3 Electrochemistry

Facts that Matter

- **Types of conductors:**

Metallic Conductors or Electronic Conductors	Electric Conductors or Ionic Conductors
1. Metallic substances which conduct electricity through them due to movement of electrons. E.g., Metals – Al, Cu, etc.	1. Substances which conduct electricity in their molten or solution form due to movement of ions. E.g., Electrolytes – NaCl, NaOH, HCl, H_2SO_4, NH_4OH, CH_3COOH
2. Metallic conductance decreases with increase in temperature.	2. Electrolytic conductance increases with increase in temperature because movement of ions increases.

- **Types of electrolytes:**

Strong Electrolytes	Weak Electrolytes
1. The electrolytes which are completely dissociated into ions in solution. E.g., Strong Acids: HCl, H_2SO_4, HNO_3. Strong Bases: NaOH, KOH. Salts: NaCl, KCl, $ZnCl_2$.	1. The electrolytes which do not dissociate completely in solution. E.g., Weak Acids: CH_3COOH, H_2CO_3, HCOOH Weak Bases: NH_4OH, $Al(OH)_3$
2. The degree of dissociation (α) = 1.	2. The degree of dissociation (α) < 1.

- **Resistance (R):** The obstruction to the flow of current.

S.I. unit of R = Ohm (Ω).

$R \propto \ell/A$ or $\mathbf{R = \rho\ell/A}$

where ℓ = length of the conductor,
A = area of cross section,
ρ = resistivity or specific resistance.

- **Resistivity (ρ):** The resistance of a conductor of 1 m length and 1 m^2 area of cross section. Its S.I. unit is Ohm m^{-1}.
- **Conductance (G):** The reciprocal of resistance (R) is called conductance.

$G = 1/R$

S.I. unit of G = S (Siemens).

- **Conductivity or Specific Conductance (κ) (kappa):** It is the conductance of solution kept between two electrodes having 1 m^2 area of cross section and at a distance of 1 m apart. It is the reciprocal of resistivity (ρ).

$\kappa = 1/\rho$.

S.I. unit of κ = S m^{-1}

- **Relation between G and κ**

  $R = \rho\ \ell/A$ $\quad 1/\rho = 1/R^*\ l/A$ $\quad \kappa = G \times G^*$

  Conductivity (κ) = Conductance (G) × Cell constant (G^*)
- **Cell constant (G^*):** It is defined as the ratio of the distance between the two **electrodes**(l) to their area of cross section (A) Its S.I. unit is m^{-1}.
- **Molar conductivity (Λ_m):** It is defined as the conductance of the solution containing one mole of the electrolyte and kept between the two electrodes with unit (1 m^2) area of cross section and a distance of unit length (1m).

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

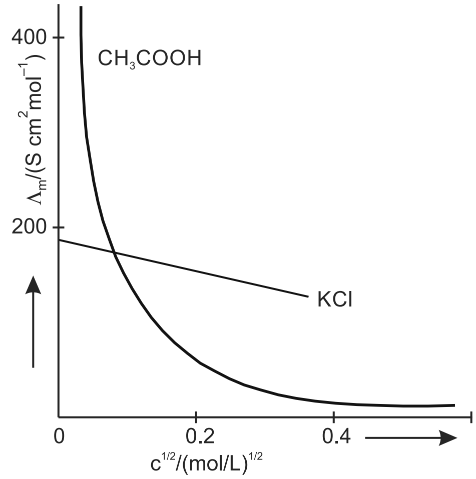
- **Limiting molar conductivity (Λ^0_m):** The molar conductivity at infinite dilution or zero concentration.
- **Variation of conductivity (κ) and molar conductivity (Λ_m) with concentration (c):**

  (*i*) **For strong electrolytes:** Λ_m increases slowly with dilution due to increase in the movement of ions on dilution.

$$\Lambda_m = \Lambda^0_m - Ac^{1/2}$$

  Where A is a constant which depends on the nature of electrolyte, *i.e.* the charges on the cation and anion.

  (*ii*) **For weak electrolytes:** Λ_m increases steeply with dilution due to increase in the number of ions (or the degree of dissociation on dilution).



- **Kohlrausch law of independent migration of ions:** The limiting molar conductivity of an electrolyte ($\Lambda^0{}_m$) is the sum of limiting molar conductivities of the cation ($\lambda^0{}_+$) and anion (λ^0_-).

$$\Lambda^0_m = v_+\ \lambda^0_+ + v_-\ \lambda^0_-$$

  Where v_+ and v_- are the no. of cations and no. of anions formed on dissociation, respectively.
- **Applications:**

  (1) This law is used to calculate Λ^0_m for any electrolyte from the λ^0 values of individual ions.

  (2) To determine the degree of dissociation (α), $\alpha = \Lambda_m/\Lambda^0_m$ where Λ_m = the molar conductivity at the concentration 'C' and Λ^o_m = the limiting molar conductivity.
- For weak electrolytes like acetic acid, $K_a = C\alpha^2/1-\alpha$.

- **Electrochemical Cells:** These are devices in which electric energy is converted to chemical energy or vice-versa. They are of two types : Galvanic cell and electrolytic cell.
  Difference between Galvanic cell and Electrolytic cell

Galvanic cell or Voltaic Cell	**Electrolytic Cell**
A device in which electrical energy is produced from a chemical reaction.	A device in which electrical energy is used to bring about a chemical reaction.
E.g., Daniel cell, Dry cell, Lead storage battery.	E.g., Electrolysis of molten NaCl, Electrolysis of dil.*aq*.H_2SO_4 solution using Pt electrodes.

- **Daniel cell:** $Zn(s) \mid Zn^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$
  $$E^o_{cell} = 1.10 \text{ V}$$
- **Electrode potential:** The potential difference between the electrode (metal) and the electrolyte (metal ion solution).
- **Cell potential:** The potential difference between the two electrodes of a galvanic cell. $E_{cell} = E_{cathode} - E_{anode}$.
- **EMF (electromotive force) of cell:** The potential difference between the two electrodes when no current is drawn (flowing) through the cell.
- **SHE (standard hydrogen electrode):** It is used as a reference electrode to measure the standard electrode potential of the other electrode by assigning standard electrode potential of SHE equal to zero (E^o_{H+} = zero). It consists of a platinum electrode (foil) coated with finely divided platinum dipped in an acidic solution with 1 M $H^+(aq)$ ions and pure hydrogen gas (at 1 bar) is bubbled through the solution.
  $$H(aq) \mid H_2(g) \mid Pt(s)$$
- **Nernst equation:** It shows the relationship between the electrode potential (electrode) and concentration of the solution.
  For the electrode reaction $M^{n+}(aq) + ne^- \longrightarrow M(s)$
  $$E_{electrode} = E^o{}_{electrode} - \frac{RT}{nF}\,\text{In}\left[\frac{M(s)}{M^{\,n+}(aq)}\right]$$
  $$E_{electrode}\text{ (at 298 K)} = E^0{}_{electrode} - \frac{0.059}{n}\log\frac{1}{[M^{n+}(aq)]} \quad [\text{Since } M(s) = 1]$$
  $$\text{EMF or } E_{cell}\text{ (at 298K)} = E^o{}_{cell} - \frac{0.059}{n}\log\frac{[\text{products}]}{[\text{reactants}]}$$
  E.g., for cell reaction $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$
  $$E_{cell} = E^o{}_{cell} - \frac{0.059}{2}\log\frac{[Cu^{2+}][Ag(s)]^2}{[Cu(s)][Ag^+]^2}$$
  Where $E^o{}_{cell} = E^o{}_{cathode} - E^o{}_{anode} = E^o{}_{Ag^+/Ag} - E^o{}_{Cu^{+2}/Cu}$ $[\because [Ag(s)] \text{ and } [Cu(s)] = 1]$
- **Relationship between standard cell potential (E^o_{cell}) and equilibrium constant (K_c)**
  $$E^o_{cell} = 2.303\frac{RT}{nF}\log K_C$$
  At 298 K, $$E^o_{cell} = \frac{0.059}{n}\log K_C$$

- **Relationship between E_{cell} and Gibbs energy ($\Delta_r G$)**

$$\Delta_r G = -nF E_{cell}$$

$$\Delta_r G^o = -nF E^\circ_{cell} \qquad \text{(at 25°C or 298 K, 1 atm)}$$

- **Relationship between $\Delta_r G$ and equilibrium constant (K_C)**

$$\Delta_r G^\circ = -2.303 \, RT \log K_C$$

- **Maximum work = $\Delta_r G^o$**
- At cathode, when there is competition between many cations or much reduction reaction the reduction with higher E^o value is preferred. Similarly, the oxidation reaction with lower E^o value is preferred.

  Electrolysis: The process of decomposition of a chemical substance into its constituent atoms/ions on passing electricity through it.
- **Faradays laws:**

  First law: The amount of substance deposited (m) or the chemical reaction that occurs at any electrode is directly proportional to the quantity of electricity (Q) passed through the electrolyte.

$$m = zQ$$

  Where z = electrochemical equivalent.

  $Q = I\,t$ where Q = quantity of electricity in coulombs (C), I = current in ampere (A) and t = time in (s).

  Second law: When the same quantity of electricity is passed through different electrolytic solutions, the amount of different substances liberated are directly proportional to their chemical equivalent weights.

  Faraday: The charge on one mole of electrons is called one faraday (1F) and its value is 96478 C mol^{-1} or approximately 96500 C mol^{-1}.
- **Applications of electrochemical series:**

  (1) The substance which has higher standard electrode potential (E^o value) is a stronger oxidising agent or has greater tendency to get reduced.

  (2) The substance which has lower standard electrode potential (E^o value) is a stronger reducing agent or has greater tendency to undergo oxidation.
- **Primary Cells:** In these the reaction occurs only once and battery then becomes dead after use over a period of time. It cannot be recharged and reused again.

  E.g., dry cell, mercury cell

(*i*) **Dry cell** (Leclanche cell)

  (1) **Anode:** Zn container.

  (2) **Cathode:** Graphite rod surrounded by powered MnO_2 and carbon.

  (3) **Electrolyte:** A moist paste of NH_4Cl and $ZnCl_2$

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

  Cathode: $MnO_2 + NH_4^+ + le^- \longrightarrow MnO(OH) + NH_3$

  Cell potential: nearly 1.5 V.

(*ii*) **Mercury cell:**

  (1) **Anode:** Zn–Hg (amalgam)

  (2) **Cathode:** A paste of HgO and carbon

  (3) **Electrolyte:** A paste of KOH and ZnO

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

  Cathode: $HgO(s) + H_2O + 2e^- \longrightarrow Hg(l) + 2\,OH^-$

  Overall cell reaction: $Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

  Cell potential is 1.35 V.

- **Secondary batteries:** After use, they can be recharged by passing current through them in opposite direction, so they can be reused again after once used. E.g., Lead storage battery, nickel–cadmium cell.

$$\text{Secondary Batteries (Rechargeable)} \begin{cases} \rightarrow \text{Lead Storage Battery} \\ \rightarrow \text{Nickel-Cadmium Cell} \end{cases}$$

(*i*) **Lead storage battery:** (1) **Anode** – Pb plate
(2) **Cathode:** Grid of lead packed with PbO_2.
(3) **Electrolyte:** 38% solution of Sulphuric acid (1.3 g/ml)

Anode: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

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

Overall cell reaction: $Pb(s) + PbO_2(s) + 2H_2SO_4(l) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$

Use: Used in automobiles and inverters. On recharging the battery, the above reaction is reversed.

(*ii*) **Nickel–Cadmium cell:**
(1) **Anode:** Cd
(2) **Cathode:** $Ni(OH)_3$

Overall cell reaction:

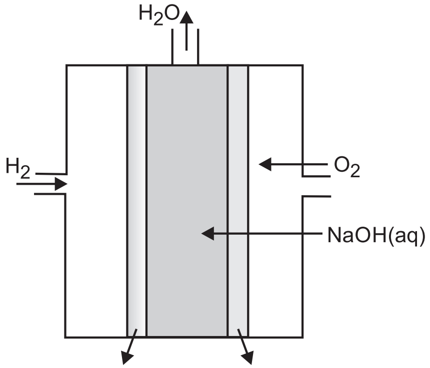
$Cd(s) + 2Ni(OH)_3(s) \longrightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$

Nickel-Cadmium cell has a longer life than lead storage cell but it is more expensive to manufacture.

- **Fuel cells:** Galvanic cells which convert the energy of combustion of fuels like hydrogen, methane, etc. directly into electrical energy.

E.g. **Hydrogen–Oxygen Fuel Cell**

Hydrogen and Oxygen gases are bubbled through a porous carbon electrode into a concentrated aqueous sodium hydroxide solution. To increase the rate of electrode reaction, catalysts like palladium or platinum are used.



Carbon Electrode Filled with Pt/Pd.

Anode: $2H_2(g) + 4OH(aq) \longrightarrow 4H_2O(l) + 4e$

Cathode: $O_2(g) + 2H_2O(l) + 4e \longrightarrow 4OH(aq)$

Overall cell reaction: $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Advantages:

1. High efficiency
2. Continuous source of energy
3. Pollution free.

- **Corrosion:** Formation of oxides or other salts of metal on the surface of metallic objects when exposed to moist air. E.g., rusting of iron, Tarnishing of silver.

Rusting of Iron: Corrosion of iron is known as rusting. Rust is hydrated ferric oxide, $Fe_2O_3.xH_2O$. It is an electrochemical phenomenon. At a particular spot oxidation takes place, which acts as anode:

Anode: $2Fe(s) \longrightarrow 2Fe^{2+} + 4e^-$, $E^o_{red} = -0.44$ V

Electrons released at anode move through the iron metal and goes to the another spot and reduces the oxygen gas in the presence of H^+ion.

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l) \quad E^o_{red} = +1.23\ V$

Overall reaction: $2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

$E^o_{cell} = +1.67\ V$

- **Methods of Preventing Corrosion:**
  (1) **Galvanisation:** The process of coating zinc over iron.
  (2) **Cathodic protection or sacrificial electrode:** In this method a more reactive metal like Mg (or) Zn are made as the sacrificial anode and are connected to the iron pipe or tank.
- **Hydrogen Economy**

  We are already aware that carbon dioxide produced by the combustion of fossil fuel is leading to the 'Greenhouse Effect'. This is responsible for the rise in temperature of the earth's surface causing polar ice to melt and ocean levels to rise. In order to avoid such a catastrophe, we need to limit our use of carbonaceous fuels. Hydrogen provides an ideal alternative as its combustion results in water only. Hydrogen can be used as a renewable and non-polluting source of energy. This is the vision of the Hydrogen Economy. Both the production of hydrogen by electrolysis of water and its combustion in a fuel cell will be important in the near future. And both these technologies are based on electrochemical principles.
- **Important Formulae:**

(1) $$R = \frac{V}{I}$$

where R = resistance
V = voltage
I = current

(2) **Conductivity** $= \dfrac{1}{R} = \dfrac{I}{V}$

units of conductance = ohm^{-1} or Siemens (S)

(3) **Cell constant** $G^* = \dfrac{l}{A} = R\kappa$

(4) **Molar conductivity** $= \lambda_m = \dfrac{\kappa}{C}$

(5) $$\lambda_m(S\ cm^2\ mol^{-1}) = \frac{\kappa\ (S\ cm^{-1}) \times 1000(cm^3)}{\text{molarity (mol/L)}}$$

(6) $$\lambda_m = \lambda_m^\circ - Ac^{1/2}.$$

where λ_m is the molar conductivity at concentration c and λ_m° is the molar conductivity at infinite dilution

(7) **Kohlrausch law.**

$$\Lambda_m^0 = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty$$

where v_+ and v_- are the number of cations and anions formed in the solution respectively whereas λ_+^∞ and λ_-^∞ are the molar conductivities of cations and anions at infinite dilution.

(8) $$W = Z\,I\,t$$

where W is the mass of substance deposited

I = current in ampere

t = time in second

(9) **Nernst equation**

$$E^{\ominus}_{cell} = \frac{2.303\ RT}{nF}\log K_c$$

K_c is the equilibrium constant

(10) $$\Delta_r G^0 = -nE^0F$$

where n is the number of electrons involved

E^0 = EMF of the cell

F = 96500 C

(11) **Faraday's second law of electrolysis:**

$$\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3} = \quad \ldots$$

where W_1 = mass of substance 1 deposited

E_1 = equivalent weight of substance 1

W_2 = mass of substance 2 deposited

E_2 = equivalent weight of substance 2

(12) **Relationship between chemical equivalent (E) and electrochemical equivalent(Z):**

$$\frac{m_1}{m_2} = \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

or

$$\boxed{\frac{E_1}{E_2} = \frac{Z_1}{Z_2}}$$

NCERT IN-TEXT QUESTIONS SOLVED

3.1. How would you determine the standard electrode potential of the system $Mg^{2+}|Mg$?

Ans. We will set up a cell consisting of $Mg|MgSO_4$(1 M) as one electrode (by dipping a magnesium wire in 1 m $MgSO_4$ solution).

Standard hydrogen electrode P*t*, H_2(1 atm) H^+(1 M) is taken as the second electrode. The EMF of the cell is measured. Direction of deflection shows that electrons flow from magnesium electrode to hydrogen electrodes, *i.e.* oxidation takes place on magnesium electrode and reduction takes place on hydrogen electrode, Hence, the cell may be represented as follows:

$Mg|Mg^{2+}\ (1M)||H^+(1M)|H_2(1atm),\ Pt$

$$E^0{}_{cell} = E^0{}_{H^{,}\ \frac{1}{2}H_2} - E^0{}_{Mg^{2+},\ Mg}$$

Put $$E^0{}_{H^+,\ \frac{1}{2}H_2} = 0$$

Hence $$E^0{}_{Mg^{2+},\ Mg} = -E^0{}_{cell}$$

3.2. Can you store copper sulphate solution in a zinc pot?

Ans. Zinc is more reactive than copper.

Hence, it displaces copper from copper sulphate solution as follows.

$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$

So, we cannot store copper sulphate solution in a zinc pot.

3.3. Consult the table of the standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.

Ans. Oxidation of ferrous ions means that following reaction should occur:

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

$$E^\circ_{ox} = -\,0.77\text{ V}$$

Only those substance can oxidise Fe^{2+} to Fe^{3+} which are stronger oxidising agents and have positive reduction potential greater than 0.77 V. So, that EMF of the cell reaction is positive.

Examples: Br_2, Cl_2 and F_2 are three of these substances.

3.4. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Ans. For hydrogen electrode: $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

Applying Nernst equation:

$$E_{H^+,\frac{1}{2}H_2} = E^\circ_{H^+,\frac{1}{2}H_2} - \frac{0.0541}{x}\log\frac{1}{\left[H^+\right]}$$

$$= 0 - \frac{0.0591}{1}\log\frac{1}{10^{-10}} \quad [\text{pH} = 10 \text{ means } [H^+] = 10^{-10}\text{M}]$$

$$= -\,0.0591 \times 10 = -\,0.591\text{ V}$$

3.5. Calculate the emf of the cell in which the following reaction takes place.

$Ni(s) + 2Ag^+(0.002\text{ M}) \longrightarrow Ni^{2+}(0.160\text{ M}) + 2Ag(s)$

Given that $E^0_{cell} = 1.05$ V

Ans. Applying Nernst equation to the given cell reaction:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{x}\log\frac{Ni^{2+}}{[Ag^+]^2} = 1.05\text{ V} - \frac{0.0591}{2}\log\frac{0.160}{(0.002)^2}$$

$$= 1.05 - \frac{0.0591}{2}\log(4 \times 10^4) = 1.05 - \frac{0.0591}{2} \times 4.6021$$

$$= 1.05 - 0.14\text{ V} = 0.91\text{ V}$$

3.6. The cell in which the following reaction occurs:

$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$ has $E^0_{cell} = 0.236$ V at 298 K.

Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.

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

or $2I^- \longrightarrow I_2 + 2e^-$

For the given cell reaction

$$x = 2$$

$$\Delta_r G^0 = -\,xFE^\circ_{cell} = -\,2 \times 96500 \times 0.236\text{ V} = -45.55\text{ kJ mol}^{-1}$$

$$\Delta_r G^0 = -2.303 \text{ RT} \log K_c$$

$$\log K_c = -\frac{\Delta_r G^\circ}{2.303 \text{ RT}}$$

or $$\log K_c = -\frac{45.55 \text{ kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3} \text{kJ K}^{-1} \text{ mol}^{-1}} \times 298 \text{ K} = 7.983$$

$\therefore$ $$K_c = \text{Antilog } (7.983) = 9.616 \times 10^7$$

3.7. Why does the conductivity of a solution decrease with dilution? [*CBSE* 2015]

Ans. Conductivity of a solution is the conductance of ions present in a unit volume of solution. On dilution the number of ions per unit volume decreases. Hence, the conductivity decreases.

3.8. Suggest a way to determine $\lambda^0{}_m$ value of water.

Ans. $$\lambda^0_m(H_2O) = \lambda^0_H + + \lambda^0_{OH^-}$$

We find out

$\lambda^0_m(HCl)$, $\lambda^0_m(NaOH)$ and $\lambda^0_m(NaCl)$

Then $$\lambda^0_m(H_2O) = \lambda^0_m(HCl) + \lambda^0_m(NaOH) - \lambda^0_m(NaCl)$$

3.9. The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate the degree of dissociation and dissociation constant. Given $\lambda^0(H^+)$ = 349.6 S cm^2 mol^{-1} and λ^0 $(HCOO^-)$ = 54.6 S cm^2 mol^{-1}

Ans. The molar conductivity of methanoic acid

$$\lambda^c_m = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda^0_m(HCOOH) = \lambda^0(H^+) + \lambda^0(HCOO^-) = 349.6 + 54.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\lambda^c_m}{\lambda^0_m} = \frac{46.1}{404.2} = 0.114$$

	HCOOH	$\rightleftharpoons$	$HCOO^-$ +	H^+
Initial conc.	n mol L^{-1}		0	0
	$n(1-\alpha)$		$n\alpha$	$n\alpha$

$\therefore$ $$k_a = \frac{x\alpha^2}{1-\alpha} = \frac{0.025 \times (0.114)^2}{1-0.114} = 3.67 \times 10^{-4}$$

3.10. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire? [*AI CBSE* 2017]

Ans. $$Q(\text{coulomb}) = 1 \text{ (ampere)} \times t(\text{sec})$$

$$= 0.5 \text{ ampere} \times 2 \times 60 \times 60 = 3600 \text{ C}$$

A flow of 1F, *i.e.* 96500 C is equivalent to the flow of 1 mole of electrons *i.e.*, 6.023×10^{23} electrons.

3600 C is equivalent to flow of electrons $= \frac{6.02 \times 10^{23}}{96500} \times 3600 = 2.246 \times 10^{22}$ electrons.

3.11. Suggest a list of metals that are extracted electrolytically.

Ans. Sodium, calcium, magnesium and aluminium.

3.12. Consider the reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7\ H_2O$$

What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$?

Ans. From the given reaction

1 mol of $Cr_2O_7^{2-}$ ions requires

$$6F = 6 \times 96500 \text{ C}$$

$$= 579000 \text{ C of electricity for the reduction of } Cr^{3+} \text{ ions.}$$

3.13. Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging?

Ans. A lead storage battery consists of anode made up of lead, cathode made up of a grid of lead packed with lead dioxide (PbO_2) and 38% solution of sulphuric acid is used as an electrolyte. When the battery is in use, the following reaction takes place:

Anode: $Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

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

On charging the battery, the reverse reaction takes place, *i.e.* $PbSO_4$ deposited on the electrode is converted back into Pb and PbO_2 and H_2SO_4 is regenerated.

3.14. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Ans. Methane and Methanol.

3.15. Explain how rusting of iron is envisaged as setting up of an electrochemical cell?

Ans. The water layer present on the surface of iron (especially in the rainy season) dissolve acidic oxides of air like CO_2, SO_2, etc. to form acids which dissociates to give H^+ ions:

$$H_2O + CO_2 \longrightarrow H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-}$$

In the presence of H^+ ions, iron start losing electrons at the same spot to form ferrous ions, *i.e.* its oxidation takes place. Hence, this spot acts as the anode:

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

The electrons thus released through the metal reaches another spot where H^+ ions and the dissolved oxygen take up these electrons and reduction reaction takes place. Hence, this spot acts as the cathode:

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

The overall reaction is:

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

Ferrous ions are further oxidised by the atmospheric oxygen to form ferric ions which combines with water molecules to form hydrated ferric oxide, $Fe_2O_3 . xH_2O$ which is rust.

NCERT TEXTBOOK QUESTIONS SOLVED

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

Ans. Mg > Al > Zn > Fe > Cu > Ag

3.2. Given the standard electrode potentials:

$$K^+/K = -2.93 \text{ V}$$

$$Ag^+/Ag = 0.80 \text{ V}$$

$$Hg^{2+}/Hg = 0.79 \text{ V}$$

$$Mg^{2+}/Mg = -2.37 \text{ V}, \; Cr^{3+}/Cr = -0.74 \text{ V}$$

Arrange these metals in their increasing order of reducing power.

Ans. Higher the oxidation potential, more easily it is oxidized and hence greater is the reducing power. Thus, increasing order of reducing power will be:

$$Ag < Hg < Cr < Mg < K$$

3.3. Depict the galvanic cell in which the reaction:

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

takes place. Further show:

(*i*) Which of the electrodes is negatively charged?
(*ii*) The carriers of current in the cell.
(*iii*) Individual reaction at each electrode.

Ans. The cell will be represented as:

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

(*i*) Anode, *i.e.* zinc electrode will be negatively charged.
(*ii*) The current will flow from silver to zinc in the external circuit.
(*iii*) At Anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
At cathode: $Ag^+(aq) + e^- \longrightarrow Ag$

3.4. Calculate the standard cell potential of galvanic cells in which the following reactions take place:

(*i*) $2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd(s)$
(*ii*) $Fe^{2+}(aq) + Ag^+(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

Given
$E^0_{Cr^{3+}, Cr} = -0.74\ V$
$E^0_{Cd^{2+}, Cd} = 0.40\ V$
$E^0_{Ag^+, Ag} = 0.80\ V$
$E^0_{Fe^{3+}, Fe^{2+}} = 0.77\ V$

Also calculate $\Delta_r G^0$ and equilibrium constant of the reactions.

Ans. (*i*)
$E^0_{cell} = E^0_{cathode} - E^0_{anode}$
$= -0.40\ V - (-0.74\ V) = +0.34\ V$
$\Delta_r G^0 = -n\ FE^0_{cell} = -6 \times 96500\ C\ mol^{-1} \times 0.34\ V$
$= -196860\ CV\ mol^{-1} = -196860\ J\ mol^{-1} = -196.86\ kJ\ mol^{-1}$
$-\Delta_r G^0 = -2.303\ RT \log K$
or $\log K = 34.5014$
$K = \text{Antilog}\ 34.5014 = 3.192 \times 10^{34}$

(*ii*)
$E^0_{cell} = +0.80\ V - 0.77\ V = +0.03\ V$
$\Delta_r G^0 = -n\ FE^0_{cell} = -(1\ mol) \times 96500\ C\ mol^{-1} \times 0.03\ V$
$= -2895\ C\ V\ mol^{-1} = -2895\ J\ mol^{-1} = -2.895\ kJ\ mol^{-1}$
$\Delta_r G^0 = -2.303\ RT \log K$
$-2895 = -2.303 \times 8.314 \times 298 \times \log K$
or $\log K = 0.5074$
or $K = \text{Antilog}\ (0.5074) = 3.22$

3.5. Write the Nernst equation and the e.m.f. of the following cells at 298 K.

(*i*) $Mg(s)|Mg^{2+}(0.001\ M)\ ||Cu^{2+}(0.0001\ M)|Cu(s)$
(*ii*) $Fe(s)|Fe^{2+}(0.001\ M)||H^+(1\ M)|H_2(g)(1\ bar)|Pt(s)$
(*iii*) $Sn(s)|Sn^{2+}(0.050\ M)||H^+(0.020\ M)|H_2(g)(1\ bar)|Pt(s)$
(*iv*) $Pt(s)|Br_2(l)|Br^-(0.010\ M)|H^+(0.030\ M)|H_2(g)(1\ bar)|Pt(s)$

Given:

$E^0_{Mg^{2+}/Mg} = -2.37\ V$
$E^0_{Cu^{2+}/Cu} = +0.34\ V$
$E^0_{Fe^{2+}, Fe} = -0.44\ V$

$$E^0_{Sn^{2+}/Sn} = -\ 0.14\ V$$

$$E^0_{\frac{1}{2}Br_2, Br^-} = +1.08\ V$$

Ans. (*i*) Cell reaction:

$$Mg + Cu^{2+} \longrightarrow Mg^{2+} + Cu\ (n = 2)$$

Nernst equation:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$E_{cell} = 0.34 - (-2.37) - \frac{0.0591}{2} \log \frac{10^{-3}}{10^{-4}}$$

$$= 2.71 - 0.02955 = 2.68\ V$$

(*ii*) Cell reaction:

$$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2\ (n=2)$$

Nernst equation:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Fe^{2+}]}{[H^+]^2}$$

$$E_{cell} = 0 - (-\ 0.44) - \frac{0.0591}{2} \log \frac{10^{-3}}{(1)^2}$$

$$= 0.44 - \frac{0.0591}{2} \times (-\ 3) = 0.44 + 0.0887 = 0.523\ V$$

(*iii*) Cell reaction:

$$Sn + 2H^+ \longrightarrow Sn^{2+} + H_2 (n = 2)$$

Nernst equation:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Sn^{2+}]}{[H^+]^2}$$

$$= 0 - (-\ 0.14) - \frac{0.0591}{2} \log \frac{0.05}{(0.02)^2} = 0.14 - \frac{0.0591}{2} \log 125$$

$$= 0.14 - \frac{0.0591}{2} (2.0969) = 0.078\ V$$

(*iv*) Cell reaction:

$$2Br^- + 2H^+ \longrightarrow Br_2 + H_2$$

Nernst equation:

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{1}{[Br]^2[H^+]^2}$$

$$E_{cell} = (0 - 1.08) - \frac{0.0591}{2} \log \frac{1}{(0.01)^2(0.03)^2}$$

$$= -\ 1.08 - \frac{0.0591}{2} \log\ (1.111 \times 10^7)$$

$$= -1.08 - \frac{0.0591}{2}(7.0457) = -1.08 - 0.208 = -1.288 \text{ V}$$

Thus, oxidation will occur at the hydrogen electrode and reduction on the Br_2 electrode.

$$E_{cell} = 1.288 \text{ V}$$

3.6. In the button cell widely used in watches and other devices the following reaction takes place:

$Zn(s) + Ag_2O(s) + H_2O(l) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

Determine $\Delta_r G^\ominus$ and $E^\ominus$ for the reaction

Given: $Zn = Zn^{2+} + 2e^-$, $E^0 = 0.76$ V

$Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-$, $E^0 = 0.344$ V

Ans. Zn is oxidised and Ag_2O is reduced (as Ag^+ ions changes to Ag)

$$E^0_{cell} = E^0_{Ag_2O/Ag(Red)} + E^\circ_{Zn/Zn^{2+}(ox)} = 0.344 + 0.76 = 1.104 \text{ V}$$

$$\Delta_r G^0 = -n\, FE^\circ cell = -2 \times 96500 \times 1.104 \text{ J} = -2.13 \times 10^5 \text{J}$$

3.7. Define conductivity and molar conductivity for solution of an electrolyte. Discuss their variation with concentration.

Ans. Conductivity of a solution is defined as the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section.

Specific conductivity:

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

In terms of SI units $= \text{S m}^{-1}$

Molar conductivity: It is defined as the conducting power of all the ions produced by one gram mole of an electrolyte in a solution and it is denoted by λ_m.

$$\lambda_m = \frac{\kappa}{C} \times 1000 \text{ S cm}^2 \text{ mol}^{-1}$$

where 'κ' is electrolytic conductivity of solution and 'C' is concentration of the solution (expressed in mol L^{-1}).

The unit of $\lambda_m = 1 \text{ S m}^2 \text{ mol}^{-1}$

Variation of conductivity and molar conductivity with concentration: Both conductivity and molar conductivity changes with change in concentration of the electrolyte. Conductivity always decreases with decrease in concentration both for weak as much as for strong electrolytes. It is because the number of ions per unit volume that carry the current in a solution decreases on dilutions. Molar conductivity increases with decreases in concentration. This is because both the number of ions as well as the mobility of ions increases with dilution. When concentration approaches zero, the molar conductivity is known as limiting molar conductivity or molar conductivity at infinite dilution.

3.8. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1}. Calculate its molar conductivity.

Ans.

$$\lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{0.0248 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.20 \text{ mol L}^{-1}} = 124 \text{ S cm}^2 \text{ mol}^{-1}$$

3.9. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}? [*Delhi* 2012]

Ans.

$$\text{Cell constant} = \frac{\text{Conductivity}}{\text{Conductance}} = \text{Conductivity} \times \text{Resistance}$$

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

3.10. The conductivity of sodium chloride at 298 K has been determined at different concentration and the results are given below:

Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa/\text{Sm}^{-1}$	1.237	11.85	23.15	55.53	106.74.

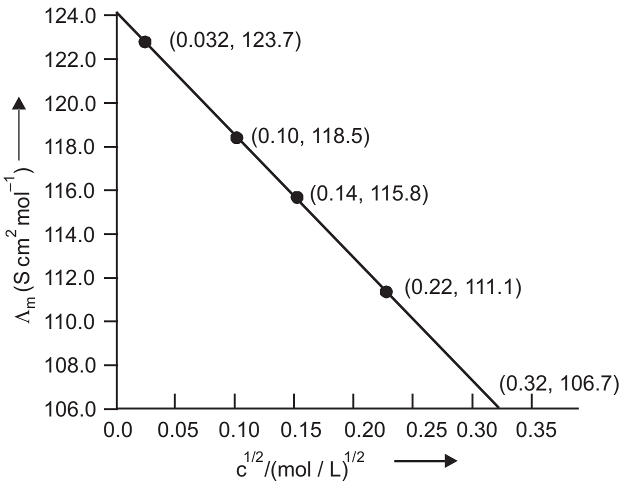
Calculate λ_m for all concentrations and draw a plot between λ_m and $C^{1/2}$. Find the value of λ_m^0.

Ans.

$$1\ \text{S cm}^{-1} = 100\ \text{S m}^{-1}$$

$$\frac{1\ \text{S cm}^{-1}}{100\ \text{S m}^{-1}} = 1\ \text{(unit conversion factor)}$$

Conc. (M)	**κ ($S\ m^{-1}$)**	**κ ($S\ cm^{-1}$)**	$\lambda_m = \frac{1000 \times K}{\text{Molarity}}$ **($S\ cm^2\ mol^{-1}$)**	**$c^{1/2}(M^{1/2})$**
10^{-3}	1.237×10^{-2}	1.237×10^{-4}	$\frac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = 123.7$	0.0316
10^{-2}	11.85×10^{-2}	11.85×10^{-4}	$\frac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = 118.5$	0.100
2×10^{-2}	23.15×10^{-2}	23.15×10^{-4}	$\frac{1000 \times 23.15 \times 10^{-4}}{2 \times 10^{-2}} = 115.8$	0.141
5×10^{-2}	55.53×10^{-2}	55.53×10^{-4}	$\frac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = 111.1$	0.224
10^{-1}	106.74×10^{-2}	106.74×10^{-4}	$\frac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = 106.7$	0.316



$$\Lambda^\circ = \text{Intercept on the } \Lambda_m \text{ axis} = 124.0 \text{ S cm}^2 \text{ mol}^{-1}$$

(on extrapolation to zero concentration)

3.11. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity, if λ^0_m for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

Ans.

$$\lambda^c_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{7.89 \times 10^{-5} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.00241 \text{ mol L}^{-1}}$$

$$= 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\lambda^c_m}{\lambda^\circ_m} = \frac{32.76}{390.5} = 8.4 \times 10^{-2}$$

$$\kappa_a = \frac{n\alpha^2}{1-\alpha} = \frac{0.00241 \times (8.4 \times 10^{-2})^2}{1-0.084} = 1.86 \times 10^{-5}$$

3.12. How much charge is required for the following reductions:

(*i*) 1 mol of Al^{3+} to Al? (*ii*) 1 mol of Cu^{2+} to Cu?

(*iii*) 1 mol of MnO_4^- to Mn^{2+}?

Ans. (*i*) The electrode reaction is:

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

∴ Quantity of charge required for the reduction of:

1 mol of Al^{3+} = 3F = 3 × 96500 C = 289500 C

(*ii*) The electrode reaction is:

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

∴ Quantity of charge required for the reduction of 1 mole of Cu^{2+} = 2F

= 2 × 96500 C = 193000 C

(*iii*) The electrode reaction is:

$$MnO_4^- \longrightarrow Mn^{2+}$$

i.e. $$Mn^{7+} + 5e^- \longrightarrow Mn^{2+}$$

∴ Quantity of charge required = 5 F = 5 × 96500 C = 482500 C

3.13. How much electricity in terms of Faraday is required to produce.

(*i*) 20.0 g of Ca from molten $CaCl_2$? (*ii*) 40.0 g of Al from molten Al_2O_3?

Ans. (*i*) $Ca^{2+} + 2e^- \longrightarrow Ca$

Thus, 1 mol of Ca, *i.e.* 40 g of Ca require electricity = 2 F

∴ 20 g of Ca will require electricity = 1 F

(*ii*) $Al^{3+} + 3e^- \longrightarrow Al$

Thus 1 mol of Al, *i.e.* 27g of Al require electricity = 3 F

∴ 40 g of Al will require electricity = $\frac{3}{27} \times 40$ = 4.44 F

3.14. How much electricity is required in coulomb for the oxidation of:

(*i*) 1 mol of H_2O to O_2? (*ii*) 1 mol of FeO to Fe_2O_3?

Ans. (*i*) The electrode reaction for 1 mol of H_2O is

$$H_2O \longrightarrow H_2 + \frac{1}{2}O_2$$

i.e. $$O^{2-} \longrightarrow \frac{1}{2}O_2 + 2e^-$$

Quantity of electricity required = 2 F

$= 2 \times 96500 \text{ C} = 193000 \text{ C}$

(*ii*) The electrode reaction for 1 mol of FeO is:

$$FeO \longrightarrow \frac{1}{2}Fe_2O_3$$

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

Quantity of electricity required = 1 F = 96500 C

3.15. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Ans. Quantity of electricity passed $= 5A \times 20 \times 60 \text{ s} = 6000 \text{ C}$

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

Thus, 2 F, *i.e.* 2 × 96500 C will deposit 1mole, *i.e.* 58.7 g of Ni

(At mass of Ni = 58.7)

Thus, 2 F, *i.e.* 2 × 96500 C will deposit Ni = 1 mole

$$\therefore \text{ 6000 C will deposit Ni} = \frac{58.7}{2 \times 96500} \times 6000 \text{ g} = 1.825 \text{ g}$$

3.16. Three electrolytic cells A, B, C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

Ans. $Ag^+ + e^- \longrightarrow Ag$,

i.e. 108 g of Ag is deposited by 1 F = 96500 C of electricity

$$\therefore \text{ 1.45 g of Ag will be deposited by} = \frac{96500}{108} \times 1.45 \text{ C of electricity} = 1295.6\text{C}$$

$$Q = I \times t$$

or $$t = \frac{Q}{I} = \frac{1295.6}{1.50} = 863.7 \text{ s} = 14 \text{ min, } 24 \text{ sec}$$

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

i.e. 2 × 96500 C will deposit Cu = 63.5 g

$$\therefore \quad \text{1295.6 C will deposit Cu} = \frac{63.5}{2 \times 96500} \times 1295.6 = 0.426 \text{ g}$$

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

$$\text{Zn deposited} = \frac{65.3}{2 \times 96500} \times 1295.6 = 0.438 \text{ g}$$

3.17. Using the standard electrode potential given in table 3.1 (of Page-69) predict if the reaction between the following is feasible:

(*i*) $Fe^{3+}(aq)$ and $I^-(aq)$ (*ii*) $Ag^+(aq)$ and $Cu(s)$ (*iii*) $Fe^{3+}(aq)$ and $Br^-(aq)$

(*iv*) $Ag(s)$ and $Fe^{3+}(aq)$ (*v*) $Br_2(aq)$ and $Fe^{2+}(aq)$

Given standard electrode potential

$$E^0_{\frac{1}{2}I_2, I^-} = 0.541 \text{ V}$$

$$E^0_{Cu^{2+},Cu} = 0.34\ \text{V}$$

$$E^0_{\frac{1}{2}Br_2,Br^-} = 1.09\ \text{V}$$

$$E^0_{Ag^+,Ag} = 0.80\ \text{V}$$

$$E^0_{Fe^{3+},Fe^{2+}} = 0.77\ \text{V}$$

Ans. A reaction is feasible if EMF of the cell reaction is +ve.

(*i*) $Fe^{3+}(aq) + I^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}I_2$

i.e. $Pt|I_2|I^-(aq)||Fe^{3+}(aq)|Fe^{2+}(aq)|Pt$

$\therefore$ $$E^0_{cell} = E^0_{Fe^{3+}/Fe^{2+}} - E^0_{\frac{1}{2}I_2,I^-}$$

$$E^0_{cell} = 0.77 - 0.54 = 0.23\ \text{V (Feasible)}$$

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

i.e. $Cu|Cu^{2+}(aq)||Ag^+(aq)|Ag$

$$E^0_{cell} = E^0_{Ag^+/Ag} - E^0_{Cu^{2+}/Cu}$$
$$= 0.80 - 0.34 = 0.46\ \text{V (Feasible)}$$

(*iii*) $Fe^{3+}(aq) + Br^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}Br_2$

$$E^0_{cell} = 0.77 - 1.09 = -0.32\ \text{V (Not feasible)}$$

(*iv*) $Ag(s) + Fe^{3+}(aq) \longrightarrow Ag^+(aq) + Fe^{2+}(aq)$

$$E^\circ_{cell} = 0.77 - 0.80 = -0.03\ \text{V (Not feasible)}$$

(*v*) $\frac{1}{2}Br_2(aq) + Fe^{2+}(aq) \longrightarrow Br^- + Fe^{3+}$

$$E^0_{cell} = 1.09 - 0.77 = 0.32\ \text{V (Feasible)}$$

3.18. Predict the products of electrolysis in each of the following:

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

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

(*iii*) A dilute solution of H_2SO_4 with platinum electrodes.

(*iv*) An aqueous solution of $CuCl_2$ with platinum electrodes.

Ans. (*i*) Electrolysis of aqueous solution of $AgNO_3$ with silver electrodes.

$AgNO_3(aq) \longrightarrow Ag^+(aq) + NO_3^-(aq)$

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

At Cathode: Ag^+ ions have lower discharge potential than H^+ ions. Hence, Ag^+ ions will be deposited as Ag in preference to H^+ ions.

At Anode: As Ag anode is attacked by NO_3^- ions, Ag of the anode will dissolve to form Ag^+ ions in the solution.

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

(*ii*) Electrolysis of aqueous $AgNO_3$ using platinum electrodes

At Cathode: Same as above

At Anode: As anode is not attacked either by OH^- or NO_3^- ions, OH^- ions have lower is charge potential. Hence, OH^- ions will be discharged in preference to NO_3^- ions which then decompose to give out O_2.

$$H_2O\ (l) \longrightarrow 2H^+ + \frac{1}{2}\ O_2(g) + 2e^-$$

(*iii*) Electrolysis of dilute H_2SO_4 with Pt electrodes.

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

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

At Cathode:

$$H^+ + e^- \longrightarrow H + H = H_2(g)$$

At Anode:

$$H_2O(l) \longrightarrow 2H^+ + \frac{1}{2}\ O_2(g) + 2e^-$$

Thus, H_2 is liberated at the cathode and O_2 at the anode.

(*iv*) Electrolysis of aqueous solution of $CuCl_2$ with platinum electrodes:

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

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

At Cathode:

Cu^{2+} ions will be reduced in preference to H^+ ions.

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

At Anode:

Cl^- ions will be oxidised in preference to OH^- ions.

$$Cl^- \longrightarrow Cl + e^-$$

$$Cl + Cl \longrightarrow Cl_2(g)$$

Thus Cu will be deposited on the cathode and Cl_2 will be liberated at the anode.

ADDITIONAL QUESTIONS SOLVED

I. Very Short Answer Type Questions

(1 *Mark*)

Q1. Define specific conductivity (specific conductance).

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

Q2. What is meant by cell constant?

Ans. Cell constant is the ratio of the distance between the electrodes (l) and the area of cross-section (A). It is denoted by $\frac{l}{A}$. Its unit is cm^{-1}. Its SI unit is m^{-1}.

Q3. Write Nernst equation for the electrodezz reaction:

$Mn^+ + ne^- \longrightarrow M(s)$ [*CBSE* 2002]

Ans. $E_{m^{n+}/M} = E^-_{M n^{n+}/M} + \frac{2.303\ RT}{nF} \log[M^{R+}]$

Q4. How does fuel cell operate?

Ans. In fuel cell, chemical energy of the fuel is converted into the electrical energy.

Q5. Under that condition will a galvanic cell send no current in the outer circuit? [*AI* 2001 *C*]

Ans. If salt bridge is not used galvanic cell will send zero current in the outer circuit after sometime.

Q6. What is the basis of obtaining electrical energy in a fuel cell?

Ans. In a fuel cell the chemical energy of fuel is converted into the electrical energy.

Q7. Name any two metals which can be used for cathodic protection of iron.

Ans. Zn and Mg

Q8. What is meant by Faraday constant?

Ans. Faraday constant is the total charge on 1 mole of electrons. It is equal to 96500 C.

Q9. Express the relationship between the degree of dissociation of an electrolyte and its molar conductivity.

Ans. $\alpha = \dfrac{(\lambda_m)_c}{(\lambda_m)_\infty} = \dfrac{\lambda}{\lambda^0}$

where $(\lambda_m)_c$ or λ is their molar conductance at conc. 'C'.

and $(\lambda_m)_\infty$ or λ^0 is the molar conductance at infinite dilution or the limiting molar conductivity.

Q10. What does the standard electrode potential of a metal being negative ($-E^0_{Zn^{2+}/Zn} = -0.7632$) indicate.

Ans. $-E^0_{Zn^{2+}/Zn} = -0.7632$ indicates that this metal acts as the anode when coupled with standard hydrogen electrode. Since oxidation takes place at anode, therefore oxidation potential is +ve but reduction potential is –ve.

Q11. Why does an alkaline solution inhibits the rusting of iron?

Ans. Rusting of iron takes place in the presence of H^+ ions. Alkaline medium will neutralise the H^+ ions and inhibit rusting.

Q12. What are primary cells?

Ans. Primary cells are those cells which are not rechargeable *i.e.* products cannot change back into the reactants.

Q13. What mass of zinc (II) ion will be reduced by 1 mole of electrons?

Ans. $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$

2 Faraday, *i.e.* 2 moles of electron will deposit 65 g of zinc.

1 Faraday, *i.e.* 1 mole of electrons will deposit 32.5 g of zinc.

Q14. Why is it impossible to obtain the electrode potential for a single electrode?

Ans. It is because e.m.f. can be measured for a complete circuit with two electrodes, but not for a single electrode.

Q15. Which electrolyte is used for electroplating of silver?

Ans. $K[Ag(CN)_2]$, i.e. potassium dicyanoargentate(I) is used as the electrolyte in silver plating process.

Q16. What is the representation of a Daniell cell?

Ans. $Zn|ZnSO_4(1M)||\ CuSO_4(1M)|Cu(s)$

Q17. What are secondary cells?

Ans. Secondary cells are those cells which can be recharged again once used, by passing direct current through them.

Q18. HCl does not give an acidic solution in benzene why?

Ans. HCl does not give acidic solution in benzene because it does not dissociate into its constituent ions in benzene as benzene is a non-polar solvent.

Q19. Write the symbolic notation for standard hydrogen electrode and its potential.

Ans. Pt, $H_2(g, 1atm)|H^+(1M)$. $E^0_{H^+/H_2} = 0$

Q20. Write the relation between cell potential and equilibrium constant.

Ans. $E_{cell} = E^0_{cell} - \dfrac{2.303\ RT}{nF} \log K_c$

Q21. What is the effect of temperature on the electrical conduction of

(*i*) metallic conductor

(*ii*) electrolytic conductor?

Ans. With increase of temperature the electrical conduction of a metallic conductor, i.e. metals decreases whereas that of an electrolytic conductor, i.e., for an electrolyte increases.

Q22. Which equation gives the relationship between equivalent or molar conductance and the concentration of a strong electrolyte?

Ans. Debye – Hukel – Onsager equation:

$\lambda = \lambda^0 - A\sqrt{C}$ where λ is the molar conductance at concentration C and A is a constant.

Q23. What is the reference electrode in determining the standard electrode potential?

Ans. Normal hydrogen electrode (NHE).

Q24. What is the standard electrode potential of NHE?

Ans. Zero.

Q25. What is the relationship between free energy change and EMF of a cell?

Ans. $-\Delta_r G = nFE_{cell}$

Q26. Which electrolyte is used in a dry cell?

Ans. A paste of NH_4Cl, MnO_2 and Carbon black.

Q27. Which cells were used in Apollo space programme? What was the product used for?

Ans. $H_2 – O_2$ fuel cell. The product H_2O was used for drinking by the astronauts.

Q28. What is the overall electrochemical reaction takes place in rusting?

Ans. $2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$

Q29. Why zinc reacts with dilute H_2SO_4 to give the gas but copper does not?

Ans. This is because zinc has a higher oxidation potential than hydrogen whereas copper has a lower oxidation potential than hydrogen.

Q30. How can you increase the reduction potential of an electrode?

Ans. By increasing the concentration of the ions.

Q31. What is EMF of a cell?

Ans. The difference between the electrode potentials of the two half cells is known as EMF of the cell.

Q32. Define corrosion. What is the chemical formula of rust?

Ans. Corrosion is the process of slow eating away of the surface of the metal due to attack of atmospheric gases. The formula of rust is $Fe_2O_3 . xH_2O$.

Q33. What is the effect of decreasing the concentration on the molar conductivity of a weak electrolyte?

Ans. On decreasing the concentration (*i.e.* on dilution) the molar conductivity will increase.

Q34. Which allotrope of carbon is used for making electrodes?

Ans. Graphite

Q35. Write the name of the electrolyte used in (*i*) fuel cell (*ii*) mercury cell:

Ans. (*i*) Concentrated KOH solution

(*ii*) Moist Mercuric oxide (HgO) mixed with KOH.

Q36. Why a cell stops working after some – time?

Ans. With the passage of time the concentration of metal ions around cathode decrease, thereby decreasing the value of $E_{cathode}$. Similarly, at anode, the concentration of metal ions increases thereby increasing value of E_{anode}. As a result, the difference between $E_{cathode}$ and E_{anode} goes on decreasing and gradually it becomes zero. At this stage the flow of current stops working.

Q37. State two advantages of $H_2 – O_2$ fuel cell over an ordinary cell.

Ans. (*i*) They do not cause any pollution.

(*ii*) They have high efficiency of 60–70%.

Q38. Rusting of iron is quicker in saline water than in ordinary water. Give reason.

Ans. In saline water, the presence of Na^+ and Cl^- ions increases the conductance of the solution in contact with the metal surface. This accelerates the formation of Fe^{2+} ions and hence that of rust, $Fe_2O_3 . xH_2O$.

Q39. What flows in the internal circuit of a galvanic cell?

Ans. Ions

Q40. How can you test whether the given electrolyte is a strong electrolyte or a weak electrolyte?

Ans. If the aqueous solution of an electrolyte conducts electricity to a large extent, it is a strong electrolyte and if to a small extent, then it is a weak electrolyte.

Q41. How is cell constant calculated from conductance values?

Ans. $\text{Cell constant} = \dfrac{\text{Specific conductance}}{\text{Observed conductance}}$

Q42. Why is chromium used for coating iron?

Ans. Chromium is a non-corroding metal which forms a protective layer over iron metal.

Q43. Define electrochemical series.

Ans. The arrangement of various electrodes in the decreasing or increasing order of their standard reduction potentials is called electrochemical series.

Q44. Write an expression to relate molar conductivity of an electrolyte to its degree of dissociation.

Ans. $\alpha = \dfrac{\lambda_m^c}{\lambda_m^\circ}$

Q45. What is the relationship between the standard EMF of the cell and the equilibrium constant of the cell reaction at 298 K?

Ans. $E^0_{cell} = \dfrac{0.0591}{n} \log K_c$

Q46. Write mathematical expression for Kohlrausch's law.

Ans. $\lambda_c^0 = \lambda_c^0 + \lambda_a^0$

or $\lambda_m^0 = \nu_c\lambda_c^0 + \nu_a\lambda_a^0$

where ν_c and ν_a are the number of cations and anions respectively in one formula unit of the compound.

Q47. What are the units of molar conductivity?

Ans. S cm^2 mol^{-1} or ohm^{-1} cm^2 mol^{-1}.

Q48. Write the electrode reactions taking place in Ni – Cd cell. Is it a primary or secondary cell?

Ans. It is a secondary cell.

$Cd + 2OH^- \longrightarrow CdO + H_2O + 2e^-$ (at anode)

$Ni(OH)_3 + e^- \longrightarrow Ni(OH)_2 + OH^-$ (at cathode)

II. Short Answer Type Questions

(2 *or* 3 *Marks*)

Q1. Define conductivity and molar conductivity for the solution of an electrolyte. [*AI* 2007]

Ans. **Conductivity:** The property by virtue of which the substance allows the passage of an electric current. The reciprocal of the resistance of a circuit is called the conductivity.

Molar conductivity: Molar conductivity is the conductance of all the ions produced by 1 mole of the electrolyte when electrodes are unit distance apart and have sufficient area of cross-section to hold the electrolyte.

Q2. The following chemical reaction is occurring in an electrochemical cell:

$$Mg(s) + 2Ag^+(0.0001\ M) \longrightarrow Mg^{2+}(0.10\ M) + 2\ Ag(s)$$

The E° values are:

$Mg^+/Mg = -2.36$ V

$Ag^+/Ag = 0.81$ V

For this cell, calculate/write

(*a*) (*i*) E° value for the 2 Ag^+/2 Ag

(*ii*) Standard cell potential E°_{cell}

(*b*) Cell potential $(E)_{cell}$

(*c*) (*i*) Symbolic representation of the above cell

(*ii*) Will the above cell reaction be spontaneous?

Ans. (*a*) (*i*) 0.81V

(*ii*) $E^\Theta_{cell} = E_{right} - E_{left}$
$= 0.81\ V - (-2.36\ V)$
$= 3.17$ V

(*b*) $E_{cell} = E^\Theta_{cell} - \dfrac{0.0591}{n} \log \dfrac{[Mg^{2+}]}{[Ag^+]^2}$

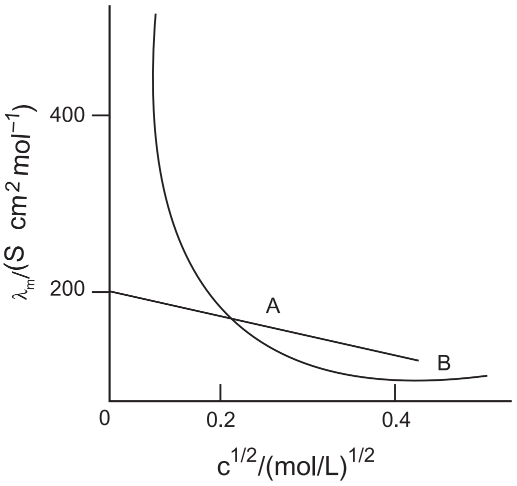
$= 3.17 - \dfrac{0.0591}{n} \log \dfrac{(0.1)}{(0.0001)^2}$

$= 2.96$ V

(*c*) (*i*) $Mg(s) \mid Mg^{2+}(0.10\ M) \parallel Ag^+ (0.0001\ M) \mid Ag(s)$

(*ii*) Yes

Q3. The following curve is obtained when molar conductivity λ_m (*y*-axis) is plotted against the square root of concentration $C^{1/2}$ (x–axis) for two electrolytes A and B.



(*a*) What can you say about the nature of the two electrolytes A and B?

(*b*) How do you account for the increase in the molar conductivity λ_m for the electrolytes A and B on dilution?

[*CBSE* 2009]

Ans.

(*a*) A is a strong electrolyte and B is a weak electrolyte.

(*b*) Molar conductivity of a strong electrolyte increases with dilution as ionic mobility increases. In a weak electrolyte molar conductivity increases steeply with dilution as the degree of dissociation increases.

Q4. What are fuel cells? Write the electrode reactions of a fuel cell which uses the reaction of hydrogen with oxygen?

[*AI* 2006, *Delhi* 2013 *C*]

Ans. A fuel cell is similar to a galvanic cell, it generates electricity directly by the electrochemical conversion of gaseous or liquid fuels fed into the cell as required.

At anode:

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

At cathode:

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

Overall reaction:

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

Q5. Predict products of electrolysis obtained at the electrodes in each case when the electrodes used are of platinum.

(*i*) An aqueous solution of $AgNO_3$

(*ii*) An aqueous solution of H_2SO_4

[*AI* 2005]

Ans.

(*i*) $AgNO_3(aq) \longrightarrow Ag^+(aq) + NO_3^-(aq)$

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

At Cathode:

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

At Anode:

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

(*ii*) $H_2SO_4(aq) \longrightarrow 2H^+(aq) + SO_4^{2-}(aq)$

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

At Cathode:

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

At Anode:

$2OH^-(aq) \longrightarrow O_2 + 2H^+(aq) + 4e^-$

Q6. Zinc rod is dipped in 0.1 M solution of $ZnSO_4$

The salt is 95% dissociated. Calculate the electrode potential. Given:

[*CBSE* 2005 (*C*)]

E^0 Zn^{2+}/Zn at 298 K = –0.76 V

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

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

$$E_{Zn+/Zn}$$

$$= E^0_{Zn+/Zn} - \frac{0.0591}{2}\log\frac{1}{[Zn^{2+}]}$$

$$= -0.76\text{ V} - \frac{0.0591}{2}\log\frac{1}{0.095}$$

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

$$= -0.76 - \frac{0.0591}{2}[3.000 - 1.9777]$$

$$= -0.76\text{ V} - \frac{0.0591}{2} \times 1.0223$$

$$= -0.76\text{ V} - \frac{0.0604}{2}$$

$$= -0.76 - 0.0302$$

$$= -0.7902\text{ V}$$

Q7. Calculate the equilibrium constant for the following reaction at 298 K.

$Cu(s) + Cl_2(g) \longrightarrow CuCl_2(aq)$

$R = 8.314\ J\ K^{-1}\ mol^{-1}$

$E^0_{Cu^{2+}/Cu} = 0.34\ V$

$E^0_{\frac{1}{2}Cl_2/Cl^-} = 1.36\ V$

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

[*AI* 2005]

Ans.

$$E^0_{cell} = E^0_{\frac{1}{2}Cl_2/Cl^-} - E^0_{Cu^{2+}/Cu}$$

$$= +1.36\ V - 0.34\ V = 1.02\ V$$

$$\log K = \frac{n\,E^0}{0.0591} = \frac{2\times 1.02}{0.0591}$$

$$= \frac{2.04}{0.0591} = 34.5177$$

$$K = \text{Antilog } 34.5177$$

$$= 3.294 \times 10^{34}$$

Q8. Calculate the emf of the following cell:

$Mg(s)|Mg^{2+}(0.2M)||Ag^+\ (1 \times 10^{-3}M)|Ag(s)$

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

$E^0_{Mg^{2+}/Mg} = -2.37\ V$

[*AI* 2005 *C*]

Ans.

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

$$2\,Ag^+(aq) + 2e^- \longrightarrow 2\,Ag(s)$$

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

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$= (E^0_{Ag^+/Ag} - E^0_{Mg^{2+}/Mg}) - \frac{0.0591}{2}\log\frac{0.2}{(10^{-3})^2}$$

$$= [+0.80\ V - (-2.37\ V) - \frac{0.0591}{2}\log(2\times 10^5)]$$

$$= +3.17\ V - \frac{0.0591}{2}[\log 2 + \log 10^5]$$

$$= +3.17\ V - \frac{0.0591}{2} \times 5.3010$$

$$= +3.17\ V - 0.1566\ V$$

$$= 3.0134\ V$$

Q9. Write the cell reaction which occur in the lead storage battery

(*i*) When the battery is in use,

(*ii*) When the battery is charging.

[*Foreign* 2004]

Ans. (*i*) $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2\,H_2O(l)$

At anode:

$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

At cathode:

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

(*ii*) $2\,PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$

Q10. Describe the composition of anode and cathode in a mercury cell. Write the electrode reactions for this cell.

[*Foreign* 2004]

Ans. Mercury cell: It consists of zinc mercury amalgam as anode, a paste of HgO and Carbon black is used as cathode. The electrolyte is a paste of KOH and ZnO.

At anode:

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

At cathode:

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

The net reaction:

$Zn(amalgam) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

Q11. State two advantages of $H_2 - O_2$ fuel cell over ordinary cells.

Ans. (*i*) It is highly efficient

(*ii*) It is pollution free.

Q12. What is corrosion? Describe the role of zinc in cathodic protection of iron. Can we use tin in place of zinc for this purpose? Give reason.

Ans. Corrosion is a process in which metal reacts with the substances present in the atmosphere to form compound at its surface.

Zinc acts as the anode. It loses electrons in preference to iron because it is more reactive than Fe.

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

If any Fe^{2+} ions are formed they again gain electrons to form iron back.

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

Tin cannot be used to protect iron because it is less reactive than Fe.

Q13. How much copper is deposited on the cathode of an electrolytic cell if a current of 5 ampere is passed through a solution of copper sulphate for 45 minutes? [*Foreign* 2003]

Ans. [Molar mass of Cu = 63.5 g mol^{-1}, 1F = 96,500 C mol^{-1}]

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

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

$$= \frac{63.5}{2\times 96500} \times 5\,\text{amp.} \times 45 \times 60$$

$$= \frac{857250}{193000} = 4.44 \text{ g}$$

Q14. How much time would it take in minutes to deposit 1.18 g of metallic copper on a metal object when a current of 2.0 A is passed through the electrolytic cell containing Cu^{2+} ions?
[Molar mass of Cu = 63.5 g mol^{-1}, 1F = 96,500 C mol^{-1}] [*Foreign* 2003]

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

$$1.18 = \frac{63.5}{2\times 96500} \times 2 \times t$$

$$t = \frac{1.18\times 2\times 96500}{2\times 63.5}$$

$$= 1793.23 \text{ sec}$$

$$= \frac{1793.23}{60} = 29.88 \text{ min}$$

Q15. Explain why electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode. Write the overall reaction.

Given $E^0_{Na^+/Na} = -2.71$ V

$E^0_{Cl_2/2Cl^-} = 1.36$ V

and $\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O(l)$ $E^0 = 1.23$ V

Ans. $NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$

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

At cathode:

$3H^+(aq) + 2e^- \longrightarrow H_2(g)$

It is because reduction potential value of $E^0_{H^+/H_2}$ is more than that $E^0_{Na^+/Na.}$

At anode:

$2Cl^-(aq) - 2e^- \longrightarrow Cl_2(g)$

It is because of over voltage, *i.e.* energy required to liberate O_2 is more than that of Cl_2.

Overall cell reaction:

$$2NaCl(aq) + 2H_2O(aq) \xrightarrow{\text{Electrolysis}} H_2(g) + Cl_2(g) + 2Na^+(aq) + 2\,OH^-(aq)$$

Q16. Calculate the standard cell potential of the galvanic cell in which the following reaction takes place.

$$2\,Cr(s) + 3\,Cd^{2+}(aq) \longrightarrow 2\,Cr^{3+}(aq) + 3\,Cd(s)$$

Also calculate the $\Delta_r G^\circ$ value of the reaction.

(Given $E^0_{Cr^{3+}/Cr} = -0.74$ V)

$E^0_{Cd^{2+}/Cd} = -0.40$ V

and F = 96500 C mol^{-1}

[*AI* 2007]

Ans. $2\,Cr(s) \longrightarrow 2\,Cr^{3+}(aq) + 6e^-$

$3\,Cd^{2+}(aq) + 6e^- \longrightarrow 3\,Cd(s)$

$$E^0_{cell} = E^0_{Cd^{2+}/Cd} - E^0_{Cr^{3+}/Cr}$$

$$= -0.40 \text{ V} - (-0.74 \text{ V})$$

$$= -0.40 \text{ V} + 0.74 \text{ V}$$

$$E^0_{cell} = 0.34 \text{ V}$$

$$\Delta_r G^0 = -nE^0F = -6 \times 0.34 \text{ V} \times 96500$$

$$\Delta_r G^0 = -196.86 \text{ kJ mol}^{-1}$$

Q17. (*a*) At 291 K, molar conductivities at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4, 108.9 ohm^{-1} cm^2, respectively. If molar conductivity of centinormal solution of NH_4OH is 9.33 ohm^{-1} cm^2, what is the degree of dissociation of NH_4OH solution?

(*b*) The standard reduction potential values of three metallic cations x, y, z, are 0.52, –3.03, –1.18V respectively. What will be the order of reducing power of the corresponding metals.

[*AI* 2006]

Ans. (*a*) $\lambda_m^\infty(NH_4Cl) = \lambda_m^\infty(NH_4^+) + \lambda_m^\infty(Cl^-)$

$$= 129.8 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_m^\infty (\text{NaOH}) = \lambda_m^\infty (\text{Na}^+) + \lambda_m^\infty (\text{OH}^-) = 217.4 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_m^\infty (\text{NaCl}) = \lambda_m^\infty (\text{Na}^+) + \lambda_m^\infty (\text{Cl}^-) = 108.9 \text{ S cm}^2 \text{ mol}^{-1}$$

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

$$\begin{aligned}\lambda_m^\infty (\text{NH}_4\text{OH}) &= \lambda_m^\infty (\text{NH}_4^+) + \lambda_m^\infty (\text{OH}^-)\\ &= \lambda_m^\infty (\text{NH}_4\text{Cl}) + \lambda_m^\infty (\text{NaOH})\\ &\quad - \lambda_m^\infty (\text{NaCl})\\ &= 129.8 + 217.4 - 108.9\\ &= 238.3 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\alpha &= \frac{(\lambda^c{}_m)}{(\lambda^\infty{}_m)}\\ &= \frac{9.33 \text{ S cm}^2 \text{ mol}^{-1}}{238.3 \text{ S cm}^2 \text{ mol}^{-1}}\\ &= 0.039 \Rightarrow \alpha = 3.9\%\end{aligned}$$

The ratio of molar conductivity at 10^{-2} M to the λ_m^∞ gives the degree of dissociation of NH_4OH.

(*b*) Y > Z > X

Q18. In the button cell widely used in watches and other devices the following reaction takes place.

$$\text{Zn}(s) + \text{Ag}_2\text{O}(s) + \text{H}_2\text{O}(l) \longrightarrow \text{Zn}^{2+}(aq) + 2\text{ Ag}(s) + 2\text{ OH}^-(aq)$$

Determine E^0 and Δ_rG^0 for the reaction.

Given

$$E^0_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$$

$$E^0_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$$

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

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

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

$$\begin{aligned}E^0_{\text{cell}} &= (E^0_{\text{SRP cathode}} - E^0_{\text{SRP anode}})\\ &= +0.80 \text{ V} - (-0.76 \text{ V})\\ &= +1.56 \text{ V}\\ \Delta_rG^0 &= -n\,E^0F\\ &= -2 \times 1.56 \text{ V} \times 96500\\ &= -301080 \text{ J mol}^{-1}\\ &= -301.080 \text{ kJ mol}^{-1}\end{aligned}$$

Q19. The E° values at 298 K corresponding to the following two reduction electrodes processes are:

(*i*) $\text{Cu}^+/\text{Cu} = +0.52$ V

(*ii*) $\text{Cu}^{2+}/\text{Cu}^+ = +0.16$ V

Formulate the galvanic cell for their combination. What will be the cell potential? Calculate the Δ_rG^0 for the cell reaction. ($1\text{F} = 96500 \text{ C mol}^{-1}$)

[*AI, Foregin* 2005]

Ans. $\text{Cu}^+|\text{Cu}^{2+}||\text{Cu}^+|\text{Cu}$

$$\begin{aligned}E^0_{\text{cell}} &= E^0_{\text{SRP(cathode)}} - E^0_{\text{SRP(anode)}}\\ &= E^0_{\text{Cu+/Cu}} - E^0_{\text{Cu}^{2+}/\text{Cu+}}\\ &= +0.52 \text{ V} - 0.16 \text{ V} = 0.36 \text{ V}\end{aligned}$$

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

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

$$\begin{aligned}n &= 1\\ \Delta_rG^0 &= -n\,E^0F\\ &= -1 \times 0.36 \text{ V} \times 96500 \text{ C}\\ &= -34740 \text{ J mol}^{-1}\\ &= -34.74 \text{ kJ mol}^{-1}\end{aligned}$$

Q20. Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity. If λ^0_{m} for acetic acid is 390.5 S cm^2 mol^{-1}, what is its dissociation constant?

[*CBSE* 2004, *Delhi* 2013]

Ans. $\kappa = 7.896 \times 10^{-5} \text{ S cm}^{-1}$

$$\begin{aligned}\lambda_m &= \frac{1000\kappa}{\text{M}}\\ &= \frac{1000 \times 7.896 \times 10^{-5}}{0.00241}\\ &= \frac{7.896 \times 10^3}{241} = \frac{7896}{241}\\ &= 32.76 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

$$\alpha = \frac{\lambda_m}{\lambda_m^0} = \frac{32.76}{390.5} = 0.0838$$

$$\begin{aligned}K_a &= \frac{C\alpha^2}{1-\alpha} = \frac{0.00241 \times (0.084)^2}{(1-0.084)}\\ &= 1.86 \times 10^{-5}\end{aligned}$$

Q21. Write the Nernst equation and calculate the e.m.f. of the following cell at 298 K:

$\text{Cu}(s)\ |\text{Cu}^{2+}(0.130 \text{ M})||\text{Ag}^+(1.00 \times 10^{-4}\text{M})|\text{Ag}(s)$

Given:

$E^0_{Cu^+/Cu}$ = + 0.34 V and

$E^0_{Ag^+/Ag}$ = + 0.80 V [*AI* 2004]

Ans. $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$

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

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$= [E^0_{Ag^+/Ag} - E^0_{Cu^{2+}/Cu}] - \frac{0.0591}{2} \log \frac{0.13}{(10^{-4})^2}$$

$$= (0.80\ V - 0.34\ V) - \frac{0.0591}{2} \log 1.3 \times 10^7$$

$$= 0.46 V - \frac{0.0591}{2} [\log 1.3 + \log 10^7]$$

$$E_{cell} = 0.46\ V - 0.21\ V = 0.25\ V$$

Q22. Calculate the equilibrium constant for the reaction.

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

Given:

$E^0_{Zn^{2+}/Zn}$ = – 0.763 V and

$E^0_{Cu^{2+}/Cu}$ = +0.34 V [*CBSE* 2004 F]

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

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

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

$$E_{cell} = E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}$$

$$= +0.34\ V - (-0.763\ V)$$

$$= 1.103\ V$$

$$\log K = \frac{nE^0}{0.0591} = \frac{2 \times 1.103}{0.0591}$$

$$\log K = \frac{2.206}{0.0591} = 37.326$$

$$K = \text{Antilog } 37.326 = 2.118 \times 10^{37}$$

Q23. Silver is electrodeposited on a metallic vessel of surface area 800 cm^2 by passing a current of 0.2 amp. for 3 hours. Calculate the thickness of silver deposited. [*AI* 2004 *C*]

Density of silver = 10.47 g cm^{-3}

Atomic mass of silver = 107.92 *u*

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

$$= \frac{107.92}{96500} \times 0.2 \text{ amp.} \times 3$$

$$= \frac{107.92}{96500} \times 0.2 \text{ amp.} \times 3 \times 60 \times 60$$

$$= 2.416\ g$$

$$d = \frac{m}{V}$$

$$m = V \times d$$

$$= A \times \text{thickness} \times \text{density}$$

$$2.416\ g = 800\ cm^2 \times \text{thickness} \times 10.47\ g\ cm^3$$

$$\text{Thickness} = \frac{2.416}{800 \times 10.47}$$

$$= \frac{24.16 \times 10^{-4}}{8.376} = 2.88 \times 10^{-4}\ cm$$

Q24. Calculate the e.m.f. at 25°C for the following cell:

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

Given:

$E^0_{Ni^{2+}/Ni}$ = – 0.25 V

$E^0_{Cu^{2+}/Cu}$ = +0.34 V

[1F = 96,500 C mol^{-1}].

Calculate the maximum work that can be accomplished by the operation of this cell. [*CBSE* 2003]

Ans. $Ni(s)|Ni^{2+}(0.01\ M)||Cu^{2+}(0.1\ M)|Cu(s)$

At anode:

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

At cathode:

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

Net cell reaction:

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

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Ni^{2+}]}{[Cu^{2+}]}$$

$$= (E^0_{Cu^{2+}/Cu} - E^0_{Ni^{2+}/Ni}) - \frac{0.0591}{2} \log \frac{0.01}{0.1}$$

$$= [+0.34\ V - (-0.25\ V)] - \frac{0.0591}{2}\log\frac{1}{10}$$

$$= 0.59\ V - \frac{0.0591}{2} \times -1$$

$$= 0.59\ V + 0.0295\ V = 0.6195\ V$$

$$\Delta G = -nEF$$

$$= -2 \times 0.6195\ V \times 96500\ C/mol$$

$$= -119563.5\ J/mol$$

$$\Delta G = -119.5635\ kJ/mol$$

$$-\Delta G = W_{max} = 119.5635\ kJ/mol$$

Q25. How long will it take an electric current of 0.15 A to deposit all the copper from 500 ml of 0.15 M copper sulphate solution?

Ans. 500 ml of 0.15 M $CuSO_4$ solution contains

$$\frac{500 \times 0.15}{1000} = 0.075 \text{ mole of Cu}$$

$$\text{Mass of Cu}(m) = 0.075 \times 63.5 = 4.7625\ g$$

$$\text{Eq. wt. of } Cu^{2+} = \frac{63.5}{2} = 31.75$$

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

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

$$t = \frac{4.7625 \times 96500}{31.75 \times 0.15} = 96500 \text{ sec}$$

$$= \frac{96500}{60 \times 60} = 26.80 \text{ hours.}$$

Q26. What is corrosion? CO_2 is always present in natural water. Explain its effect (increases, stops or no effect) on rusting of Fe.

Ans. Corrosion is a process of slowly eating away of the metal due to the attack of atmospheric gases on the surface of metal resulting into the formation of compounds such as oxides, sulphides, carbonates, sulphates, etc.

Factors affecting corrosion are:

(*i*) Reactivity of metal
(*ii*) Presence of impurities
(*iii*) Presence of air and moisture
(*iv*) Strains in metals
(*v*) Presence of electrolytes

CO_2 increases the rusting of iron because greater the number of H^+ ions, faster the rusting will take place.

Q27. What do you understand by sacrificial, cathodic and barrier protection of corrosion? [*CBSE* 2005 *C*]

Ans. **Sacrifical protection:** Sacrificial protection means covering the iron surface with a layer of metal which is more active (electropositive) than iron and thus prevents iron from losing electrons. The metal which is most often used for covering iron with more active metal is zinc and the process is called galvanisation.

Cathodic protection or Electrical protection: This method of metal protection is based upon the fact that there is no dissolution of metal ions from the cathode of an electrochemical cell, since the cathode is more negative than the electrode potential of the particular metal. Cathodic protection is used to prevent corrosion of submerged or underground metal works.

Barrier protection: In barrier protection method, the metal surface is not allowed to come in contact with moisture, oxygen and carbon dioxide. This can be achieved by applying paint, grease, oiling or coating the surface of iron with non-corroding metals such as nickel, chromium, aluminium, etc.

Q28. What do you understand by the term 'conductance'? What are its units?

Ans. The reciprocal of electrical resistance is called conductance. It is usually represented by the symbol 'G'.

$$\text{Thus } G = \frac{1}{R}$$

Units: The unit of conductance is reciprocal of ohm written as

ohm^{-1} or mho

or 'Siemens (S)

$1\ S = 1\ \Omega^{-1}$

Q29. What is a Galvanic cell? Give the symbolic representation of the Daniell cell.

Ans. Galvanic cell: A galvanic cell is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device, the Gibbs energy of the spontaneous redox reaction is converted into electrical work.

Symbolic representation of a Daniell cell:

$$Zn|Zn^{2+}_{(C_1)}||Cu^{2+}_{(C_2)}|Cu$$

Q30. What are the differences between Galvanic cell (Electrochemical cell) and Electrolytic cell?

Ans.

Electrochemical cell	Electrolytic cell
(1) It is a device used to convert chemical energy into electrical energy.	(1) It is a device used to convert electrical energy into chemical energy.
(2) It is based upon the redox reaction, which is spontaneous.	(2) The redox reaction is non-spontaneous and takes place only when electric energy is supplied
(3) To set up this cell, a salt bridge or porous pot is used.	(3) No salt bridge is used in this case.

Q31. What is understood by a Normal Hydrogen Electrode? Give its significance.

Ans. It is used as a reference electrode. Its electrode potential is taken as 0.000 volt. Hydrogen electrode consists of platinum wire coated with finely divided platinum black containing pure hydrogen gas at 1 atm and a solution of HCl (1M) so as to maintain the equilibrium between H^+ ions and $H_2(g)$.

Significance: It is used in the measurement of electrode potential of different metals/metal ions.

Q32. Write the chemical equation for all the steps involved in the rusting of iron. Give any one method to prevent rusting of iron. [*CBSE* 2008]

Ans. At anode:

$$2Fe(s) \longrightarrow 2Fe^{2+} + 4e^-$$

$$(E^{\circ}_{Fe^{2+}/Fe} = -0.44\ V)$$

Cathode:

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

$$E^{\circ}_{H^+/O_2/H_2O} = 1.23\ V$$

The overall reaction being:

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

$$E^{\ominus}_{cell} = 1.67\ V$$

The ferrous ions are further oxidised by oxygen the atmospheric oxygen into ferric ions which came out as rust in the form of hydrated ferric oxide. ($Fe_2O_3 . xH_2O$) One method used to prevent rusting of iron is *by Barrier protection method*.

Q33. What is a salt bridge? What is it used for?

Ans. A salt bridge is a U-shaped tube containing concentrated solution of an inert electrolyte like KCl, KNO_3, K_2SO_4, etc. or a solidified solution of an electrolyte such as agar-agar and gelatine

It is used: (*i*) To complete the electrical circuit by allowing ions to flow from one solution to the other without mixing the two solutions.

(*ii*)To maintain the electrical neutrality of the solutions in the two half cells.

Q34. What is an electrochemical series? How does it help in calculating the e.m.f. of a standard cell?

Ans. The series of elements which have been arranged on the basis of their electrode potential is called electrochemical series or activity series.

Standard EMF of the cell = [Standard reduction potential of the right hand side electrode] – [Standard reduction potential of the left hand side electrode]

$$E^0_{cathode} - E^0_{anode}$$

Q35. How Nernst equation can be applied in the calculation of equilibrium constant of any cell reaction?

Ans. $$E^0_{cell} = \frac{0.0591}{n}\log K_c \text{ at 298 K}$$

Thus knowing the standard EMF of the cell, equilibrium constant K_c can be calculated.

Q36. Why λ^0_m for CH_3COOH cannot be determined experimentally?

Ans. Molar conductivity of weak electrolytes keeps on increasing with dilution and does not become constant even at very large dilution.

Q37. Which will have greater molar conductivity and why?

Sol. (A) 1 mol KCl dissolved in 200 cc of the solution.

Sol. (B) 1 mol KCl dissolved in 500 cc of the solution.

Ans. Sol. B will have greater molar conductivity because

$$\lambda_m = k \times V$$

with dilution k decreases but V increases, so that product will increase more.

Q38. What is cell constant? How is it determined?

Ans. It is the ratio of the distance between electrodes (l) to the cross-sectional area between the electrodes.

$$\text{Cell constant} = \frac{l}{A} \text{ in cm}^{-1} \text{ or m}^{-1}$$

or Conductivity (κ) = Conductance (G) × Cell constant (G*)

Cell constant of any particular cell can be found by measuring the conductance of a solution whose conductivity is known.

Q39. Derive an expression for the pH of electrolyte in the following half cell. Pt, H_2(1 atm)|$H^+(aq)$. The reduction potential is –0.30 V.

Ans. $$E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{0.0591}{2}\log\frac{1}{[H^+]^2}$$

$$-0.30\text{ V} = 0 - \frac{0.0591}{2}\log\frac{1}{[H^+]^2}$$

$$\log\frac{1}{[H^+]^2} = \frac{0.60}{0.0591} = 10$$

$$\log\frac{1}{[H^+]^2} = \log 10^{10} \Rightarrow \frac{1}{[H^+]^2}$$

$$= 10^{10} = [H^+] = 10^{-5}\text{ mol}^{-1}$$

$$pH = -\log [H^+] = -\log 10^{-5}$$

$$= (5 \times \log 10) = 5$$

Q40. Molar conductance of 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. What would be the specific conductance of this solution?

[*AI* 2014]

Ans. $$\lambda_m = \frac{1000\kappa}{M} = \kappa = \frac{\lambda_m \times M}{1000}$$

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

$$\kappa = 0.20835\text{ S cm}^{-1}$$

$$= 2.0835 \times 10^{-1}\text{ S cm}^{-1}$$

Q41. Explain Kohlrausch's law of independent migration of ions. Mention one application of Kohlrausch's law.

Ans. It states that at infinite dilution molar conductivity of an electrolyte is equal to the sum of contributions due to cation as well as anion.

$$\lambda^\infty_m (Na_2SO_4) = 2\lambda^\infty_m (Na^+) + \lambda^\infty_m (SO_4^{2-})$$

Application: It helps in calculating the λ^∞_m of weak electrolytes.

E.g., $\lambda^\infty_m (NaCl) = \lambda^\infty_m (Na^+) + \lambda^\infty_m (Cl^-)$ ...(1)

$$\lambda^\infty_m (CH_3COONa) = \lambda^\infty_m (CH_3COO^-) + \lambda\ (Na^+) \quad ...(2)$$

$$\lambda_m^\infty(\mathrm{HCl}) = \lambda_m^\infty(\mathrm{H^+}) + \lambda_m^\infty(\mathrm{Cl^-}) \quad ...(3)$$

$\lambda_m^\infty(CH_3COOH)$ can be determined by adding equations (2) and (3) and substracting (1).

Q42. The measured resistance of a conductance cell containing 7.5×10^{-3}M solution of KCl at 25°C was 1005 ohms. Calculate (*a*) specific conductance, (*b*) molar conductance of the solution cell constant = $1.25\ \mathrm{cm^{-1}}$.

Ans. $M = 7.5 \times 10^{-3}$, R = 1005 ohms

(*a*) Specific conductance

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

where $\frac{l}{A}$ is a cell constant

$$\kappa = \frac{1}{1005\ \text{ohm}} \times 1.25\ \mathrm{cm^{-1}}$$
$$= 1.2437 \times 10^{-3}\ \mathrm{ohm^{-1}\ cm^{-1}}$$
$$= 1.2437 \times 10^{-3}\ \mathrm{S\ cm^{-1}}$$

$$(b)\ \lambda_m = \frac{1000 \times \kappa}{M}$$
$$= \frac{1000 \times 1.2437 \times 10^{-3}}{7.5 \times 10^{-3}}$$
$$= \frac{1243.7}{7.5}$$
$$= 165.826\ \mathrm{S\ cm^2\ mol^{-1}}$$
$$\therefore\ \lambda_m = 165.826\ \mathrm{S\ cm^2\ mol^{-1}}$$

Q43. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The free energy change for the decomposition reaction

$$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2 \text{ is}$$

$\Delta G = +\ 960$ kJ

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

Ans. $\Delta G^\circ = +\ 960\ \text{kJ} = 960 \times 10^3 J$

$E^\circ = ?$

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

$$\frac{4}{3}Al^{3+} + 4e^- = \frac{4}{3}Al$$

$$\Delta G^\circ = -\ nE^\circ F$$
$$960 \times 10^3 J = -4 \times E^\circ \times 96500$$
$$E^\circ_{cell} = \frac{-960 \times 10^3}{4 \times 96500}$$
$$E^\circ_{cell} = \frac{-9600}{3860} = -\ 2.48\ V$$

Q44. Following reactions occur at cathode during the electrolysis of aqueous silver chloride, solution:

$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad E^\ominus = +0.80\ V$$

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g) \qquad E^\ominus = +0.00\ V$$

On the basis of their standard reduction electrode potential ($E^\ominus$) value, which reaction is feasible at the cathode and why? [*CBSE* 2015]

Ans. Since $E^\ominus_{Ag+/Ag}$ is positive that means Ag^+ is undergoing reduction therefore the reaction at cathode:

$Ag^+ + e^- \longrightarrow Ag(\downarrow)$ is feasible.

Q45. Define limiting molar conducting. Why conducting of an electrolyte solution decreases with decrease in concentration. [*CBSE* 2015]

Ans. Conductivity of solution of infinite dilution is known as limiting molar conductivity.

As the dilution increases or concentration decreases the number of ions per unit volume decreases. So, the conductance decreases.

Q46. Calculate emf of the following cell of 25°C:

$Fe|Fe^{2+}$ (0.001M) || H^+ (0.01M) | $H_2(g)$(1 bar)pt

$E^\circ_{(Fe^{2+}/Fe)} = -0.44V$

$E^\circ_{(H^+/H_2)} = 0.00V$ (*CBSE* 2015)

Ans. Cell Reaction

$$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$$
$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= 0.00 - (0.44)$$

$$E_{cell} = 0.44 - \frac{0.0591}{2} 10\text{ g } \frac{[10^{-3}]}{[10^{-2}]^2}$$

$$= 0.44 - \frac{0.0591}{2} 10\text{ g } 10$$

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

$$E_{cell} = 0.4105\text{ V}$$

Q47. (*a*) Calculate E°_{cell} for the following reaction at 298 K:

$$2Cr(s) + 3Fe^{2+}\ (0.01M) \longrightarrow 2Cr^{3+}(0.01M) + 3Fe(s)$$

When: $E_{cell} = 0.261$ V

(*b*) Using the $E^\ominus$ values of A and B, predict which one is better for coating the surface of iron $[E^\circ_{(Fe^{2+}/Fe)} = -0.44V]$ to prevent corrosion and why?

When : $E^\ominus_{(A^{2+}/A)} = -2.37$ V

$E^\ominus_{(B^{2+}/B)} = -0.14$ V

[*CBSE* 2016]

Ans. (*a*) $E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[\text{product}]}{[\text{reaction}]}$

$$E^\circ_{cell} = E_{cell} - \frac{0.0591}{6}\log\frac{[0.01]^2}{[0.01]^3}$$

$$= 0.261 + 0.009\ \log\frac{10^{-4}}{10^{-6}}$$

$$= 0.261 + 0.009\ \log 10^2$$

$$= 0.261 + 0.009 \times 2$$

$$= 0.2806\text{ V}$$

(*b*) When

$[E^\circ_{Fe^{2+}/Fe}] = -0.44$ V

$E^\circ_{(A^{2+}/A)} = -2.37$ V

$E^\circ_{(B^{2+}/B)} = -0.14$ V

∴ 'A' will prevent iron from corrosion, so we can coat the iron metal by element 'A' because it is having more negative value of reduction potential than iron.

Q48. (*a*) The conductivity of 0.001 mol/L solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α). When $\lambda^o(H^+) = 349.6$ s cm^2 mol^{-1} and $\lambda^o(CH_3COO^-) = 40.9$ s cm^2 mol^{-1}

(*b*) Define electrochemical cell. What happens it external potential applied becomes greater than E°_{cell} of electrochemical cell.

Ans. (*a*) Given, molarity (M) = 0.001 mol/L

Conductivity $= 3.905 \times 10^{-5}$ s cm^{-1}

$\lambda^o(H^+) = 349.65$ cm^2 mol^{-1}

$\lambda^o(CH_3COO^-) = 40.95$ cm^2 mol

Molar conductivity

$$(\lambda_m) = \text{Conductivity} \times \frac{1000}{M}$$

$$= 3.905 \times 10^{-5} \times \frac{1000}{0.001}$$

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

$$\alpha = \frac{\lambda_m}{\lambda_m^o} \quad [\lambda^o_{CH_3COOH} = \lambda^o_{H^+} + \lambda^o_{CH_3COO^-}$$

$$= 349.65 + 40.9 = 390.5]$$

$$= \frac{39.05}{390.5} = 0.1 = 10\%$$

(*b*) **Electrochemical cell:** Cell which convert chemical energy into electrical energy, if E°_{cell} (External) > E°_{cell}.

(*i*) Electron flow is from cathode to anode and current will flow from anode to cathode.

III. *Long Answer Type Questions*

(*5 Marks*)

Q1. (*a*) Explain why electrolysis of an aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode.

Given: $E^0_{Na^+/Na}$ 2.71 V,

$E^0_{H_2O/H_2} = -0.83$ V

$E^0_{Cl_2/2Cl^-} = +1.36$ V,

$E^\circ_{H^+/\frac{1}{2}O_2/H_2O} = +1.23$ V

(*b*) The resistance of a conductivity cell when filled with 0.05 M solution of an electrolyte X is 100 ohms at 40°C. The same conductivity cell filled with 0.01 M solution of an electrolyte Y has a resistance of 50 ohms. The conductivity of 0.05 M solution of electrolyte X is 1.0×10^{-4} S cm^{-1}. Calculate

(*i*) Cell constant

(*ii*) Conductivity of 0.01M Y solution

(*iii*) Molar conductivity of 0.01M Y solution. [*AI* 2008]

Ans. (*a*) Following reaction takes place at cathode:

$$Na^+(aq) + e^- \longrightarrow Na(s) \qquad E^0 = -2.71 \text{ V}$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E^0 = -0.83 \text{ V}$$

Because second reaction has higher value of E^0, therefore H_2 is liberated at cathode.

Following reaction takes place at:

Anode:

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^- \qquad E^0 = 1.36 \text{ V}$$

Cathode:

$$H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+ + 2e^- \qquad E^0 = 1.23 \text{ V}$$

Because first reaction has higher value of E^0, therefore Cl_2 is liberated at anode.

(*b*) **For an electrolyte X**

Molarity = 0.05 M

Resistance = 100 Ω

Conductivity = 1.0×10^{-4} S cm^{-1}

For an electrolyte Y

Molarity = 0.01 M

Resistance = 50 Ω

Conductivity = ?

(*i*) Cell constant = Conductivity (κ) × resistance (R)

$$G^* = 1.0 \times 10^{-4} \times 100 = 10^{-2} \text{ cm}^{-1}$$

(*ii*) Conductivity of solution Y is

$$\kappa = \frac{G^*}{R} = \frac{10^{-2}}{50} = 0.02 \times 10^{-2} = 2 \times 10^{-4} \text{ S cm}^{-1}$$

Concentration, C = 0.01 M

$$= 0.01 \text{ mol L}^{-1}$$
$$= 0.01 \times 1000 \text{ mol ml}^{-3}$$
$$= 10 \text{ mol cm}^{-3}$$

(*iii*) Molar concentration

$$\lambda_m = \frac{\kappa}{C} = \frac{2 \times 10^{-4}}{10} = 0.2 \times 10^{-4} \text{ S cm}^2 \text{ mol}^{-1}$$

Q2. (*a*) State Kohlrausch's law of independent migration of ions. How can the degree of dissociation of acetic acid in a solution be calculated from its molar conductivity data?

(*b*) (*i*) Formulate an electrochemical cell representing the reaction:

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

(*ii*) Calculate E^0_{cell},

(*iii*) Calculate E_{cell} at 25°C if

$[Cr^{3+}] = 0.1$ M

$[Fe^{2+}] = 0.01$ M

Given $E^0_{Cr^{3+}/Cr} = -0.74$ V

$E^0_{Fe^{2+}/Fe} = -0.44$ V [*CBSE* 2008]

Ans. (*a*) **Kohlrausch law of independent migration of ions:** It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contribution of the anion and cation of the electrolyte. If $\lambda^0_{Na^+}$ and $\lambda^0_{Cl^-}$ are limiting molar conductivity for sodium chloride is given by:

$$\lambda^\circ_m \text{ (NaCl)} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$$

Calculation of degree of dissociation of a weak electrolyte like acetic acid. The α is given by:

$$\alpha = \frac{\lambda_m}{\lambda^0_m}$$

where λ_m is the molar conductivity and λ°_m is the limiting molar conductivity.

(*b*) (*i*) The cell can be represented as:

$Cr(s)|Cr^{3+}(aq)||Fe^{+}(aq)|Fe(s)$

(*ii*)
$$E^0 = E^0_{cathode} - E^0_{anode}$$
$$= -0.44 - (-0.74)$$
$$= -0.44 + 0.74 = 0.30\ V$$

(*iii*)
$$E_{cell} = E^0_{cell} - \frac{0.059}{n}\log\frac{[Cr^{3+}(aq)]^2}{[Fe^{2+}(aq)]^3}$$
$$= 0.30 - \frac{0.059}{6}\log\frac{(0.1)^2}{(0.01)^3}$$
$$= 0.30 - 0.009\log\frac{0.01}{0.0000001}$$
$$= 0.30 - 0.009\log 10^4$$
$$= 0.30 - 0.009 \times 4\log 10$$
$$= 0.30 - 0.036\ [\therefore \log 10 = 1]$$
$$= 0.264\ V$$

Q3. (*a*) What type of a cell is the lead storage battery? Write the anode and cathode reactions and the overall reaction occurring in a lead storage battery while it is operating.

(*b*) A voltaic cell is set up at 25°C with two half cells, $Al|Al^{3+}$ (0.001M) and $Ni|Ni^{+}$(0.50 M). Write the equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

Given: $E^0_{Ni^{2+}/Ni} = -0.25\ V$
$E^0_{Al^{3+}/Al} = -1.66\ V$

[*CBSE* 2009, 2012]

Ans. (*a*) The lead storage battery is the most important secondary cell. The cell reaction when the battery is in use are given below:

At anode:

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$$

At cathode:

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

The overall cell reaction is:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

(*b*) Half cell reactions are:

$$Al \longrightarrow Al^{3+} + 3e^- \quad \text{(At Anode)}$$
$$Ni^{2+} + 2e^- \longrightarrow Ni \quad \text{(At cathode)}$$

$$2Al + 3Ni^{2+} \longrightarrow 2Al^{3+} + 3Ni \quad \text{(Overall reaction)}$$

The cell may be represented as:

$Al|Al^{3+}||Ni^{2+}|Ni$

$$E^\circ_{cell} = E^\circ_{right} - E^\circ_{left}$$
$$= (-0.25) - (-1.66)$$
$$= -0.25 + 1.66$$
$$= 1.41\ V$$

Q4. (*a*) Define molar conductivity of a substance and describe how for weak and strong electrolytes, molar conductivity changes with concentration of the solute. How is such change explained?

(*b*) A volatic cell is set up at 25°C with the following half cells:

$Ag^{+}(0.001\ M)|Ag$ and

$Cu^{2+}(0.10\ M)|Cu$

What would be the voltage of this cell? ($E^\circ_{cell} = 0.46\ V$) [*CBSE* 2009, 2012]

Ans. (*a*) **Molar conductivity:** Molar conductivity of a solution is defined as the conductance of the solution which contains one mole of the electrolyte such that the entire solution is placed between the two electrodes kept one centimeter apart. It is denoted by λ_m.

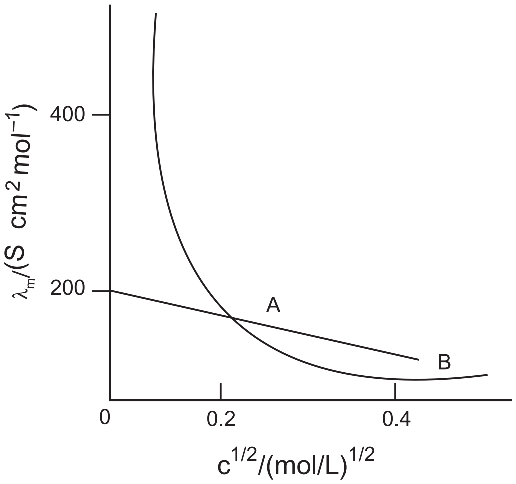
Molar conductivity,

$$\lambda_m = \frac{\kappa\,(\text{kappa})}{C}$$

Its unit is $S\ cm^2\ mol^{-1}$.

Weak electrolytes: When the concentration of a weak electrolyte becomes very low, its degree of ionisation rises sharply. There is a sharp increase in the number of ions in the solution.

Hence the molar conductivity of a weak electrolyte rises steeply at low concentration.



Strong electrolytes: The molar conductivity of a strong electrolyte decreases slightly with the increase in concentration.

(*b*) The reaction that takes place in cell is

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

Here $n = 2$

$$E^0_{cell} = 0.46\ V$$

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[Ag^+]^2}{[Cu^{2+}]}$$

$$= 0.46 - \frac{0.059}{2} \log \frac{[0.001]^2}{0.10}$$

$$= 0.46 - \frac{0.059}{2} \log 10^{-5}$$

$$= 0.46 - \frac{0.059}{2} \times (-5) \log 10$$

$$= 0.46 + 0.0295\ (-5)\ [\because \log 10 = 1]$$

$$= 0.608\ V$$

Q5. (*a*) Express the relationship amongst cell constant, resistance of the solution in the cell and conductivity of the solution?

(*b*) Calculate the equilibrium constant for the reaction:

$$Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$$

[*CBSE* 2009]

Given:

$E^0_{Cd^{2+}|Cd} = 0.40$ V,

$E^0_{Fe^{2+}|Fe} = -0.44$ V

Ans. (*a*) The relationship between cell constant of a cell (G*), resistance of the solution in the cell (R) and conductivity (κ) is given by:

$$\kappa = \frac{\text{Cell constant}}{R} = \frac{G^*}{R}$$

The relationship between molar conductivity (λ_m) and conductivity of the solution (κ) is given by:

$$\lambda_m = \frac{\kappa}{C}$$

where C is the concentration of the solution.

(*b*)

$$E^0_{cell} = E_{cathode} - E_{anode}$$

$$= -0.40 - (-0.44)$$

$$= -0.40 + 0.44 = 0.04\ V$$

Since

$$E^0_{cell} = \frac{0.059}{n} \log K_c$$

$$\log K_c = \frac{2 \times 0.04}{0.059} = 1.356$$

$$K_c = \text{antilog}\ (1.356)$$

$$= 22.70$$

Q6. (*a*) Calculate the emf of the cell $Mg(s) | Mg^{2+}(0.1M) || Cu^{2+}(1 \times 10^{-3}M) | Cu(s)$

Given:

$E^0_{Cu^{2+}/Cu} = +0.34$ V

$E^0_{Mg^{2+}/Mg} = -2.37$ V

(*b*) Explain with examples the terms weak and strong electrolytes. [*CBSE* 2007]

Ans. (*a*)

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

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

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

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$$

$$E^0_{cell} = [E^0_{Cu^{2+}/Cu} - E^0_{Mg^{2+}/Mg}]$$

$$E_{cell} = [+0.34\ V - (-2.37\ V)] - \frac{0.0591}{2} \log 10^2$$

$$= 2.71\ V - 0.0591\ V = 2.66\ V$$

(*b*) **Weak electrolytes:** Weak electrolytes are those which do not dissociate into ions completely in aqueous solution, *e.g.* CH_3COOH, NH_4OH.

Strong electrolytes: Strong electrolytes are those which dissociate into ions completely in aqueous solution or in melton state *e.g.*, NaCl, H_2SO_4, NaOH, etc.

Q7. (*a*) Write the formulation for the galvanic cell in which the reaction:

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

takes place.

Identify the cathode and the anode reactions in it.

(*b*) Write Nernst equation and calculate the emf of the following cell:

$Sn(s)|Sn^{2+}(0.04\ M)||\ H^+(0.02\ M)|H_2(g)|PE(s)$

(Given $E^{-}_{Sn^{2+}/Sn} = -\ 0.14\ V$)

[*Foreign* 2007]

Ans.

(*a*) $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$ [At anode]

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

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

'Cu' is acting as anode whereas 'Ag' is acting as cathode.

(*b*) $Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$

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

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\frac{[Sn^{2+}]}{[H^+]^2}$$

$$= [E^0_{H^+/H_2} - E^0_{Sn^{2+}/Sn}] - \frac{0.0591}{2}\log\frac{0.04}{(0.02)^2}$$

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

$$= 0.14\ V - 0.0591\ V = 0.0809\ V$$

Q8. (*a*) Explain with one example each the terms weak and strong electrolytes.

(*b*) Write the Nernst equation and calculate the emf of the following cell:

$Fe(s)|Fe^{2+}(0.001\ M)||H^+(1M)|H_2(g)|Pt(s)$ (1 bar)

($E^{2/3}_{Fe^{2+}/Fe} = -\ 0.44\ V$)

[*Foreign* 2007, *Delhi* 2013]

Ans. (*a*) **Weak electrolytes:** Those electrolytes which do not dissociate into ions completely in aqueous solution, *e.g.*, CH_3COOH, NH_4OH.

Strong electrolytes: Strong electrolytes are those which dissociate into ions completely in aqueous solution or in molten state, *e.g.*, NaCl, H_2SO_4, NaOH etc.

(*b*) $Fe(s)+2H^+(aq) \longrightarrow Fe^{2+}(aq)+H_2(g)$

$$E_{cell} = [E^0_{H^+/H_2} - E^0_{Fe^{2+}/Fe}] - \frac{0.0591}{2}\log\frac{[Fe^{2+}]}{[H^+]^2}$$

$$= [0 - (0.44)] - \frac{0.0591}{2}\log\frac{0.001}{1^2}$$

$$= +\ 0.44\ V + \frac{0.1773}{2}$$

$$= 0.44\ V + 0.0886\ V = 0.5286\ V$$

Q9. (*a*) Explain why electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode. Write the overall reaction.

($E^0_{Na^+/Na} = -2.71\ V$;

$E^0_{H_2O/H_2} = -\ 0.83\ V$)

$E^0_{Cl_2/2Cl^-} = +1.36\ V$;

$E^0_{H^+ + O_2/H_2O} = 1.23\ V$

(*b*) Calculate the emf of the cell $Zn|Zn^{2+}(0.1M)||Cd^{2+}(0.01M)|Cd$ at 298 K, [Given $E^0_{Zn^{2+}/Zn} = -\ 0.76\ V$; $E^0_{Cd^+/Cd} = -\ 0.40\ V$]

Ans. (*a*) $NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$

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

At cathode:

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

It is because reduction potential value of $E^0_{H^+/H_2}$ is more than that of $E^0_{Na^+/Na}$.

At anode:

$2Cl^-(aq) - 2e^- \longrightarrow Cl_2(g)$

It is because of over voltage, *i.e.* energy required to liberate O_2 is more than that for Cl_2.

Overall reaction:

$$2\ NaCl(aq) + 2H_2O(aq) \xrightarrow{Electrolysis} H_2(g) + Cl_2(g) + 2Na^+(aq) + 2OH^-(aq)$$

(*b*) $Zn|Zn^{2+}(0.1M)||Cd^{2+}(0.01M)|Cd$

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

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

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

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cd^{2+}]}$$

$$= [E^0_{Cd^{2+}/Cd} - E^0_{Zn^{2+}/Zn}] - \frac{0.0591}{2}\log\frac{0.1}{0.01}$$

$$= [-0.40\ V - (-0.76\ V)] - \frac{0.0591}{2}\log 10$$

$$= +0.36\ V - 0.0295\ V$$

$$= 0.3305\ V$$

Q10. (*a*) Account for the following

(*i*) Alkaline medium inhibits the rusting of iron.

(*ii*) Iron does not corrode even if zinc coating is broken in a galvanised iron pipe.

$Cu^{2+} + 2e^- \longrightarrow Cu;\ E^0 = +0.34\ V$

$Ag^{2+} + e^- \longrightarrow Ag;\ E^0 = +0.80\ V$

(*b*) (*i*) Construct the galvanic cell using the above data.

(*ii*) For what concentration of Ag^+ ions will emf of the cell be zero at 25°C if the concentration of Cu^{2+} is 0.01 M? [log 3.919 =0.593] [*CBSE* 2006]

Ans. (*a*) (*i*) H^+ ions are required for rusting to take place. Alkaline medium will react with H^+ ions, therefore it inhibits rusting.

(*ii*) Zinc acts as anode because it is more reactive.

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

Even if any Fe^{2+} ion is formed it will gain electrons and again changes into Fe and thus corrosion will be prevented.

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

(*b*) (*i*) $Cu(s)|Cu^{2+}(aq)\ ||Ag^+(aq)|Ag(s)$

(*ii*)
$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$

$$2Ag^+(aq) + 2e^- \longrightarrow Ag(s)$$

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

$$E_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{2+}/Cu}$$

$$= +\ 0.80\ V - 0.34\ V$$

$$E_{cell} = 0.46\ V$$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$= 0.46V - \frac{0.0591}{2}\log\frac{0.01}{[Ag^+]^2}$$

$$\log\frac{0.01}{[Ag^+]^2} = \frac{0.46V \times 2}{0.0591} = \frac{0.92}{0.0591}$$

$$= 15.567$$

$$\Rightarrow \quad \frac{0.01}{[Ag^+]^2} = \text{Antilog } (15.54)$$

$$= 3.690 \times 10^{15}$$

$$[Ag^+]^2 = \frac{0.01}{3.688 \times 10^{15}}$$

$$= 0.271 \times 10^{-17}$$

$$= 2.71 \times 10^{-18}$$

$$[Ag^+] = 1.65 \times 10^{-9}\ mol\ L^{-1}$$

Q11. (*a*) State two advantages of $H_2 - O_2$ fuel cell over ordinary cell.

(*b*) Silver is electrodeposited on a metallic vessel of total surface area 900 cm^2 by passing a current of 0.5 amp for two hours.

Calculate the thickness of silver metal deposited.

[Given: Density of silver = 10.5 g cm^{-3}

Atomic mass of silver = 108 *u*

1F = 96500 C mol^{-1}.]

[*AI* 2006]

Ans. (*a*) (*i*) It is highly efficient and do not produce pollution.

(*ii*) The H_2O so produced can be used by astronauts for drinking purpose.

(*b*)
$$m = Z \times I \times t$$

$$m = \frac{108}{96500} \times 0.5 \times 2 \times 60 \times 60$$

$$= \frac{108 \times 5}{965 \times 10} \times 2 \times 6 \times 6$$

$$= 4.03\ g$$

$$4.03\ g = V \times d$$

$$4.03\ g = V \times 10.5\ g\ cm^{-3}$$

$$V = \text{Area} \times \text{thickness}$$

$$V = \frac{4.03}{10.5}$$

$$\frac{4.03}{10.5} = 900\ \text{cm}^2 \times \text{thickness}$$

$$\text{Thickness} = \frac{0.338\ \text{cm}^3}{900\ \text{cm}^2}$$

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

Q12. (*a*) Give reasons for the following:

(*i*) Rusting of iron is quicker in saline water than in ordinary water.

(*ii*) Aluminium metal cannot be produced by the electrolysis of aqueous solution of aluminium salt.

(*b*) Resistance of a conductivity cell filled with 0.1 M KCl solution is 100 ohms. If the resistance of the same cell when filled with 0.02 M KCl solution is 520 ohms, calculate the conductivity and molar conductivity of 0.02 M KCl solution. Conductivity of 0.01 M KCl solution is 1.29 S m^{-1} [*AI CBSE* 2006]

Ans. (*a*) (*i*) It is because in saline water, there are more H^+ ions. Greater the number of H^+ ions, quicker the rusting will take place.

(*ii*) It is because aluminium metal is more reactive than hydrogen and it will react with H_2O.

(*b*) Cell constant = Conductivity(κ) × Resistance (R)

$$= 1.29\ \text{S m}^{-1} \times 100\ \Omega$$
$$= 129\ \text{m}^{-1} = 1.29\ \text{cm}^{-1}$$

$$\lambda_m = \frac{100\ \kappa}{M}$$

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

$$\kappa = \frac{1}{520\ \Omega} \times 1.29\ \text{cm}^{-1},\ \text{where}$$

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

$$\therefore \quad \kappa = 2.48 \times 10^{-3}\ \text{S cm}^{-1}$$

$$\lambda_m = \frac{100 \times 0.248 \times 10^{-2}}{0.02}$$

$$= 124\ \text{S cm}^2\ \text{mol}^{-1}$$

Q13. (*a*) (*i*) Represent the galvanic cell in which the following reaction:

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

takes place.

(*ii*) Which electrode is negatively charged?

(*iii*) Write reactions taking place at each electrode.

(*b*) Calculate the number of coloumbs required for the oxidation of 1 mole of water to produce oxygen as per equation:

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

(Given 1F = 96,500 C mol^{-1})

[*Foreign* 2006]

Ans. (*a*) (*i*) $Zn(s)|Zn^{2+}(aq)||Ag^+(aq)|Ag(s)$

(*ii*) Anode is the negatively charged electrode

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

At cathode:

$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$

(*b*) $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$

2 moles of H_2O require 4 × 96500 C of electricity

∴ 1 mole of H_2O will require

$$= \frac{4 \times 96500}{2}$$

= 193000 Coloumbs of electricity

Q14. (*a*) Write the reactions taking place at cathode and anode when the Lead-acid storage battery is in use.

(*b*) Consider a cell composed of two half cells.

$Cu(s)|Cu^{2+}(aq)$ and $Ag(s)|Ag^+(aq)]$

Calculate:

(*i*) The standard potential

(*ii*) The cell potential at 298 K when Cu^{2+} is 2 M and Ag^+ is 0.05 M

$E^0_{Cu^{2+}/Cu} = +0.34$ V,

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

R = 8.314 J K^{-1} mol^{-1}

[*Foreign* 2006]

Ans. (*a*) **At anode:**

$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-$

At cathode:

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

(*b*) (*i*) $E^0_{cell} = E^0_{Ag^+/Ag} - E^0_{Cu^{2+}/Cu}$

$= +0.80\ V - 0.34\ V$

$= 0.46\ V$

(*ii*) $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$

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

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$= +0.46\ V - \frac{0.0591}{2} \log \frac{2}{(0.05)^2}$$

$$= +0.46\ V - \frac{0.0591}{2} \log \frac{2 \times 100 \times 100}{5 \times 5}$$

$$= +0.46\ V - \frac{0.0591}{2} \log 800$$

$$= +0.46\ V - \frac{0.0591}{2}\ 2.9031$$

$$= +0.46\ V - 0.0857$$

$$= 0.3743\ V$$

Q15. (*a*) Define the terms: specific conductance and molar conductivity for a solution consisting of an electrolyte.

(*b*) Write the cell formulation and calculate the standard cell potential of the galvanic cell in operation which the following reaction takes place.

$2Cr(s) + 3Cd^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cd(s)$

Calculate Δ_rG^0 for the above reaction. (Given $E^0_{Cr^{3+}/Cr} = -0.74\ V$), $E^0_{Cd^{2+}/Cd} = -0.40\ V$, 1F = 96500C mol^{-1})

[*AI* 2006 *C*]

Ans. (*a*) **Specific conductance:** It is defined as the conductance of an electrolyte when the electrodes are 1 cm apart and have an area of cross-section of 1 cm^2.

Molar conductivity: It is defined as the conductance of all the ions produced from 1 mole of the electrolyte when electrodes are unit distance apart and have sufficient area of cross-section to hold the electrolyte.

(*b*) $Cr(s)|Cr^{3+}(1M)||Cd^{2+}(1M)|Cd(s)$

$E^0_{cell} = E^0_{Cd^{2+}/Cd} - E^0_{Cr^{3+}/Cr}$

$= -0.40\ V - (-0.74\ V)$

$= +0.34\ V$

Q16. (*a*) Explain with an example how weak and strong electrolytes can be distinguished.

(*b*) In the button cell used in watches the following reactions occurs:

$Zn(s) + Ag_2O(s) + H_2O(l) \longrightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

Determine E^0 for the cell and Δ_rG^0 for the reaction.

(Given: $Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$; $E^0 = -0.76\ V$

$Ag_2O(s) + 2H_2O(l) + 2e^- \longrightarrow 2Ag(s) + 2OH^-(aq)$

$E^0 = +0.80\ V$

1F = 96500 C mol^{-1})

[*CBSE* 2006 *C*]

Ans. (*a*) **Strong electrolytes:** Those electrolytes which dissociate into ions completely into aqeous solution or in molten state are called strong electrolytes. For example:

KCl, NaOH, H_2SO_4, etc.

Weak electrolytes: Those electrolytes which do not dissociate into ions completely into aqueous solution are weak electrolytes. For example: CH_3COOH, NH_4Cl

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

$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$

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

$E^0_{cell} = (E^0_{SRP\ cathode} - E^0_{SRP\ anode})$

$= +0.80\ V - (-0.76\ V)$

$= +1.56\ V$

$\Delta_rG^0 = -nE^0F$

$= -2 \times 1.56\ V \times 96500$

$= -301080\ J\ mol^{-1}$

$= -301.080\ kJ\ mol^{-1}$

Q17. (*a*) State the products of electrolysis obtained on the cathode and the anode in the following cases:

(*i*) A dilute soluton of H_2SO_4 with platinum electrodes.

(*ii*) An aqueous solution of $AgNO_3$ with silver electrodes.

(*b*) Write the cell formulation and calculate the standard cell potential of the galvanic cell in which the following reaction takes place:

$Fe^{2+}(aq) + Ag^{+}(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$

Calculate Δ_rG^0 for the above reaction

[Given: $E^0_{Ag+/Ag} = +0.80$ V

$E^0_{Fe^{3+}/Fe^{2+}} = +0.77$ V

[1F = 96500 C mol^{-1}]

[*AI* 2006 *C*]

Ans. (*a*) (*i*) At cathode:

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

At anode:

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

$H_2(g)$ is evolved at cathode and $O_2(g)$ is evolved at anode.

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

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

(*b*)

$$\begin{aligned} E^0_{cell} &= E^0_{Ag^+/Ag} - E^0_{Fe^{3+}/Fe^{2+}} \\ &= +0.80\text{ V} - (+0.77\text{ V}) \\ &= +0.03\text{ V} \\ \Delta_rG^0 &= -nFE^0 \\ &= -2\times 0.03\text{ V}\times 96500 \\ &= -5790\text{ J mol}^{-1} \\ &= 5.79\text{ kJ mol}^{-1}. \end{aligned}$$

IV. Value-Based Questions

Q1. Shyam bought a dry cell which was very old. He puts it in the torch. The torch did not glow. He found that the cell was dead. Its potential was zero.

(*a*) Why did this happen?

(*b*) Write down the value associated with it.

Ans. (*a*) As the dry cell (zinc and graphite) contains ions, over a period of time it gets consumed. Hence it gets completely used up even on long standing.

(*b*) Be thrifty and buy only the required amount of things.

Q2. Raju and his father were going in a boat in the river. Raju's father was going to throw away the cell used in watches and hearing aids into the water. Raju prevented him from doing so.

(*a*) As a student of chemistry, why would you advise Raju's father not to throw the cell in the water body?

(*b*) What is the value associated with the above decision?

Ans. (*a*) The watch cells are made up of mercury. This mercury will pollute the water. Water contaminated with mercury leads to accumulation of mercury in the body of fishes and other aquatic life.

(*b*) It helps in keeping the environment safe from pollution due to mercury.

Q3. Manu went with his father to a shopkeeper who showed them two types of batteries, one with lead plates and the other with cadmium plates. The battery with cadmium plates was more expensive than the lead battery. Manu's father wanted to purchase lead battery as it was cheaper.

(*a*) As a student of chemistry, why would you suggest to Manu's father to buy the expensive cadmium plate battery? Give two reasons.

(*b*) What are the values associated with the above decision?

Ans. (*a*) Cadmium plate battery though expensive is not a strong pollutant like lead. Lead salts being insoluble in water if ingested into our system cannot be excreted out. However, Cd salts being water-soluble easily get excreted and hence do not get biomagnified in the body.

(*b*) Keeping the environment safe from pollution due to lead.

Q4. One can utilise the electrochemical principles in preserving fossil fuels. Explain.

Ans. Hydrogen provides an ideal alternate, as on combustion it forms only water. It is a renewable and non-polluting source of energy. We can use it in place of fossil fuels such as coil, petroleum etc.

Q5. Ram's father wants to buy a battery for his inverter. Why is it suggested to buy cadmium plates battery in place of lead storage batteries? Give reasons.

Ans. Lead has harmful effects on human being as well as on the environment. That is why it is wise to choose cadmium battery instead of lead storage battery.

V. HOTS Questions

Q1. The standard reduction potential for the half-cell having reaction.

$NO_3^-\ (aq) + 2H^+\ (aq) + e^- \longrightarrow NO_2(g) + H_2O$ is 0.78 volt.

Calculate the reduction potential in 8 M H^+ ions.

Ans. Applying the formula,

$$E_{red} = E^0_{red} + \frac{0.0591}{n} \log [H^+]^2$$

$$= 0.78 + \frac{0.0591}{2} \log 8^2$$

$$= 0.78 + 0.0591 \times 3 \times 0.3010$$

$$= 0.833 \text{ volt}$$

Q2. The emf of a cell corresponding to the reaction:

$Zn + 2H^+\ (aq) \longrightarrow Zn^{2+}\ (0.1\ M) + H_2(g)\ 1\ atm$

is 0.28 volt at 25° C. Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.

$E^0_{Zn^{2+}/Zn} = -\ 0.76$ volt and $E^0_{H^+/H_2} = 0$

Ans. $E^0_{cell} = 0.76$ volt $[\because E^\circ_{H^+/H_2} = 0V]$

Applying Nernst equation,

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log \frac{[Zn^{2+}][H_2]}{[H^+]^2}$$

$$0.28 = 0.76 - \frac{0.0591}{2} \log \frac{(0.1)\times 1}{[H^+]^2}$$

$$\log \frac{0.1}{[H^+]^2} = \frac{2\times 0.48}{0.0591}$$

$$\log 0.1 - \log [H^+]^2 = 16.2436$$

[Since, $-\log [H^+] = pH$]

$$2pH = 16.2436 - \log 0.1$$

$$pH = \frac{17.2436}{2} = 8.6218$$

Q3. Calculate the solubility product constant of AgI from the following values of standard electrode potentials.

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

$E^0_{AgI/Ag} = -\ 0.15$ volt at 25° C.

Ans. Solubility product of AgI = $[Ag^+]\ [I^-]$

Two half reactions for the cell are:

$$\text{At anode}: \underset{AgI}{Ag} \longrightarrow \underset{(Oxidation)}{Ag^+ + e^-}$$

$$\text{At cathode}: +e^- \longrightarrow \underset{(Reduction)}{Ag + I^-}$$

Cell reaction: $AgI \longrightarrow Ag^+ + I^-$

Applying Nernst equation,

$$E_{cell} = E^0_{cell} - \frac{0.0591}{1} \log \frac{[Ag^+][I^-]}{[AgI]}$$

At equilibrium, $E_{cell} = 0$ and $[AgI] = 1$

$$\text{So, } \log [Ag^+]\ [I^-] = \frac{E^0_{cell}}{0.0591}$$

$$E^0_{cell} = -\ 0.80 - 0.15$$

$$= -\ 0.95 \text{ volt}$$

$\therefore \log [Ag^+][I^-] = 16.101$

or $[Ag^+][I^-] = \text{Antilog } [16.101]$

$= 1.21$