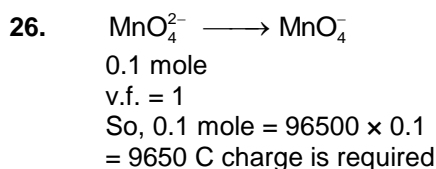


$$E_{\text{H}_2/\text{H}^+} = 0 - \frac{0.059}{2} \log \frac{(10^{-10})^2}{1}$$

$$E_{\text{H}_2/\text{H}^+} = +0.59 \text{ V}$$

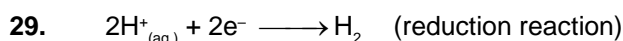
24.  $\alpha = \frac{\Lambda_{\text{M}}}{\Lambda_{\text{M}}^{\infty}} = \frac{9.54}{238} = 0.04008 = 4.008 \%$

25.  $E_{\text{Cell}}^{\circ} = E_{\text{OP}}^{\circ} + E_{\text{RP}}^{\circ}$   
 $= 0.76 + 0.34 = 1.10 \text{ V}$



27.  $n_{\text{O}_2} = \frac{5600}{22400} = \frac{1}{4}$   
 $\frac{W_{\text{Ag}}}{108} \times 1 = \frac{W_{\text{O}_2}}{M_{\text{O}_2}} \times 4 \quad (2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-)$   
 $\frac{W_{\text{Ag}}}{108} = \frac{1}{4} \times 4$   
 $W_{\text{Ag}} = 108 \text{ g}$

28. Fuel cell convert chemical energy of fuel like  $\text{H}_2$ ,  $\text{CH}_4$  into electrical energy



$$E = E^{\circ} - \frac{0.059}{2} \log \frac{P_{\text{H}_2}}{[\text{H}^+_{(\text{aq.})}]^2}$$

$$0 = 0 - \frac{0.059}{2} \log \frac{P_{\text{H}_2}}{[10^{-7}]^2}$$

(In order to make  $\log 1 = 0$ )

$$P_{\text{H}_2} = (10^{-7})^2 = 10^{-14} \text{ atm}$$

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

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

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

32.  $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$

$$E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V}$$

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

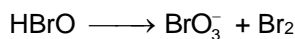
33. Nernst equation for the given cell representation is given as

$$E = E^0 - \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

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

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

For HBrO :



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

$$= 1.595 - 1.5 > 0 \text{ (Positive)}$$

So reaction is spontaneous.

35. The standard Gibb's energy ( $\Delta_r G^0$ ) =  $-nFE_{cell}^0$

Value of n = 2

$$\Delta_r G^0 = -2 \times 96500 \times 0.24 = -46320J = -46.32 \text{ kJ}$$

36. Nernst equation :

$$E_{cell}^0 = E_{cell}^0 - \frac{0.059}{n} \log Q_C$$

at equilibrium  $E_{cell} = 0$ ,  $Q_C = K_C$

$$E_{cell}^0 = \frac{0.059}{n} \log K_C \quad \text{Value of } E_{cell}^0 = 0.59 \text{ V}$$

$$0.59 = \frac{0.059}{1} \log K_C \quad \text{Value of } n = 1$$

$$K_C = \text{antilog } 10$$

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

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

$$E_{Al^{3+}/Al}^0 = -1.66 \text{ V}$$

$$E_{Ag^+/Ag}^0 = 0.80 \text{ volt}$$

$$E_{K^+/K}^0 = -2.93 \text{ volt}$$

$$E_{Cr^{3+}/Cr}^0 = 0.74 \text{ volt}$$

The decreasing order of reducing power

$K > Al > Cr > Ag$

38.  $\lambda_{M(CH_3COOH)}^\infty \rightleftharpoons \lambda_{CH_3COO^-}^\infty + \lambda_{H^+}^\infty \quad \dots\dots(1)$

$$x = \lambda_{H_2SO_4}^\infty \rightleftharpoons \lambda_{SO_4^{2-}}^\infty + 2\lambda_{H^+}^\infty \quad \dots\dots(2)$$

$$y = \lambda_{K_2SO_4}^\infty \rightleftharpoons \lambda_{SO_4^{2-}}^\infty + 2\lambda_{K^+}^\infty \quad \dots\dots(3)$$

$$Z = \lambda_{M(CH_3COOH)}^\infty \rightleftharpoons \lambda_{CH_3COO^-}^\infty + \lambda_{K^+}^\infty \quad \dots\dots(4)$$

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

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



## PART - II

- $$2\text{AgCl(s)} + \text{H}_2\text{(g)} (1 \text{ bar}) \longrightarrow 2\text{HCl(aq)} + 2\text{Ag(s)}$$

The cell with this cell reaction can be represented as :

$$\text{Pt(s)} | \text{H}_2\text{(g)} (1 \text{ bar}) | 1\text{MHCl(aq)}, || \text{Ag}^+\text{(aq)} || \text{Ag(s)}$$

(anode) (cathode)

silver is undergoing reduction ( $\text{Ag}^+ \longrightarrow \text{Ag}$ ) 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  $\text{Ag}^+$  and at cathode oxidation does not take place hence it is also incorrect.

**Note :** Remember LEO  $\longrightarrow$  loss of electrons is oxidation.
- We know that,

standard Gibbs energy,  $\Delta G^\circ = -nEF^\circ_{\text{cell}}$

For the cell reaction,

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

$$\Delta G^\circ = -2 \times 96500 \times 0.46 = -88780 \text{ J} = -88.7 \text{ kJ} - 89.0 \text{ kJ}$$
- Galvanised iron i.e. iron coated with zinc does not rust easily as zinc has more negative electrode potential ( $-0.7\text{V}$ ) than iron. ( $-0.41\text{V}$ ) i.e., zinc is less reactive than iron.
- $$\text{NaBr} \rightleftharpoons \text{Na}^+ + \text{Br}^-$$

$$\left. \begin{array}{l} 2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{OH}^- \\ \text{Na}^+ + \text{OH}^- \longrightarrow \text{NaOH} \end{array} \right\} \text{at cathode}$$

$$\text{Br}^- - \text{e}^- \longrightarrow \text{Br}$$

$$\text{Br} + \text{Br} \longrightarrow \text{Br}_2 \quad (\text{at anode})$$

So, the products are  $\text{H}_2$ ,  $\text{Br}_2$  and  $\text{NaOH}$ .  $\text{H}_2$  at cathode,  $\text{Br}_2$  at anode and  $\text{NaOH}$  in solution.
- In a Daniel cell  $\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}$

$$E_{\text{cell}} = 1.1 \text{ V}$$

The reaction of oxidation half cell

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

The reaction of reduction half cell

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

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

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.
- The correct reason is the current carried by cation and anion is equal to their transport number.
- $$\text{Zn(l)} + \text{Hg(g)} \longrightarrow \text{ZnO(s)} + \text{Hg(l)}$$

The cell potential remains constant during its life as the overall reaction does not involve any ion in solution whose concentration changes during its life time.
- Given,  $\text{pH} = 14$ ;  $\therefore \text{pOH} = 0$  and  $[\text{OH}^-] = 1 \text{ M}$

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

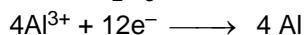
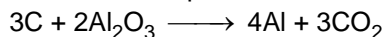
$$\therefore [\text{Cu}^{2+}] = 1.0 \times 10^{-19} \text{ M}$$

For the half-reaction,

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

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

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



$$\begin{aligned}\therefore \Delta G^\circ &= 3\Delta G_f^\circ(\text{CO}_2) - 2\Delta G_f^\circ(\text{Al}_2\text{O}_3) \\ &= 3(-394) - 2(-1520) \\ &= 1858 \text{ kJ}\end{aligned}$$

$$\Delta G^\circ = nFE_{\text{cell}}^\circ$$

$$-E_{\text{cell}}^\circ = \frac{1858 \times 1000}{12 \times 96500} = 1.60 \text{ V}$$

11.  $2\text{NaCl} + 2\text{H}_2\text{O} \xrightarrow{\text{electrolysis}} \text{H}_2 + \text{Cl}_2 + 2\text{NaOH}$

Weight of NaCl present in 0.5 L = 0.5 mol

$$\text{charge} = 965 \times 5 = 4825 \text{ C}$$

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

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

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

$$\text{pOH} = 1, \text{pH} = 13$$

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

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

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

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

Therefore, for  $E_{\text{cell}} = +ve$ ,  $\Delta G$  is always negative.

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

24.  $E_{\text{cell}}^\circ = \frac{0.059}{2} \log k$

$$E_{\text{B}^+/\text{B}}^\circ - E_{\text{A}^{+2}/\text{A}}^\circ = \frac{0.059}{2} \log$$

$$E_{\text{B}^+/\text{B}}^\circ - 0.34 = \frac{0.059}{2} \times 15.6$$

$$E_{\text{B}^+/\text{B}}^\circ = 0.80$$

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

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

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

M = Molarity

$\kappa$  = specific conductivity

$$\kappa = \frac{1}{R} \times \text{cell constant}$$

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

$$= \frac{1}{5 \times 10^3 \Omega} \times \frac{1 \text{ cm}}{100 \text{ cm}^2}$$

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

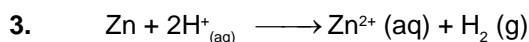
$$26. \quad E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{RT}{nF} \ln Q$$

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

### PART - III

$$1. \quad E_{\text{cell}}^0 = 0.77 + 0.14 = 0.91 \text{ volt.}$$

$$2. \quad \Lambda_{\text{NaBr}}^0 = 126 + 152 - 150 = 128 \text{ S cm}^2 \text{ mol}^{-1}.$$



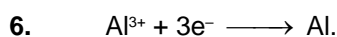
$$E = E^0 - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} \text{ pH}_2$$

Adding  $\text{H}_2\text{SO}_4$  means increasing  $\text{H}^+$  and therefore  $E_{\text{cell}}$  will increase and reaction will shift to forward direction.

$$4. \quad \begin{array}{ll} \text{Cr}^{2+} | \text{Cr}^{3+} = +0.41\text{V} & \text{Mn}^{2+} | \text{Mn}^{3+} = -1.57\text{V} \\ \text{Fe}^{2+} | \text{Fe}^{3+} = -0.77\text{V} & \text{Co}^{2+} | \text{Co}^{3+} = -1.97\text{V} \end{array}$$

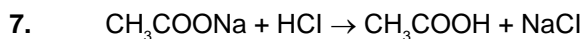
As Cr will have maximum oxidation potential value, therefore its oxidation will be easiest.

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



$$\frac{5.12 \times 10^3}{27} = 189.62 \text{ mol.}$$

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



From the reaction,

$$\Lambda_{\text{CH}_3\text{COONa}}^0 + \Lambda_{\text{HCl}}^0 - \Lambda_{\text{CH}_3\text{COOH}}^0 = \Lambda_{\text{NaCl}}^0 \quad \text{or} \quad \Lambda_{\text{CH}_3\text{COOH}}^0 = \Lambda_{\text{CH}_3\text{COONa}}^0 + \Lambda_{\text{HCl}}^0 - \Lambda_{\text{NaCl}}^0$$

Thus to calculate the value of  $\Lambda_{\text{CH}_3\text{COOH}}^0$  one should know the value of  $\Lambda_{\text{NaCl}}^0$  along with  $\Lambda_{\text{CH}_3\text{COONa}}^0$  and  $\Lambda_{\text{HCl}}^0$ .

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

$$9. \quad C = 0.1 \text{ M,} \quad R = 100 \, \Omega$$

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

$$C = 0.02 \text{ M,} \quad R = 520 \, \Omega.$$

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

$$\Lambda_{\text{M}} = \frac{\frac{1}{520} \times 129}{1000 \times 0.02} = 124 \times 10^{-4} \text{ Sm}^2 \text{ mol}^{-1}.$$

10. According to Kohlrausch's law the molar conductivity at infinite dilution ( $\Lambda^0$ ) for weak electrolyte  $\text{CH}_3\text{COOH}$  is

$$\Lambda_{\text{CH}_3\text{COOH}}^0 = \Lambda_{\text{CH}_3\text{COONa}}^0 + \Lambda_{\text{HCl}}^0 - \Lambda_{\text{NaCl}}^0$$

So for calculating the value of  $\Lambda_{\text{CH}_3\text{COOH}}^0$ , value of  $\Lambda_{\text{NaCl}}^0$  should also be known.

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

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

$$13. \quad \begin{aligned} \text{Fe}^{3+} + 3\text{e}^- &\longrightarrow \text{Fe} & \Delta G_1 &= -3 \times F \times E^{\circ}_{\text{Fe}^{3+}/\text{Fe}} \\ \text{Fe}^{2+} &\longrightarrow \text{Fe} & \Delta G_2 &= -2 \times F \times E^{\circ}_{\text{Fe}^{2+}/\text{Fe}} \\ \text{Fe}^{3+} + \text{e}^- &\longrightarrow \text{Fe}^{2+} & \Delta G &= \Delta G_1 - \Delta G_2 \\ \Delta G &= 3 \times 0.036F - 2 \times 0.439 \times F = -1 \times E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+}) \times F \\ E^{\circ}(\text{Fe}^{3+}/\text{Fe}^{2+}) &= 2 \times 0.439 - 3 \times 0.036 = 0.878 - 0.108 = 0.770 \text{ V} \end{aligned}$$

$$14. \quad \frac{2}{3} \text{Al}_2\text{O}_3 \longrightarrow \frac{4}{3} \text{Al} + \text{O}_2$$

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

$$\Delta G = -nFE_{\text{cell}}$$

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

$$E_{\text{cell}} = 2.5 \text{ V}$$

$$15. \quad 2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow \text{H}_2(\text{g})$$

$$E_{\text{red}} = E^{\circ}_{\text{red}} - \frac{0.0591}{n} \log \frac{P_{\text{H}_2}}{(\text{H}^+)^2}; E_{\text{red}} = 0 - \frac{0.0591}{2} \log \frac{2}{(1)^2}; \quad E_{\text{red}} = -\frac{0.0591}{2} \log 2$$

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

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

For reaction to be spontaneous  $E^{\circ}$  must be positive.

$$E^{\circ}_{\text{Zn} / \text{Zn}^{2+}} + E^{\circ}_{\text{Ni}^{2+} / \text{Ni}} = 0.76 + (-0.23) = +0.53 \text{ (positive)}$$

17. Higher the SRP, better is oxidising agent. Hence  $\text{MnO}_4^-$  is strongest oxidising agent

$$18. \quad x = 1.4 \text{ S/m.}$$

$$R = 50 \Omega$$

$$M = 0.2$$

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

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

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

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

20. Reason : Higher the position of element in the electrochemical series, more difficult is the reduction of its cations.  
If  $\text{Ca}^{2+}(\text{aq})$  is electrolysed, water is reduced in preference to it. Hence it cannot be reduced electrolytically from an aqueous solutions.

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

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

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

$$\frac{2F}{1 \text{ mole}} = 63.5 \text{ g.}$$

23. Galvanization is applying a coating of Zn.

24. For strongest reducing agent  $E_{OP}^\circ$  should be maximum.

$$E_{OP Cr/Cr^{+3}}^\circ = 0.74 \text{ V}$$

Whereas

$$E_{OP Mn^{2+}/MnO_4^-}^\circ = -1.51 \text{ V}$$

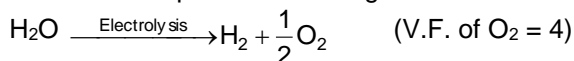
$$E_{OP Cr^{3+}/Cr_2O_7^{2-}}^\circ = -1.33 \text{ V}$$

$$E_{OP Cl^-/Cl_2}^\circ = -1.36 \text{ V}$$

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  $B_2H_6$



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

$$\left[ \frac{(100A) \times t \text{sec.}}{96500} \right] \times \frac{1}{4} = 3 \quad \therefore t = \frac{3 \times 96500 \times 4}{100 \times 3600} \text{ hr.} = 3.22 \text{ hrs.}$$

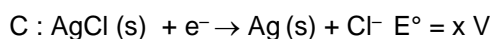
26.  $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}$

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

$$\text{For } 0.05F; PbSO_4 \text{ electrolyzed} = \frac{0.05 \times 303}{2} = 7.6 \text{ g}$$

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

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



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

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

$$0.92 = x + 0.72$$

$$x = 0.92 - 0.72 = 0.2 \text{ Volts}$$

29. Fact

30.  $E_{\text{cell}}^\circ = E_{Zn(s)|Zn^{+2}}^\circ + E_{Au^{+3}/Au(s)}^\circ$

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

$$= 0.76 \text{ V} + 1.4 \text{ V} = 2.16 \text{ V}$$

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

31.  $\lambda^\circ_{\text{m}}(\text{HA}) = \lambda^\circ_{\text{m}}(\text{HCl}) + \lambda^\circ_{\text{m}}(\text{NaA}) - \lambda^\circ(\text{NaCl})$   
 $= 425.9 + 100.5 - 126.4$   
 $= 400$

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

$$= 50$$

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