Very Short Answer Questions

Very Short Answer Questions (PYQ)

Q.1.What is primary cell? Give an example.

[CBSE Delhi 2008]

Ans. A primary cell is one in which the redox reaction occurs only once and the cell becomes dead after some time and cannot be used again, e.g., dry cell.

Q.2. How much charge is required for the reduction of 1 mol of Zn^{2+} to Zn?

[*CBSE Patna 2015*]

Ans.

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

Quantity of charge required for the reduction of one mole of Zn^{2+} = 2F = 2 × 96500 C = 193000 C

Q.3. How much charge in Faradays is required for the reduction of 1 mol of Al^{3+} to Al?

[*CBSE Chennai 2015*]

Ans.

$$\mathrm{Al^{3+}} + 3e^- \rightarrow \mathrm{Al}$$

Quantity of charge required for reduction of 1 mol of Al^{3+} = 3F

= 3 × 96500 C = 289500 C

Q.4. What is meant by 'limiting molar conductivity'?

[*CBSE (AI) 2010*]

Ans. When concentration of an electrolyte approaches zero, the molar conductivity is known as limiting molar conductivity $(\wedge_m^o)$.

Very Short Answer Questions (OIQ)

Q.1. What is meant by cell constant?

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

Q.2. Define specific conductance or conductivity.

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

Q.3. How is the unit of molar conductivity arrived at?

Ans.

$$\Lambda_m = k \times V = \text{ohm}^{-1}\,\text{cm}^{-1} \times \text{cm}^3\,\text{mol}^{-1}$$

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

Q.4. Write the equation showing the relationship between equivalent or molar conductance and concentration of a strong electrolyte.

Ans. Debye-Huckel-Onsager equation, $\Lambda = \Lambda^o - b\sqrt{c}$ in which Λ is the molar conductance at concentration *c*and *b* is the constant, Λ° is the conductance at infinite dilution.

Q.5. Why on dilution the Λm of CH_3COOH increases drastically while that of CH_3COONa increases gradually?

[*NCERT Exemplar*]

Ans. In the case of CH_3COOH, which is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation.

$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$

Q.6. Write the mathematical expression for Kohlrausch's law.

Ans. $\Lambda_m^o = v_c\Lambda_c^o + v_a\Lambda_a^o$ where v_c and v_a are the number of cations and anions respectively in one formula unit of the compound.

Q.7. Why is alternating current used for measuring resistance of an electrolytic solution?

[*NCERT Exemplar*]

Ans. Alternating current is used to prevent electrolysis so that concentration of ions in the solution remains constant.

Q.8. Why electrolysis of NaBr and NaI gives Br_2 and I_2 respectively while that of NaF gives O_2 instead of F_2?

Ans. Br^- and I^- ions have higher oxidation potentials than water. Hence, they are more easily oxidised. But F^- ions have lower oxidation potential than H_2O. So, H_2O is easily oxidised to give O_2 gas.

Q.9. Why does an aqueous solution of NaCl on electrolysis give H_2 gas at the cathode and not sodium metal?

Ans. This is because of the fact that standard reduction potential of water is greater than that of sodium.

Q.10. What are the products of electrolysis of molten and aqueous sodium chloride?

Ans. (i) Na and Cl_2 (ii) H_2 and Cl_2.

Q.11. Consider a cell given below:

$Cu \mid Cu^{2+} \mid\mid Cl^- \mid Cl_2, Pt$

Write the reactions that occur at anode and cathode.

[*NCERT Exemplar*]

Ans. Anode: $Cu \rightarrow Cu^{2+} + 2e^-$

Cathode: $Cl_2 + 2e^- \rightarrow 2Cl^-$

Q.12. What is the necessity to use a salt bridge in a Galvanic cell?

Ans. To complete the inner circuit and to maintain the electrical neutrality of the electrolytic solutions of the half-cells we use a salt bridge in a Galvanic cell.

Q.13. What is the reference electrode in determining the standard electrode potential?

Ans. Normal hydrogen electrode (NHE).

Q.14.

What does the negative sign in the expression $E^{o}_{Zn^{2+}/Zn} = -\ 0.76\ V$ mean?

[*NCERT Exemplar*]

Ans. It means that Zn is more reactive than hydrogen. When zinc electrode will be connected to SHE, Zn will get oxidised and H^+ will get reduced.

Q.15. State the factors that influence the value of cell potential of the following cell:

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

Ans. Concentration of Mg 2+ and Ag+ ions in the solution and temperature.

Q.16. Define electrochemical series.

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

Q.17. What would happen if no salt bridge were used in an electrochemical cell (like Zn–Cu cell)?

Ans. The metal ions (Zn^{2+}) formed by the loss of electrons will accumulate in one electrode and the negative ions (SO_4^{2-}) will accumulate in the other. Thus, the solutions will develop charges and the current will stop flowing. Moreover, the inner circuit will not be completed.

Q.18. What flows in the internal circuit of a galvanic cell?

Ans. Ions.

Q.19. In operation of a galvanic cell, at one of the electrodes oxidation takes place. What is the name of this electrode and what is its polarity?

Ans. Anode is the electrode at which oxidation, *i.e.*, loss of electron takes place. It is –ve terminal.

Q.20. Why is it not possible to measure the single electrode potential?

Ans. Oxidation or reduction cannot take place alone. Moreover, electrode potential is a relative tendency and can be measured with respect to a reference electrode only.

Q.21.

What does the negative value of E^o_{cell} indicate?

Ans.

Negative E^o_{cell} value means $\Delta_r G^o$ will be +ve, and the cell will not work.

Q.22. Write Nernst equation for single electrode potential.

Ans.

For the electrode reaction $M^{n+} + \text{ne}^- \rightarrow M$

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303\ \text{RT}}{\text{nF}} \log \frac{[M]}{[M^{n+}]} = E^o_{M^{n+}/M} - \frac{2.303\ \text{RT}}{\text{nF}} \log \frac{1}{[M^{n+}]}$$

Q.23. Write Nernst equation for the general cell reaction

$\text{aA} + \text{bB} \xrightarrow{\text{ne}} \text{xX} + \text{yY}$.

Ans. If n moles of electrons are transferred, Nernst equation is

$$E_{\text{cell}} = E^0_{\text{Cell}} - \frac{\text{RT}}{\text{nF}} \ln \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

Q.24. How can the reduction potential of an electrode be increased?

Ans.

$$M^{n+} + \text{ne}^- \rightarrow M,$$
$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{\text{RT}}{\text{nF}} \ln \frac{1}{[M^{n+}]} = E^o_{M^{n+}/M} + \frac{\text{RT}}{\text{nF}} \ln [M^{n+}]$$

Thus, electrode potential can be increased by increasing the metal ion concentration.

Q.25. Write Nernst equation for the reaction

$2\text{Cr} + 3\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 3\text{Fe}$

Ans.

$$E_{\text{cell}} = E^o_{\text{cell}} - \frac{RT}{6F}\ln\frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3} \qquad (\because\ n = 6)$$

Q.26. Write the Nernst equation for the cell reaction in the Daniel cell. How will the E_{cell} be affected when concentration of Zn^{2+} ions is increased?

[*NCERT Exemplar*]

Ans. $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

$$E_{\text{cell}} = E^o_{\text{cell}} - \frac{0.059}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \quad E_{\text{cell}}$$

decreases when concentration of Zn^{2+} ions, $[Zn^{2+}]$ increases.

Q.27. Why does a galvanic cell become dead after some time?

Ans. As the reaction proceeds, concentration of ions in anodic half keeps on increasing while in the cathodic half it keeps on decreasing. Hence, their electrode potentials also keep on changing till ultimately they become equal and then e.m.f. of the cell becomes zero.

Q.28. What are secondary cells?

Ans. Secondary cells are those cells which are rechargeable, *i.e.*, the products can be changed back to reactants.

Q.29. Can E^o_{cell} or $\Delta_r G$ for cell reaction ever be equal to zero?

[NCERT Exemplar]

Ans. No.

Q.30. Why does a dry cell become dead after a long time even if it has not been used?

Ans. Even though not in use, a dry cell becomes dead after some time because the acidic NH_4Cl corrodes the zinc container.

Q.31. What is the role of $ZnCl_2$ in a dry cell?

Ans. $ZnCl_2$ combines with the NH_3 produced to form the complex salt $[Zn(NH_3)_2Cl_2]$ otherwise the pressure developed due to NH_3 would crack the seal of the cell.

Q.32. Unlike dry cell, the mercury cell has a constant cell potential throughout its useful life. Why?

[*NCERT Exemplar*]

Ans. Ions are not involved in the overall cell reaction of mercury cells.

Q.33. Write the name of the electrolyte used in (*i*) fuel cell (*ii*) mercury cell.

Ans. (i) Concentrated aqueous KOH solution.

(ii) Moist mercuric oxide (HgO) mixed with KOH.

Q.34. What is the overall electrochemical reaction taking place in rusting?

Ans.

$$2\mathrm{Fe}(s)+O_2(g)+4H^+(\mathrm{aq})\rightarrow 2\mathrm{Fe}^{2+}(\mathrm{aq})+2H_2O(I)$$

Q.35. Write the chemical formula of rust.

Ans. $Fe_2O_3 . xH_2O$

Q.36. What is galvanization?

Ans. The process of coating zinc over iron is called galvanization.

Q.37. What is cathodic protection?

Ans. A process in which a metal is connected with a more reactive metal which acts as anode and the metal to be protected acts as a cathode is known as cathodic protection.

Q.38. Which type of a metal can be used in cathodic protection of iron against rusting?

Ans. A metal which is more electropositive than iron such as Al, Zn, Mg can be used in cathodic protection of iron against rusting.

Q.39. Value of standard electrode potential for the oxidation of Cl^- ions is more positive than that of water, even then in the electrolysis of aqueous sodium chloride, why is Cl^- oxidised at anode instead of water?

[*NCERT Exemplar*]

Ans. On electrolysis of aqueous sodium chloride, oxidation of water at anode requires over potential hence Cl^- is oxidised instead of water.

Q.40. Depict the galvanic cell in which the cell reaction is $Cu + 2Ag^+ \rightarrow 2Ag + Cu^{2+}$.

[*NCERT Exemplar] [HOTS*]

Ans. Cu | Cu^{2+}(conc.) | | Ag^{+}(conc.) | Ag

Q.41. How will the pH of brine (aq. NaCl solution) be affected when it is electrolysed?

[*NCERT Exemplar] [HOTS*]

Ans. The pH of the solution will increase as NaOH is formed in the electrolytic cell.

Q.42. Three iron sheets have been coated separately with three metals *A*, *B* and *C* whose standard electrode potentials are given below.

Metal	***A***	***B***	***C***	**Iron**
***E*^{o}**	**– 0.46 V**	**– 0.66 V**	**– 0.20 V**	**– 0.44 V**

Identify in which case rusting will take place faster when coating is damaged.

[*HOTS*]

Ans. As iron (– 0.44 V) has lower standard reduction potential than C (– 0.20 V) only therefore when coating is broken, rusting will take place faster.

Short Answer Questions-I

Short Answer Questions-I (PIQ)

Q.1. Define the following terms:

[*CBSE (AI) 2014*]

Q. Molar conductivity (Λ_m)

Ans. Molar conductivity, Λ_m of a solution at a dilution *V* is defined as the conductance of all the ions produced from one gram mole of the electrolyte dissolved in *V* cm^3 of the solution when the electrodes are one centimetre apart and the area of the electrodes is so large that the whole of the solution is contained between them.

$$\Lambda_m = k \times V \quad \text{or} \quad \Lambda_m = \frac{k \times 1000}{\text{Molarity}}$$

Molarity where k is the conductivity and *V* is the volume of the solution containing 1 mole of the electrolyte.

Q. Secondary batteries

Ans. Secondary batteries are those batteries which can be recharged by passing electric current through them and hence can be used over again *e.g.*, lead storage battery.

Q.2. Express the relation among cell constant, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solution related to its conductivity?

[*CBSE Delhi 2011; (AI) 2012*]

Ans.

$$\text{Conductivity (k)} = \frac{1}{\text{Resistance } (R)} \times \text{Cell constant}$$

$$\text{Molar conductivity } (\Lambda_m) = \frac{\text{Conductivity } (k) \times 1000}{\text{Molarity } (M)}$$

Q.3. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution?

[*CBSE (AI) 2014*]

Ans. Kohlrausch law states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of cation and anion of the electrolyte.

In general, if an electrolyte on dissociation gives v_+ cations and v_- anions then its limiting molar conductivity is given by

$$\Lambda_m^o = \nu_+\lambda_+^o + \nu_-\lambda_-^o$$

where λ_+^o and λ_-^o are the limiting molar conductivities of cations and anions respectively.

Conductivity of a solution decreases with dilution. This is due to the fact that the number of ions per unit volume that carry the current in a solution decreases with dilution.

Q.4. Define the following terms:

[CBSE (AI) 2014]

Q. Fuel cell

Ans. A fuel cell is a device which converts the energy produced during the combustion of fuels like hydrogen, methanol, methane etc. directly into electrical energy. One of the most successful fuel cell is H_2—O_2 fuel cell.

Q. Limiting molar conductivity

$$(\mathbf{\Lambda}_m^o)$$

Ans. When concentration approaches zero, the molar conductivity is known as limiting molar conductivity. It is represented by $(\mathbf{\Lambda}_m^o)$

$$\Lambda_m^o = (\Lambda_m)_{\text{when } c\to 0}$$

Q.5. For the given cells:

Lead storage cell, Mercury cell, Fuel cell and Dry cell

Answer the following:

- **i. Which cell is used in hearing aids?**
- **ii. Which cell was used in Apollo space programme?**
- **iii. Which cell is used in automobiles and inverters?**

iv. **Which cell does not have long life?**

[*CBSE Delhi 2016; South 2016*]

Ans.

i. Mercury cell
ii. Fuel cell
iii. Lead storage cell
iv. Dry cell

Q.6. What is the effect of catalyst on:

[*CBSE Delhi 2017*]

Q. Gibbs energy (ΔG) and

Ans. No effect

Q. Activation Rnergy of a Reaction?

Ans. Decreases

Q.7. Write the name of the cell which is generally used in hearing aids. Write the reactions taking place at the anode and the cathode of this cell.

[*CBSE (AI) 2017*]

Ans.

Mercury cell

At *anode:* $\mathrm{Zn(Hg)} + 2\,\mathrm{OH}^- \rightarrow \mathrm{ZnO}(s) + H_2O + 2e^-$

At cathode: $\mathrm{HgO}(s) + H_2O + 2e^- \rightarrow \mathrm{Hg}(l) + 2\,\mathrm{OH}^-$

$$\mathrm{Zn(Hg)} + \mathrm{HgO}(s) \rightarrow \mathrm{ZnO}(s) + \mathrm{Hg}(l)$$

Q.8. Answer the following questions

[CBSE Delhi 2015]

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

$$\mathrm{Ag^+}\,(\mathrm{aq}) + e^- \rightarrow \mathrm{Ag}\,(s) \qquad E^\circ = +0.80\ V$$

$$H^+(\mathrm{aq}) + e^- \rightarrow \tfrac{1}{2}H_2(g) \qquad E^\circ = 0.00\ V$$

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

Ans. The reaction, $\mathrm{Ag^+}\,(\mathrm{aq}) + e^- \rightarrow \mathrm{Ag}\,(s)$ is feasible at cathode as cathodic reaction is one which has higher standard reduction electrode potential (E^o_{red}).

Q. Define limiting molar conductivity. Why conductivity of an electrolyte solution decreases with the decrease in concentration?

Ans. The value of molar conductivity when the concentration approaches zero is known as limiting molar conductivity. Conductivity of an electrolytic solution decreases with decrease in concentration as the number of ions per unit volume that carry the current in the solution decreases with decrease in concentration.

Q.9. Answer the following questions

[CBSE Panchkula 2015]

Q. Following reactions occur at cathode during the electrolysis of aqueous sodium chloride solution:

$$\mathrm{Na^+}\,(\mathrm{aq}) + e^- \rightarrow \mathrm{Na}\,(s) \qquad E^0 = -2.71\ V$$

$$H^+(\mathrm{aq}) + e^- \rightarrow \tfrac{1}{2}H_2(g) \qquad E^0 = +0.00\ V$$

On the basis of their standard reduction electrode potential (E^0) values, which reaction is feasible at the cathode and why?

Ans. The reaction $H^+(\mathrm{aq}) + e^- \rightarrow \tfrac{1}{2}H_2(g)$ is feasible at cathode as it has higher standard reduction potential than other reaction.

Q. Why does the cell potential of mercury cell remain constant throughout its life?

Ans. As the overall reaction does not involve any ion in the solution whose concentration changes during its life period.

Q.10. Calculate the time to deposit 1.27 g of copper at cathode when a current of 2 A was passed through the solution of $CuSO_4$

(Molar mass of Cu = 63.5 g mol^{-1}, 1 F = 96500 C mol^{-1})

[*CBSE Allahabad 2015*]

Ans.

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

63.5 g of copper is deposited by 2 × 96500 C.

$\therefore$ 1.27 g of copper will be deposited by $\frac{2\times96500\times1.27}{63.7}C = 3860\ C$

I = 2 A, Q = 3860 C

$$\therefore\quad t = \frac{Q}{I} = \frac{3860}{2} = 1930\ s$$

Q.11. Two half-reactions of an electrochemical cell are given below:

MnO_4^- (*aq*) + $8H^+$(*aq*) + 5*e*$^-$ → Mn^{2+}(*aq*) + $4H_2O$(*l*); *E*^{o} = +1.51 V

Sn^{2+} (*aq*) Sn*4*+(*aq*) + 2*e*$^-$, *E*^{o} = +1.51 V

Construct the redox equation from the standard potential of the cell and predict if the reaction is reactant favoured or product favoured.

[*CBSE (AI) 2009; Delhi 2011*]

Ans.

At anode: $[Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-] \times 5$

At cathode: $[MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)] \times 2$

Cell reaction:

$$2\,MnO_4^-(aq) + 5\,Sn^{2+}(aq) + 16H^+(aq) \rightarrow 2\,Mn^{2+}(aq) + 5\,Sn^{4+}(aq) + 8H_2O(l)$$

$$E^{o}_{cell} = E^{o}_{cathode} - E^{o}_{anode} = 1.51\ V - 0.15\ V$$

$$= 1.36\ V$$

As cell potential is positive therefore the reaction is product favoured.

Q.12. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 ampere for 20 minutes. What mass of nickel will be deposited at the cathode?

(Given: At. Mass of Ni = 58.7 g mol^{-1}, 1 F = 96500 C mol^{-1})

[*CBSE (F) 2014*]

Ans.

$$Q = I \times t = 5\ A \times 20 \times 60\ s = 6000\ C$$

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

$$2 \times 96500\ C\ \text{deposit Ni} = 58.7\ g$$

$$\therefore\quad 6000\ C\ \text{will deposit Ni} = \frac{58.7\ g\ \ mol^{-1}}{2 \times 96500\ C\ \ mol^{-1}} \times 6000\ C = 1.825\ g$$

Q.13.Determine the values of equilibrium constant (*K_C*) and $\Delta G°$ for the following reaction:

$Ni(s)+2Ag^{+}(aq) \rightarrow Ni^{2+}(aq)+2Ag(s), E° = 1.05V$

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

[*CBSE Delhi 2011*]

Ans.

$$Ni\ (s) + 2\ Ag^{+}\ (aq) \rightarrow Ni^{2+}\ (aq) + 2\ Ag\ (s);\ E^{\circ} = 1.05\ V$$

Here, $n = 2$

$$\log\ K_c = \frac{n}{0.059}\ E^0_{\text{cell}}$$

$$\log\ K_c = \frac{2}{0.059} \times 1.05 = 39.5932$$

$$K_c = \text{antilog } 39.5932 = 3.919 \times 10^{39}$$

$$K_c = 3.92 \times 10^{39}$$

$$\Delta G^0 = -n\,\text{FE}^0_{\text{cell}}$$

$$\Delta G^0 = -2 \times 96500 \times 1.05 = -202650\ \text{J}$$

$$\Delta G0 = -\mathbf{202.65\ kJ}$$

Q.14. The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution.

[*CBSE (AI) 2012*]

Ans.

$$\wedge_m = \frac{k \times 1000}{M}$$

$$k = \frac{\wedge_m \times M}{1000}$$

$$k = \frac{138.95\ S\ \ \text{cm}^2\ \text{mol}^{-1} \times 1.5\ \ \text{mol}\ \ L^{-1}}{1000\ \ \text{cm}^3\ \ L^{-1}}$$

$$= 0.208455\ \ \text{cm}^{-1}$$

Q.15. The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate its molar conductivity.

[*CBSE Delhi 2013*]

Ans.

$$\wedge_m = \frac{k \times 1000}{C} = \frac{0.025\ \ S\ \ \text{cm}^{-1} \times 1000\ \ \text{cm}^3\ \ L^{-1}}{0.2\ \ \text{mol}\ \ L^{-1}} = 125\ S\ \ \text{cm}^2\ \ \text{mol}^{-1}$$

Q.16. The standard electrode potential (E°) for Daniell cell is + 1.1 V. Calculate the $\triangle G°$ for the reaction

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

(1 F = 96500 C mol^{-1}).

[*CBSE (AI) 2013*]

Ans.

$$\Delta_r G^o = -\mathrm{nFE}^o_{(\,\mathrm{cell}\,)}$$

In the given equation, $n = 2$, F = 96500 C mol^{-1} and $E^o_{\mathrm{cell}} = 1.1V$

Therefore, $\Delta_r G^\circ = -\,2 \times 96500\ \mathrm{C\ mol^{-1}} \times 1.1\ \mathrm{V}$

$$= -\,212300\ \mathrm{J\ mol^{-1}} = \mathbf{-\,212.3\ kJ\ mol^{-1}}$$

Q.17. The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere.

[CBSE Delhi 2011]

Ans. According to electrochemical theory of rusting the impure iron surface behaves like small electrochemical cell in the presence of water containing dissolved oxygen or carbon dioxide. In this cell pure iron acts as anode and impure iron surface acts as cathode. Moisture having dissolved CO_2 or O_2 acts as an electrolyte. The reactions are given below.

At anode: $\mathrm{Fe} \longrightarrow \mathrm{Fe}^{2+} + 2e^-;\ E^o_{\mathrm{Fe^{2+}}/\mathrm{Fe}} = -\,0.44\ \mathrm{V}$

At cathode: $2\mathrm{H}^+ + \frac{1}{2}\mathrm{O}_2 + 2e^- \longrightarrow \mathrm{H}_2\mathrm{O};\ E^o_{H^+/O_2/H_2O} = 1.23\ \mathrm{V}$

Overall reaction: $\mathrm{Fe} + 2H^+ + \frac{1}{2}O_2 \rightarrow \mathrm{Fe}^{2+} + H_2O;\ E^o_{\mathrm{cell}} = 1.67\ V$

The Fe^{2+} ions are further oxidised by atmospheric oxygen to Fe^{3+} ions, which comes out in the form of hydrated ferric oxide (rust).

$$2Fe^{2+} + \frac{1}{2} O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + {}_xH_2O \rightarrow Fe_2O_3.\ xH_2O\ (Rust)$$

Q.18. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^2 mol^{-1}.

[*CBSE Delhi 2017*]

$$\text{Given } \lambda^o_{(H^+)} = 349.6\ S\ cm^2\ mol^{-1} \text{ and } \lambda^o_{(CH_3COO^-)} = 40.9\ S\ cm^2\ mol^{-1}$$

Ans.

$$\Lambda^o_{(CH_3COOH)} = \lambda^o_{(CH_3COO^-)} + \lambda^o_{(H^+)}$$

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

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

$$\alpha = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{39.05\ S\ cm^2\ mol^{-1}}{390.5\ S\ cm^2\ mol^{-1}} = 0.1 \qquad \alpha = 10\%$$

Short Answer Questions-I (OIQ)

Q.1. Write electrode reactions taking place in

i. **Ni–Cd cell,**
ii. **Lead Acid Accumulator.**

Ans.

i. $Cd(s) + 2OH^-(aq) \rightarrow Cd(OH)_2(s) + 2e^-$
$NiO_2(s) + 2H_2O + 2e^- \rightarrow Ni(OH)_2(s) + 2OH^-(aq)$

ii. $Pb \rightarrow Pb^{2+} + 2e^-$ (at anode)PbO_2 +
$SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$ (at cathode)

Q.2. Account for the following:

i. **Alkaline medium inhibits the rusting of iron.**
ii. **Iron does not rust even if the zinc coating is broken in a galvanized iron pipe.**

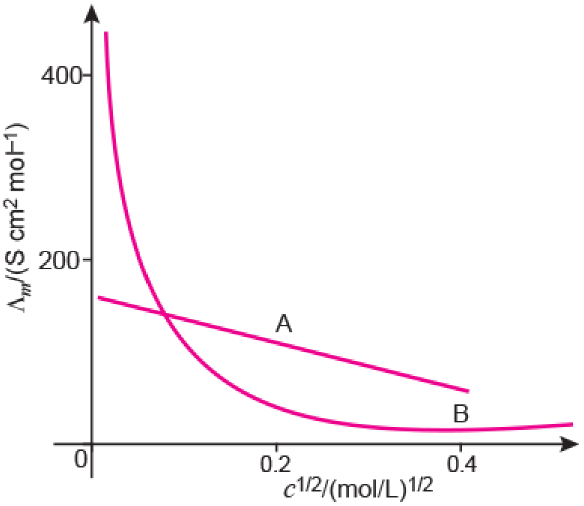
Ans. (i) The alkalinity of the solution prevents the availability of H+ ions.

(ii) Zinc has lower reduction potential than iron. Therefore, zinc coating acts as anode and the exposed iron portions act as cathode. If zinc coating is broken, zinc still undergoes oxidation, protecting iron from rusting. No attack occurs on iron till all the zinc is corroded.

Q.3. The following curve is obtained when molar conductivity (Λm) is plotted against the square root of concentration, $c^{1/2}$ for two electrolytes A and B.

i. **How do you account for the increase in the molar conductivity of the electrolyte A on dilution?**
ii. **As seen from the graph, the value of limiting molar conductivity ($\Lambda^0 m$) for electrolyte B cannot be obtained graphically. How can this value be obtained?**

[*CBSE Sample Paper 2016*]



Ans.

i. As seen from the graph, electrolyte ‘A’ is a strong electrolyte which is ionised almost completely in solutions. For strong electrolyte ‘A’, the number of ions does not increase appreciably on dilution and only mobility of ions increases due to decrease in interionic attraction. Therefore, molar conductivity increases a little as shown in graph by a straight line.
ii. Limiting molar conductivity ($\Lambda^o{}_m$) for weak electrolyte ‘B’ can be obtained by using Kohlrausch law of independent migration of ions which says that limiting molar conductivity of an electrolyte is equal to the sum of the individual contribution of the cation and anion of the electrolyte.

Q.4. Answer the following questions

Q. For a weak electrolyte, molar conductance in dilute solution increases sharply as its concentration in solution is decreased. Give reason.

Ans. Because with dilution, there is increase in degree of dissociation and consequently the number of ions in total volume of solution increases and hence molar conductivity increases sharply.

Q. Write overall cell reaction for lead storage battery when the battery is being charged.

Ans.

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

Q. 5. When a current of 0.75 A is passed through a $CuSO_4$ solution for 25 min, 0.369 g of copper is deposited at the cathode. Calculate the atomic mass of copper.

Ans.

$$W = Z \times I \times t$$

$$0.369 = \frac{M}{2 \times 96500} \times 0.75 \times 25 \times 60 \qquad (M = \text{molar mass of copper})$$

$$\mathbf{M = 63.3\ g/mol}$$

Q.6. At what pH of HCl solution will hydrogen gas electrode show electrode potential of –0.118 V? H_2 gas is passed at 298 K and 1 atm pressure.

Ans.

$$H^+ + e^- \rightarrow \tfrac{1}{2}H_2$$

Applying Nernst equation,

$$E_{H^+/\frac{1}{2}H_2} = E^o_{H^+/\frac{1}{2}H_2} - \frac{0.059}{n} \log \frac{1}{[H^+]}$$

$$-0.118 = 0 - \frac{0.059}{1} \log \frac{1}{[H^+]}$$

$$-0.118 = 0.059 \log [H^+] \text{ or } -0.118 = -0.059 \text{ pH}$$

$$\text{pH} = 2$$

Q.7. Calculate the electrode potential of copper electrode dipped in 0.1 M $CuSO_4$ solution at 298 K. Given that $E^o_{Cu^{2+}/Cu}$ = 0.34V.

Ans.

$$Cu^{2+} + 2e^- \rightarrow Cu; \quad n = 2$$

$$E_{Cu^{2+}/Cu} = E^o_{Cu^{2+}/Cu} - \frac{0.059}{n} \log \frac{1}{[Cu^{2+}]}$$

$$E_{Cu^{2+}/Cu} = 0.34 - \frac{0.059}{2} \log \frac{1}{0.1}$$

$$E_{Cu^{2+}/Cu} = 0.34 - 0.0295 = 0.3105V$$

Q.8. How many molecules of chlorine should be deposited from molten sodium chloride in one minute by a current of 300 milliampere?

Ans.

$$Q = I \times t$$

$$\text{Here, } I = \frac{300}{1000} = 0.3\ A;\ t = 60\ s;\ Q = 0.3\ A \times 60\ s = 18\ C$$

$$2 \times 96500\ C \text{ deposit } Cl_2 = 1 \text{ mol}$$

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$\therefore 18\ C \text{ will deposit } Cl_2 = \frac{1 mol \times 18\ C \times 6.022 \times 10^{23}}{2 \times 96500\ C} \text{ molecules mol}^{-1}$$

$$= 5.616 \times 10^{19} \text{ molecules}$$

Q.9. **A current of 5 ampere is flowing though a wire for 193 seconds. Calculate the number of electrons flowing through the cross section of wire for 193 seconds.**

[*HOTS*]

Ans. $Q = I \times t$ = 5 A × 193 s = 965 C

96500 C is equivalent to flow of 6.022 × 10^{23} electrons.

∴ 965 C will be equivalent to flow of electrons

$$= \frac{6.022 \times 10^{23}}{96500} \times 965 = \mathbf{6.022 \times 1021.}$$

Q.10. Calculate the equilibrium constant for the reaction

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

$$\textbf{If } E^o_{\mathrm{Cd}^{2+}/\mathrm{Cd}} = -0.403\ \mathrm{V};\ E^o_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.763\ \mathrm{V}$$

Ans.

$$\mathrm{E^o}_{\mathrm{cell}} = E^o_{\mathrm{Cd}^{2+}/\mathrm{Cd}} - E^o_{\mathrm{Zn}^{2+}/\mathrm{Zn}} = -0.403\ \mathrm{V} - (-0.763\ \mathrm{V}) = 0.360\ \mathrm{V},\ n = 2$$

$$\log K_c = \left(\frac{\mathrm{nE^o_{cell}}}{0.059}\right) = \left(\frac{2 \times 0.360}{0.059}\right) = \left(\frac{0.720}{0.059}\right) = 12.20$$

$$K_c = \text{antilog}\ (12.20) = \mathbf{1.585 \times 10^{12}}$$

Short Answer Questions-II

Short Answer Questions-II (PYQ)

Q.1.Answer the following questions

[CBSE (AI) 2017]

Q. The cell in which the following reaction occurs:

$$2\,\mathrm{Fe}^{3+}\,(\mathrm{aq}) + 2I^{-}\,(\mathrm{aq}) \rightarrow 2\,\mathrm{Fe}^{2+}\,(\mathrm{aq}) + I_2\,(s)$$

has $E^0_{\mathrm{cell}} = 0.236$ V at 298 K. Calculate the standard Gibbs energy of the cell reaction.

(Given : 1 F = 96,500 C mol^{-1})

Ans.

Given, n = 2, $E^0_{\mathrm{cell}} = 0.236$ V, F = 96,500 C mol^{-1}

$$\therefore \quad \Delta G^\circ = -\mathrm{nFE}^o_{\mathrm{cell}}$$

$$= -\,2 \times 96500\ \mathrm{C\ mol^{-1}} \times 0.236\ \mathrm{V} = -\,45548\ \mathrm{J\ mol^{-1}} = \mathbf{-\,45.548\ kJ\ mol^{-1}}$$

Q. How many electrons flow through a metallic wire if a current of 0.5A is passed for 2 hours?

(Given : 1 F = 96,500 C mol^{-1})

[*CBSE (AI) 2017*]

Ans. $Q = I \times t = 0.5\ \mathrm{A} \times 2 \times 60 \times 60\ \mathrm{s} = 3600\ \mathrm{C}$

Number of electrons flowing through the wire on passing a charge of 96500 C = 6.022×10^{23}

∴ Number of electrons flowing through the wire on passing a charge of 3600 C

$$= \frac{6.022 \times 10^{23} \times 3600\ C}{96500\ C} = 2.246 \times 10^{22}\ \text{electrons}$$

Q.2.

i. Write two advantages of $H_2 - O_2$ fuel cell over ordinary cell.

ii. Equilibrium constant (K_c) for the given cell reaction is 10. Calculate E^o_{cell}.

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

[*CBSE (F) 2014*]

Ans. (i) The two main advantages of H_2–O_2 fuel cell over ordinary cell are as follows:

- It has high efficiency of 60%–70%.
- It does not cause any pollution.

ii. $A(s) + B^{2+}(aq) \rightleftharpoons A^{2+}(aq) + B(s)$

Here, $n = 2$, $K_c = 10$

$$E^{0}{}_{\text{cell}} = \frac{0.059}{n} \times \log K_c$$

$$E^{0}{}_{\text{cell}} = \frac{0.059}{n} \times \log 10 = \times 1 = 0.0295\ \text{V}$$

Q.3. Conductivity of 2.5 × 10^{-4} M methanoic acid is 5.25 × 10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation.

Given: $\lambda^o(H^+) = 349.5$ S cm^2 mol^{-1} and $\lambda^o(HCOO^-) = 50.5$ S cm^2 mol^{-1}.

[*CBSE Allahabad 2015*]

Ans.

$$= \Lambda^c_m \frac{k \times 1000}{M}$$

$$\Lambda^c_m = \frac{5.25 \times 10^{-5}\ S\ cm^{-1} \times 1000\ cm^3\ L^{-1}}{2.5 \times 10^{-4}\ mol\ L^{-1}}$$

$$\Lambda^c_m = 210\ \text{S cm}^2\ \text{mol}^{-1}$$

$$\Lambda_m^c\ (\mathrm{HCOOH}) = \Lambda^o_{\mathrm{HCOO}^-} + \Lambda^o_{H^+}$$

$$= 50.5\ \mathrm{S\ cm^2\ mol^{-1}} + 349.5\ \mathrm{S\ cm^2\ mol^{-1}}$$

$$= 400\ \mathrm{S\ cm^2\ mol^{-1}}$$

Degree of dissociation, $\alpha = \frac{\Lambda_m^c}{\Lambda_m^o} = \frac{210\ S\ \mathrm{cm^2\ mol^{-1}}}{400\ S\ \mathrm{cm^2\ mol^{-1}}} = 0.525$

or $\alpha = \mathbf{52.5\%}$

Q.4. Answer the following questions

[CBSE (AI) 2014]

Calculate $\Delta_r G^\circ$ for the reaction

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

Given: $E^o_{\mathrm{cell}} = +2.71$ V, 1 F = 95600 C $\mathrm{mol^{-1}}$

Ans.

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

$$\Delta r\, G^\circ = -\, nFE^o_{\mathrm{cell}}$$

Here, $n = 2$, $F = 96500\ \mathrm{C\ mol^{-1}}$ and $E^o_{\mathrm{cell}} = 2.71$ V

$$\therefore \qquad \Delta r\, G^\circ = -\,2 \times 96500\ \mathrm{C\ mol^{-1}} \times 2.71\ \mathrm{V}$$

$$= -\,523030\ \mathrm{J\ mol^{-1}} = \mathbf{-\,523.03\ kJ\ mol^{-1}}$$

Q. Name the type of cell which was used in Apollo space programme for providing electrical power.

Ans. H_2—O_2 fuel cell

Q.5. Conductivity of 0.00241 M acetic acid solution is 7.896 × 10^{-5} S cm^{-1}. Calculate its molar conductivity in this solution. If Λ_m^o for acetic acid is 390.5 S cm^2 mol^{-1}, what would be its dissociation constant?

[*CBSE Delhi 2008*]

Ans.

$c = 0.00241\ M,\ k = 7.896 \times 10^{-5}\ S\ \text{cm}^{-1},\ \Lambda_m^o = 390.5\ S\ \text{cm}^2\ \text{mol}^{-1}$

$$\Lambda_m = \frac{k \times 1000}{c}$$

Substituting the values

$$\Lambda_m = \frac{7.896 \times 10^{-5} \times 1000}{0.002} = 32.76\ S\ \text{cm}^2\ \text{mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^o} = \frac{32.76}{390.5} = 0.084$$

α = 8.4%

$$\begin{array}{llll} \text{CH}_3\ \text{COOH} & \rightleftharpoons & \text{CH}_3\ \text{COO}^- & + \quad H^+ \\ c & & 0 & \quad 0 \\ c(1-\alpha) & & c\alpha & \quad c\alpha \end{array}$$

$$K_a = \frac{[\text{CH}_3 - \text{COO}^-]\ [H^+]}{[\text{CH}_3 - \text{COOH}]} = \frac{c\alpha\ .\ c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$K_a = \frac{0.0241\ (0.084)^2}{(1-0.084)} = 1.86\ \times\ 10^{-5}$$

Q.6.

alculate $\Delta r\ G^\circ$ and log K_c for the following reaction at 298 K:

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

Given: $E^\circ_{\text{cell}} = 0.30$ V

[*CBSE (F) 2016*]

Ans.

$$\begin{array}{lll}
\mathrm{Cr}\,(s) & \rightarrow & \mathrm{Cr}^{3+}\,(\mathrm{aq}) + 3e^{-}\,]\times 2 \\
\mathrm{Fe}^{2+}\,(\mathrm{aq}) + 2e^{-} & \rightarrow & \mathrm{Fe}\,(s) \qquad\qquad]\times 3 \\
\hline
\multicolumn{3}{l}{2\,\mathrm{Cr}\,(s) + 3\,\mathrm{Fe}^{2+}\,(\mathrm{aq}) \rightarrow 2\,\mathrm{Cr}^{3+}\,(\mathrm{aq}) + 3\,\mathrm{Fe}\,(s), \quad n = 6} \\
\hline
\end{array}$$

Here, $n = 6$, $E^{o}_{\text{cell}} = 0.30\ \text{V}$

Substituting the values in the expression, $\log K_c = \frac{n}{0.059}\ E^{o}_{\text{cell}}$, we get

$\log K_c = \frac{6}{0.059} \times 0.30$ or $\log K_c = 30.5084$

$K_c = \text{Antilog}\ (30.5084)$ or $K_c = 3.224 \times 10^{30}$

$\Delta G^{\circ} = -\ nFE^{o}_{\text{cell}}$

$= -\ 6 \times 96500 \times 0.30 = -\ 173700\ \text{J mol}^{-1}$

$\Delta G^{\circ} = \mathbf{-\ 173.7\ kJ\ mol^{-1}}$

Q.7. One half-cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. The other half-cell consists of a zinc electrode in a 0.10 M solution of $Zn(NO_3)_2$. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver ions in the solution.

$$\left(\textbf{Given: } = E^{o}_{\mathrm{Zn^{2+}}/\mathrm{Zn}}\ -0.763\ \text{V},\ E^{o}_{\mathrm{Ag^{+}}/\mathrm{Ag}} = +\,0.80\ \text{V}\right)$$

[*CBSE (F) 2010*]

Ans.

Electrochemical cell

$$Zn(s) \mid Zn^{2+}\ (0.10\ M) \mid\mid Ag^{+}\ (conc.) \mid Ag(s)$$

$$E^{o}_{cell} = E^{o}_{R} - E^{o}_{L} = E^{o}_{Ag^{+}/Ag} - E^{o}_{Zn^{2+}/Zn}$$

$$= 0.80\ V - (-\ 0.763)V = 1.563\ V$$

We know that,

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Ag^{+}]^{2}}$$

$$1.48 = 1.563 - \frac{0.0591}{2}\log\frac{[0.10]}{[Ag^{+}]^{2}}$$

$$\log = \frac{[0.10]}{[Ag^{+}]^{2}} = \frac{0.083}{0.02955}\ 2.8087$$

Or $$\frac{[0.10]}{[Ag^{+}]^{2}} = \text{antilog } 2.8087 = 643.7$$

$$[Ag^{+}]^{2} = \frac{0.10}{643.7} = 1.553 \times 10^{-4}$$

$$[Ag^{+}] = \mathbf{1.247 \times 10^{-2}\ M}$$

Q.8. A strip of nickel metal is placed in a 1-molar solution of $Ni(NO_3)_2$ and a strip of silver metal is placed in a 1-molar solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter.

- **i. Write the balanced equation for the overall reaction occurring in the cell and calculate the cell potential.**
- **ii. Calculate the cell potential, *E*, at 25°C for the cell if the initial concentration of $Ni(NO_3)_2$ is 0.100 molar and the initial concentration of $AgNO_3$ is 1.00 molar.**

$$\left[\, E^o_{\mathrm{Ni^{2+}}/\mathrm{Ni}} = -\,0.25\ \mathrm{V};\ E^o_{\mathrm{Ag^+}/\mathrm{Ag}} = 0.80\ \mathrm{V},\ \log 10^{-1} = -\,1 \right]$$

[CBSE (F) 2012]

Ans.

i. At anode: $\mathrm{Ni} \longrightarrow \mathrm{Ni^{2+}} + 2e^-$

At cathode: $[\mathrm{Ag^+} + e^- \longrightarrow \mathrm{Ag}] \times 2$

Cell reaction: $\mathrm{Ni} + 2\mathrm{Ag^+} \longrightarrow \mathrm{Ni^{2+}} + 2\mathrm{Ag}$

$E^o{}_{\text{cell}} = E^o{}_{\text{cathode}} - E^o{}_{\text{anode}}$

$= E^o_{\mathrm{Ag^+}/\mathrm{Ag}} - E^o_{\mathrm{Ni^{2+}}/\mathrm{Ni}} = 0.80\ \mathrm{V} - (-\,0.25\ \mathrm{V})$

$E^o{}_{\text{cell}} = \mathbf{1.05\ V}$

ii. $E_{\text{cell}} = E^o_{\text{cell}} - \frac{0.059}{n} \log \frac{/\,\mathrm{Ni^{2+}}\,/}{/\,\mathrm{Ag^+}\,/^2}$

Here, $n = 2$, $E^o{}_{\text{cell}} = 1.05\ \mathrm{V}$, $[\mathrm{Ni^{2+}}] = 0.1\ \mathrm{M}$, $[\mathrm{Ag^+}] = 1.0\ \mathrm{M}$

$E_{\text{cell}} = 1.05\ \mathrm{V} - \frac{0.059}{2} \log \frac{(0.1)}{(1)^2}$

$E_{\text{cell}} = 1.05\mathrm{V} - 0.0295 \log 10^{-1}$

$= 1.05 + 0.0295\ \mathrm{V} = \mathbf{1.0795\ V}$

Q.9. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55 × 10^3ohm. Calculate its resistivity, conductivity and molar conductivity.

[*CBSE (AI) 2012*]

Ans.

$A = \pi r^2 = 3.14 \times \left(\frac{1}{2}\mathrm{cm}\right)^2 = 0.785\ \ \mathrm{cm}^2\ ;\ l = 50\ \ \mathrm{cm}$

Resistivity, $\rho = \frac{R \times A}{l} = \frac{5.55 \times 10^3 \mathrm{ohm} \times 0.785\ \ \mathrm{cm}^2}{50\ \ \mathrm{cm}} = 87.135\ \ \mathrm{ohm}\ \ \mathrm{cm}$

Conductivity, $k = \frac{1}{\rho} = \frac{1}{87.135\ \ \mathrm{ohm}\ \ \mathrm{cm}} = 0.01148\ S\ \ \mathrm{cm}^{-1}$

Molar Conductivity, $\Lambda_m = \frac{k \times 1000}{M} = \frac{0.01148\ S\ \ \mathrm{cm}^{-1} \times 1000\ \ \mathrm{cm}^3\ \ L^{-1}}{0.05\ \ \mathrm{mol}\ \ L^{-1}}$

$= \mathbf{229.\ 6\ S\ cm^2\ mol^{-1}}$

Q.10. A voltaic cell is set up at 25°C with the following half cells:

Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.50 M)

Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

$$E^o_{Ni^{2+}/Ni} = -0.25\text{ V};\ E^o_{Al^{3+}/Al} = -1.66\text{ V}\ (\log 8 \times 10^{-6} = -0.54)$$

[*CBSE (AI) 2012*]

Ans.

At anode: $[Al \longrightarrow Al^{3+} + 3e^-] \times 2$

At cathode: $[Ni^{2+} + 2e^- \longrightarrow Ni] \times 3$

Cell reaction: $\overline{\underline{2Al + 3Ni^{2+} \rightarrow 2Al^{3+} + 3Ni}}$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = E^o_{Ni^{2+}/Ni} - E^o_{Al^{3+}/Al}$$

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

$$[Al^{3+}] = 1 \times 10^{-3}\text{ M};\ [Ni^{2+}] = 0.5\text{ M};\ n = 6$$

Substituting the values in the Nernst equation,

$$E_{cell} = E^o_{Ni^{2+}/Ni} - E^o_{Al^{3+}/Al}$$

$$E_{cell} = 1.41\text{ V} - \frac{0.059}{6}\log\frac{(10^{-3})^2}{(0.5)^3}$$

$$= 1.41\text{ V} - \frac{0.059}{6}\log(8 \times 10^{-6}) = 1.41\text{ V} - \frac{0.059}{6}(-0.54)$$

$$E_{cell} = 1.41\text{ V} + 0.0053\text{ V} = \mathbf{1.4153\ V}$$

Short Answer Questions-II (OIQ)

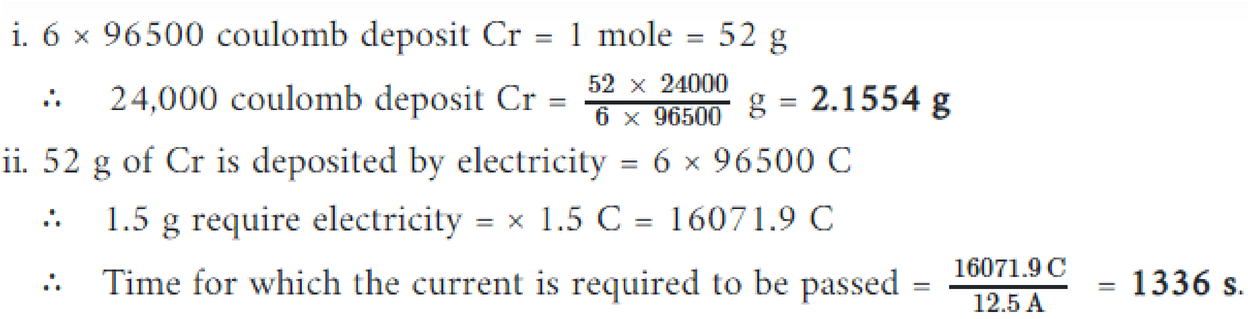
Q.1. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following equation:

$CrO_3(aq) + 6H^+(aq) + 6e^- \rightarrow Cr(s) + 3H_2O$

Calculate (*i*) how many grams of chromium will be plated out by 24,000 coulombs and (*ii*) how long will it take to plate out 1.5 g of chromium by using 12.5 A current?

(At. mass of Cr = 52).

Ans.



i. 6 × 96500 coulomb deposit Cr = 1 mole = 52 g

∴ 24,000 coulomb deposit Cr = $\frac{52 \times 24000}{6 \times 96500}$ g = **2.1554 g**

ii. 52 g of Cr is deposited by electricity = 6 × 96500 C

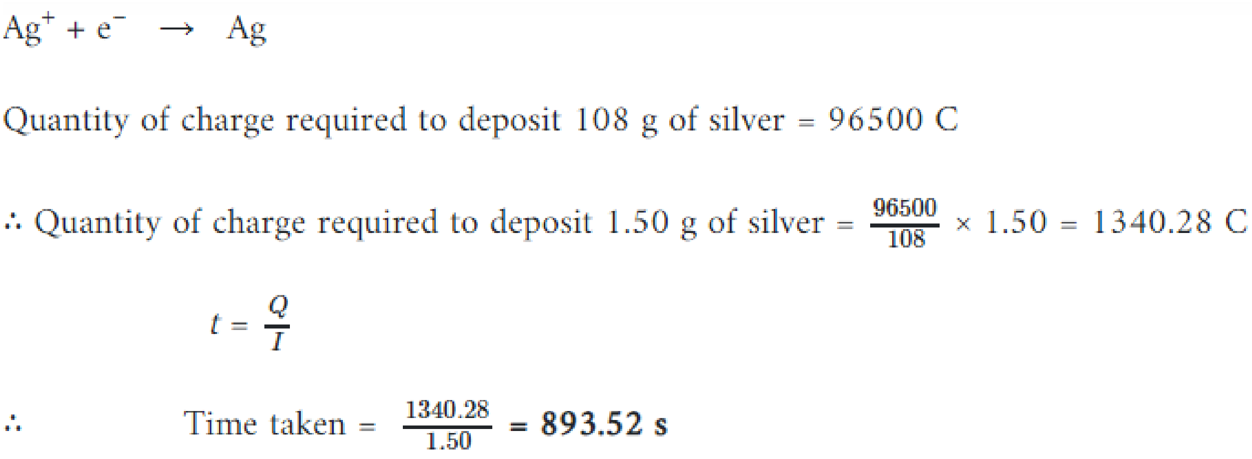
∴ 1.5 g require electricity = × 1.5 C = 16071.9 C

∴ Time for which the current is required to be passed = $\frac{16071.9\ C}{12.5\ A}$ = **1336 s**.

Q.2. Answer the following questions

Q. A current of 1.50 A was passed through an electrolytic cell containing $AgNO_3$ solution with inert electrodes. The weight of Ag deposited was 1.50 g. How long did the current flow?

Ans.



$Ag^+ + e^- \rightarrow Ag$

Quantity of charge required to deposit 108 g of silver = 96500 C

∴ Quantity of charge required to deposit 1.50 g of silver = $\frac{96500}{108} \times 1.50$ = 1340.28 C

$$t = \frac{Q}{I}$$

∴ Time taken = $\frac{1340.28}{1.50}$ = **893.52 s**

Q. Write the reactions taking place at the anode and cathode in the above cell.

Ans.

Inert electrodes

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

Cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$

Q. Give reactions taking place at the two electrodes if these are made up of Ag.

Ans.

Ag electrodes

Anode: $Ag(s) \rightarrow Ag^+(aq) + e^-$

Cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$

Q.3. A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential $\left(E^o_{Zn^{2+}/Zn} = -0.76\ V\right)$.

Ans.

The electrode reaction written as reduction reaction is

$$Zn^{2+} + 2e^- \rightarrow Zn \ (n = 2)$$

Applying Nernst equation, we get

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

As 0.1 M $ZnSO_4$ solution is 95% dissociated, this means that in the solution,

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

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

$$= -\ 0.76 - 0.02955\ (\log 1000 - \log 95)$$

$$= -\ 0.76 - 0.02955\ (3 - 1.9777) = -\ 0.76 - 0.03021 = \mathbf{-\ 0.79021\ V}$$

Q.4. The conductivity of 0.001028 mol L^{-1} acetic acid is 4.95 × 10^{-5} S cm^{-1}. Calculate its dissociation constant Λ^o_m if for acetic acid is 390.5 S cm^2 mol^{-1}.

[*HOTS*]

Ans.

$$\Lambda_m = \frac{k \times 1000}{c} = \frac{4.95 \times 10^{-5}\ S\ cm^{-1}}{0.001028\ mol\ L^{-1}} \times \frac{1000\ cm^3}{L} = 48.15 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^o_m} = \frac{48.15\ S\ cm^2\ mol^{-1}}{390.5\ S\ cm^2\ mol^{-1}} = 0.1233$$

$$K = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.001028\ mol\ L^{-1} \times (0.1233)^2}{1 - 0.1233} = \mathbf{1.78 \times 10^{-5}\ mol\ L^{-1}}$$

Q.5. 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 $\frac{4}{3}$ Al + O2 is 960 kJ (F = 96,500 C mol–1). [HOTS]

Ans.

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

$$\therefore \quad \frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2,\ n = \frac{2}{3} \times 6e^- = 4e^-$$

$$\Delta_r G = 960 \times 1000 = 960000 \text{ J}$$

Now, $\Delta_r G = -nFE_{cell}$

$\Rightarrow$ $E_{cell} = -\dfrac{\Delta_r G}{nF} = \dfrac{-960000}{4 \times 96500}$

$\Rightarrow$ $E_{cell} = \mathbf{-2.487\ V}$

$\therefore$ Minimum potential difference needed to reduce Al_2O_3 is **– 2.487 V.**

Q.6.

The emf of a cell corresponding to the reaction.

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(0.1\ M) + H_2\ (g, 1\ atm)$ is 0.28 volt at 25°C.

Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.

$E^o_{Zn^{2+}/Zn} = -0.76$ V, $E^o_{H^+/H_2} = 0$ V [*HOTS*]

Ans.

Half-cell reactions:

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

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

Cell reaction: $\overline{\underline{Zn + 2H^+ \rightarrow Zn^{2+} + H_2}}$

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

$$= \left(E^o_{H^+/H_2} - E^o_{Zn^{2+}/Zn}\right) - \frac{0.0591}{2} \log \frac{0.1}{[H^+]^2}$$

$$= [0 - (-0.76)] - 0.02955\ [\log 10^{-1} - 2 \log (H^+)]$$

$$0.28 = 0.76 - 0.02955\ (-1 + 2\ \mathrm{pH}) \qquad [\because \mathrm{pH} = -\log\ (\mathrm{H}^+)]$$

$$2\ \mathrm{pH} - 1 = 16.244$$

$$\mathrm{pH} = 8.62$$

Q.7.

From the following molar conductivities at infinite dilution, calculate Λ_m^0 for NH_4OH.

Λ_m^0 for $Ba(OH)_2$ = 457.6 $\Omega^{-1}\ cm^2\ mol^{-1}$

Λ_m^0 for $BaCl_2$ = 240.6 $\Omega^{-1}\ cm^2\ mol^{-1}$

Λ_m^0 for NH_4Cl = 129.8 $\Omega^{-1}\ cm^2\ mol^{-1}$

Ans.

$$\Lambda^o_{m(NH_4OH)} = \lambda^o_{NH_4^+} + \lambda^o_{OH^-}$$

$$= (\lambda^o_{NH_4^+} + \lambda^o_{Cl^-}) + \frac{1}{2}(\lambda^o_{Ba^{2+}} + 2\lambda^o_{OH^-}) - \frac{1}{2}(\lambda^o_{Ba^{2+}} + 2\lambda^o_{Cl^-})$$

$$= \Lambda^o_{m(NH_4Cl)} + \frac{1}{2}[\Lambda^o_{m(Ba(OH)_2)}] - \frac{1}{2}[\Lambda^o_{m(BaCl_2)}]$$

$$129.8 + \frac{1}{2} \times 457.6 - \frac{1}{2} \times 240.6 = 238.3\ \mathrm{ohm}^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$$

Long Answer Questions

Long Answer Questions

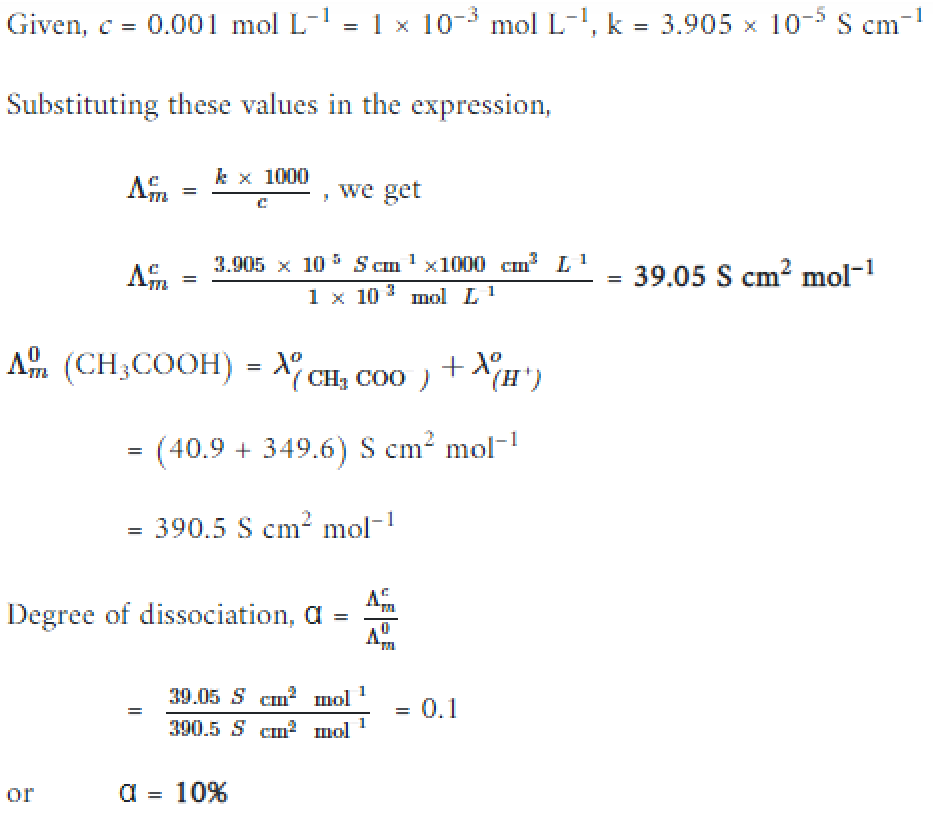
Q.1. Answer the following questions

[*CBSE Central 2016*]

Q. The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is 3.905×10^{-5} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).

Given $\lambda^0(H^+) = 349.6$ S cm^2 mol^{-1} and $\lambda^0(CH_3COO^-) = 40.9$ S cm^2 mol^{-1}

Ans.



Given, $c = 0.001 \text{ mol L}^{-1} = 1 \times 10^{-3} \text{ mol L}^{-1}$, $k = 3.905 \times 10^{-5} \text{ S cm}^{-1}$

Substituting these values in the expression,

$$\Lambda_m^c = \frac{k \times 1000}{c}, \text{ we get}$$

$$\Lambda_m^c = \frac{3.905 \times 10^{5}\ S\,cm^{1} \times 1000\ cm^3\ L^{1}}{1 \times 10^{3}\ mol\ L^{1}} = \mathbf{39.05\ S\ cm^2\ mol^{-1}}$$

$$\Lambda_m^0\ (CH_3COOH) = \lambda^o_{(CH_3COO\ )} + \lambda^o_{(H^+)}$$

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

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

Degree of dissociation, $\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^0}$

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

or $\alpha = \mathbf{10\%}$

Q. Define electrochemical cell. What happens if external potential applied becomes greater than E^o_{cell} of electrochemical cell?

Ans. A device which is used to convert chemical energy produced in a redox reaction into electrical energy is called an electrochemical cell.

If external potential applied becomes greater than E^o_{cell} of electrochemical cell, the reaction gets reversed and the electrochemical cell function as an electrolytic cell.

Q. 2.

Calculate e.m.f and $\triangle G$ for the following cell at 298 K:

$\text{Mg(s)} \mid \text{Mg}^{2+}\ (0.01\ \text{M}) \mid\mid \text{Ag}^{+}\ (0.0001\ \text{M}) \mid \text{Ag(s)}$

Given: $[\ E^o_{\text{Mg}^{2+}/\text{Mg}} = -\ 2.37\ \text{V},\ E^o_{\text{Ag}^{+}/\text{Ag}} = +\ 0.80\ \text{V}]$

[CBSE Guwahati 2015]

Ans.

At anode : $\text{Mg} \longrightarrow \text{Mg}^{2+} + 2e^{-}$

At cathode: $[\text{Ag}^{+} + e^{-} \longrightarrow \text{Ag}] \times 2$

$$\overline{\underline{\text{Mg} + \ 2\text{Ag} + \rightarrow + \text{Mg}\,2 + +2\,\text{Ag}\ ;}}\ n = 2$$

$$E^o_{\text{cell}} = E^o_{\text{cathode}} - E^o_{\text{anode}} = E^o_{\text{Ag}^{+}/\text{Ag}} - E^o_{\text{Mg}^{2+}/\text{Mg}} = 0.80\ \text{V} - (-\ 2.37\ \text{V}) = 3.17\ \text{V}$$

Substituting $E^o_{\text{cell}} = 3.17$ V, $n = 2$, $[\text{Mg}^{2+}] = 1 \times 10^{-2}$ M, $[\text{Ag}^{+}] = 1 \times 10^{-4}$ M in Nernst equation for above cell reaction,

$$E_{\text{cell}} = E^o_{\text{cell}} - \frac{0.059}{n} \log \frac{/\ \text{Mg}^{2+}\ /}{/\ \text{Ag}^{+}\ /^{2}}, \text{ we get}$$

$$E_{\text{cell}} = 3.17 - \frac{0.059}{2} \log \frac{10^{-2}}{(10^{-4})^{2}}$$

$$E_{\text{cell}} = 3.17 - 0.0295 \log 10^{6}$$

$$E_{\text{cell}} = 3.17 - 0.177\ \text{V} = 2.993\ \text{V}$$

$$E_{\text{cell}} = \mathbf{2.993\ V}$$

Substituting $n = 2$, $F = 96500$ C mol^{-1}, $E_{\text{cell}} = 2.993$ V in the expression, $\Delta G = -nFE_{\text{cell}}$ we ge

$$\Delta G = -nFE_{\text{cell}} = -2 \times 96500 \text{ C mol}^{-1} \times 2.993 \text{ V}$$

$$\Delta G = -577649 \text{ J mol}^{-1} = -577.649 \text{ kJ mol}^{-1}$$

Q.3. Answer the following questions

Q. State the relationship amongst cell constant of a cell, resistance of the solution in the cell and conductivity of the solution. How is molar conductivity of a solute related to conductivity of its solution?

Ans.

$k = \frac{1}{R} \times \left(\frac{l}{A}\right)$ = where, k = Conductivity, $\frac{l}{A}$ = Cell constant, R = Resistance

$\Lambda_m = \frac{k \times 1000}{M}$ where, Λm = Molar conductivity, k = Conductivity, M = Molarity of solution

Q.

A voltaic cell is set up at 25°C with the following half-cells:

Al | Al^{3+} (0.001 M) and Ni | Ni^{2+} (0.50 M)

Calculate the cell voltage $E^o_{Ni^{2+}/Ni}$ [= − 0.25 V, $E^o_{Al^{3+}/Al}$ = − 1.66 V]

Ans.

At anode: $[Al(s) \rightarrow Al^{3+}(aq) + 3e^-] \times 2$

At cathode: $[Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)] \times 3$

$$\underline{\overline{2\,AL\,(s) + 3\,Ni^{2+}\,(aq) \rightarrow 2\,Al^{3+}\,(aq) + 3\,Ni\,(s),}}\quad n = 6$$

$$E_{\text{cell}} = E^o_{\text{cell}} - \frac{0.0591}{n} \log \frac{/\,Al^{3+}\,/^2}{/\,Ni^{2+}\,/^3}$$

Here, $n = 6$, $[Al^{3+}] = 0.001\ M = 1\times 10^{-3}\ M$, $[Ni^{2+}] = 0.5\ M$

$$E^{o}_{cell} = E^{o}_{Ni^{2+}/Ni} - E^{o}_{Al^{3+}/Al} = -0.25\ V - (-1.66\ V) = 1.41\ V$$

$$E_{cell} = 1.41 - \frac{0.0591}{6}\log\frac{(10^{-3})^2}{(0.5)^3} = 1.41 - \frac{0.0591}{6}\log\frac{10^{-6}}{0.125}$$

$$= 1.41\ \frac{0.0591}{6} - \log(10^{-6}\times 8) = 1.41 - \frac{0.0591}{6}\log(10^{-6} + \log 2^3)$$

$$= 1.41 - \frac{0.0591}{6}\log(-6\log 10 + 3\log 2)$$

$$= 1.41 - \frac{0.0591}{6}\log(-6 + 3\times 0.3010)$$

$$= 1.41 - \frac{0.0591}{6}(-5.097)$$

$$= 1.41 + \frac{0.3012}{6} = 1.41 + 0.0502 = 1.4602\ V$$

$$E_{cell} = \mathbf{1.46\ V}$$

Q.4.

Given that Λ^0_m (HCl) = 426 S cm^2 mol^{-1}, Λ^0_m (NaCl) = 126 S cm^2 mol^{-1}

Λ^0_m (CH_3COONa) = 91 S cm^2 mol^{-1}

Ans.

$$\Lambda^0_m\ (CH_3COOH) = \Lambda^o_{CH_3COO^-} + \Lambda^o_{H^+}$$

$$= \Lambda^o_{CH_3COO^-} + \Lambda^o_{Na^+} + \Lambda^o_{H^+} + \Lambda^o_{Cl^-} - (\Lambda^o_{Na^+} + \Lambda^o_{Cl^-})$$

$$= \Lambda^o_{m(CH_3COONa)} + \Lambda^o_{m(HCl)} - \Lambda^o_{m(NaCl)}$$

$$= (91 + 426 - 126)\ S\ cm^2\ mol^{-1}$$

$$= \mathbf{391\ S\ cm^2\ mol^{-1}}$$

Q.5. A voltaic cell is set up at 25°C with the following half-cells Al^{3+} (0.001 M) and Ni^{2+} (0.50 M). Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

$$\left(\text{Given: } E^o_{Ni^{2+}/Ni} =-\ 0.25\ V,\ E^o_{Al^{3+}/Al} =-\ 1.66\ V\right)$$

Ans.

At anode: $[Al \rightarrow Al^{3+} + 3e^-] \times 2$

At cathode: $[Ni^{2+} + 2e^- \rightarrow Ni] \times 3$

Cell reaction: $\overline{\underline{2Al + 3Ni^{2+} \rightarrow 2Al^{3+} + 3Ni}}$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = E^o_{Ni^{2+}/Ni} - E^o_{Al^{3+}/Al}$$

$$= -\ 0.25\ V - (-\ 1.66\ V) = 1.41\ V$$

$$[Al^{3+}] = 1 \times 10^{-3}\ M;\ [Ni^{2+}] = 0.5\ M;\ n = 6$$

Substituting the values in the Nernst equation,

$$E_{cell} = E^o_{Ni^{2+}/Ni} - E^o_{Al^{3+}/Al}$$

$$E_{cell} = 1.41\ V - \frac{0.059}{6} \log \frac{(10^{-3})^2}{(0.5)^3}$$

$$= 1.41\ V - \frac{0.059}{6} \log (8 \times 10^{-6}) = 1.41\ V - \frac{0.059}{6} (-\ 0.54)$$

$E_{cell} = 1.41\ V + 0.0053\ V =$ **1.4153 V**

Q.6. Calculate the potential for half-cell containing

0.10M $K_2Cr_2O_7$ (*aq*), 0.20 M Cr^{3+}(*aq*) and 1.0 × 10^{-4} M H^+(*aq*). The half cell reaction is

$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

and the standard electrode potential is given as E^o =1.33V.

Ans.

For half cell reaction

$$Cr_2O_7^{2} (aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{[Cr^{3+}]^2}{[Cr_2O_7^{2}][H^+]^{14}}$$

Here, $E^o = 1.33$ V, n = 6, $[Cr^{3+}] = 0.2$ M

$[Cr_2O_7^{2}] = 0.1$ M, $[H^+] = 1 \times 10^{-4}$ M

Substituting these values in the given expression, we get

$$E_{cell} = 1.33\ V - \frac{0.0591}{6} \log \frac{(0.20)^2}{(0.1)(10^{-4})^{14}}$$

$$= 1.33\ V\ \frac{0.0591}{6} - \log\left(4 \times 10^{55}\right) = 1.33\ V - \frac{0.0591}{6}\left[\log 4 + \log 10^{55}\right]$$

$$= 1.33\ V - \frac{0.0591}{6}\left[2 \log 2 + 55 \log 10\right] = 1.33\ V - \frac{0.0591}{6}\left[2 \times 0.3010 + 55\right]$$

$$= 1.33\ V - 0.548\ V = \mathbf{0.782\ V}$$

Q.7.

Using the E^o values of A and B, predict which is better for coating the surface of iron

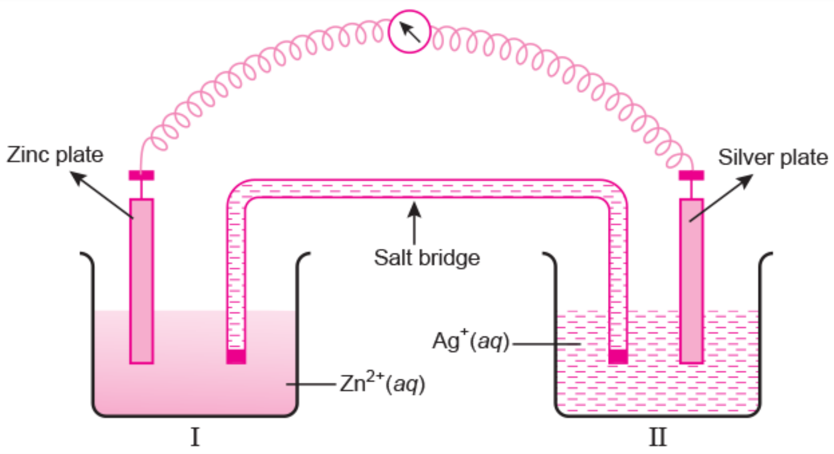
$\left[E^o_{Fe^{2+}/Fe} = -0.44\ V\right]$ to prevent corrosion and why?

Given: $\left[E^o_{A^{2+}/A} = -2.37\ V, E^o_{B^{2+}/B} = -0.14\ V\right]$

Ans. A, as its standard reduction potential is less than B, therefore, it will undergo oxidation more easily than B.

Long Answer Question (OIQ)

Q.1. Consider the figure given below and answer the questions (i) to (vi):



i. Write the direction of electron flow.
ii. Is silver plate the anode or cathode?
iii. What will happen if salt bridge is removed?
iv. When will the cell stop functioning?
v. How will concentration of Zn^{2+} ions and Ag^{+} ions be affected when the cell functions?
vi. How will the concentration of Zn^{2+} ions and Ag^{+} ions be affected after the cell becomes ‘dead’?

[*NCERT Exemplar] [HOTS*]

Ans.

i. Electrons move from Zn to Ag.
ii. Ag is the cathode.
iii. Cell will stop functioning.
iv. When Ecell = 0.
v. Concentration of Zn^{2+} ions will increase and concentration of Ag^{+} ions will decrease.
vi. When Ecell = 0, equilibrium is reached and concentration of Zn^{2+} ions and Ag^{+} ions will not change.

Q.2. The electrochemical cell given alongside converts the chemical energy released during the redox reaction

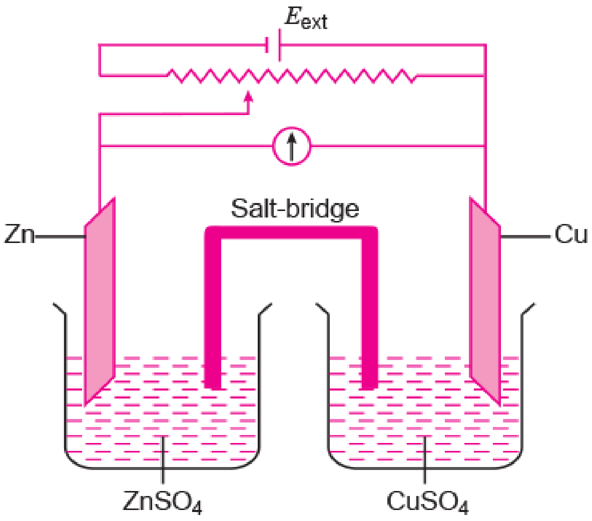
$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

to electrical energy. It gives an electrical potential of 1.1 V when concentration Zn^{2+} and Cu^{2+} ions is unity. State the direction of flow of current and also specify whether zinc and copper are deposited or dissolved at their respective electrodes when:

i. an external opposite potential of less than 1.1 V is applied.

ii. **an external potential of 1.1 V is applied.**
iii. **an external potential of greater than 1.1 V is applied.**

[*HOTS*]



Ans.

- **i.** Reaction continues to take place. Electrons flow from Zn electrode to copper electrode, hence current flows from Cu to Zn. Zn dissolves and copper deposits at their respective electrodes.
- **ii.** The reaction stops and no current flows. A state of equilibrium is achieved and no change is observed at zinc and copper electrodes.
- **iii.** Reaction takes place in opposite directions. Electrons flow from copper electrode to zinc electrode and hence current flows from Zn to Cu. Zinc deposits and copper dissolves at their respective electrodes. The cell functions as an electrolytic cell.

Q.3. Answer the following questions

Q. Define the following terms:

a. Limiting molar conductivity

b. Fuel cell

Ans.

- **a.** The molar conductivity when concentration approaches to zero is called limiting molar conductivity.
- **b.** A fuel cell is a device which converts energy produced during the combustion of fuels like hydrogen, methane, methyl alcohol etc. directly into electrical energy. One such successful fuel cell is hydrogen-oxygen fuel cell.

Q. Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 Ω, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is $1.29 \times 10^{-2}\ \Omega^{-1}\ \text{cm}^{-1}$.

Ans. For 0.1 mol L^{-1} KCl solution,

Conductivity, k = $1.29 \times 10^{-2}\ \Omega^{-1}\ \text{cm}^{-1}$, Resistance, *R* = 100 W

Cell constant = Conductivity × resistance

= $1.29 \times 10^{-2}\ \Omega$–1 $\text{cm}^{-1} \times 100\ \Omega = 1.29\ \text{cm}^{-1}$

For 0.02 mol L^{-1} solution,

Resistance = 520 Ω, Cell constant = $1.29\ \text{cm}^{-1}$,

$$\text{Conductivity, k} = \frac{\textit{Cellconstant}}{\text{Resistance}}$$

$$= \frac{129\ \text{cm}^{-1}}{520\ \Omega} = 0.00248\ \Omega^{-1}\ \text{cm}^{-1}$$

$$\text{Molar conductivity, } \Lambda m = \frac{\text{Conductivity } (k) \times 1000\ \text{cm}^3\ L^{-1}}{\text{Molarity}}$$

$$= \frac{0.00248\ \Omega^{-1}\ \text{cm}^{-1} \times 1000\ \text{cm}^3\ L^{-1}}{0.02\ \text{mol}\ L^{-1}}$$

$$= 124\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Q.4. Answer the following questions

[*HOTS*]

Q. Calculate the standard free energy change for the following reaction at 25°C.

$$\text{Au}(s) + \text{Ca}^{2+}(1\ \text{M}) \quad \rightarrow \quad \text{Au}^{3+}(1\ \text{M}) + \text{Ca}(s)$$

$$E^o_{\text{Au}^{3+}/\text{Au}} = +\ 1.50\ \text{V}\ , = E^o_{\text{Ca}^{2+}/\text{Ca}}\ -\ 2.87\ \text{V}$$

Predict whether the reaction will be spontaneous or not at 25ºC. Which of the above two half cells will act as an oxidising agent and which one will be a reducing agent?

Ans.

$$E^{o}_{cell} = E^{o}_{Ca^{2+}/Ca} - E^{o}_{Au^{3+}/Au}$$

$$= (-2.87\ V) - (1.50\ V) = -4.37\ V$$

$$\Delta_r G^{o}_{cell} = -6 \times 96500 \times (-4.37\ V)$$

$$= +2530.230\ kJ/mol$$

Since $\Delta_r G^{o}$ is positive, therefore, reaction is non-spontaneous.

Au^{3+}/Au half cell will be an oxidising agent while Ca^{2+}/Ca half cell will be a reducing agent.

Q. Tarnished silver contains Ag_2S. Can this tarnish be removed by placing tarnished silver ware in an aluminium pan containing an inert electrolytic solution such as NaCl? The standard electrode potential for half reaction:

$$Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-} \text{ is } -0.71V$$

$$\text{and for} \quad Al^{3+} + 3e^- \rightarrow 2Al(s) \text{ is } -1.66V$$

Ans. E^{o}_{cell} for reaction of tarnished silver ware with aluminium pan is

(– 0.71 V) – (– 1.66 V) *i.e.*, + 0.95 V

Tarnished silver ware, therefore, can be cleaned by placing it in an aluminium pan as E^{o}_{cell} is positive.

Q.5. At 291 K, the molar conductivities at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 S cm^2 mol^{-1} respectively. If the molar conductivity of a centinormal solution of NH_4OH is 9.33 S cm2 mol^{-1}, what is the percentage dissociation of NH_4OH at this dilution? Also calculate the dissociation constant of NH_4OH.

[*HOTS*]

Ans.

Here, we are given:

Λ_m^0 for $NH_4Cl = 129.8\ S\ cm^2\ mol^{-1}$

Λ_m^0 for $NaOH = 217.4\ S\ cm^2\ mol^{-1}$

Λ_m^0 for $NaCl = 108.9\ S\ cm^2\ mol^{-1}$

By Kohlrausch's law,

Λ_m^0 for $NH_4OH = \lambda^o_{NH_4^+} + \lambda^o_{OH^-}$

$= \Lambda_m^o(NH_4Cl) + \Lambda_m^o(NaOH) - \Lambda_m^o(NaCl)$

$= [129.8 + 217.4 - 108.9]\ S\ cm^2\ mol^{-1}$

$= 238.3\ S\ cm^2\ mol^{-1}$

$\Lambda_m^c = 9.33\ S\ cm^2\ mol^{-1}$ (Given)

$\therefore$ Degree of dissociation $(\alpha) = \frac{\Lambda_m^c}{\Lambda_m^o} = \frac{9.33}{238.3} = 0.0392$

or Percentage dissociation = 0.0392×100 = **3.92%**

Calculation of dissociation constant

	NH_4OH	$\rightleftharpoons$	NH_4^+	$+\ OH^-$
Initial conc.	c		0	0
Equilibrium conc.	$c - c\alpha$		$c\alpha$	$c\alpha$
	$= c(1-\alpha)$			

$$K = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

Substituting, $c = 0.01\ \text{N} = 0.01\ \text{M}$, and $\alpha = 0.0392$, we get

$$\text{We get,}\quad K = \frac{(0.01)\ (0.0392)^2}{1 - 0.0392}$$

$$= \frac{10^{-2} \times (3.92 \times 10^{-2})^2}{0.9608}$$

$$= 1.599 \times 10^{-5}$$

Q.6. Answer the following questions

Q. State two advantages of H_2–O_2 fuel cell over ordinary cell.

Ans. Advantages of fuel cell:

- **a.** It is a pollution-free device since no harmful products are formed.
- **b.** Its efficiency is about 75% which is considerably higher than conventional cells.
- **c.** It is a continuous source of energy if the supply of gases is maintained. (Any Two)

Q. Silver is electrodeposited on a metallic vessel of total surface area 500 cm^2 by passing a current of 0.5 amp for two hours. Calculate the thickness of silver deposited.

[Given: Density of silver = 10.5 g cm^{-3}, Atomic mass of silver = 108 amu, *F* = 96,500 C mol^{-1}]

Ans.

$$m = Z\ I\ t = \frac{108}{96500} \times 0.5 \times 2 \times 3600 = 4.029\ \text{g}$$

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

$$V = \frac{4.029\ g}{10.5\ g\ \ cm^{-3}} = 0.3837\ \text{cm}^3$$

Let the thickness of silver deposited be x cm.

$$\therefore \quad V = A \times x \quad \text{or} \quad x = \frac{V}{A}$$

$$x = \frac{0.3837}{500} = 7.67 \times 10^{-4}\ \text{cm.}$$