1   Represent the galvanic cell in which the reactions is   1

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

ANS: Zn | ZnSO$_4$ (1M) || CuSO$_4$ (1M) | Cu(s)

2   What is primary cell? Give an example.   1

ANS: It is a cell in which products cannot be changed back into reactants, i.e. it is not rechargeable, e.g. dry cell and mercury cell. In this cell, electrical energy is produced by the redox reaction occurring in the cell.

3   What are secondary cells?   1

ANS: Those cells which are rechargeabe, i.e. products can be converted back into reactants.

4   Arrange the following metals in the order in which they displace each other from the solution of their salts.   1
Al, Cu, Fe, Mg and Zn.

ANS: Mg, Al, Zn, Fe, Cu is the decreasing order of their reactivity.

5   How much charge in Faraday is required for reduction of 1 mole of Al^{3+} to Al?   1

ANS: Al^{3+} + 3e$^-$ $\rightarrow$ Al(s), i.e. 3 Faradays of charge is required.

6   Define specific conductivity (specific conductance).   1

ANS: Specific conductance is defined as the conductance of electrolyte when distance between electrodes is 1 cm and area of cross section is 1 cm^2.

7   Complete: $\Lambda°$ Na$_2$SO$_4$ =   1

ANS: $\Lambda_m^{\infty} Na_2SO_4 = 2\lambda_m^{\infty} Na^+ + \lambda_m^{\infty} SO_4^{2-}$ or $\Lambda° Na_2SO_4 = 2\lambda° Na^+ + \lambda° SO_4^{2-}$

8   How many Faradays of charge are required to convert:
1 mole of MnO_4^- to Mn^{2+} ion,   1

ANS: $MnO_4^- \longrightarrow Mn^{2+}, \quad Mn^{7+} + 5e^- \longrightarrow Mn^{2+}$
$MnO_4^- + 5e^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$ That is, when 1 mole of MnO_4^-
changes to Mn^{2+}, 5 Faradays of charge is required.

9   Why does alkaline medium inhibit rusting of iron?   1

ANS: It will remove H$^-$ which are essential for rusting.

10   (a) Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution: 2
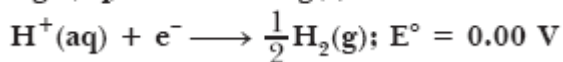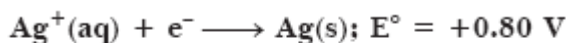
$$Ag^+(aq) + e^- \longrightarrow Ag(s); \quad E° = +0.80 \text{ V}$$
$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g); \quad E° = 0.00 \text{ V}$$

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?
(b) Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration?
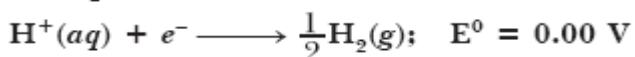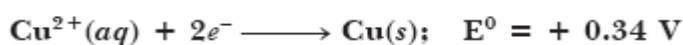
$$E°_{Cell} = E°_{Ag^+/Ag} - E°_{H^+/\frac{1}{2}H_2} = +0.80 - 0.00 = +0.80 \text{ V}$$
$$\frac{1}{2}H_2 + Ag^+ \longrightarrow H^+(aq) + Ag(s)$$
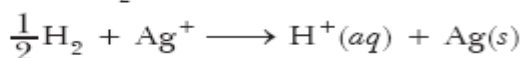
This reaction is feasible because $E°_{Cell}$ is +ve.

ANS: (a) Therefore, ΔG will be –ve, since $\Delta G° = -nE°F$. (b) Limiting molar conductivity is the maximum conductivity when solution is infinitely dilute, such that on further dilution, there is no increase in Λm. Conductivity decreases with decrease in concentration because the number of ions per unit volume decreases.

11   (a) Following reactions occur at cathode during the electrolysis of aqueous copper (II) chloride solution:

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s); \quad E° = +0.34 \text{ V}$$
$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g); \quad E° = 0.00 \text{ V}$$

2

On the basis of their standard reduction electrode potential (E^2) values, which reaction is feasible at the cathode and why?
(b) State Kohlrausch law of independent migration of ions. Write its one application.

ANS: (a) At cathode: $Cu^{2+} + 2e^- \longrightarrow Cu(s)$ The above reaction is feasible at cathode because $E°_{Cu^{2+}/Cu} = +0.34$, i.e. reduction potential of Cu^{2+} is higher than H+ as $E°_{H^+/H_2} = 0$.
(b) Kohlrausch law: It states, 'The limiting molar conductivity of an electrolyte is equal to the sum of contribution of cations as well as anions'.
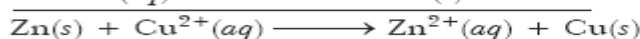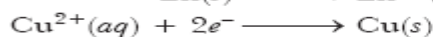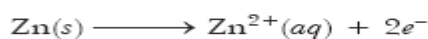Application: It helps in calculating L° (limiting molar conductivities) of weak electrolytes.

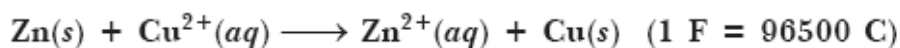12   Following reactions occur at cathode during electrolysis of aqueous sodium chloride solution:

$$Na^+ + e^- \longrightarrow Na(s); \quad E° = -2.71 \text{ V}$$
$$H^+ + e^- \longrightarrow \frac{1}{2}H_2(g); \quad E° = 0.00 \text{ V}$$

2
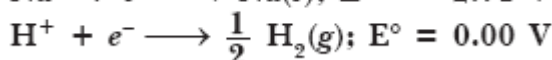
On the basis of their standard electrode potential (E°) values, which reaction is feasible at the cathode and why?

ANS: $H^+ + e^- \longrightarrow \frac{1}{2}H_2$ is feasible at cathode because it has higher reduction potential.

13   The standard electrode potential (E°) for Daniel cell is +1.1 V. Calculate the ΔG° for the reaction:

2

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \quad (1 \text{ F} = 96500 \text{ C})$$

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$
$$\overline{Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)}$$
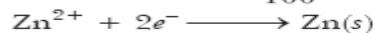$$E°_{cell} = 1.10 \text{ V}$$
$$\Delta G° = -nE°F = \frac{-2 \times 1.10 \text{ V} \times 96500 \text{ C}}{1000} = -212.3 \text{ kJ mol}^{-1}$$

ANS:

14   Zinc rod is dipped in 0.1 M solution of ZnSO4. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential. Given $E°_{Zn^{2+}/Zn} = -0.76$ V.

2

ANS:

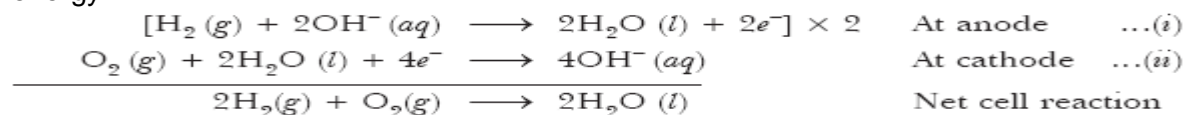$$[\text{Zn}^{2+}] = 0.1 \times \frac{95}{100} = 0.095 \text{ M}$$

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

$$E_{\text{Zn}^{2+}/\text{Zn}} = E^\circ_{\text{Zn}^{2+}/\text{Zn}} - \frac{0.0591}{2} \log \frac{1}{[\text{Zn}^{2+}]}$$

$$= -0.76 \text{ V} - \frac{0.0591}{2} \log \frac{1}{0.095} = -0.76 \text{ V} - \frac{0.0591}{2} [\log 1000 - \log 95]$$

$$= -0.76 \text{ V} - \frac{0.0591 \text{ V}}{2} [3.000 - 1.9777] = -0.76 \text{ V} - \frac{0.0591 \text{ V}}{2} \times 1.0223$$

$$= -0.76 \text{ V} - \frac{0.0604}{2} \text{ V} = -0.76 \text{ V} - 0.0302 \text{ V} = -0.7902 \text{ V}$$
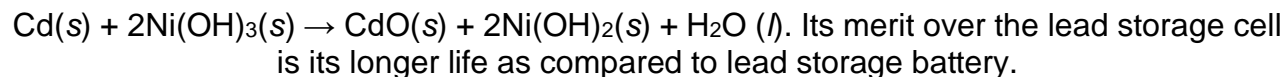
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15   Give an example of a fuel cell and write the cathode and anode reactions for it.   2

ANS: Fuel cells are those cells in which chemical energy of a fuel is converted into electrical energy.
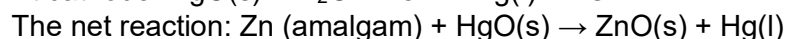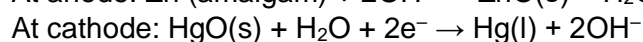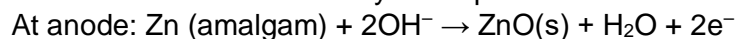
$$[\text{H}_2\,(g) + 2\text{OH}^-\,(aq) \longrightarrow 2\text{H}_2\text{O}\,(l) + 2e^-] \times 2 \qquad \text{At anode} \qquad ...(i)$$
$$\underline{\text{O}_2\,(g) + 2\text{H}_2\text{O}\,(l) + 4e^- \longrightarrow 4\text{OH}^-\,(aq) \qquad\qquad \text{At cathode} \quad ...(ii)}$$
$$2\text{H}_2(g) + \text{O}_2(g) \longrightarrow 2\text{H}_2\text{O}\,(l) \qquad\qquad\quad \text{Net cell reaction}$$

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16   Write the overall reaction that occurs during use (discharging) of nickelcadmium cell. Is it a primary or a secondary cell. Mention its one merit over the lead storage cell.   2

ANS: Nickel-cadmium cell: It is another type of secondary cell which has longer life than lead storage cell but more expensive to manufacture. The overall reaction during discharge is

$$\text{Cd}(s) + 2\text{Ni(OH)}_3(s) \rightarrow \text{CdO}(s) + 2\text{Ni(OH)}_2(s) + \text{H}_2\text{O}\,(l). \text{ Its merit over the lead storage cell}$$
is its longer life as compared to lead storage battery.

17   Mention the reactions occurring at (i) anode, (ii) cathode, during working of a mercury cell. Why does the voltage of a mercury cell remain constant during its operation?   2

ANS: Mercury cell: It consists of zinc mercury amalgam as anode, a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The reaction of the cell is
At anode: $\text{Zn (amalgam)} + 2\text{OH}^- \rightarrow \text{ZnO}(s) + \text{H}_2\text{O} + 2e^-$
At cathode: $\text{HgO}(s) + \text{H}_2\text{O} + 2e^- \rightarrow \text{Hg}(l) + 2\text{OH}^-$
The net reaction: $\text{Zn (amalgam)} + \text{HgO}(s) \rightarrow \text{ZnO}(s) + \text{Hg}(l)$
It gives constancy in voltage over long period because no ions are involved in net cell reaction. It is used in watches and hearing aids.

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18   The conductivity of 0.20 M KCl at 298 K is 0.025 S cm⁻¹. Calculate its molar conductivity.   2

ANS: $$\Lambda_m = \frac{1000 \times \kappa}{M} = \frac{1000 \times 0.025 \times 10^{-2}}{0.20} = 125 \text{ S cm}^2 \text{ mol}^{-1}$$

---

19   The conductivity of 0.001 M acetic acid is 4×10^{-5} S cm⁻¹. Calculate the dissociation constant of an acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm² mol⁻¹.   2

$$\Lambda_m = \frac{1000\,\kappa}{M} = \frac{1000 \times 4 \times 10^{-5}}{0.001} = 40 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{(\Lambda_m)}{(\Lambda_m)^\circ} = \frac{40}{390} = 0.1026$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.001 \times (0.1026)^2}{1 - 0.1026} = \frac{10^{-3} \times 1.053 \times 10^{-2}}{0.8974}$$

ANS: $$= \frac{1.053 \times 10^{-5}}{0.8974} = 1.17 \times 10^{-5} \text{ mol L}^{-1}$$

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20   Calculate the time to deposit 1.27 g of copper at cathode when a current of 2 A was passed through the solution of CuSO₄.
(Molar mass of Cu = 63.5 g mol⁻¹, 1 F = 96500 C mol⁻¹)   2

$$t = ?, \quad m = 1.27 \text{ g}, \quad I = 2 \text{ A}$$
$$m = Z \times I \times t$$
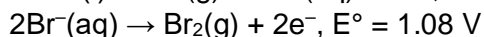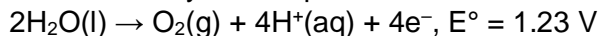$$\Rightarrow \quad 1.27 = \frac{\text{Eq. Wt}}{96500} \times 2 \times t.$$
$$\Rightarrow \quad 1.27 \times 96500 = \frac{\text{Atomic Wt}}{\text{Valency}} \times 2 \times t.$$
$$\Rightarrow \quad 1.27 \times 96500 = \frac{63.5}{2} \times 2 \times t$$
$$\Rightarrow \quad t = \frac{1.27 \times 96500}{63.5} = \frac{127 \times 10 \times 96500}{100 \times 635}$$

ANS: ∴
$$t = 2 \times 965 = 1930 \text{ seconds.}$$

21   In the electrolysis of aqueous sodium bromide, there are two possible anodic reactions:
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$, E° = 1.23 V
$2Br^-(aq) \rightarrow Br_2(g) + 2e^-$, E° = 1.08 V
Which reaction occurs at anode and why?

    2

    ANS: $2Br^-(aq) \rightarrow Br_2 + 2e^-$ occurs at anode because it has lower reduction potential. Liberation of O_2 requires over voltage.

22   The molar conductivity of 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution.

    2

$$\Lambda_m = \frac{1000 \, \kappa}{M}$$
$$\Rightarrow \quad 138.9 \text{ S cm}^2 \text{ mol}^{-1} = \frac{1000 \times \kappa}{1.5}$$
$$\therefore \quad \kappa = \frac{138.9 \times 1.5}{1000} = \frac{208.35}{1000} = 2.0835 \times 10^{-1} \text{ S cm}^{-1}.$$
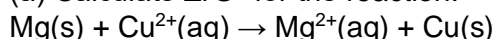ANS:

23   The specific conductivity of 0.40 M solution of KCl at 258 K in 4.96×10^{-2} Scm^{-1}. Calculate its molar conductivity.

    2

Molar conductivity $\Lambda_m = \dfrac{1000 \, \kappa}{M} = \dfrac{1000 \times 4.96 \times 10^{-2}}{0.4} = 124$ S cm^2 mol^{-1}.
ANS:

24   (a) Calculate ΔrG° for the reaction:
$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$
Given: E°$_{cell}$ = + 2.71 V, 1 F = 96500 C mol^{-1}
(b) Name the type of cell which was used in Apollo space programme for providing electrical power.

    3
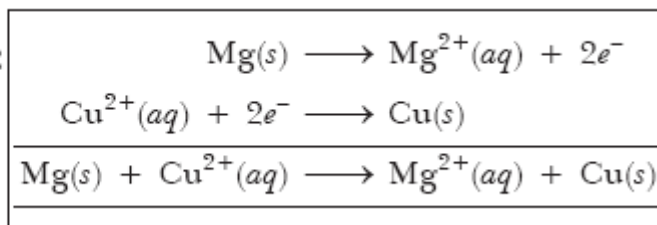
    ANS: (a)
$$\Delta_r G° = - nE°F$$
$$= -2 \times 2.71 \text{ V} \times 96500 \text{ C}$$
$$= -523030 \text{ J}$$
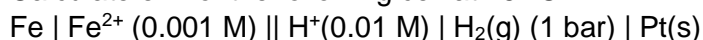$$= -523.030 \text{ kJ mol}^{-1}$$

$$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$$
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$
$$\overline{Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)}$$
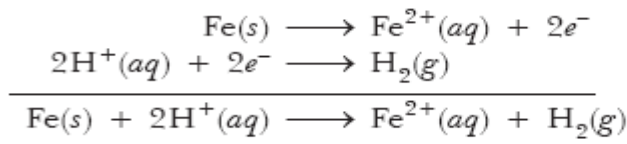
(b) H2—
O2 Fuel Cell was used in Apollo space programme for providing electrical power.

25   Calculate emf of the following cell at 25 °C:
Fe | Fe^{2+} (0.001 M) || H$^+$(0.01 M) | H$_2$(g) (1 bar) | Pt(s)
E°(Fe^{2+} | Fe) = −0.44 V   E°(H$^+$ | H$_2$) = 0.00 V

    3

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$$
$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$
$$\overline{Fe(s) + 2H^+(aq) \longrightarrow Fe^{2+}(aq) + H_2(g)}$$

Here, $\quad n = 2$

$$E_{Cell} = E°_{Cell} - \frac{0.0591}{2} \log \frac{[Fe^{2+}]}{[H^+]^2}$$

$$= (E°_{H^+/H_2} - E°_{Fe^{2+}/Fe}) - \frac{0.0591}{2} \log \frac{10^{-3}}{[10^{-2}]^2}$$

$$= [0 - (-0.44 \text{ V})] - \frac{0.0591}{2} \log 10$$

$$= +0.44 \text{ V} - 0.0295 = 0.4105 \text{ V.}$$

ANS:
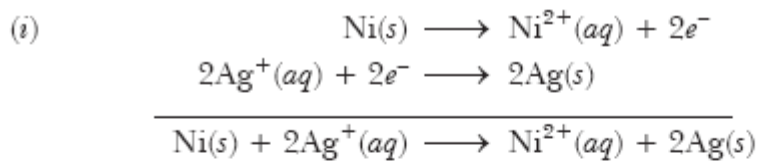
26 A strip of nickel metal is placed in a 1 molar solution of $Ni(NO_3)_2$ and a strip of silver metal is placed in a 1-molar solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter.
(i) Write the balanced equation for the overall reaction occurring in the cell and calculate the cell potential.
(ii) Calculate the cell potential, E, at 25 °C for the cell if the initial concentration of $Ni(NO_3)_2$ is 0.100 molar and the initial concentration of $AgNO_3$ is 1.00 molar.
$[E°_{Ni^2/Ni} = -0.25 \text{ V}; E°_{Ag^+/Ag} = 0.80 \text{ V}; \log 10^{-1} = -1]$

3

(i)
$$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$$
$$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$$
$$\overline{Ni(s) + 2Ag^+(aq) \longrightarrow Ni^{2+}(aq) + 2Ag(s)}$$

$$E°_{cell} = E°_{(cathode)} - E°_{(anode)} = +0.80V - (-0.25V) = 1.05 \text{ V}$$

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

$$E_{cell} = E°_{cell} - \frac{0.0591 \text{ V}}{2} \log \frac{0.1}{(1)^2} = 1.05 \text{ V} - \frac{0.0591 \text{ V}}{2} \log 10^{-1}$$

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

$$= 1.05V + 0.0295 \text{ V} = 1.0795V$$

ANS:

27 Conductivity of 2.5×10^{-4} M methanoic acid is 5.25×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation.
Given: $\lambda_0(H^+) = 349.5$ S cm^2 mol^{-1} and $\lambda_0(HCOO^-) = 50.5$ S cm$_2$ mol^{-1}.

3

$$\kappa = 5.25 \times 10^{-5} \text{ S cm}^{-1}, M = 2.5 \times 10^{-4} \text{ M.}$$

$$\lambda°_{HCOOH} = \lambda°_{(HCOO^-)} + \lambda°_H+$$

$$= 349.5 + 50.5 = 400 \text{ S cm}^2 \text{ mol}^{-1}.$$

$$\therefore \quad \Lambda_m = \frac{1000 \kappa}{M} = \frac{1000 \times 5.25 \times 10^{-5}}{2.5 \times 10^{-4}} = \frac{1000 \times 525}{10 \times 2.5 \times 100}$$

$$\Rightarrow \quad \Lambda_m = \frac{525}{2.5} = \frac{5250}{25} = 210 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda°_m} = \frac{210}{400} = \frac{21}{40} = 0.525$$

ANS: $\Rightarrow \quad \alpha = 0.525 \times 100\% = 52.5\%$

28 When a certain electrolytic cell was filled with 0.1 M KCl, it has resistance of 85 ohms at 25 °C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration. [Specific conductance of 0.1 M KCl = 1.29×10^{-2} ohm^{-1} cm^{-1}]   3

$$\kappa = 1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\kappa = \frac{1}{R} \times \frac{l}{A}$$

$$\Rightarrow \quad \frac{l}{A} = \kappa \times R = 1.29 \times 10^{-2} \times 85 = 109.65 \times 10^{-2} = 1.0965 \text{ cm}^{-1}$$

$$\Rightarrow \quad \Lambda_m = \frac{1000\,\kappa}{M} = \frac{1000}{M} \times \frac{1}{R} \times \frac{l}{A}$$

$$\Rightarrow \quad \Lambda_m = \frac{1000 \times 1 \times 1.0965}{0.052 \times 96} = \frac{1096.50}{4.992} = 219.65 \text{ S cm}^2 \text{ mol}^{-1}$$

ANS:

29 The electrical resistance of a column of 0.05 mol L^{-1} NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.   3

$$A = \pi r^2 = 3.14 \times (0.5)^2 \text{ cm}^2 = 0.785 \text{ cm}^2$$

$$\rho \text{ (resistivity)} = \frac{R \times A}{l} = \frac{5.55 \times 10^3 \Omega \times 0.785 \text{ cm}^2}{50 \text{ cm}} = 87.135 \ \Omega \text{ cm}.$$

$$\kappa = \frac{1}{\rho} = \frac{1}{87.135 \ \Omega \text{ cm}} = 0.01148 \text{ S cm}^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{0.01148 \times 1000}{0.05 \text{ M}} = 229.6 \text{ S cm}^2 \text{ mol}^{-1}$$
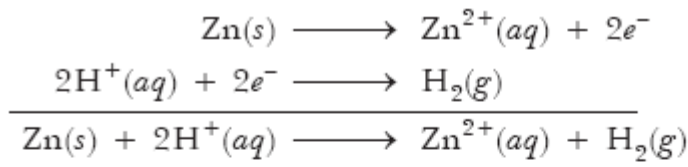
ANS:

30 An aqueous solution of copper sulphate, $CuSO_4$ was electrolysed between platinum electrodes using a current of 0.1287 ampere for 50 minutes. (Atomic mass of Cu = 63.5 g mol^{-1}]
(a) Write the cathodic reaction.
(b) Calculate: 3
(i) Electric charge passed during electrolysis
(ii) Mass of copper deposited at the cathode
[Given: 1F = 96,500 C mol^{-1}]

$$t = 50 \times 60 = 3000 \text{ s}$$
$$I = 0.1287 \text{ A}$$

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

(b) (i) $Q = I \times t = 0.1287 \times 3000 = 386.1 \text{ C}$

(ii) $m = Z \times I \times t = \dfrac{63.5}{2 \times 96500} \times 386.1 = 0.127 \text{ g}$

ANS:

31 Calculate the emf of the following cell at 25 °C: Zn | Zn^{2+} (0.001 M) || H$^+$ (0.01 M) | H$_2$(g) (1 bar) | Pt(s) $E^0_{(ZN^{2+}/Zn)} = -0.76 \text{ V}; \ E^0_{(H^+/H_2)} = 0.00 \text{ V}$ 3

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

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

$$\text{Zn}(s) + 2\text{H}^+(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)$$

$$n = 2$$

Now,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

$$= (E^\circ_{\text{H}^+/\text{H}_2} - E^\circ_{\text{Zn}^{2+}/\text{Zn}}) - \frac{0.0591}{2} \log \frac{10^{-3}}{[10^{-2}]^2}$$

$$= [0 - (-0.76\ \text{V})] - \frac{0.0591}{2} \log 10$$

$$= +0.76\ \text{V} - 0.0295 = 0.7305\ \text{V}$$

ANS:

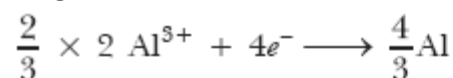32   Estimate potential difference needed to reduce Al_2O_3 at 500 °C and equilibrium constant 'K'.

$$\frac{2}{3}\ \text{Al}_2\text{O}_3 \longrightarrow \frac{4}{3}\ \text{Al}(s) + \text{O}_2(g),\ \Delta_r G = 960\ \text{kJ},\ F = 96500\ \text{C}$$

3

ANS:

$$\frac{2}{3} \times 2\ \text{Al}^{3+} + 4e^- \longrightarrow \frac{4}{3}\text{Al}$$

$$n = 4$$
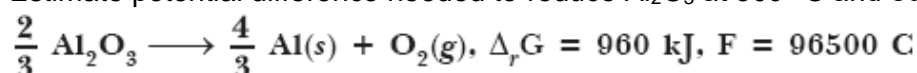
$$\Delta_r G^\circ = 960 \times 1000\ \text{J} = -nE^\circ F$$

$$\Rightarrow \quad 960 \times 1000 = -4 \times E^\circ \times 96500$$

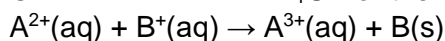$$\therefore \quad\quad E^\circ = -\frac{960 \times 1000}{4 \times 96500} = -2.487\ \text{V}$$

$$\text{Also, } \log K = \frac{nE^\circ}{0.0591} = \frac{4 \times -2.487}{0.0591} = \frac{-9.948}{0.0591} = -168.3248 + 1 - 1$$

$$K = \overline{169}.6752\ \text{(Antilog)}.$$
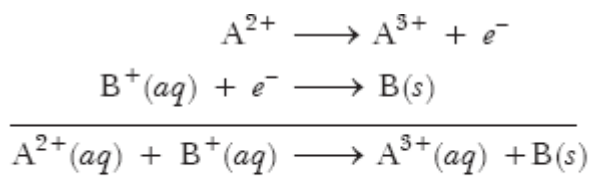
$$\Rightarrow \quad\quad K = 4.739 \times 10^{-169}.$$

33   Calculate E°cell and $\Delta_r G^\circ$ for the following reaction at 25°C.
$\text{A}^{2+}(aq) + \text{B}^+(aq) \rightarrow \text{A}^{3+}(aq) + \text{B}(s)$
[Given $K_C = 10^{10}$, 1F = 96500 C, R = 8.314 JK^{-1} mol^{-1}]

3

$$\text{A}^{2+} \longrightarrow \text{A}^{3+} + e^-$$

$$\underline{\text{B}^+(aq) + e^- \longrightarrow \text{B}(s)}$$

$$\text{A}^{2+}(aq) + \text{B}^+(aq) \longrightarrow \text{A}^{3+}(aq) + \text{B}(s)$$

$$\log K_C = \frac{0.0591}{nE^\circ} = \frac{0.0591}{1 \times E^\circ}$$

ANS:

$$\log 10^{10} = \frac{0.0591}{1 \times E^\circ}$$

$$E^\circ \times 10 = 0.0591$$

$$E^\circ = 0.00591\ \text{V}$$

$$\Delta G^\circ = -nE^\circ F$$

$$= 1 \times 0.00591 \times 96500$$

$$= -510.315\ \text{J}.$$

34   Limiting molar conductivities of NH_4Cl, NaOH and NaCl are respectively 129.8, 217.4 and 108.9 S cm^2 and the molar conductivity of 10^{-2} M solution of NH_4OH is 9.33 S cm^2 mol^{-1}. Calculate the   3 degree of dissociation of NH_4OH.

$$\Lambda° \, NH_4OH = \Lambda° \, NH_4Cl + \Lambda° \, NaOH - \Lambda° \, NaCl$$
$$= 129.8 + 217.4 - 108.9 = 238.3 \text{ S cm}^2 \text{ mol}^{-1}$$

$\therefore$ Degree of dissociation

$$\therefore \quad \alpha = \frac{\Lambda_m}{\Lambda_m°} = \frac{9.33}{238.3} = 0.03915 = 0.03915 \times 100\%$$

ANS: $\Rightarrow$ $\alpha = 3.915\%$

35   How long a current of 3 amperes has to be passed through a solution of silver nitrate to coat a metal surface of 80 cm^2 with a 0.005 mm thick layer? Density of Ag is 10.5 g cm^{-3}. At. Wt. of Ag =   3 108.0 u.

ANS:

$$\text{Volume} = \text{Area} \times \text{thickness} = 80 \text{ cm}^2 \times 0.005 \times \frac{1}{10} \text{ cm} = 0.04 \text{ cm}^3$$
$$\text{Mass of Ag} = \text{Volume} \times \text{Density} = 0.04 \text{ cm}^3 \times 10.5 \text{ g cm}^{-3} = 0.42 \text{ g}$$
$$m = Z \times I \times t$$

$$\Rightarrow \quad 0.42 = \frac{108}{96500} \times 3 \times t, \left[\text{Eq. Wt. of Ag} = \frac{\text{Atomic weight}}{\text{Valency}} = \frac{108}{1} = 108 \right]$$
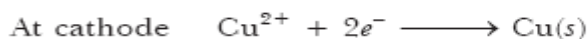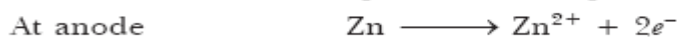
$$\Rightarrow \quad t = \frac{0.42 \times 96500}{3 \times 108} = \frac{40530}{324} = 125.09 \text{ seconds.}$$

36   Calculate the equilibrium constant, K for the reaction at 298 K,

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

Given $E°_{Zn^{2+}/Zn} = -0.76$ V   3

$$E°_{Cu^{2+}/Cu} = +0.34 \text{ V}$$

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

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

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

$$E°_{cell} = (E°_{Cu^{2+}/Cu} - E°_{Zn^{2+}/Zn})$$
$$= +0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$$
$$E°_{cell} = \frac{0.0591}{2} \log K$$

$$\Rightarrow \quad \log K = \frac{2 \times E°_{cell}}{0.0591} = \frac{2 \times 1.10 \text{ V}}{0.0591} = 37.2250$$

$$\Rightarrow \quad K = \text{Antilog of } 37.2250$$
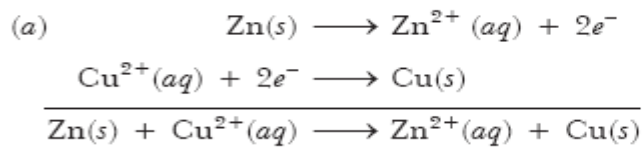
ANS: $\Rightarrow$ $K = 1.679 \times 10^{37}$

37   For the cell: $Zn(s) \mid Zn^{2+}(2M) \parallel Cu^{2+}(0.5 \text{ M}) \mid Cu(s)$
(a) Write equation for each half-reaction.
(b) Calculate the cell potential at 25 °C.   3
[Given: $E°_{Zn^{2+}/Zn} = -0.76$ V; $E°_{Cu^{2+}/Cu} = +0.34V$]

(a)
$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$
$$\underline{Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)}$$
$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

(b) $E_{cell} = E°_{cell} - \dfrac{0.0591}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]} = (E°_{Cu^{2+}/Cu} - E°_{Zn^{2+}/Zn}) - \dfrac{0.0591\,V}{2} \log \dfrac{2}{0.5}$

$= [+0.34\,V + 0.76] - \dfrac{0.0591\,V}{2} \log 4 = +1.10\,V - \dfrac{0.0591\,V}{2} \times 0.6021$

ANS: $= 1.10\,V - 0.018\,V = 1.082\,V$

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38   Consider the cell: Mg(s) | Mg^{2+} (0.13 M) || Ag$^+$ (1.0 × 10^{-4}) M | Ag(s)   3
Its emf is 2.96 V. Calculate E°cell.
(R = 8.314 JK^{-1} mol^{-1}, 1F = 96500 C mol^{-1})

$$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$$
$$\underline{2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)}$$
$$Mg(s) + 2Ag^+(aq) \longrightarrow Mg^{2+}(aq) + 2Ag(s)$$
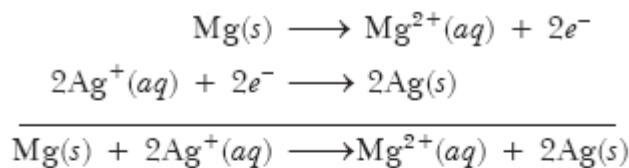
$$E_{cell} = E°_{cell} - \dfrac{0.0591}{2} \log \dfrac{[Mg^{2+}]}{[Ag^+]^2}$$

$\Rightarrow \quad +2.96\,V = E°_{cell} - \dfrac{0.0591}{2} \log \dfrac{0.13}{(10^{-4})^2}$

$\Rightarrow \quad 2.96\,V = E°_{cell} - \dfrac{0.0591}{2} [\log 1.3 + 7.000]$

$= E°_{cell} - 0.0295\,[0.1139 + 7.000]$

$\Rightarrow \quad 2.96\,V = E°_{cell} - 0.0295 \times 7.1139$

$\Rightarrow \quad E°_{cell} = +2.96 + 0.209 = 3.169\,V.$

ANS:

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39   A conductivity cell was filled with 0.1 M NaCl solution at 25 °C. Its resistance was found to be
176.6 ohms. The conductivity of the solution is 9.2 × 10^{-3} S cm^{-1}. The cross-sectional area of the   3
electrode used was 4 cm^2. What must be distance between the electrodes and calculate molar
conductivity.

$$K = \dfrac{1}{R} \times \dfrac{l}{A}$$

$$9.2 \times 10^{-3} = \dfrac{1}{176.6} \times \dfrac{l}{4}$$

$\Rightarrow \quad l = 9.2 \times 10^{-3} \times 176.6 \times 4 = 6.5\,cm$

$$\Lambda_m = \dfrac{1000\,\kappa}{M} = \dfrac{9.2 \times 10^{-3} \times 1000}{0.1} = 92\,S\,cm^2\,mol^{-1}$$

ANS:

---

40   How long will it take an electric current of 0.15 A to deposit all the copper from 500 mL of 0.15 M   3
copper sulphate solution?

$$500 \text{ mL of } 0.15 \text{ M CuSO}_4 \text{ solution contains } \frac{500 \times 0.15}{1000} = 0.075 \text{ mole of Cu}$$

Mass of Cu $= 0.075 \times 63.5 = 4.7625$ g; Eq. Wt. of $Cu^{2+} = \frac{63.5}{2} = 31.75$

$$m = Z \times I \times t$$

$$\Rightarrow \quad 4.7625 = \frac{31.75}{96500} \times 0.15 \times t$$

$$\Rightarrow \quad t = \frac{4.7625 \times 96500}{31.75 \times 0.15} = 96500 = \frac{96500}{60 \times 60} = 26.80 \text{ hours.}$$

ANS:

41   (a) Define the following terms:
(i) Limiting molar conductivity (ii) Fuel cell
(b) Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is 1.29 × 10^{-2} $Ω^{-1}$ cm^{-1}.

5

ANS: (a) (i) Limiting molar conductivity: It is defined as the maximum molar conductance of an electrolyte when solution is infinitely dilute, i.e. concentration approaches zero when electrolyte solution is kept in cell, unit distance apart having large area of cross-section to hold enough electrolyte.
(ii) Fuel cell is a cell in which chemical energy of a fuel is converted into electrical energy.
(b) R = 100 ohms, M = 0.1 mol L^{-1} of KCl

$$\kappa = \frac{1}{R} \times \frac{l}{A}$$

$$\Rightarrow \quad 1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1} = \frac{1}{100 \text{ ohm}} \times \frac{l}{A}$$

$$\Rightarrow \quad \frac{l}{A} = 1.29 \text{ cm}^{-1}$$

Again, $\quad \kappa = \frac{1}{R} \times \frac{l}{A} = \frac{1}{520} \times 1.29 = \frac{1.29}{5.20} \times 10^{-2}$

$$= 2.48 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$$

Now, M = 0.02 mol L^{-1}, $\Lambda_m = \frac{1000 \kappa}{M} = \frac{1000 \times 2.48 \times 10^{-3}}{0.02}$
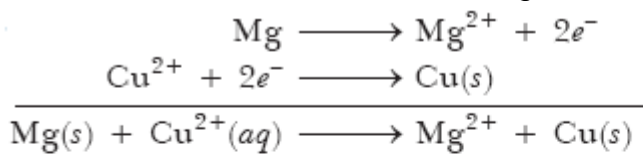
$$= 124 \text{ S cm}^2 \text{ mol}^{-1}$$

42   (a) State Faraday's first law of electrolysis. How much charge in terms of Faraday is required for the reduction of 1 mol of Cu^{2+} to Cu?
(b) Calculate emf of the following cell at 298 K:

5

  Mg(s) | Mg^{2+} (0.1 M) || Cu^{2+} (0.01) | Cu(s) [Given E°$_{cell}$ = + 2.71 V, 1 F = 96500 C mol^{-1}]

ANS: (a) It states that the mass of the substance deposited is directly proportional to charge passed through electrolyte.

$Cu^{2+} + 2e^- \rightarrow Cu(s)$ 2 Faraday of charge is required to deposite 1 mole of copper, i.e. 63.5 g of Cu. (b)

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

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$= 2.71\ V - \frac{0.0591}{2} \log \frac{0.1}{0.01}$$

$$= 2.71\ V - \frac{0.0591}{2} \log 10 = 2.71\ V - 0.0295 = 2.68\ V$$

43   (a) State Kohlrausch law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch law.

(b) Calculate Λ°_m for acetic acid.

Given that $\Lambda^\circ_m(HCl)$ = 426 S cm^2 mol^{-1}

$\Lambda^\circ_m(NaCl)$ = 126 S cm^2 mol^{-1}

$\Lambda^\circ_m(CH_3COONa)$ = 91 S cm^2 mol^{-1}

5

ANS:

(a) **Kohlrausch's law of independent migration of ions:** According to this law, molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of the contributions from its individual ions. If the molar conductivity of the cations is denoted by λ^∞_+ and that of the anions by λ^∞_-, then the law of independent migration of ions is

$$\Lambda^\infty_m = v_+\lambda^\infty_+ + v_-\lambda^\infty_-$$
or $$\Lambda^\circ = v_+ \lambda^\circ_+ + v_- \lambda^\circ_-$$

where v_+ and v_- are the number of cations and anions per formula of electrolyte

$$\Lambda^\circ_m\ CH_3COOH = \lambda^\circ_m\ CH_3COO^- + \lambda^\circ_m H^+$$

The degree of dissociation α can be calculated by the formula $\alpha = \dfrac{(\Lambda_m)_C}{(\Lambda_m)_\infty}$

where $(\Lambda_m)_C$ is molar conductivity of a particular conc. and $(\Lambda_m)_\infty$ is the maximum molar conductivity of infinite dilution. It is also denoted by Λ°_m, called limiting molar conductivity.

(b) $\Lambda^\circ_m(NaCl) = \lambda^\circ(Na^+) + \lambda^\circ(Cl^-) = 126$ S cm^2 mol^{-1} ...(i)

$\Lambda^\circ_m(HCl) = \lambda^\circ(H^+) + \lambda^\circ(Cl^-) = 426$ S cm^2 mol^{-1} ...(ii)

$\Lambda^\circ_m(CH_3COONa) = \lambda^\circ(Na^+) + \lambda^\circ(CH_3COO^-) = 91$ S cm^2 mol^{-1} ...(iii)

Adding (ii) and (iii) and subtracting (i), we get

$$\Lambda^\circ_m(CH_3COOH) = \lambda^\circ(H^+) + \lambda^\circ(CH_3COO^-)$$
$$= \Lambda^\circ_m(HCl) + \Lambda^\circ_m(CH_3COONa) - \Lambda^\circ_m(NaCl)$$
$$= (426 + 91 - 126) = 391 \text{ S cm}^2 \text{ mol}^{-1}$$

44   (a) What type of a battery is lead storage battery ? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery.

(b) Calculate the potential for half-cell containing 0.10 M $K_2Cr_2O_7(aq)$, 0.20 M $Cr^{3+}(aq)$ and 1.0 × 10^{-4} M $H^+(aq)$

The half-cell reaction is

5

$Cr_2O_7^{2-}$(aq) + 14 H⁺(aq) + 6e⁻ → 2Cr³⁺(aq) + 7H₂O(l) and the standard electrode potential is given as E° = 1.33 V.

ANS: (a) Lead storage battery: It is a secondary cell. It consists of a lead anode and a grid of lead packed with lead dioxide as cathode. A solution of sulphuric acid (38% by mass) is used as electrolyte.
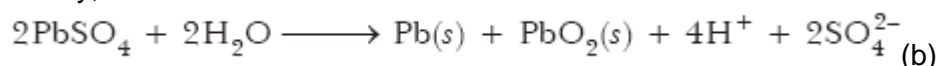The cell reactions when the battery is in use are given below:

Anode : $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$
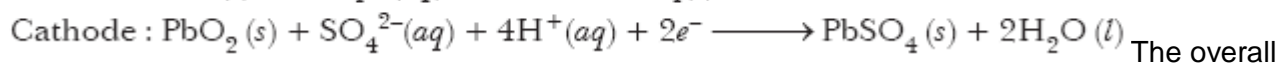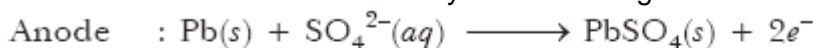
Cathode : $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$ The overall cell reaction consisting of cathode and anode reactions is:
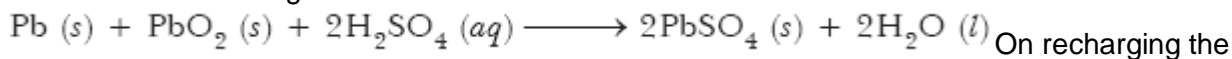
$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$ On recharging the battery, the reaction is reversed.

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

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591\,V}{6} \log \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$= 1.33\,V - \frac{0.0591\,V}{6} \log \frac{(0.2)^2}{(0.1)(1.0\times10^{-4})^{14}}$$

$$= 1.33\,V - \frac{0.0591\,V}{6} \log \frac{4\times10^{-2}}{1.0\times10^{-57}}$$

$$= 1.33\,V - \frac{0.0591\,V}{6} \log 4 \times 10^{55}$$

$$= 1.33\,V - \frac{0.0591\,V}{6} \times 55.6021$$

$$= 1.33\,V - \frac{3.286\,V}{6} = 1.33\,V - 0.5476\,V = 0.7824\,V$$

45 (a) How many moles of mercury will be produced by electrolysing 1.0 M Hg(NO₃)₂ solution with a current of 2.00 A for 3 hours ? [Hg(NO₃)₂ = 200.6 g mol⁻¹]
(b) A voltaic cell is set up at 25° C with the following half-cells Al³⁺ (0.001 M) and Ni²⁺ (0.50 M). Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.
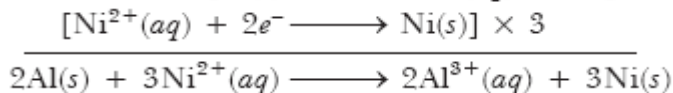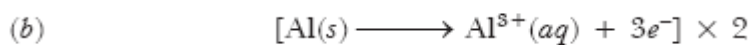(Given; $E^{\circ}_{Ni^{2+}/Ni} = -0.25\,V$, $E^{\circ}_{Al^{3+}/Al} = -1.66\,V$)

5

(a) $$m = Z \times I \times t = \frac{200.6 \times 2 \times 3 \times 60 \times 60}{2 \times 96500}$$

$$\Rightarrow \quad m = \frac{43329.6}{1930} = 22.45\,g$$

$$\text{Number of moles} = \frac{22.45}{200.6} = 0.112\,mol$$

(b) $$[Al(s) \longrightarrow Al^{3+}(aq) + 3e^-] \times 2$$
$$[Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)] \times 3$$
$$\overline{2Al(s) + 3Ni^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Ni(s)}$$

ANS:

$$E_{cell} = (E^{\circ}_{Ni^{2+}/Ni} - E^{\circ}_{Al^{3+}/Al}) - \frac{0.0591}{6} \log \frac{[Al^{3+}]^2}{[Ni^{2+}]^3}$$

$$= [-0.25\,V - (-1.66\,V)] - \frac{0.0591\,V}{6} \log \frac{(10^{-3})^2}{(0.50)^3}$$

$$= 1.41\,V - \frac{0.0591\,V}{6} \log \frac{8\times10^{-6}}{1}$$

$$= 1.41\,V - \frac{0.0591\,V}{6} [\log 8 + \log 10^{-6}]$$

$$= 1.41\,V - \frac{0.0591\,V}{6} [0.9031 - 6.0000]$$

$$= 1.41\,V - \frac{0.0591\,V}{6} \times [-5.0969]$$

$$= 1.41\,V + \frac{0.3012\,V}{6}$$

$$= 1.41\,V + 0.0502\,V$$

$$= 1.4602\,V$$

$$= 1.46\,V$$

46 (a) Define the term conductivity and molar conductivity of the solution of an electrolyte. Comment on its variation with temperature.
(b) The measured resistance of conductivity cell was 100 ohms. If 7.45 g of KCl is dissolved per litre of solution. Calculate (i) specific conductance (ii) molar conductance. [$\frac{l}{A}$ = 1.25 cm^{-1}, Molar mass of KCl is 74.5 g mol^{-1}]

5

ANS: (a) Refer Answer to 3.7 (NCERT Exercises).
Conductivity and molar conductivity increase with increase in temperature because degree of ionisation and mobility of ions will increase.

(i) $\kappa = \dfrac{1}{R} \times \dfrac{l}{A} = \dfrac{1}{100} \times 1.25 = 1.25 \times 10^{-2}$ S cm^{-2}

(ii) $\Lambda_m = \dfrac{1000\,\kappa}{M} = \dfrac{1000 \times 1.25 \times 10^{-2}}{\dfrac{7.45}{74.5} \times \dfrac{1}{1}} = 1000 \times 1.25 \times 10^{-2} \times 10$

(b) $= 125$ S cm^2 mol^{-1}.

47 A new galvanic cell of E°$_{cell}$ more than E°$_{cell}$ of Daniel cell is connected to Daniel cell in a manner that new cell gives electrons to cathode, what will happen
(a) E$_{cell}$ will increase
(b) E$_{cell}$ will decrease
(c) No change will take place
(d) Daniel cell will work as electrolytic cell where Zn will be deposite on zinc rod and copper will dissolve from copper rod.

1

ANS: (d) is correct.
∵ external emf is greater than emf of Daniel cell.

48 Ag$^+$(aq) + e$^-$ → Ag(s) E° = + 0.80 V
Fe^{2+}(aq)$^+$ + 2e$^-$ → Fe(s) E° = – 0.44 V
What is emf of
Fe(s) + 2Ag$^+$ (aq) → Fe^{2+}(aq) + 2Ag(s)
(a) 1.16 V (b) 1.24 V
(c) 2.04 V (d) –1.16 V

1

(b) $E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Fe^{2+}/Fe}$
ANS: $= 0.80$ V $- (-0.44) = 1.24$ V

49 Which of the following expression is correct for 'Ka' in terms of Λ° and Λ, where 'C' is molarity.

(a) $K_a = \dfrac{C\Lambda_m^\circ}{\Lambda_m(\Lambda_m^\circ - \Lambda)}$ (b) $K_a = \dfrac{C\Lambda_m^2}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m)}$

(c) $K_a = \dfrac{C\Lambda_m^2}{\Lambda_m^\circ}$ (d) $K_a = \dfrac{C\Lambda_m^2}{(\Lambda_m^\circ - \Lambda_m)}$

1

(b) $\alpha = \dfrac{\Lambda_m}{\Lambda_m^\circ}$ $K_a = \dfrac{C\alpha^2}{1-\alpha} = \dfrac{C \times \left(\dfrac{\Lambda_m}{\Lambda_m^\circ}\right)^2}{1 - \dfrac{\Lambda_m}{\Lambda_m^\circ}}$

$= \dfrac{C \times \Lambda_m^2}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m)} = \dfrac{C\Lambda_m^2}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m)}$

ANS:

| 50 | What is pH of the half cell $Pt|H_2(g)|H^+$ if $E^\circ_{H^+/H_2}$ $= -0.0295$ V | 1 |

(a) 1   (b) 2   (c) 0.5   (d) 3

ANS: (c)

$$E_{H^+/H_2} = E^\circ_{H^+|H_2} - \frac{0.0591}{1} \log \frac{1}{[H^+]}$$

$$-0.0295 \text{ V} = 0 - \frac{0.0591 + 1}{1} \times pH$$

$$pH = \frac{0.0295}{0.0591} = \frac{1}{2} = 0.5$$

51

$X(s) + 2Y^+(aq) \rightleftharpoons X^{2+}(aq) + 2Y(s)$; ($E^\circ_{cell} = 0.059$ V) What is the value of 'K' for above reaction?

(a) 1×10^8 (b) 1×10^2
(c) 4×10^3 (d) 3×10^4

1

ANS:

(b) $X \longrightarrow X^{2+} + 2e^-$

$2Y^+ + 2e^- \longrightarrow 2Y$

$n = 2$

$$\log K = \frac{nE^\circ}{0.0591} = \frac{2 \times 0.059 \text{ V}}{0.0591} = 2$$
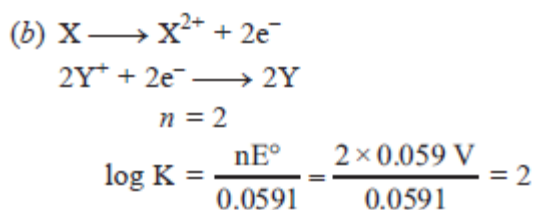
$$K = 10^2.$$

52

Which of the following statement is correct?
(a) E_{Cell} and $\Delta_r G$ of cell reaction both are extensive properties.
(b) E_{Cell} and $\Delta_r G$ of cell reaction both are intensive properties.
(c) E_{Cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive property.
(d) E_{Cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property.

1

ANS: (c) E°_{cell} depends upon concentration (amount) of substance therefore, intensive property but ΔG is extensive property.

53

While charging the lead storage battery _____.
(a) $PbSO_4$ anode is reduced to Pb.
(b) $PbSO_4$ cathode is reduced to Pb.
(c) $PbSO_4$ cathode is oxidised to Pb.
(d) $PbSO_4$ anode is oxidised to PbO_2.

1

ANS: (a) $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

54

On the basis of following E°values, the strongest oxidising agent is

$[Fe(CN)_4]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + e^- \quad E^\circ = -0.35$ V

$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad E^\circ = -0.77$ V

1
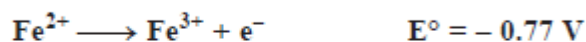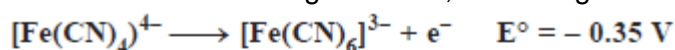
(a) Fe^{2+} (b) Fe^{3+}
(c) $[Fe(CN)_6]^{3-}$ (d) $[Fe(CN)_6]^{4-}$

ANS: (b) It is because $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$ V, it means Fe^{3+} can gain electron early to form Fe^{2+}.

55

Λ_m of M/32 solution of weak acid is 8 S cm^2 mol^{-1} and limiting molar conductivity is 400 S cm^2 mol^{-1}. K_a for acid is (a) 1.25×10^{-6} (b) 6.25×10^{-4}
(c) 1.25×10^{-4} (d) 1.25×10^{-5}

1

(d) $\alpha = \dfrac{\Lambda_m}{\Lambda_m^\circ} = \dfrac{8}{400} = \dfrac{1}{50}$

$K_a = \dfrac{C\alpha^2}{1-\alpha} \qquad \alpha <<< 1 \quad (1-\alpha = 1)$

$K_a = C\alpha^2$

$K_a = \dfrac{1}{32} \times \dfrac{1}{50} \times \dfrac{1}{50} = \dfrac{1}{800} \times 10^{-2} = \dfrac{1000}{800} \times 10^{-5}$
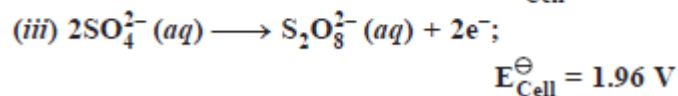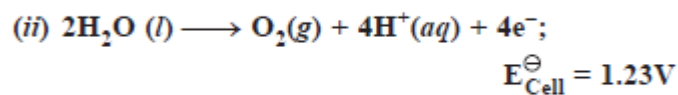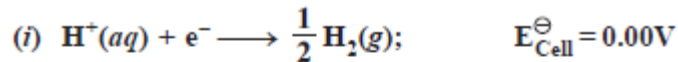
ANS: $\qquad K_a = 1.25 \times 10^{-5}$

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56 The positive value of the standard electrode potential of Cu^{2+}/Cu indicates that _____. (a) this redox couple is a stronger reducing agent than the H^+/H_2 couple.

(b) this redox couple is a stronger oxidising agent than H^+/H_2.   **1**

(c) Cu can displace H_2 from acid.

(d) Cu cannot displace H_2 from acid.

ANS: (b) and (d) are correct.

Cu is less reactive than H_2 so cannot displace H_2 from acid. Redox couple is good oxidising agent as $Cu^{2+} + 2e^- \rightarrow Cu(s)$ is possible due to +ve emf.

---

57 E°_{cell} for some half cell reactions are given below. On the basis of these mark the correct answer.

(i) $\mathbf{H^+(aq) + e^- \longrightarrow \dfrac{1}{2} H_2(g)}$; $E^\ominus_{Cell} = 0.00V$

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

$\qquad\qquad\qquad\qquad E^\ominus_{Cell} = 1.23V$

(iii) $\mathbf{2SO_4^{2-}\ (aq) \longrightarrow S_2O_8^{2-}\ (aq) + 2e^-}$;   **1**

$\qquad\qquad\qquad\qquad E^\ominus_{Cell} = 1.96\ V$

(a) In dilute sulphuric acid solution, hydrogen will be reduced at cathode.

(b) In concentrated sulphuric acid solution, water will be oxidised at anode.

(c) In dilute sulphuric acid solution, water will be oxidised at anode.

(d) In dilute sulphuric acid solution, SO_4^{2-} ion will be oxidised to tetrathionate ion at anode.

    (a) and (c) are correct.

     At cathode: $2H^+ + 2e^- \longrightarrow H_2(g)$

     At anode: $H_2O \longrightarrow \dfrac{1}{2}O_2 + 2H^+ + 2e^-$.
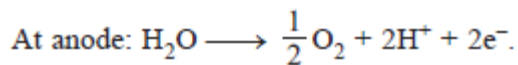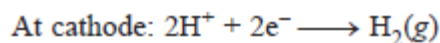
ANS:

---

58 $E^\ominus_{Cell} = 1.1V$ for Daniel cell. Which of the following expressions are correct description of state of

    (a) $1.1 = K_c$

    (b) $\dfrac{2.303RT}{2F}\ \log K_c = 1.1$

    (c) $\log K_c = \dfrac{2.2}{0.059}$ **1**

equilibrium in this cell?   (d) $\log K_c = 1.1$

    (b) and (c).

    (c) $\log K_c = \dfrac{nE^\circ}{0.0591} = \dfrac{2 \times 1.10}{0.0591} = \dfrac{2.20}{0.0591}$

    (b) $\qquad E^\circ = \dfrac{0.591 \log K_c}{n} = \dfrac{2.303\ RT}{2F} \log K_c$

    $1.10\,V = \dfrac{2.303\ RT}{2F} \log K_c$

ANS:

59 $\Lambda^0_m H_2O$ is equal to _____.

(a) $\Lambda^0_{m\ (HCl)} + \Lambda^0_{m\ (NaOH)} - \Lambda^0_{m\ (NaCl)}$

(b) $\Lambda^0_{m\ (HNO_3)} + \Lambda^0_{m\ (NaNO_3)} - \Lambda^0_{m\ (NaOH)}$

(c) $\Lambda^0_{(HNO_3)} + \Lambda^0_{m\ (NaOH)} - \Lambda^0_{m\ (NaNO_3)}$

(d) $\Lambda^0_{m\ (NH_4OH)} + \Lambda^0_{m\ (HCl)} - \Lambda^0_{m\ (NH_4Cl)}$

1

ANS:　(a) and (c).

$$\lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} + \lambda^\circ_{Na^+} + \lambda^\circ_{OH^-} - \lambda^\circ_{Na^+} - \lambda^\circ_{Cl^-} = \Lambda^\circ_{H_2O}$$

$$\lambda^\circ_{H^+} + \lambda^\circ_{NO_3^-} + \lambda^\circ_{Na^+} + \lambda^\circ_{OH^-} - \lambda^\circ_{Na^+} - \lambda^\circ_{NO_3^-} = \Lambda^\circ_{H_2O}$$

60 Match the terms given in Column I with the units given in Column II.

Column I　Column II

(a) Λ_m　(i) S cm^{-1}

(b) E_{Cell}　(ii) m^{-1}

(c) κ　(iii) S cm^2 mol^{-1}

(d) G*　(iv) V

1

ANS:　Λ_m – S cm^2 mol^{-1}, E_{Cell} – V, κ – S cm^{-1}, G* – m^{-1}

61 Match the terms given in Column I with the items given in Column II.

Column I　Column II

(a) Λ_m　(i) intensive property

(b) $E^{\ominus}_{Cell}$　(ii) depends on number of ions/volume

(c) κ　(iii) extensive property

(d) $\Delta_r G_{Cell}$　(iv) increases with dilution

1

ANS:　(a) Λ_m increases with dilution.
(b) E°_{Cell} is intensive property.
(c) κ depends upon number of ions/volume.
(d) $\Delta_r G_{Cell}$ is extensive property.

62 Match the items of Column I and Column II

Column I	Column II
(a) Lead storage battery	(i) maximum efficiency
(b) Mercury cell	(ii) prevented by galvanisation

1

16

| (c) Fuel cell | (iii) gives steady potential |
| (d) Rusting | (iv) Pb is anode, PbO_2 is cathode |

ANS: (a) Lead storage battery – Pb is anode, PbO_2 is cathode
(b) Mercury cell gives steady potential (Constant value)
(c) Fuel cell has maximum efficiency.
(d) Rusting is prevented by galvanisation.

63   In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. (Q.18 to Q.20)
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.
Assertion: E_{Cell} should have a positive value for the cell to function.
Reason: $E_{cathode} < E_{anode}$

1

ANS: (c) Assertion is correct statement but reason is wrong statement.

64   In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. (Q.18 to Q.20)
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.
Assertion: Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.
Reason: For weak electrolytes degree of dissociation increases with dilution of solution.

1

ANS: (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

65   In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. (Q.18 to Q.20)
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.
Assertion: For measuring resistance of an ionic solution an AC source is used.
Reason: Concentration of ionic solution will change if DC source is used.

1

ANS: (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

66   Λ_m° for weak electrolyte is determined by _____.

1

ANS: Kohlrausch law

67. The quantity of change required to obtain 1 mole of Al from Al_2O_3 is _____.   1

ANS: 3F

68. $$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + 2O_2,$$ number of moles of electrons gained or lost = _____.   1

ANS: n = 4

69. If $E^°_{Cell}$ is –ve, cell will not work. [True/False]   1

ANS: True.

70. If external emf opposing Daniel cell is less than 1.10 V, cell will keep in working. [True/False]   1

ANS: True.

71. Salt bridge completes internal circuit and prevents accumulation of charges. [True/False]   1

ANS: True.

72. Inert electrolyte in salt bridge reacts with solution of half cells. [True/False]   1

ANS: False, (Inert electrolyte does not react with any of the electrolyte present in half cell).

73. Calculate the time in hours for collecting 24g of Mg from $MgCl_2$ using 10 amp current? (Mg = 2 hr)
(a) 2 hrs (b) 4 hrs
(c) 5 hrs (d) 5.36 hour   1

ANS:
$$(d) \quad m = Z \times I \times t$$
$$24\ g = \frac{24}{2 \times 96000} \times 10 \times t$$
$$\Rightarrow \quad t = \frac{19300}{60 \times 60} = \frac{193}{36} = 5.36 \text{ hours}$$

74.
$$(a)\ \frac{\Delta G}{\Delta S} \qquad\qquad (b)\ \frac{\Delta G}{\Delta H}$$
$$(c)\ \frac{\Delta S}{\Delta G} \qquad\qquad (d)\ \frac{\Delta H}{\Delta G}$$
Efficiency of fuel cell is equal   1

ANS: (b) It is ratio of ΔG (useful work) to ΔH (total work)

75 Which cell will measure standard electrode potential of copper electrode?   [NCERT Exemplar Problem]

(a) $Pt(s)|H_2 (g, 0.1\ bar)|H^+ (aq., 1\ M)||Cu^{2+}(aq., 1M)|Cu$

(b) $Pt(s)|H_2 (g, 1\ bar)|H^+ (aq., 1\ M)||Cu^{2+} (aq., 2\ M)|Cu$

(c) $Pt(s)|H_2 (g, 1\ bar)|H^+ (aq., 1\ M)||Cu^{2+} (aq., 1\ M)|Cu$

(d) $Pt(s)|H_2 (g, 1\ bar)|H^+ (aq., 0.1\ M)||Cu^{2+} (aq., 1\ M)|Cu$

1

ANS: (c) because conc. of Cu^{2+} = 1M, H^+ = 1M, pH_2 = 1 bar

76 Electrode potential for Mg electrode varies according to the equation

$$E_{Mg^{2+}|Mg} = E^{\ominus}_{Mg^{2+}|Mg} - \frac{0.059}{2} \log \frac{1}{[Mg^{2+}]}.$$

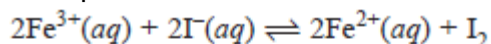The graph of $E_{Mg^{2+}|Mg}$ vs log $[Mg^{2+}]$ is
[NCERT Exemplar Problem]

(a)

(b)

1

(c)

(d)
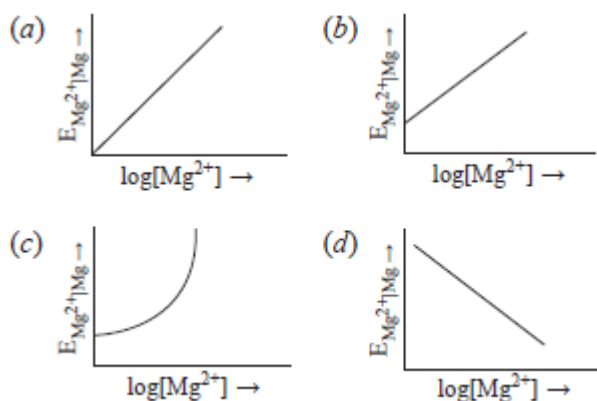
ANS: (b) $E^{\circ}_{Mg^{2+}|Mg}$ is directly proportional to log $[Mg^{2+}]$ but it can't be zero.

77 The equilibrium constant of the following reaction at 298 K is 1×10^8 for

$$2Fe^{3+}(aq) + 2I^-(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_2$$

$$E^{\circ}_{I_2|I^-} = + 0.54\ V \quad E^{\circ}_{Fe^{3+}|Fe} = ?$$

1

(a) + 1.006 V   (b) + 0.77 V

(c) – 0.77 V   (d) – 0.625 V

(b) $\log K = \dfrac{nE^{\circ}}{0.0591} = \dfrac{2 \times E^{\circ}}{0.0591}$

$\Rightarrow \log 10^8 = \dfrac{2 \times E^{\circ}}{0.0591} \Rightarrow 8 = 2 \times \dfrac{E^{\circ}}{0.0591}$

$E^{\circ} = 4 \times 0.0591 = 0.2364\ V$

$E^{\circ}_{Cell} = E^{\circ}_{Fe^{3+}|Fe^{2+}} - E^{\circ}_{I_2^+|I^-}$

$0.2364\ V = E^{\circ}_{Fe^{3+}|Fe^{2+}} - 0.54\ V$
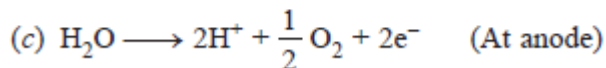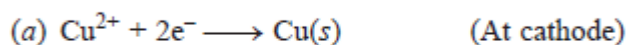
$E^{\circ}_{Fe^{3+}|Fe^{2+}} = 0.7764\ V$

ANS:

78   What will happen during the electrolysis of aqueous solution of $CuSO_4$ by using platinum electrodes? [NCERT Exemplar Problem]
(a) Copper will deposit at cathode.
(b) Copper will deposit at anode.
(c) Oxygen will be released at anode.
(d) Copper will dissolve at anode.
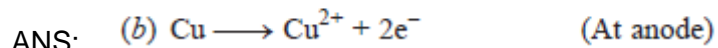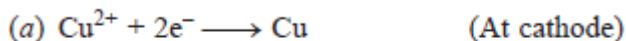
      1

ANS: (a) and (c).

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

$$(c)\ H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- \qquad \text{(At anode)}$$

79   What will happen during the electrolysis of aqueous solution of $CuSO_4$ in the presence of Cu electrodes?
(a) Copper will deposit at cathode.
(b) Copper will dissolve at anode.
(c) Oxygen will be released at anode.
(d) Copper will deposit at anode.

      1

ANS:
$$(a)\ Cu^{2+} + 2e^- \longrightarrow Cu \qquad \text{(At cathode)}$$
$$(b)\ Cu \longrightarrow Cu^{2+} + 2e^- \qquad \text{(At anode)}$$

80   For the given cell, $Mg|Mg^{2+}||Cu^{2+}|Cu$
(a) Mg is cathode
(b) Cu is cathode
(c) The cell reaction is
      $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$
(d) Cu is the oxidising agent

      1

ANS: (b) Copper is cathode. $Cu^{2+} + 2e^- \rightarrow Cu(s)$
(c) Cell reaction is $Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu$

81   Match the items of Column I and Column II.
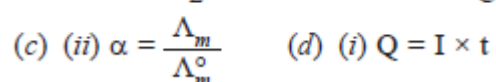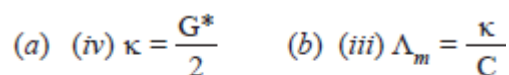
Column I	Column II
(a) κ	(i) $I \times t$
(b) Λ_m	(ii) $\Lambda_m / \Lambda_m^\circ$
(c) α	(iii) $\dfrac{\kappa}{C}$
(d) Q	(iv) $\dfrac{G^*}{2}$

      1

ANS:
$$(a)\ (iv)\ \kappa = \frac{G^*}{2} \qquad (b)\ (iii)\ \Lambda_m = \frac{\kappa}{C}$$
$$(c)\ (ii)\ \alpha = \frac{\Lambda_m}{\Lambda_m^\circ} \qquad (d)\ (i)\ Q = I \times t$$

82   Match the items of Column I and Column II.

Column I	Column II
(a) Lechlanche cell	(i) cell reaction $2H_2 + O_2 \rightarrow 2H_2O$

      1

(b) Ni–Cd cell	(ii) does not involve any ion in solution and is used in hearing aids.
(c) Fuel cell	(iii) rechargeable
(d) Mercury cell	(iv) reaction at anode, Zn → Zn²⁺ + 2e⁻
	(v) converts energy of combustion into electrical energy

ANS: (a) (iv) (b) (iii) (c) (i) (d) (ii)

83   Match the items of Column I and Column II on the basis of data given below:

$$E^{\ominus}_{F_2/F^-} = 2.87 \text{ V}, \qquad E^{\ominus}_{Li^+/Li} = -3.5 \text{ V},$$

$$E^{\ominus}_{Au^+/Au} = 1.4 \text{ V}, \qquad E^{\ominus}_{Br_2/Br^-} = 1.09 \text{ V}$$

Column I   Column II

(a) F_2 (i) metal is the strongest reducing agent

(b) Li   (ii) metal ion which is the weakest oxidising agent

(c) Au^{3+} (iii) non-metal which is the best oxidising agent

(d) Br^- (iv) unreactive metal

(e) Au   (v) anion that can be oxidised by Au^{3+}

(f) Li^+ (vi) anion which is the weakest reducing agent

(g) F^- (vii) metal ion which is an oxidising agent

1

ANS: (a) (iii) (b) (i) (c) (vii) (d) (v) (e) (iv) (f) (ii) (g) (vi)

84   In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices. (Q.12 and Q.13)
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.
Assertion: $E_{Ag^+/Ag}$ increases with increase in concentration of Ag^+ ions.
Reason: $E_{Ag^+/Ag}$ has a positive value.

1

ANS: (e) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

85      $Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$, number of Faradays required = _____ .

1

ANS: 6F

86   Dil. HNO_3, on electrolysis liberates _____ at anode.   1

ANS: O_2

87   Agar – Agar is gum like substance which holds inert electrolyte. [True/False]   1

ANS: True

88   KCl is used in salt bridge because K^+ and Cl^- have almost equal mobility. [True/False]   1

ANS: True.

89   Anode is on left side and cathode is on right side of galvanic cell. [True/False]   1

ANS: True.