Electrochemistry

Question 71.

(a) Define molar conductivity of a solution and explain how molar conductivity changes with change in concentration of solution for a weak and a strong electrolyte.

(b) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if the conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1} ?

Answer:

(a) Molar conductivity: Conductivity of 1 M electrolytic solution placed between two electrodes 1 cm apart and have enough area of cross-section to hold the entire volume is known as molar conductivity or conductivity observed for one molar solution of electrolyte. Molar conductivity increases with decrease in concentration of solute for both weak and strong electrolytes.

(b) $R = \rho\ (l/a)$

Cell constant $la = R\rho = R_K$

$$= (1500\ \Omega) \times 0.146 \times 10^{-3}\ S\ cm^{-1} = 0.219\ cm^{-1}$$

Question 72.

(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 $1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$.

Answer:

(a) (i) Fuel cells : These cells are the devices which convert the energy produced during combustion of fuels like H_2, CH_4, etc. directly into electrical energy.

(ii) The molar conductivity of a solution at infinite dilution is called limiting molar conductivity and is represented by the symbol Λ°_m.

(b) For 0.1 M KCl solution

R = 100 Q, K = $1.29 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$

Formula : Cell constant = Conductivity × Resistance

$= 1.29 \times 10^{-2} \times 100 = 1.29\ cm^{-1}$ or $129\ m^{-1}$

For 0.2 M KCl solution, conductivity

$$K = \frac{\text{Cell constant}}{\text{Resistance}} = \frac{129 m^{-1}}{520 \Omega}$$
$$= 0.248\ \Omega^{-1}\ cm^{-1} = 0.248\ Sm^{-1}$$

$$\text{Molar conductivity} = \frac{K}{C_m} = \frac{0.248 Sm^{-1}}{20 \text{mol}\ m^{-3}}$$
$$= \mathbf{1.24 \times 10^{-2}\ Sm^{-1}\ mol^{-1}}$$

[∵ Concentration of solution
$= 0.02\ M = 0.02\ mol\ L^{-1}$
$= 0.02 \times 10^3\ mol^{-3} = 20\ mol\ m^{-3}$

Question 73.

(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 :

$Mg(s) | Mg^{2+} (0.1\ M) || Cu^{2+} (0.01) | Cu (s)$

[Given $E^0_{cell} = +2.71$ V, 1 F = 96500 C mol^{-1}]

Answer:

According to first law of Faraday's "the amount of chemical reaction and hence the mass of any substance deposited/liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolyte."

The quantity of charge required for reduction of 1 mol of Cu^{2+}

= 2 faradays (∵ $Cu^{2+} + 2e^- \rightarrow Cu$)

= 2 × 96500 C = 193000 C

Cell reaction : $Mg + Cu^{2+}\ Mg^{2+} + Cu$(n = 2)

Using Nernst equation,

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$
$$\Rightarrow E_{cell} = 2.71 - \frac{0.0591}{2} \log \frac{0.1}{0.01}$$
$$\Rightarrow E_{cell} = 2.71 - \frac{0.0591}{2} \log 10$$
$$\Rightarrow E_{cell} = 2.71 - 0.02955 \quad \therefore \mathbf{E_{cell} = 2.68\ V}$$

Question 74.

(a) Define the terms conductivity and molar conductivity for the solution of an electrolyte. Comment on their variation with temperature.

The measured resistance of a conductance cell was 100 ohms. Calculate (i) the specific conductance and (ii) the molar conductance of the solution.

($KC1 = 74.5\ g\ mol^{-1}$ and cell constant = $1.25\ cm^{-1}$)

Answer:

(a) Conductivity : Reciprocal of resistivity is called conductivity

k = 1R×lA

Molar conductivity : It is defined as the conductivity of solution containing 1 mole solute dissolved per litre when placed between two electrodes of unit area separated by 1 cm.

Molar conductivity and conductivity of solution increase on increasing the temperature.

(b) Given : R = 100 Ω, Cell constant = $1.25\ cm^{-1}$, Molarity = $74.5\ g\ mol^{-1}$

$$(i)\ \text{Specific conductance, } K = \frac{1}{R} \times \text{Cell constant}$$

$$= \frac{1}{100} \times 1.25$$

$$\therefore \quad = \mathbf{0.0125\ \Omega^{-1}\ cm^{-1}}$$

$$(ii)\ \text{Molar conductance } (\Lambda_m) = \frac{K \times 1000}{\text{Molarity}}$$

$$= \frac{0.0125 \times 1000}{74.5}$$

$$= \mathbf{0.167\ \Omega^{-1}\ cm^2\ mol^{-1}}$$

Question 75.

(a) Predict the products of electrolysis in each of the following:

(i) An aqueous solution of $AgNO_3$ with platinum electrodes.

(ii) An aqueous solution of H_2SO_4 with platinum electrodes.

(b) Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The Gibbs energy change for the decomposition reaction

$23\ Al_2O_3 \rightarrow 43\ Al + O_2$ is 960 kJ ($F = 96500\ C\ mol^{-1}$)

Answer:

(a) (i) *At anode :* $AgNO_3(aq) \longrightarrow Ag^+ + NO_3^-$

$$H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$$

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

Product of electrolysis of aq soln of H_2SO_4 is H^+ and SO_4^{2-} and OH^-

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

(ii) *At anode :* $H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

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

(b) $Al_2O_3\ (2Al^{3+} + 3O^{2-}) \longrightarrow 2Al + \frac{3}{2}O_2,\ n = 6e^-$

$$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2, \qquad n = 4e^-$$

Substituting $\Delta G = +960$ KJ $= +960{,}000$ J, $n = 4$

Formula : $\Delta G = -nFE$

$\therefore \quad 960000 = -4 \times 96500 \times E$

$\therefore \quad E = -\frac{960000}{4 \times 96500} = -$ **2.487 V**

Question 76.

(a) Define the following terms :

(i) Molar conductivity (Λ_m) (ii) Secondary batteries (iii) Fuel cell

(b) State the following laws :

(i) Faraday first law of electrolysis

(ii) Kohlrausch's law of independent migration of ions

Answer:

(a) (i) Molar conductivity Λ_m): Molar conductivity can be defined as the conductance of the volume V of electrolytic solution kept between two electrodes of a conducting cell at distance of unit length but having area of cross section large enough to accommodate sufficient volume of solution that contains one mole of the electrolyte. $\Lambda_m = KV$

(ii) Secondary batteries: Those cells which can be recharged on passing electric current through them in opposite direction and can be used again are called secondary batteries, e.g. Lead-acid storage cell.

(iii) Fuel cell : Galvanic cells that are designed to convert the chemical energy of combustion of fuels like hydrogen, methane etc. into electrical energy are called fuel cells, e.g. $H_2 - O_2$ fuel cell

(b) (i) Faraday first law of electrolysis : According to this law the mass of the substance deposited or liberated at any electrode during electrolysis is directly proportional to the quantity of charge passed through the electrolyte.

$\omega \propto Q$ ($\because Q = I \times t$) $\omega = = ZIt$

(ii) Kohlrausch's law of independent migration of ions : According to this law limiting molar conductivity of an electrolyte can be represented as the sum of the limiting ionic conductivities of the cation and the anion each multiplied with the number of ions present in one formula unit of electrolyte.

$\Lambda^{o}m$ for $AxBy=x\lambda o++y\lambda o-$

Question 77.

Calculate $\Delta_r G°$ and e.m.f. (E) that can be obtained from the following cell under the standard conditions at 25°C :

Zn (s) | Zn^{2+} (aq) || Sn^{2+} (aq) | Sn (s)

Answer:

Given : $E^o_{Zn^{2+}/Zn} = -0.76\,V$, $E^o_{Sn^{2+}/Sn} = -0.14\,V$,

$F = 96500\ C\ mol^{-1}$, $\Delta_r G° = ?$ $E = ?$

Cell Reaction :

Zn (s) | Zn^{2+} (aq) || Sn^{2+} (aq) | Sn (s)

$$E^o_{Cell} = E^o_{Cathode} - E^o_{Anode}$$
$$= -0.14\ V - (-0.76\ V) = 0.62\ V$$

Using formula :

$$\Delta_r G° = -nF\,E^o_{Cell}$$
$$= -2 \times 96500\ C\ mol^{-1} \times 0.62\ V$$

$\therefore$ $\Delta_r G° = -119660\ J\ mol^{-1}$ [$\because$ CV = 1 Joule]

$E_{Cell} = E^o_{Cell} = \mathbf{0.62}$

****