

(11)

n

electrochemistry-CBSE(Solutions)

Explanations

1. The galvanic cell for the given reaction is

- 2. Refer to text on page 30.
- Electrochemical cell is a device that converts the chemical energy of a spontaneous redox reaction into electrical energy.

If the external applied potential becomes greater than E_{cell}° of electrochemical cell, the reaction gets reversed and electrochemical cell now functions as an electrolytic cell. (1)

4. Given
$$E_{\text{Fe}^{2+}/\text{Fe}}^0 = -0.44\text{V}$$
, $E_{\chi^{2+}/\chi}^0 = -2.36\text{V}$
 $E_{\chi^{2+}/\chi}^0 = -0.14\text{V}$

'X' is a better for coating the surface of iron because standard oxidation potential of X is greater than that of Fe so before oxidation of iron takes place, oxidation of X occurs. (2)

5.
$$\operatorname{Zn}(s) + \operatorname{Cu}^{2+}(aq) \longrightarrow \operatorname{Zn}^{2+}(aq) + \operatorname{Cu}(s)$$

 $E^{\circ} = +1.1 \text{ V, } \Delta G^{\circ} = ?$

 $1F = 96500C \text{ mol}^{-1}, n = 2$

$$\Delta G^{\circ} = -nFE^{\circ} = -2 \times 96500 \times 1.1$$
 (1)
= -212300 Jmol⁻¹ = -212.3 kJ mol⁻¹

• The electrode reaction involved is

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

Thus, n=2

By using Nernst equation, we get,

$$E_{\text{Zn}^{2+}/\text{Zn}} = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} - \frac{0.0591}{2} \log \frac{1}{(\text{Zn}^{2+})}$$
 (1)

Give that 0.1 M ZnSO₄ solution is 95% dissociated that means

$$[Zn^{2+}] = \frac{95}{100} \times 01 = 0.095 M$$

$$\therefore E_{zn^{2+}/zn} = -0.76 - \frac{0.0591}{2} \log \frac{1}{0.095}$$

$$= -0.76 - 0.0295 [\log 1000 - \log 95]$$

$$= -0.76 - 0.0295 \times 1.022$$

$$[\because \log 1000 = 3, \log 95 = 1.978]$$

(1)

Reducing power $\approx \frac{1}{\text{Reduction potential}}$, i.e. as the reduction potential decreases, reducing power increases. So, arrange the given metals on this basis.

= -0.79015 V

Metals in an increasing order of their reducing

Ag⁺ /Ag,
$$Cu^{2+}$$
 / Cu , Fe^{2+} / Fe , Cr^{3+} / Cr ,

Mg²⁺ / Mg, K⁺ / K

Ag < Cu < Fe < Cr < Mg < K

(More negative E° means that the redox couple is a stronger reducing agent). (2)

8. Given,
$$E_{Cd^{2+}/Cd}^{\circ} = -0.403 \text{ V}$$

$$E_{Zn^{2+}/Zn}^{\circ} = -0.763 \text{ V}$$

$$E_{Cell}^{\circ} = -0.403 - (-0.763)$$

$$E_{Cell}^{\circ} = 0.36 \text{ V}$$

$$\Delta_r G^{\circ} = -nFE_{Cell}^{\circ}$$
(1)

where n = number of moles of electrons used

$$n = 2 \text{ (Here)} \implies F = 96500 \text{ C mol}^{-1}$$

 $\Delta_r G^\circ = -2 \times 96500 \times 0.36 = 69480 \text{ J/mol}$

Also,
$$E_{\text{Cell}}^{\circ} = \frac{0.0591}{n} \log K_{\text{C}}$$

$$\therefore \log K_C = \frac{n \times E_{Cell}^\circ}{0.0591} = \frac{2 \times 0.36}{0.0591} = 12.18$$

$$\log K_C = 12.18$$
 (1)

- **9.** (i) $Cu/Cu^{2+}(aq, 1M) \mid Ag^{+}(aq, 1M) \mid Ag$ (1)
 - (ii) Direction of flow of current is from silver to copper. (1)
 - (iii) At anode Cu (s) \longrightarrow Cu²⁺ (aq) + 2e⁻ (1/2)

At cathode
$$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$$
 (1/2)

Net reaction

Cu (s) +
$$2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag$$
 (s) [1/2]

10. Since, oxidation of Cr is taking place in the given reaction, the chromium electrode is anode and as Fe is reduced in the reaction, Fe electrode is cathode. The half-cell reactions are as follows

At anode
$$Cr \longrightarrow Cr^{3+} + 3e^{-}] \times 2$$

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

Overall reaction

$$2Cr + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe$$
 (1)

$$E^{\circ} = E_{\text{cathode}} - E_{\text{anode}} = -0.44 - (-0.74) = 0.3 \text{ V}$$
 (1/2)

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{\left[\text{Cr}^{3+}\right]^{2}}{\left[\text{Fe}^{2+}\right]^{3}}$$
 (1/2)

Here, n = number of electrons transferred, i.e. equal to 6.

$$= 0.3 - \frac{0.0591}{6} \log \frac{(0.01)^2}{(0.1)^3}$$
$$= 0.309 \approx 0.31 \text{ V}$$
 (1)

11. Write Nernst equation and find the number of electrons to find E_{cell}.

At anode, Fe(s) \longrightarrow Fe²⁺(aq) + 2e⁻

At cathode,
$$\left[H^{+}(aq) + e^{-} \longrightarrow \frac{1}{2}H_{2}(g)\right] \times 2$$

Overall reaction

$$Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(q)$$

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

$$E_{\rm H^+/H_2}^{\rm o} = 0.00 \, \rm V$$

$$E_{\text{ceil}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2^{+}}]}{[\text{H}^{+}]^{2}}$$
 (1)

$$= [0.00 - (-0.44)] - \frac{0.0591}{2} \log \frac{10^{-3}}{(10^{-2})^2}$$

$$=0.44-\frac{0.0591}{2}$$

$$E_{\text{cell}} = 0.4104 \,\text{V} \tag{1}$$

12. At anode $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$

At cathode
$$\left[H^{+}(aq) + e^{-} \longrightarrow \frac{1}{2} H_{2}(g) \right] \times 2$$

Net equation

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^{+}]^{2}}$$
$$= 0.76 - \frac{0.0591}{2} = 0.731 \text{ V}$$

13. Write Nernst equation and find the n_{umber} electrons to find E_{cell} .

Anode half reaction, $Fe(s) \longrightarrow Fe^{2+}(aq) + \lambda$.

$$\left[H^{+}(aq)+e^{-}\longrightarrow \frac{1}{2}H_{2}(g)\right],$$

Net reaction

Fe (s) + 2 H⁺ (aq)
$$\longrightarrow$$
 Fe²⁺ (aq) + H₂(g)

$$E_{cell} = E_{cell}^{\circ} - \left(\frac{2.303 \, RT}{nF}\right) \log \frac{[Fe^{2+}]}{[H^{+}]^{2}}$$

$$E_{cell} = E_{cell}^{\circ} - \left(\frac{0.05912}{n}\right) \log \frac{[Fe^{2+}]}{[H^{+}]^{2}}$$

$$= 0.44 - \frac{0.05912}{2} \log \frac{0.001}{1}$$

$$\therefore E_{cell} = 0.44 - [0.02956 \times (-3)]$$

$$= 0.44 + 0.08868$$

Write Nernst equation and find the number electrons to find E_{cell} .

 $= 0.52868 \text{ V} \approx 0.53 \text{ V}$

As per the condition given,

$$Ag(s) |Ag^{+}(10^{-3}M)| |Cu^{2+}(10^{-1}M)| |Cu(s)|$$

At anode Ag(s)
$$\longrightarrow$$
 Ag⁺(aq) + e⁻] × 2

At cathode
$$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$$

Overall reaction

$$2Ag(s) + Cu^{2+}(aq) \longrightarrow 2Ag^{+} + Cu(s)$$

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{2} \log \frac{[Ag^{+}]^{2}}{[Cu^{2+}]}$$

$$= 0.46 - \frac{0.0591}{2} \log \frac{(10^{-3})^{2}}{10^{-1}}$$

$$= 0.46 - \frac{0.0591}{2} \log 10^{-5}$$

 $E_{\text{cell}} = 0.608 \text{V}$

(3)

15. (i) Calculate E_{coll}° by using the formula,

Ecel = Ecathode - Eanode

- (ii) Calculate the number of electrons by writing electrode reactions then write Nernst equals and find $E_{\rm cell}$.
- (i) At anode $Ni(s) \longrightarrow Ni^{2+}(aq) + 2^{2}$ At cathode $2Ag^{+}(aq) + 2e^{-} \longrightarrow 2Ag^{(s)}$

Overall reaction

Ni (s) +
$$2Ag^{+}(aq) \longrightarrow Ni^{2+}(aq) + 2Ag$$
 (s) (1/2)
 $E_{cell}^{o} = E_{cathede}^{o} - E_{anode}^{o}$
= + 0.80 V - (-0.25 V) = 1.05 V (1)

(ii)
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^{+}]^{2}}$$

$$= E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{(0.1)}{(1)^{2}}$$

$$= 1.05 - \frac{0.0591}{2} \times -1$$

$$= 1.05 + 0.0295 = 1.0795 \text{ V}$$
(1)

16.

- (i) Calculate E_{cell}° by using the formula, $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} E_{\text{anode}}^{\circ}$
- (ii) Calculate $\Delta_r G^\circ$ by using the formula, $\Delta_r G^\circ = -nFE^\circ_{cell}$

The given reaction, shows that zinc is oxidised and silver is reduced in the button cell.

The reactions occurring are:

At anode

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}; E^{\circ}_{Zn^{2+}/Zn} = -0.76 \text{ V}$$
(1/2)

At cathode

$$Ag_{2}O(s) + H_{2}O(l) + 2e^{-} \longrightarrow$$

$$2Ag(s) + 2OH^{-}(aq); E_{Ag^{+}/Ag}^{\circ} = + 0.80 \text{ V}_{(1/2)}$$

Now,
$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$
 (1/2)

$$= E_{\text{Ag}^{+}/\text{Ag}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

$$= 0.80 - (-0.76) = 1.56 \text{ V}$$
 (1/2)

We know that,
$$\Delta_r G^\circ = -nE^\circ F$$
 (1/2)

Here, n = 2 F = 96500 C mol⁻¹

$$\Delta_r G^\circ = -2 \times 1.56 \times 96500 \text{ J mol}^{-1}$$

= -301080 J mol⁻¹ = -301 kJ mol⁻¹ (1/2)

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(i) Calculate E_{cell}° by using the formula,

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

 (ii) Calculate the number of electrons by writing the electrode reactions then write Nernst equation and find E_{cell}.

For the cells,

Al | Al³⁺ (0.001 M) || Ni²⁺ (0.50 M) | Ni⁻ the cell reaction is

$$2Al(s) + 3Ni^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Ni(s)$$
 (1/2)

Thus, n = 6

$$E_{\text{cell}}^{\circ} = E_{\text{Ni}^{2+}/\text{Ni}}^{\circ} - E_{\text{Al}^{3+}/\text{Al}}^{\circ}$$

$$= -0.25 \text{ V} - (-1.66 \text{ V}) = 1.41 \text{ V}$$
 (1)

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{\text{n}} \log \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3}$$
 (1/2)

$$E_{\text{cell}} = 1.41 \text{ V} - \frac{0.0591 \text{ V}}{6} \log \frac{(10^{-3})^2}{(0.50)^3}$$

$$= 1.41 \text{ V} - \frac{0.0591 \text{ V}}{6} \log \frac{8 \times 10^{-6}}{1} \left(\because \frac{1}{0.125} = 8 \right)$$

$$E_{\text{cell}} = 1.41 \text{ V} - \frac{0.0591 \text{ V}}{6} \times (-5.0969)$$

= 1.41 V + 0.0502 V = 1.4602 V (1)

18.

- (i) Find ΔG° using the formula, $\Delta G^{\circ} = -nFE^{\circ}$
- (ii) Find $\log K_C$ by using the formula, - $nFE^\circ = -2.303 \, RT \log K_C$
- (iii) Find K_C using the antilog table.

Here,
$$n=2$$

$$\Delta G^{\circ} = -nFE^{\circ}$$
(1/2)

$$\Delta G^{\circ} = -2 \times 96500 \, \text{C} \times 1.05 \, \text{V}$$

$$\Delta G^{\circ} = -202.65 \text{ kJ mol}^{-1}$$
 (1/2)

$$-nFE^{\circ} = -2.303 RT \log K_{c}$$
 (1/2)
[∴∆G° = -2.303 RT log K_c]

$$\log K_C = \frac{nE^{\circ}}{0.0591}$$

$$= \frac{2 \times 1.05}{0.0591} = 35.5329$$
(1/2)

$$K_C = \text{antilog } 35.5329$$
 $K_C = 3.412 \times 10^{35}$ (1)

19. Given, $[Cr_2O_7^{2-}] = 0.10 \text{ M}$, $[Cr^{3+}] = 0.20 \text{ M}$ and

$$[H^+] = 1 \times 10^{-4} \text{ M}, E_{cell}^{\circ} = 1.33 \text{ V}, n = 6$$

Half-cell reaction,

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$$

$$\longrightarrow 2 \operatorname{Cr}^{3+}(aq) + 7 \operatorname{H}_2 O(1)$$

By using Nernst equation, we get

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591 \,\text{V}}{n} \log \frac{\left[\text{Cr}^{3+}\right]^{2}}{\left[\text{Cr}_{2}\text{O}_{7}^{2-}\right] \left[\text{H}^{+}\right]^{14}}$$

$$= 1.33 \,\text{V} - \frac{0.0591 \,\text{V}}{6} \log \frac{(0.2)^{2}}{(0.1) (1.0 \times 10^{-4})^{14}}$$
(1)

= 1.33 V -
$$\frac{0.0591 \text{V}}{6} \log \frac{4 \times 10^{-2}}{1.0 \times 10^{-57}}$$

= 1.33 V - $\frac{0.0591 \text{V}}{6} \log 4 \times 10^{59}$
= 1.33 V - $\frac{0.0591 \text{ V}}{6} \times 55.6021$
= 1.33 V - 0.5477 V = 0.7823 V (1)

20.

(i) Calculate E_{coll}^{o} by using the formula,

(ii) Calculate the number of electrons by writing the electrode reactions then write Nernst equation and find Ecol

(i) The cell reactions are as

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$$
 (Anode)

$$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s) \qquad (Cathode)$$

(ii) $E_{\text{cell}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ}$

$$E_{\text{cell}}^{\circ} = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$$
 (1/2)

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$
(1/2)

$$E_{\text{celi}} = 1.10 \text{ V} - \frac{0.0591 \text{ V}}{2} \log \frac{2}{0.5}$$

= 1.10 V - $\frac{0.0591 \text{ V}}{2} \times 0.6021$

(1)

- (i) Find log K_C using the formula, ΔG° = -2.303 log K_C
 (ii) Find K_C using the antilog table.

$$\Delta G^{\circ} = -2.303 \, RT \, \log K_C \tag{1}$$

 $-212300 = -2.303 \times 8.314 \times 298 \times \log K_C$

$$\log K_C = \frac{212300}{2.303 \times 8.314 \times 298} = 37.2074 \tag{1}$$

$$K_C = \text{antilog } 37.2074, K_C = 1.6 \times 10^{37}$$
 (1)

22. Cell reaction is

$$\operatorname{Sn} + 2\operatorname{H}^+ \longrightarrow \operatorname{Sn}^{2+} + \operatorname{H}_2; (n=2)$$

$$E_{\text{cell}}^a = E_R - E_L = 0 - (-0.144) = 0.144 \text{ V}$$
 (1/2)

According to Nernst equation,

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591 \text{ V}}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^{+}]^{2}}$$
(1/2)

$$E_{cell} = 0.144 \text{ V} - \frac{0.0591 \text{ V}}{2} \log \frac{(0.05)}{(0.02)^2}$$
 (1)

$$= 0.144 \text{ V} - \frac{0.0591 \text{ V} \times 2.0969}{2} = 0.078 \text{ V}$$

23.

- (i) Write the cell reaction for the given cell
- (ii) Calculate E o by using the formula,

$$E_{\text{cell}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ}$$

(iii) Calculate Ag + ion concentration by using Nernst equation.

Cell reaction is

$$Cu(s) + 2Ag^{+}(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

$$E_{\text{cell}}^{\circ} = E_R - E_L = +0.80 - (+0.34) = 0.46 \text{ V}$$

Number of electrons taking part, n = 2By using Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591 \text{ V}}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^{2}}$$

(1/2

(1/

$$0.422 \text{ V} = 0.46 \text{ V} - \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^{2}}$$

$$0.422 \text{ V} = 0.46 \text{ V} - 0.0295 \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^{2}}$$

$$\log \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{0.46 - 0.422}{0.0295} = 1.288$$

$$\frac{[Cu^{2+}]}{[Ag^+]^2}$$
 = antilog 1.288

$$\frac{[Cu^{2+}]}{[Ag^+]^2} = 19.41$$

$$\frac{0.10}{[Ag^+]^2} = 19.41$$

$$[Ag^+]^2 = 0.00515$$

$$[Ag^+] = 0.0717 = 7.17 \times 10^{-2} M$$

24. According to given information, cell can be represented as

 $Zn(s) |Zn^{2+}(aq)(1M)| |Ag^{+}(aq)|Ag(s)$

Given,
$$E^{\circ}_{Zn^{2+}/Zn} = -0.763V$$
, $E^{\circ}_{Ag^{+}/Ag} = +0.80V$

$$E^{\circ}_{\text{Cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$= 0.80 - (-0.76) = 1.56 \text{ V}$$

By using Nernst equation, we get

$$E_{\text{Cell}} = E^{\circ}_{\text{Cell}} - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^{+}]^{2}}$$

$$1.48 = 1.56 - \frac{0.0591}{2} \log \frac{1}{[Ag^+]^2}$$

$$0.08 = +0.0295 \log \frac{1}{\left[Ag^{+}\right]^{2}}$$

$$\frac{0.08}{0.0295} = -2\log[Ag^+]$$

$$-\frac{0.08}{0.0295 \times 2} = \log[Ag^+]$$

$$\log[Ag^+] = -1.356$$

$$[Ag^+] = \text{Anti} \log[-1.356]$$

$$= 0.0441 = 4.4 \times 10^{-2} \text{ M}$$

25.
$$E_{\text{cell}}^{\circ} = 1.05 \text{ V}, n = 2$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

$$E_{\text{cell}} = 1.05 - \frac{0.0591}{2} \log \frac{(0.160)}{(0.002)^2}$$

$$E_{\text{cell}} = 1.05 - 0.0295 \log 4 \times 10^4$$

$$E_{\text{cell}} = 1.05 - 0.0295 \times 4.6021$$

= 0.91 V

26. Given,
$$E^{\circ}_{Cell} = 0.46 \text{ V}$$
, $[Ag^{+}] = 0.001 \text{ M}$, $[Cu^{2+}] = 0.10 \text{ M}$

Cell reaction is

$$Ag^+(aq) + Cu(s) \longrightarrow Cu^{2+}(aq) + Ag(s)$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^{2}}$$

$$= 0.46 - \frac{0.0591}{2} \log \frac{0.10}{(10^{-3})^{2}}$$

$$= 0.46 - 0.148 = 0.312V$$
(1)

27. At anode $Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^{-}$

At cathode $Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$

Overall reaction

$$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$$
 (1/2)

$$E^{\circ}_{\text{cell}} = 0.34 - (-2.37) = + 2.71 \text{ V}$$
 (1/2)

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{0.001}{0.0001}$$

$$E_{\text{cell}} = 2.71 - 0.0295 \log 10$$
(1)

$$E_{\text{cell}} = 2.71 - 0.0295 \times 1$$

 $E_{\text{cell}} = 2.68 \approx 2.70 \text{ V}$ (1)

(ii)
$$\Delta G = -nFE_{cell}$$

 $\Delta G = -2 \times 96500 \times 2.70$ (::1F = 96500 C mol⁻¹)
 $\Delta G = 521.10 \text{ kJ mol}^{-1}$ (2)

28. At anode
$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$$

At cathode
$$\operatorname{Sn}^{2+}(aq) + 2e^{-} \longrightarrow \operatorname{Sn}(s)$$
 (1)

Overall reaction

(1)

(1)

(1)

(1)

$$Zn(s) + Sn^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Sn(s)$$
 (1)

$$E_{\text{cell}}^{\circ} = E_{\text{Sn}^{2+}/\text{Sn}}^{\circ} - (-E_{\text{Zn}^{2+}/\text{Zn}}^{\circ})$$

= -0.14 + 0.76

$$= 0.62 \text{ V}$$
 (1)

(2)

$$\Delta G^{\circ} = -nFE^{\circ}$$

$$= -2 \times 96500 \times 0.62 \tag{1}$$

$$\Delta G^{\circ} = -119660 \,\mathrm{J \, mol^{-1}} \tag{1}$$

(i) Calculate Ecol by using the formula,

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

- (ii) Calculate the number of electrons by writing the electrode reactions, then write Nernst equation and find E_{cell} .
- (i) Refer to solution 9 (iii)

(ii) At anode
$$\operatorname{Sn}(s) \longrightarrow \operatorname{Sn}^{2+}(aq) + 2e^{-}$$
 (1/2)

At cathode $2H^+(aq) + 2e^- \longrightarrow H_2(q)$ (1/2)

Net reaction

$$Sn(s) + 2H^{+}(aq) \longrightarrow Sn^{2+}(aq) + H_{2}(g)$$
 (1/2)

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^{+}]^{2}}$$

$$= (E_{\text{H}^{+}/\text{H}_{2}}^{\circ} - E_{\text{Sn}^{2+}/\text{Sn}}^{\circ}) - \frac{0.0591}{2} \log \frac{0.04}{(0.02)^{2}}$$

$$= [0\text{V} - (-0.14\text{V})] - \frac{0.0591}{2} \log \frac{4}{100} \times \frac{100}{2} \times \frac{100}{2}$$

$$= + 0.14\text{V} - 0.0591\text{V} = 0.0809\text{ V}$$
(1)

Explanations

1. Conductivity,

$$\kappa = \frac{1}{R} \times \frac{l}{A}$$
 $\left(\text{As } \kappa = \frac{1}{\rho} \text{ and } \rho = \frac{RA}{l} \right)$

(1)

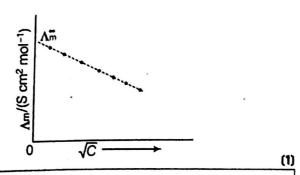
where, $\kappa = \text{conductivity}$, R = resistance

and
$$\frac{l}{A}$$
 = cell constant

- 2. Limiting molar conductivity The conductivity of a solution at infinite dilution is called limiting molar conductivity and is represented by the symbol Am .
- 3. Strong electrolytes are completely ionised in all concentrations. For strong electrolytes, Λ_m increases slowly with dilution. It is found to vary with concentration according to the Debye-Huckel-Onsager equation.

$$\Lambda_{\rm m} = \Lambda_{\rm m}^{\infty} - [A + B\Lambda_{\rm m}^{\infty}] \sqrt{C}$$

 $\Lambda_{\rm m} = \Lambda_{\rm m}^{\infty} - [A + B\Lambda_{\rm m}^{\infty}] \sqrt{C}$ (1) where, A and B are called Debye-Huckel constants. If solution is diluted (concentration is decreased), there is decrease in ionic attractions hence, molar conductivity increases with decrease in concentration.



4. To find out the degree of dissociation of acetic acid, we first need to calculate the $\Lambda_m^*(CH_3COOH)$ with the help of Kohlrausch law.

According to the question

Given, $\Lambda_m = 39.05 \text{ S cm}^2 \text{ mol}^{-1}$ $\lambda^{\circ}(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ $\lambda^{\circ}(\text{CH}_3\text{COO}^-) = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$ (1)

 $\Lambda_{\rm m}^{\circ}({\rm CH_3COOH}) = \lambda^{\circ}({\rm H}^+) + \lambda^{\circ}({\rm CH_3COO}^-)$ $= 349.6 \text{ S cm}^2 \text{ mol}^{-1} + 40.9 \text{ S cm}^2 \text{ mol}^{-1}$ $= 390.5 \text{ S cm}^2 \text{ mol}^{-1}$ $\alpha = \frac{\Lambda_{\rm m}}{\Lambda_{\rm m}^{\circ}} = \frac{39.05 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}}$ $\Rightarrow \alpha = 0.1$ (1)

5. Kohlrausch's law of independent migration of ions states that the limiting molar conductivity of an electrolyte can be expressed as the sum of the individual contributions of the anion and the cation of the electrolyte, e.g.

$$\Lambda_{m (CH_3COOH)}^{\circ} = \lambda_{CH_3COO^-}^{\circ} + \lambda_{H^+}^{\circ}$$
 (1)

The conductivity of a solution is related with the number of ions present per unit volume of the solution. When the solution is diluted, the number of ions per unit volume decreases. Hence, conductivity or specific conductance of the solution decreases. (1)

 (i) First we find out molar conductivity at given concentration using the formula,

$$\Lambda_{\rm m}^{\rm C} = \frac{\kappa \times 1000}{M}$$

(ii) Then, we find out the degree of dissociation (α) using the formula, $\alpha = \frac{\Lambda_m^C}{\Lambda_m^\infty}$

(iii) After dissociation of acetic acid into ions, we will find out the dissociation constant using the formula, $K_a = \frac{C \alpha^2}{1-\alpha}$

Molar conductivity at 0.001 M,

$$\Lambda_{\rm m}^{C} = \frac{\kappa \times 1000}{M}$$

$$= \frac{4 \times 10^{-5} \times 1000}{0.001} \text{S cm}^{2} / \text{mol}$$

$$= 40 \text{ S cm}^{2} / \text{mol}$$

Degree of dissociation,

$$\alpha = \frac{\Lambda_{\rm m}^C}{\Lambda_{\rm m}^\infty} = \frac{40}{390} = 0.10256$$

For the dissociation of acetic acid, CH₃COOH₁

CH₃COOH \(\sum_{1}^{\text{COO}} CH_{3}COO^{-} + H^{+} \)

170

Can

Initial(conc.)
$$C \text{ mol}^{-1}$$
 0 0

After time,
$$t(C-C\alpha)$$
 $C\alpha$ $C\alpha$

Dissociation constant, $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

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

$$K_a = \frac{0.001 \times (0.103)^2}{(1 - 0.103)}$$

$$=\frac{1.061\times10^{-5}}{0.897}$$

$$=1.18\times10^{-5}$$

7. The resistance, R of a conductor varies direct with length (l) and inversely with area cross-section A, i.e.

$$R \propto \frac{l}{A}$$
 or $R = \rho \frac{l}{A}$

where,
$$\rho = \text{resistivity}$$
; $\rho = \frac{RA}{I}$

Conductivity (x) is the reciprocal of resistivity (p). So,

$$\kappa = \frac{1}{\rho} = \frac{1}{RA/l} = \frac{l}{RA} = \frac{1}{R} \cdot \left(\frac{l}{A}\right)$$

$$\therefore \qquad \kappa = \frac{1}{R} \cdot \left(\frac{l}{A}\right) = \frac{1}{R} \cdot G^*$$

where,
$$G^* = \frac{l}{A} = \text{cell constant}$$

The molar conductivity of a solution is related to its conductivity by the following relation

$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{M} \, \rm S \, cm^2 \, mol^{-1}$$

where, M = molarity

8. Use formula
$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{M}$$
 to find the value of κ .

Given
$$\Lambda_{\rm m} = 138.9 \,\mathrm{S \, cm^2 mol^{-1}}$$

Molarity,
$$M = 1.5 \text{ M} = 1.5 \text{ mol } / \text{ L}$$

We know that,
$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{M}$$
 (1)

$$_{138.9 \text{ S cm}^2\text{mol}^{-1}} = \frac{\kappa \times 1000}{1.5 \text{ mol cm}^{-3}}$$

$$\kappa = \frac{138.9 \text{ S cm}^2 \text{mol}^{-1} \times 1.5 \text{ mol cm}^{-3}}{1000}$$

$$= 138.9 \times 1.5 \times 10^{-3} \text{ S cm}^{-1}$$

$$= 0.208 \text{ S cm}^{-1}$$

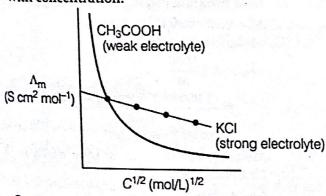
(1)

10. Conductivity The inverse of resistivity is called conductivity. It is denoted by κ (kappa). It is also known as specific conductance. $\kappa = 1/\rho$ SI unit of conductivity is S m⁻¹ or ohm⁻¹ m⁻¹. (1/2)

Molar conductivity It is defined as the conductance of the solution which contains one mole of the electrolyte such that entire solution is in between the two electrodes kept one centimetre apart, and large enough to contain all the electrolytes.

Molar conductivity,
$$\Lambda_{\rm m} = \frac{\kappa}{C}$$
 (1/2)

Variation of conductivity and molar conductivity with concentration.



Conductivity and molar conductivity change with change in concentration of electrolyte.

Conductivity always decreases with decrease in concentration for both weak as well as strong electrolytes.

But molar conductivity increases with decrease in concentration. For strong electrolytes, $\Lambda_{\rm m}$ increases slowly with dilution but for weak electrolyte, $\Lambda_{\rm m}$ increases steeply on dilution, especially near lower concentrations. (1/2)

11. (i) First, we calculate Λ_m^C using the formula

$$\Lambda_{\rm m}^{\rm C} = \frac{\kappa \times 1000}{M}$$

(ii) Then, degree of dissociation is calculated using the relation given below.

$$\alpha = \frac{\Lambda_{\rm m}^{\rm C}}{\Lambda_{\rm m}^{\rm \infty}}$$

Molar conductivity of 2.5×10^{-4} M solution is

$$\Lambda_{\rm m}^{\rm C} = \frac{\kappa \times 1000}{M} = \frac{5.25 \times 10^{-5} \times 1000}{2.5 \times 10^{-4}}$$

$$\Lambda_{\rm m}^{\rm C} = 210 \, \text{S cm}^{2} \text{mol}^{-1}$$

$$\Lambda_{\rm m \, (HCOOH)}^{\infty} = \lambda_{\rm (HCOO^{-})}^{\circ} + \lambda_{\rm (H^{+})}^{\circ}$$

$$\Lambda_{\rm m}^{\infty} = 50.5 + 349.5$$

$$\Lambda_{\rm m}^{\infty} = 400$$

$$\alpha = \frac{\Lambda_{\rm m}^{\rm C}}{\Lambda_{\rm m}^{\infty}} = \frac{210}{400} \tag{1}$$

$$\alpha = 0.525 \tag{1}$$

(i) First find conductivity using the formula conductivity, $\kappa = 1/R \times I/A$

(ii) Then, find molar conductivity of solution by using the formula,

$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{\text{Molarity}}$$

Given, Resistance (R) = 200 Ω

Molarity of NaCl solution = 0.01 M

Cell constant =
$$\frac{l}{A} = 1 \text{ cm}^{-1}$$
 (1)

Conductivity (k) = $\frac{1}{R} \times \frac{l}{A} = \frac{1}{200 \Omega} \times 1 \text{ cm}^{-1}$

$$= 5.0 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$$
 (1)

Molar conductivity (Λ_m)

$$= \frac{\kappa \times 1000}{\text{Molarity}} = \frac{(5.0 \times 10^{-3} \text{ S cm}^{-1}) (1000 \text{ cm}^3 \text{L}^{-1})}{0.01 \text{ mol L}^{-1}}$$
$$= 500 \text{ S cm}^2 \text{mol}^{-1}$$

13. Given, Λ_{m}° of Al₂(SO₄)₃ = 858 S cm² mol⁻¹

$$\lambda_{m(SO_4^{2-})}^{\circ} = 160 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{m[Al_2(SO_4)_3]}^{\circ} = 2\lambda_{m(Al^{3+})}^{\circ} + 3\lambda_{m(SO_4^{2-})}^{\circ}$$
(1)

$$858 = 2\lambda^{\circ}_{m(Al^{3+})} + 3 \times 160$$

$$858 = 2\lambda^{\circ}_{m(Al^{3+})} + 480$$

$$\lambda_{m(Al^{3+})}^{\circ} = \frac{858 - 480}{2} = 189 \text{ S cm}^{2} \text{ mol}^{-1}$$
 (2)

14. Given, conductance of cell when electrolyte of 0.1 M KCl is filled = 85 ohm's

Conductance of cell when unknown electrolyte of 0.052 M is filled = 96 ohm's

Specific conductance (κ) of 0.1 M KCl = 1.29×10⁻² Ω^{-1} cm⁻¹

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

Cell constant =
$$\kappa \times R$$

= 0.0129 S cm⁻¹ × 85 = 1.0965 cm⁻¹ (1)
= 109.65 m⁻¹

In case of second solution,

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

$$= \frac{1}{96} \times 109.65 \,\text{m}^{-1} = 0.01142 \,\Omega^{-1} \,\text{cm}^{-1}$$

$$\Lambda_{\text{m}} = \frac{\kappa \times 1000}{M}$$

$$= \frac{0.01142 \,\Omega^{-1} \,\text{cm}^{-1} \times 1000 \,\text{cm}^{3} \,\text{L}^{-1}}{0.052 \,\text{mol L}^{-1}}$$

$$= 219.61 \text{ Scm}^2 \text{ mol}^{-1}$$
 (1)

- **15.** (i) Find area from radius by using, $A = \pi r^2$
 - (ii) Find resistivity from the formula, $\rho = \frac{RA}{I}$
 - (iii) Find conductivity (κ) from resistivity as $\kappa = 1/\rho$
 - (iv) Find molar conductivity, $\Lambda_{\rm m}$ by using the formula, $\Lambda_{\rm m} = \frac{\kappa \times 1000}{M}$

Given, concentration of NaOH = 0.05 M, diameter = 1 cm, length = 50 cm, resistance = $5.55 \times 10^3 \Omega$

Area,
$$A = \pi r^2 = 3.14 \times \left(\frac{1}{2}\right)^2 \text{ cm}^2 = 0.785 \text{ cm}^2$$

Resistivity, $\rho = \frac{RA}{I}$

$$= \frac{5.55 \times 10^{3} \Omega \times 0.785 \text{ cm}^{2}}{50 \text{ cm}} = 87.135 \Omega \text{ cm}$$
(1/2)

Conductivity,

$$\kappa = \frac{1}{\rho} = \frac{1}{87.135} \Omega^{-1} \text{cm}^{-1}$$

$$= 0.01148 = 1.148 \times 10^{-2} \text{ S cm}^{-1} (1/2)$$

(1/2)

Molar conductivity,

$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{M}$$

$$= \frac{1.148 \times 10^{-2} \times 1000}{0.05} = 229.6 \text{ S cm}^2 \text{mol}^{-1}$$
(1/2)

16. Given, $\Lambda_{\text{m(CH}_3\text{COOH)}} = 11.7 \text{ S cm}^2 \text{ mol}^{-1}$ $\Lambda_{\text{m(CH}_3\text{COO}^-)}^{\circ} = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$

$$\Lambda_{m(H^+)}^{\circ} = 349.1 \text{ S cm}^2 \text{ mol}^{-1}$$

Degree of dissociation $\alpha = \Lambda_m$

Degree of dissociation, $\alpha = \frac{\Lambda_m}{\Lambda_m^o}$

$$\begin{split} &\Lambda_{m \, (CH_3COOH)}^{\circ} = \Lambda_{m \, (CH_3COO^-)}^{\circ} + \Lambda_{m \, (H^+)}^{\circ} \\ &\Lambda_{m \, (CH_3COOH)}^{\circ} = (40.9 + 349.1) = 390 \, \text{S cm}^2 \, \text{mol}^{-1} \\ &\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}} = \frac{11.7}{390} = 3.0 \times 10^{-2} \end{split}$$

17. Recall Kohlrausch's law to find the conductance of weak electrolyte.

Given, $\Lambda_{m(HCl)}^{\circ} = 426 \text{S cm}^2 \text{ mol}^{-1}$; $\Lambda_{m(NaCl)}^{\circ} = 126 \text{ S cm}^2 \text{ mol}^{-1}$, $\Lambda_{m(CH_3COON_a)}^{\circ} = 91 \text{ S cm}^2 \text{ mol}^{-1}$ $\Lambda_{m(CH_3COOH)}^{\circ} = \Lambda_{H^+}^{\circ} + \Lambda_{CH_3COO^-}^{\circ}$ (1/2) $\Lambda_{m(HCl)}^{\circ} + \Lambda_{m(CH_3COON_a)}^{\circ} + \Lambda_{Na^+}^{\circ} - \Lambda_{Cl^-}^{\circ} - \Lambda_{Na^+}^{\circ}$ $\Lambda_{m(HCl)}^{\circ} + \Lambda_{m(CH_3COON_a)}^{\circ} - \Lambda_{m(NaCl)}^{\circ}$ (1) $\Lambda_{m(HCl)}^{\circ} + \Lambda_{m(CH_3COON_a)}^{\circ} - \Lambda_{m(NaCl)}^{\circ}$ (1)

18. (i) Given: Conductivity of CH₃COOH solution, $\kappa = 3.905 \times 10^{-5} \text{S cm}^{-1}$

Concentration of CH₃COOH solution,

 $M = 0.001 \text{ mol } L^{-1} = 0.001 M$

Molar conductivity,

$$\lambda_{\rm m} = \kappa \times \frac{1000}{M}$$

$$= \frac{(3.905 \times 10^{-5} \text{S cm}^{-1}) \times (1000)}{0.001 \text{ M}}$$

$$= 39.05 \text{ S cm}^2 \text{ mol}^{-1}$$

Molar conductivity at infinite dilution (λ°_{m}) for CH₃COOH,

$$\lambda_{\text{m CH}_3\text{COOH}}^{\circ} = \lambda_{\text{CH}_3\text{COO}^-}^{\circ} + \lambda_{\text{H}^+}^{\circ}$$

$$= 40.9 + 349.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$

Degree of dissociation, $\alpha = \frac{\lambda_m}{\lambda_m^{\circ}}$

$$= \frac{39.05 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.1$$

(ii) A device used to convert the chemical energy produced in a spontaneous redox reaction into electrical energy is called an electrochemical cell.

When external potential applied becomes greater than E_{cell}° of electrochemical cell, electrons flow from cathode to anode, i.e. electrochemical cell behaves like an electrolytic cell. (2)

(i) Degree of dissociation The ratio of molar conductivity (Λ_m) at a specific concentration C to the molar conductivity at infinite dilution, i.e. limiting molar conductivity, Λ^o_m, is known as degree of dissociation.
(1) At any concentration C, if α is the degree of dissociation, then for a weak electrolyte, α = Λ_m/Λ^o_m

(ii) Given,
$$E_{\text{Ni}^2+/\text{Ni}}^{\circ} = 0.25 \text{ V} \text{ and } E_{\text{Ag}^+/\text{Ag}}^{\circ} = 0.80 \text{ V}$$

At anode Ni(s) \longrightarrow Ni²⁺(aq) + 2e⁻

At cathode
$$[Ag^+(aq) + e^- \longrightarrow Ag(s)] \times 2$$

Overall reaction

Ni (s) + 2Ag⁺ (aq)
$$\longrightarrow$$
 Ni²⁺ (aq) + 2Ag(s) (1)
 $E_{\text{cell}}^{\circ} = E_{\text{Ag}^{+}/\text{Ag}}^{\circ} - E_{\text{Ni}^{2+}/\text{Ni}}^{\circ} = 0.80 - 0.25$
 $E_{\text{cell}}^{\circ} = 0.55$

Equilibrium constant (K) =

Antilog
$$\left(\frac{nE^{\circ}}{0.0591}\right)$$
 = antilog $\left(2 \times \frac{0.55}{0.0591}\right)$
 $K = 4 \times 10^{18}$ (1)

Maximum work
$$(\Delta G^{\circ}) = -nFE^{\circ}$$

= -2 × 96500 × 0.55= - 106150 J mol⁻¹ (1)

20. (i) Refer to solution 10. (2)
(ii)
$$Fe^{2+}$$
 $(aq) + Ag^{+}$ $(aq) \longrightarrow Fe^{3+}$ $(aq) + Ag(s)$

$$E_{\text{cell}}^{\circ} = E_{\text{Ag}^{+}/\text{Ag}}^{\circ} - (E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ})$$

= 0.80 V - 0.77 V = 0.03 V (1)

$$\Delta_r G^\circ = -nFE^\circ = -1 \times 96500 \times 0.03$$
 (1)
= -2895 J mol⁻¹

Equilibrium constant (K) = antilog
$$\left(\frac{nE^{\circ}}{0.0591}\right)$$

 $K = 3.21$

(ii) Given, conductivity,

$$\kappa = 0.146 \times 10^{-3} \text{ S cm}^{-1}$$

Resistance,
$$R = 1500 \Omega$$

∴ Cell constant, $G^* = \kappa \times R$
= $0.146 \times 10^{-3} \times 1500 = 0.219 \text{ cm}^{-1}$ (3)

Explanations

1. Given, w = 1.50 g; I = 1.50 A

Molar mass of $Ag = 108 \text{ g mol}^{-1}$

$$Z = \frac{\text{Equivalent weight}}{F}$$

where, $F = 96500 \, \text{C}$

As we know, $w = Z \times I \times t$

or $t = \frac{w}{Z \times I} = \frac{1.50 \times 96500}{108 \times 1.50}$ = 893.51 s

2. Given, conductivity of CH₃COOH solution, $\kappa = 1.65 \times 10^{-4} \text{ S cm}^{-1}$

Concentration of CH3COOH solution,

 $M = 0.01 \, M$

(2)

Molar conductivity,
$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{M}$$

$$= \frac{(1.65 \times 10^{-4}) \times 1000}{0.01 \text{ M}}$$

$$= 16.5 \text{ S cm}^2 \text{ mol}^{-1}$$
(2)

3. Mercury cell is suitable for low current devices like hearing aids, watches, etc.

The electrode reactions of a mercury cell can be written as

At anode

$$Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$$
 (1)

At cathode

$$HgO(s) + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$$
 (1/2)

Overall reaction of the cell is written as

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$
 (1/2)

Leclanche cell is commonly used in transistors.
 The electrode reactions of Leclanche cell can be written as

At anode
$$Zn(s) \longrightarrow Zn^{2+} + 2e^{-}$$
 (1)

At cathode

 $MnO_2 + NH_4^+ + e^- \longrightarrow MnO (OH) + NH_3$

NH₃ formed in reaction at cathode combines with Zn^{2+} to form the complex like $[Zn(NH_3)_4]^{2+}$ (1)

5. (i) Mercury cell (1/2)

(ii) Fuel cell (1/2)

(iii) Lead storage cell (1/2)

(iv) Dry cell (1/2)

6. Given, w = 1.27 g, I = 2A

Molar mass of $Cu = 63.5 \text{ g mol}^{-1}$,

$$Z = \frac{\text{Equivalent weight}}{E}$$

$$F = 96500 \,\mathrm{C \, mol^{-1}}$$

$$w = Z \times I \times t \tag{1}$$

$$t = \frac{w}{Z \times I} = \frac{1.27 \times 2 \times 96500}{63.5 \times 2}$$

$$t = 1930 \text{ s}$$

$$= 32.1 \, \text{min}$$
 (1)

7. (i) Electrolysis of an aqueous solution of AgCl.

AgCl
$$(aq) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

On passing electricity, Ag⁺(aq) and H⁺(aq) move towards the cathode. Since, the discharge potential of Ag⁺ ion is lower than

that of H⁺ ions. In the other words, Ag⁺ ions have more value of standard reduction potential. Therefore, Ag⁺ ions are discharged in preference of H⁺ ions.

At cathode $Ag^+(aq) + e^- \longrightarrow Ag(s)$

At anode
$$Cl^- - e^- \longrightarrow {}^{\bullet}Cl$$

 ${}^{\bullet}Cl + {}^{\bullet}Cl \longrightarrow Cl_2$ (g)

Hence, reduction of Ag⁺(ion) is feasible at cathode.

(ii) Limiting molar conductivity Refer to solution 2 of topic 2.
 Conductivity of an electrolyte solution decreases with the decrease in concentration due to the fact that the number of ions per

unit volume that carry the current in a solution decreases on dilution.

8. (i) Electrolysis of aqueous solution of CuCl₂

$$CuCl_2(aq) \Longrightarrow Cu^{2+} (aq) + 2Cl^{-} (aq)$$

 $H \cdot O(l) \Longrightarrow H^{+}(aq) + OH^{-} (aq)$

On passing electricity, $Cu^{2+}(aq)$ and $H^{+}(aq)$ move towards the cathode. Since, the discharge potential of Cu^{2+} ion is lower than that of H^{+} ions, or Cu^{2+} ion have more value of standard reduction potential.

Therefore, Cu²⁺ ions are discharged in the presence of H⁺ ions.

(ii) Kohlrausch's law of independent migration of ions Refer to solution 5 of topic2

Application Using this law, it is possible to calculate Λ_m^o for weak electrolyte from the λ^o of individual ions at infinite dilution.

9. Dry cell (Leclanche cell) consists of a zincontainer which acts as anode and cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by a moist paste of NH₄Cl and ZnCl₂.

The reactions are:

At anode $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$

At cathode $2e^- + 2NH_4^+ (aq) \longrightarrow 2NH_3(g) + H_2(g)$

 $2NH_3(g) + Zn^{2+}(aq) \longrightarrow [Zn(NH_3)_2]^{2+}(aq)$

 $H_2(g) + 2MnO_2 \longrightarrow Mn_2O_3(s) + H_2O(l)$ Overall reaction

 $Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) \longrightarrow$

 $[Zn(NH_3)_2]^{2+}(aq) + Mn_2O_3(s) + H_2O(1)$

By using Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 \, RT}{nF} \ln \frac{[\text{Zn}(\text{NH}_3)_2]^{2+}}{[\text{NH}_A^+]^2}$$

Due to the presence of ions in the overall reaction, its voltage decreases with time.

- 10.
- (i) First find the amount of charge by $Q=l\times t$
- (ii) Then, mass of copper deposited using the formula, m = Zlt

$$= \frac{\text{Equivalent weight}}{96500} \times I \times t$$

Given, Current, I = 5.0 A

time (t) =
$$20 \times 60 = 1200 \text{ s}$$

$$Q = I \times t \Rightarrow Q = 5.0 \times 1200 = 6000 \text{ C}$$

$$m = Z \times I \times t = \frac{\text{Equivalent weight}}{96500} \times Q$$

$$= \frac{58.7}{2 \times 96500} \times 6000 = 1.82 \text{ g}$$
(1)

11. Those galvanic cells in which chemical energy of combustion of fuels like hydrogen, methane, etc. is converted into electrical energy are called fuel cells.

The electrode reactions involved in the working of H₂-O₂ fuel cell are as follows:

At cathode.

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(ag)$$

At anode,

$$2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(1) + 4e^-$$
 (1)

12. $CaCl_2 \longrightarrow Ca^{2+} + 2Cl^{-}$

$$Ca^{2+} + 2e^{-} \longrightarrow Ca_{40g}$$

The electricity required to produce 40 g = 2 F

Therefore, electricity required to produce 20g =
$$(2 \times 20) / 40 = 1F$$
 (2)

13. Electrode reaction,

$$Ag^{+} + e^{-} \longrightarrow Ag$$
180 g

:.96500 C (1F) of electricity deposit Ag = 108 g

Quantity of current passed = Current × Time

$$= 0.5 \times 60 \times 60 \times 2 = 3600 \,\mathrm{C}$$

3600 C of electricity will deposit Ag

$$=\frac{108}{96500}\times3600=4.03g\tag{1}$$

Now, let the thickness of deposition be a cm

Mass = volume × Density or Area × Thickness

× density

$$4.03g = 900 \text{ cm}^2 \times a \text{ cm} \times 10.5 \text{ g cm}^{-3}$$

 $a = 4.26 \times 10^{-4} \text{ cm}$

(1)

(1)

(1)

14. Lead storage battery is a secondary cell. Thus, it can be recharged by passing direct current through it. Therefore, it can be reused. It is used in automobiles.

In a lead storage cell, the anode is made of spongy lead and the cathode is a grid of lead packed with lead dioxide. The electrolyte used is H_2SO_4 (38% by mass).

At anode

Pb (s) +
$$SO_4^{2-}$$
 (aq) \longrightarrow PbSO₄(s) + $2e^-$

At cathode

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

$$PbSO_4(s) + 2H_2O(l)$$
 (1/2)

The overall cell reaction

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

On recharging the battery, the reaction is reversed.

$$2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$$
 (1/2)

15. The chemistry of corrosion of iron is essentially an electrochemical phenomenon. In which a metal oxide or other salt of metal forms a coating on metal oxide. The reactions occurring during the corrosion of iron in the atmosphere are as follows:

At anode.

2 Fe(s)
$$\longrightarrow$$
 2 Fe²⁺ + 4e⁻; $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V}$

At cathode

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l);$$

$$E_{\rm H^+/O_2/H_2O}^{\rm o} = 1.23 \text{ V}$$

Overall reaction

2Fe(s) + O₂(g) + 4H⁺(aq)
$$\longrightarrow$$
 2 Fe²⁺(aq)
+ 2H₂O(l);
 $E_{cell}^{\circ} = 1.67 \text{ V}$ (1)

The ferrous ions are further oxidised to ferric ions by atmospheric oxygen. Reaction is as follows:

$$2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow$$

$$Fe_2O_3(s) + 4H^+(aq)$$

Time =
$$3 h = 3 \times 60 \times 60 s$$

$$m = ZIt = \frac{E}{96500} It$$
(1/2)

$$=\frac{200.6\times2\times3\times60\times60}{2\times96500}$$
 (1/2)

$$= 22.45 g$$
 (1/2)

Number of moles =
$$\frac{22.45}{200.6}$$
 = 0.112 mol (1/2)

17. In the electrolysis of NaBr,

$$2Br^{-}(aq) \longrightarrow Br_2 + 2e^{-}$$

occurs at anode because it has lower reduction potential, and liberation of O2 requires over voltage.

18. Mercury cell

Anode Zinc-mercury amalgam Cathode Paste of HgO and carbon Electrolyte Paste of KOH and ZnO Electrode reactions are as follows

At anode

$$Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$$

$$HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$$
 (1/2)

Overall reaction

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$
 (1/2)

The voltage of a mercury cell remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life-time. (1/2)

19. Fuel cells Galvanic cells that are designed to convert the chemical energy from combustion of fuels like hydrogen, methane, methanol directly into electrical energy are called fuel cells. The efficiency of fuel cell is higher than that of galvanic cell, e.g. hydrogen-oxygen fuel cell, in which hydrogen and oxygen are bubbled through porous carbon electrodes into conc. KOH solution. Finely divided Pt or Pd metals are incorporated into the electrodes for increasing . the rate of electrode reactions. (1)

At cathode

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

At anode

$$2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$$

Overall reaction

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$
 (1)

20. Nickel-cadmium cell is a secondary cell. It has longer life than the lead storage cell but more expensive to manufacture. (1/3) The overall reaction during discharging is

$$Cd(s) + 2Ni(OH)_{3}(s) = \frac{Discharge}{Recharge} CdO(s) + 2Ni(OH)_{2}(s) + H_{2}O(l)$$

21. Refer to solution 18.

22. Refer to solution 20.

(2)

(1/2)

23. Given, Charge (Q) = 24000 C and

Mass of chromium (Cr) deposited = 1.5 gMolar mass of (Cr) = 52 g mol^{-1}

and 1 $F = 96500 \text{ Cmol}^{-1}$

 $: 6 \times 96500$ C charge deposit Cr = 52 g

:. 24000 C charge deposit
$$Cr = \frac{52 \times 24000}{6 \times 96500}$$

$$=\frac{1248000}{6\times 96500}$$

(1)

...(i)

(14

Mass of chromium deposited = 2.16 g Also,

Charge
$$(Q) = i \times t$$
 (time)

$$t = \frac{Q}{i} = \frac{24000}{12.5} = 1920 \text{ s}$$

Duration of current = 32 min

24. (i) Standard Gibbs Free energy is given by $\Delta G^{\circ} = -nFE^{\circ}_{cell}$ where, n = number of moles of electrons transfered, F = Faraday's constant

 $= 96500 \, \text{Cmol}^{-1}$ $E^{\circ}_{\text{cell}} = \text{Cell potential}$ Two half-reactions for the given redox reaction can be written as

$$2 \operatorname{Fe}^{3+}(aq) + 2e^{-} \longrightarrow 2 \operatorname{Fe}^{2+}(aq) + 2\operatorname{I}^{-}(aq) \longrightarrow \operatorname{I}_{2}(s) + 2e^{-}$$

2 moles of electrons are involved in the reaction, hence n = 2

Therefore, by substituting all the values in Eq. (i) we get

$$\Delta_r G^\circ = - (2 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.236 \text{ V})$$

= -45548 J

$$\Delta_r G^\circ = -4555 \,\mathrm{kJ}$$

(ii) Given, current (i) = 0.5 A, time (t) = 2h Quantity of charge (Q) passed = Current (i) \times time (t) = $(0.5 \text{ A}) \times (2 \times 60 \times 60 \text{ s}) = 3600 \text{ C}$

Again, $Q = ne^$ where, n = number of electrons e^- = charge on electron

$$\therefore n = \frac{Q}{e^{-}} = \frac{3600\text{C}}{1.6 \times 10^{-19}\text{C}} = 2250 \times 10^{19}$$

Thus, number of electrons = 2.250×10^{22} (11/2)

To find out the mass of Ag deposited at 25.(i) cathode, we first need to find the quantity of electricity passed (Q) using faraday's law. The value of Q helps in determining the mass of 108 g of Ag.

> Given, current (I) = 2Atime $(t) = 15 \min$

Quantity of electricity passed will be

 $Q = It = 2 \times 15 \times 60 = 1800 \text{ C}$

Electrolysis of AgNO3

$$Ag^+ + e^- \longrightarrow Ag(s)$$

(Atomic mass of $Ag=108 g \text{ mol}^{-1}$)

As, 96500 C deposit 108 g of Ag

∴ 1800 C will deposit =
$$\frac{108 \times 1800}{96500}$$
 g of Ag

= 2.014 g of Ag $(1\frac{1}{2})$

(ii) A Fuel cell Refer to solution 11.

The overall reaction of the cell is $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ $(1\frac{1}{2})$

6. (i) For the reaction,

$$Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$$

$$n = 2$$

$$E_{\text{cell}}^{\circ} = +2.71\text{V}, 1\text{F} = 96500 \text{ C} \text{ mol}^{-1} \text{ (given)}$$

 $\Delta G^{\circ} = -nF E_{\text{cell}}^{\circ}$

$$=-2 \times 96500 \times 2.71 = -523030 \text{ J mol}^{-1}$$

= $-523.030 \text{ kJ mol}^{-1}$

- (ii) H2-O2 fuel cell was used in Apollo space programme for providing electrical power.
- 7. (i) Advantages of fuel cells
 - (a) Because of the continuous supply of fuels, these cells never become dead. These cells are usually operated at a temperature of 70-140°C and gives a potential of about 0.9 V.
 - (b) Fuel cells do not cause any pollution unlike thermal plant which burn fossil fuels like coal gas, oil, etc. 1 mon

(ii) The reaction

$$A(s) + B^{2+}(aq) \Longrightarrow A^{2+}(aq) + B(s)$$

By using Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{[A^{2+}]}{[B^{2+}]}$$
 (1)

At equilibrium, $E_{cell} = 0$ $E_{\text{cell}}^{\circ} = \frac{0.059}{0.000} \log K_C$ $K_c = 10 \text{ and } n = 2$ $E_{\text{cell}}^{\circ} = \frac{0.059}{2} \log 10$ $(\because \log 10 = 1)$

$$E_{\text{cell}}^{\circ} = \frac{0.059}{2} = 0.0295$$
 (1)

28. Refer to solution 14.

(3)

29.

- (i) Cathode is the site of reduction.
 - (ii) Use Q = It to find the amount of charge passed and m = ZIt

$$= \frac{\text{Equivalent weight} \times \textit{lt}}{96500}$$

to find the mass of copper deposited.

Given that, $t = 50 \times 60 = 3000$ s, I = 0.1287A

(i)
$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$
 (s)

(ii) (a)
$$Q = It = 0.1287 \times 3000 = 386.1 \text{ C}$$

(b)
$$m = Z \times I \times t = \frac{\text{Equivalent weight}}{96500} \times Q$$

$$=\frac{63.5}{2\times96500}\times386.1=0.127 \text{ g}$$
 (1)

30. (i) $Sn(s) \mid Sn^{2+}(0.004 M) \mid H^{+}(0.020 M)$

$$|H_2(g)|$$
 (1 bar) | Pt (s)

Cell reaction is

$$Sn + 2H^+(0.020 M) \longrightarrow Sn^{2+}(0.004 M)$$

$$E_{\text{cell}}^{\circ} = E_{\text{H}^{+}, \frac{1}{2}\text{H}_{2}}^{\circ} - E_{\text{Sn}^{2} + /\text{Sn}}^{\circ}$$

$$= 0 - (-0.14 \text{ V}) = 0 + 0.14 \text{ V} = 0.14 \text{ V}$$

For calculation of emf, apply Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Sn}^{2+}] \times p_{\text{H}_2}}{[\text{H}^{+}]^2}$$

$$= 0.14 - \frac{0.0591}{2} \log \frac{[0.004] \times 1}{[0.020]^2}$$

$$= 0.14 - \frac{0.0591}{2} \log \frac{0.004}{0.0004}$$

$$= 0.14 - \frac{0.0591}{2} \log 10$$

$$= 0.14 - \frac{0.0591}{2} = 0.110 \text{ V}$$

 $(2\frac{1}{2})$ (ii) (a) From standard oxidation potential it is clear that oxygen gas should be liberated at anode, but its rate of production is very

low. In order to increase that we increase the voltage of external battery. Because of which chloride ions get oxidised easily and Cl₂ gas is liberated at anode.

- (b) Conductivity of solution is conductance of ions present in unit volume of solution.

 On dilution number of CH₃COOH ions per unit volume decreases. Hence conductivity decreases. (2½)
- 31. (i) Gibbs energy of reaction is

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} \qquad \dots (i)$$

Given,
$$\Delta G^{\circ} = -43600 \text{ J}$$
, $n = 2$, $E_{\text{cell}}^{\circ} = ?$, $E = 96500 \text{ C}$ mol⁻¹

On putting the above values in Eq. (i), we get

$$-43600 J = -2 \times 96500 \times E^{\circ}$$

$$E^{\circ} = \left(\frac{43600}{2 \times 96500}\right) V$$

$$E^{\circ} = 0.22 \text{ V}$$

Now using Nernst equation,

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[Product]}{[Reactant]}$$

$$E = E^{\circ} - \frac{0.0591}{n} \log \left[\frac{[H^{+}]^{2} [Cl^{-}]^{2}}{H_{2}(g)} \right] (n = 2)$$

Putting values, we get

$$E = 0.22 - \frac{0.0591}{2} \log \left[\frac{(0.1)^2 (0.1)^2}{1} \right]$$

$$E = 0.22 - \frac{0.0591}{2} \log (10^{-4})$$

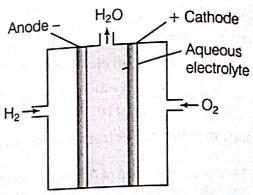
$$(\log 10^{-x} = -x)$$

$$E = 0.22 - \frac{0.0591}{2} (-4) = 0.3382 \text{ V}$$

∴
$$E = 0.3382 \text{ V}$$
 (2½)

(ii) It is a galvanic cell in which chemical energy from combustion of fuels is converted into electrical energy. In this type of galvanic cells, reactants are continuously feed to the electrodes, which react to produce electricity and product thus formed are continuously removed. Fuel cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc.

directly into electrical energy are highly efficient (70%) when compared to efficiency thermal power plants (40%).



Fuel cell using

and

produces electricity

Their two advantages are:

- (a) fuel cells are pollution free.
- (b) They never become dead due to continuous supply of fuel.

There have been tremendous progress in the development of new electrode materials, better catalyst and electrolytes for increasing the efficiency of fuel cells.

32. For the reaction,

$$Mg(s) + Cu_{(0.01M)}^{2+} \longrightarrow Mg_{(0.001M)}^{2+} + Cu(s)$$

Given,
$$E^{\circ}_{cell} = 2.71 \text{ V}$$

 $E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$
 $E_{cell} = 2.71 - \frac{0.0591}{2} \log \frac{[0.001]}{[0.01]}$
 $E^{\circ}_{cell} = 2.71 + \frac{0.0591}{2} \log 10$
 $E^{\circ}_{cell} = 2.74 \text{ V}$

- (i) When $E_{\text{ext}} < 2.71 \text{ V}$; the current flows from to Mg as the electron flows from Mg to Curo
- (ii) When $E_{\rm ext} > 2.71$ V, the reactions are reversand so, the polarity of the electrodes. Thus, current will flow from Mg to Cu.

33. (a)
$$Fe^{2+} + 2e^{-} \longrightarrow Fe_{56g}$$

∴56 g of Fe is deposited by 2F or 2×96500€ charge

∴ 2.8 g of Fe will be deposited by

Now,
$$\frac{96500 \times 2 \times 2.8}{56} \text{ C charge} = 9650 \text{ C}$$

$$Q = It$$

Time,
$$t = \frac{9650}{2} = 4825 \text{ s}$$

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

 $:: 2 \times 96500 \text{ C}$ charge deposits Zn = 6538

:. 9650 C charge will deposit

$$Zn = \frac{65.3 \times 9650}{96500 \times 2} = 3.27g$$

- (b) (i) 'A' is a strong electrolyte since there is a small increase in Λ_m with dilution while 'B' is a weak electrolyte since Λ_m increases sharply near high dilution.
- (ii) For strong electrolyte (A) the plot becomes linear near high dilution and we can determine the value of Λ°_{m} on extrapolation of Λ_{m} to $C \rightarrow 0$.
 - For weak electrolyte, Λ_m increases sharply near high dilution. Hence, an extrapolation of Λ_m to $C \to 0$ is not possible.

34. (i)
$$2Al(s) + 3Cu^{2+}(0.01M) \longrightarrow$$

 $2Al^{3+}(0.01M) + 3Cu(s)$
 $E_{cell} = 1.98 \text{ V}$

Applying Nernst equation for the given cell reaction,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3}$$

$$E_{\text{cell}}^{\circ} = E_{\text{cell}} + \frac{0.0591}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3}$$
(1)

Here, n = 6 (n = number of electrons

transferred)

$$=1.98 + \frac{0.0591}{6} \log \frac{(0.01)^2}{(0.01)^3}$$
$$=1.98 + \frac{0.0591}{6} \log 100 = 1.98 + \frac{0.0591}{6} \times 2$$

$$[\log 100 = \log 10^2 = 2\log 10 = 2, \text{ as } \log 10 = 1]$$

$$=1.9997 V \approx 2.0 V$$
 (2)

(ii) Lower the reduction potential, more reactive is the metal. Coating the surface of iron with a more active metal prevents the iron from losing electrons and hence from corrosion.

As reduction potential of A is lower than that of iron, therefore A would be used for coating the surface of iron to prevent it from corrosion. This is because lower the reduction potential of an element, more reactive is the element. Therefore, A would be more reactive than iron as well as B and hence, A protects the iron metal from corrosion. (2)

- 5. (i) (a) Refer to solution 10 of Topic '2'.
 - (b) Secondary batteries After use, they can be recharged by passing current through it in the opposite direction so that it can be used again. Secondary cell undergo a large number of discharging and charging cycles. The most important secondary cell

is the lead storage battery. Other example includes nickel-cadmium cell. (1)

- (c) Refer to solution 11. (1)
- (ii) (a) Faraday's first law of electrolysis The amount of substance deposited during electrolysis is directly proportional to quantity of electricity passed.

$$m \propto Q$$
, $m \propto It$, $m = ZIt$,

where, Z is electrochemical equivalent, I is current in ampere, t is time in seconds and Q is charge in coulomb.

Electrochemical equivalent (Z) It is amount of substance deposited in grams when 1 ampere current is passed for 1 second, i.e. when 1 coulomb of charge is passed. Its unit is gC^{-1} .

- (b) Kohlrausch's law of independent migration of ions Refer to solution 5 of Topic 2. (1)
- 36. (i) (a) Electrolysis of AgNO₃(aq) using Pt electrodes AgNO₃(aq) \longrightarrow Ag⁺(aq) + NO₃⁻ (aq) At cathode, Ag⁺(aq) + e⁻ \longrightarrow Ag (s) At anode, 2H₂O (l) \longrightarrow O₂(g) +4H⁺(aq) + 4e⁻ [11/2]
 - (b) Electrolysis of $H_2SO_4(aq)$ using Pt electrodes. $2H_2O(l) \longrightarrow 2H_2(g) + O_2(g)$ At cathode, $H_2O + e^- \longrightarrow \frac{1}{2}H_2 + OH^-$

At anode,
$$2 \text{ H}_2\text{O} \longrightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$$
 (112)

(2)

(1)

(ii) Reaction involved, $\frac{2}{3}\text{Al}_2\text{O}_3 \longrightarrow \frac{4}{3}\text{Al} + \text{O}_2$

Here,
$$n = 4$$

Given, $\Delta G = -960 \text{ kJ} \implies \Delta G = -nFE^\circ$
 $-960000 \text{ J} = -4 \times 96500 \times E^\circ$
 $E^\circ = \frac{960000 \text{ J}}{4 \times 96500 \text{ J}} = 2.48 \text{ V} \approx 2.5 \text{ V}$

- 37. (i) (a) Limiting molar conductivity The molar conductivity of a solution at infinite dilution is called limiting molar conductivity and is represented by the symbol Λ_m° . (1)
 - (b) Fuel cell Refer to solution 19.
 - (ii) (a) First calculate the cell constant using relation, I/A (cell constant) = $R \times \kappa$ then, find conductivity (κ).
 - (b) Find molar conductivity of solution by the formula, $\Lambda_{\rm m} = \frac{\kappa \times 1000}{\rm Molarity}$

(1) (a) Cell constant, $G^* =$ conductivity \times resistance $= 1.29 \text{ Sm}^{-1} \times 100 \Omega = 129 \text{ m}^{-1} = 1.29 \text{ cm}^{-1}$

(b) Conductivity of 0.02 M KCl solution,

$$\kappa = \frac{\text{Cell constant}}{\text{Resistance}} = \frac{1.29 \text{ cm}^{-1}}{520 \Omega}$$
$$= 2.48 \times 10^{-3} \text{ S cm}^{-1} \tag{1}$$

(c) Molar conductivity,
$$\Lambda_{\rm m} = \frac{\kappa \times 1000}{M}$$

= $\frac{2.48 \times 10^{-3} \times 1000}{0.02} = 124 \text{ S cm}^2 \text{ mol}^{-1}$ (1)

38. (i) Faraday's first law of electrolysis Refer to solution 35 (ii) (a) Charge required for the reduction of 1 mole of

(1)

 $Cu^{2+} \text{ to } Cu = 2F$ (ii) $Cu^{2+} + Mg \longrightarrow Mg^{2+} + Cu$ Given, $E^{\circ}_{Ceil} = +2.71 \text{ V}$ By using Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$$
 (1)

Here, n = 2 and $E_{cell}^{\circ} = + 2.71 \text{ V}$

$$E_{\text{cell}} = 2.71 - \frac{0.059}{2} \log \frac{(0.1)}{(0.01)}$$

$$= 2.71 - \frac{0.059}{2} \log 10$$

$$= 2.71 - 0.0295 = 2.68 \text{ Y} \quad [\because \log 10 = 1]$$