Choose and write the correct option(s) in the following questions.

1. An electrochemical cell can behave like an electrolytic cell when _____.

   [NCERT Exemplar; CBSE 2020 (56/4/2)]

   (a) $E_{cell} = 0$ (b) $E_{cell} > E_{ext}$

   (c) $E_{ext} > E_{cell}$ (d) $E_{cell} = E_{ext}$

2. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called _____.   *[NCERT Exemplar]*

   (a) Cell potential   (b) Cell emf

   (c) Potential difference   (d) Cell voltage

3. A hypothetical electrochemical cell is shown below:

   $A \mid A^+(x M) \parallel B^+(y M) \mid B$

   The emf measured is +0.20 V. The cell reaction is

   (a) $A + B^+ \longrightarrow A^+ + B$ (b) The cell reaction cannot be predicted.

   (c) $A^+ + e^- \longrightarrow A, \ B^+ + e^- \longrightarrow B$ (d) $A^+ + B \longrightarrow A + B^+$

4. Which cell will measure standard electrode potential of copper electrode?   *[NCERT Exemplar]*

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

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

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

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

5. The positive value of the standard electrode potential of Cu^{2+}/Cu indicates that _____.

   [NCERT Exemplar]

   (a) this redox couple is a stronger reducing agent than the H^+/H_2 couple.

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

   (c) Cu can displace H_2 from acid.

   (d) Cu cannot displace H_2 from acid.

6. Standard electrode potential for Sn^{4+}/Sn^{2+} couple is +0.15 V and that for the Cr^{3+}/Cr couple is $- 0.74$ V. The two couple in their standard states are connected to make cell. The cell potential will be:

   (a) +1.19 V   (b) 0.89 V

   (c) +0.18 V   (d) +1.83 V

7. Which of the following statement is not correct about an inert electrode in a cell? *[NCERT Exemplar]*

   (a) It does not participate in the cell reaction.

   (b) It provides surface either for oxidation or for reduction reaction.

   (c) It provides surface for conduction of electrons.

   (d) It provides surface for redox reaction.

8. Using the data given below find out the strongest reducing agent.   *[NCERT Exemplar]*

   $E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V $E^o_{Cl_2/Cl^-} = 1.36$ V

   $E^o_{MnO_4^-/Mn^{2+}} = 1.51$ V $E^o_{Cr^{3+}/Cr} = - 0.74$ V

   (a) Cl^- (b) Cr   (c) Cr^{3+} (d) Mn^{2+}

9. Using the data given in Q. 8 find out in which option the order of reducing power is correct.

   [NCERT Exemplar]

   (a) $Cr^{3+} < Cl^- < Mn^{2+} < Cr$ (b) $Mn^{2+} < Cl^- < Cr^{3+} < Cr$

   (c) $Cr^{3+} < Cl^- < Cr_2O_7^{2-} < MnO_4^-$ (d) $Mn^{2+} < Cr^{3+} < Cl^- < Cr$

10. Use the data given in Q. 8 find out the most stable oxidised species.   *[NCERT Exemplar]*

    (a) Cr^{3+} (b) MnO_4^- (c) $Cr_2O_7^{2-}$ (d) Mn^{2+}

Electrochemistry

11. The electrode potential data are given below

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}, \qquad E^o = +0.77 \text{ V}$$

$$Al^{3+} + 3e^- \longrightarrow Al, \qquad E^o = -1.66 \text{ V}$$

$$Br_2 + 2e^- \longrightarrow 2Br^-, \qquad E^o = +1.80 \text{ V}$$

Based on the data, the reducing power of Fe^{2+}, Al, Br^- will increase in the order.

(a) $Br^- < Fe^{2+} < Al$ (b) $Fe^{2+} < Al < Br^-$ (c) $Al < Br^- < Fe^{2+}$ (d) $Al < Fe^{2+} < Br^-$

12. Which one of the following is always true about the spontaneous cell reaction in a galvanic cell?

(a) $E^o_{cell} > 0, \Delta G^o < 0, Q > K_c$

(b) $E^o_{cell} < 0, \Delta G^o < 0, Q < K_c$

(c) $E^o_{cell} > 0, \Delta G^o > 0, Q > K_c$

(d) $E^o_{cell} > 0, \Delta G^o < 0, Q < K_c$

13. The standard emf of a galvanic cell involving 3 moles of electrons in a redox reaction is 0.59 V. The equilibrium constant for the reaction of the cell is:

(a) 10^{10} (b) 10^{20} (c) 10^{30} (d) 10^{15}

14. The SI unit of conductivity is

(a) Sm^{-1} (b) Scm^{-1} (c) Sm (d) Scm

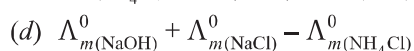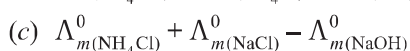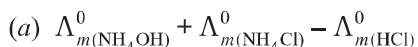15. Which of the statements about solutions of electrolytes is not correct?   [*NCERT Exemplar*]

(a) Conductivity of solution depends upon size of ions.

(b) Conductivity depends upon viscosity of solution.

(c) Conductivity does not depend upon solvation of ions present in solution.

(d) Conductivity of solution increases with temperature.

16. On increasing temperature,

(a) ionic conductance increases and electronic conductance decreases.

(b) ionic conductance decreases and electronic conductance increases.

(c) both ionic and electronic conductance increase.

(d) both ionic and electronic conductance decrease.

17. $\Lambda^0_{m(NH_4OH)}$ is equal to _____.   [*NCERT Exemplar*]

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

(b) $\Lambda^0_{m(NH_4Cl)} + \Lambda^0_{m(NaOH)} - \Lambda^0_{m(NaCl)}$

(c) $\Lambda^0_{m(NH_4Cl)} + \Lambda^0_{m(NaCl)} - \Lambda^0_{m(NaOH)}$

(d) $\Lambda^0_{m(NaOH)} + \Lambda^0_{m(NaCl)} - \Lambda^0_{m(NH_4Cl)}$

18. Charge carried by 1 mole of electrons is

(a) 6.023×10^{23} coulomb

(b) 9.65×10^4 coulomb

(c) 1.6×10^{-19} coulomb
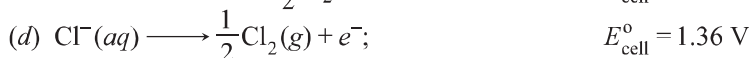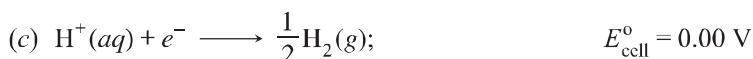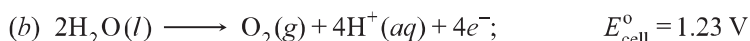
(d) 6.28×10^{19} coulomb

19. The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is _____.   [*NCERT Exemplar*]
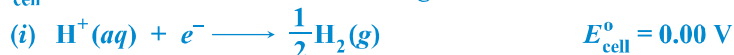
(a) 1F   (b) 6F   (c) 3F   (d) 2F

20. In the electrolysis of aqueous sodium chloride solution, which of the following half cell reaction will occur at anode?   [*NCERT Exemplar*]

(a) $Na^+(aq) + e^- \longrightarrow Na(s)$; $E^o_{cell} = -2.71 \text{ V}$

(b) $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$; $E^o_{cell} = 1.23 \text{ V}$

(c) $H^+(aq) + e^- \longrightarrow \dfrac{1}{2}H_2(g)$; $E^o_{cell} = 0.00 \text{ V}$

(d) $Cl^-(aq) \longrightarrow \dfrac{1}{2}Cl_2(g) + e^-$; $E^o_{cell} = 1.36 \text{ V}$

21. E^o_{cell} for some half cell reactions are given below. On the basis of these mark the correct answer.

(i) $H^+(aq) + e^- \longrightarrow \dfrac{1}{2}H_2(g)$ $E^o_{cell} = 0.00 \text{ V}$

(ii) $2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E^o_{cell} = 1.23 \text{ V}$

(iii) $2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$; $E^o_{cell} = 1.96 \text{ V}$ [*NCERT Exemplar*]

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

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

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

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

22. The electrolyte used in the mercury cell is

(*a*) paste of NH_4Cl and $ZnCl_2$ (*b*) paste of HgO and carbon

(*c*) paste of KOH and ZnO   (*d*) paste of PbO and H_2SO_4

23. A device that converts energy of combustion of fuels like hydrogen and methane directly into electrical energy is known as:

(*a*) dynamo   (*b*) Ni-Cd cell   (*c*) fuel cell   (*d*) electrolytic cell

24. Which metal is used as electrode which do not participate in the reaction but provides surface for conduction of electrons?

(*a*) Cu   (*b*) Pt   (*c*) Zn   (*d*) Fe

Answers

1. (*c*)	**2.** (*b*)	**3.** (*a*)	**4.** (*c*)	**5.** (*b*), (*d*)	**6.** (*b*)	**7.** (*d*)	**8.** (*b*)	**9.** (*b*)	**10.** (*a*)
11. (*a*)	**12.** (*d*)	**13.** (*c*)	**14.** (*a*)	**15.** (*c*)	**16.** (*a*)	**17.** (*b*)	**18.** (*b*)	**19.** (*c*)	**20.** (*b*)
21. (*a*), (*c*)	**22.** (*c*)	**23.** (*c*)	**24.** (*b*)						

Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

(*a*) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

(*b*) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

(*c*) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

(*d*) *Assertion (A) is incorrect, but Reason (R) is correct statement.*

1. **Assertion** (*A*) : E_{cell} should have a positive value for the cell to function.

   Reason (*R*) : $E_{cathode} < E_{anode}$

2. **Assertion** (*A*) : Mercury cell does not give steady potential.

   Reason (*R*) : In the cell reaction, ions are not involved in solution.

3. **Assertion** (*A*) : Cu is less reactive than hydrogen.

   Reason (*R*) : $E^o_{Cu^{2+}/Cu}$ is negative.

4. **Assertion** (*A*) : Copper sulphate cannot be stored in zinc vessel.

   Reason (*R*) : Zinc is less reactive than copper.

5. **Assertion** (*A*) : $E_{Ag^+/Ag}$ increases with increase in concentration of Ag^+ ions.

   Reason (*R*) : $E_{Ag^+/Ag}$ has a positive value.

6. **Assertion** (*A*) : Current stops flowing when $E_{cell} = 0$.

   Reason (*R*) : Equilibrium of the cell reaction is attained.

7. **Assertion** (*A*) : For measuring resistance of an ionic solution an AC source is used.

   Reason (*R*) : Concentration of ionic solution will change if DC source is used.

8. **Assertion** (*A*) : Conductivity of all electrolytes decreases on dilution.

   Reason (*R*) : On dilution number of ions per unit volume decreases.

9. **Assertion** (*A*) : Conductivity decreases for weak electrolyte and increases for strong electrolyte with decrease in concentration.

   Reason (*R*) : On dilution, the number of ions per unit volume that carry the current decreases.

Electrochemistry

10. **Assertion** (*A*) : Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.

   Reason (*R*) : For weak electrolytes degree of dissociation increases with dilution of solution.

11. **Assertion** (*A*) : Electrolysis of NaCl solution gives chlorine at anode instead of O_2.

   Reason (*R*) : Formation of oxygen at anode requires overvoltage.

12. **Assertion** (*A*) : The following reaction takes place at cathode during the electrolysis of aqueous sodium chloride:

$$H_2O(l) + e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-$$

   Reason (*R*) : The reaction with lower value of E^o is preferred at cathode.

Answers

1. (*c*)	**2.** (*d*)	**3.** (*c*)	**4.** (*c*)	**5.** (*b*)	**6.** (*a*)	**7.** (*a*)	**8.** (*a*)	**9.** (*d*)	**10.** (*a*)
11. (*a*)	**12.** (*c*)								

Passage-based/Case-based Questions

Read the given passages and answer the questions that follow.

PASSAGE–1

The conductivity or specific conductivity of an electrolytic solution varies with the concentration of the solutions of different electrolytes. For comparing the conductances of the solutions of different electrolytes, it is essential that the solutions should have equal volumes and they must contain definite amount of the electrolytes which give ions carrying the same total charge. The conducting power of an electrolytic solution can be expressed in terms of equivalent conductance and molar conductance. The equivalent conductance of a solution does not vary linearly with concentration and it is related with specific conductance. The effect of equivalent conductance can be studied by plotting values against the square root of the concentration. Following two figures show the behaviour of strong and weak electrolytes with change of concentration.
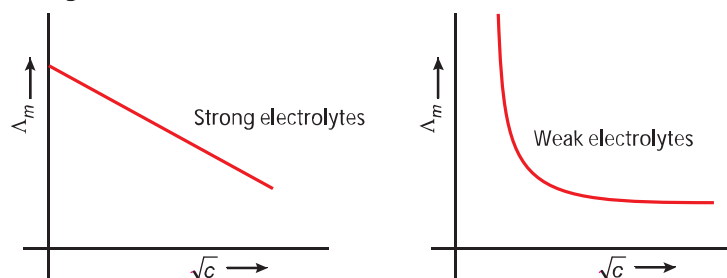
1. **Write the relationship between specific conductivity and equivalent conductivity?**

Ans. $\Lambda = \kappa \times \dfrac{1000}{N}$

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

Ans. The molar conductivity of a weak electrolyte increases with decrease in concentration.

3. **Write the mathematical expression for Kohlrausch's law in terms of equivalent conductivities.**

Ans. $\Lambda^o_{eq} = \lambda^o_+ + \lambda^o_-$

4. **What is meant by limiting molar conductivity?**

Ans. The molar conductivity of a solution at infinite dilution is called limiting molar conductivity.

5. **Which equation gives the relationship between equivalent or molar conductivity and concentration of a strong electrolyte?**

**Ans.** Debye-Huckel Onsager equation

$$\Lambda = \Lambda^o - A\sqrt{c}$$

Redox reactions play an important role in chemistry. Whenever a redox reaction takes place directly in a single beaker, chemical energy in the form of heat is produced. By suitable means, it is possible to bring about the redox reactions indirectly so as to convert the chemical energy into electrical energy. A device used to convert the chemical energy produced in a redox reaction into electrical energy is called an electrochemical cell. If a redox reaction is allowed to take place in such a way that oxidation half reaction takes place in one beaker and the reduction half reaction in another beaker, the electrons given out by the former will be taken by the latter and the current will flow. The two portions of the cell are called half cells. The values of standard redox potential (E^o) of two half cell reactions decides in which way the reaction will proceed. A redox reaction is feasible when the substance having higher reduction potential gets reduced and the one having lower reduction potential gets oxidised. For example, In Daniel cell, zinc goes into solution and copper gets deposited.

1. **Formulate the galvanic cell in which the following reaction takes place:**

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

Ans. The cell is represented as

$$Zn(s)\,|\,Zn^{2+}(aq)\,\,||\,Ag^+(aq)\,|\,Ag(s)$$
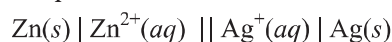
2. **Is it safe to stir $AgNO_3$ solution with a copper spoon? Why or why not?**

Given: $E^o_{Ag^+/Ag} = 0.80$ volt and $E^o_{Cu^{2+}/Cu} = 0.34$ volt

Ans. No, it is not safe to stir $AgNO_3$ solution with copper, because copper is more reactive than Ag and can displace Ag from $AgNO_3$ solution.

3. **Two half cell reactions of an electrochemical cell are given below:**

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l), \quad E^o = +1.51\ V$$
$$Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e^-, \qquad E^o = +0.15\ V$$

Construct the redox reaction from the two half cell reactions and predict if this reaction favours formation of reactants or products shown in the equation.

Ans. The redox reaction will be

$$2MnO_4^-(aq) + 16H^+(aq) + 5Sn^{2+}(aq) \longrightarrow 2Mn^{2+}(aq) + 5Sn^{4+}(aq) + 8H_2O(l)$$
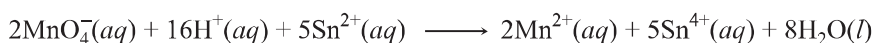
$E^o_{Cell} = E^o_{Cathode} - E^o_{Anode} = 1.51\ V - 0.15\ V = 0.36\ V$, *i.e.*, it will be positive.

Hence, reaction will favour formation of products.

4. **State the factors that influence the value of cell potential of the following cell:**

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

Ans. The factors that influence the value of cell potential are concentration of Mg^{2+} and Ag^+ ions in the solution and temperature.

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

Ans. No, E^o_{cell} or $\Delta_r G^o$ for cell reaction can never be zero.

$$\Delta G^o = -nFE^o$$

E^o is never zero hence ΔG^o will also be not equal to zero.

Very Short Answer Questions   [1 mark]

Q. 1. **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. 2. **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 keeps on changing until they become equal and then e.m.f. of the cell becomes zero.

Electrochemistry

Q. 3. **Consider a cell given below:**

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

Write the reactions that occur at anode and cathode.

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

Cathode: $\qquad Cl_2 + 2e^- \longrightarrow 2Cl^-$

Q. 4. **Depict the galvanic cell in which the cell reaction is** $Cu + 2Ag^+ \longrightarrow 2Ag + Cu^{2+}$.

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

Q. 5. **What is the reference electrode in determining the standard electrode potential?**

Ans. Normal hydrogen electrode (NHE).

Q. 6. **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. 7. **Define electrochemical series.**

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

Q. 8. **Write Nernst equation for single electrode potential.**

Ans. For the electrode reaction $M^{n+} + ne^- \longrightarrow M$

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

Q. 9. **Write Nernst equation for the general cell reaction** $aA + bB \xrightarrow{ne^-} xX + yY.$

Ans. If n moles of electrons are transferred, Nernst equation is $E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln\frac{[X]^x[Y]^y}{[A]^a[B]^b}.$

Q. 10. **Write Nernst equation for the reaction**

$$2Cr + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe$$

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

Q. 11. **How can the reduction potential of an electrode be increased?**

Ans. $M^{n+} + ne^- \longrightarrow M,$

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

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

Q. 12. **What flows in the internal circuit of a galvanic cell?**

Ans. Ions.

Q. 13. **What does the negative value of** E^o_{cell} **indicate?**

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

Q. 14. **Why is alternating current used for measuring resistance of an electrolytic solution?**

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

Q. 15. **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. 16. **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. 17. **What is the effect of temperature on ionic conductance?** [*CBSE 2019 (56/3/2)*]

Ans. The ionic conductance increases with increase in temperature because the degree of dissociation increases with increase in temperature.

Q. 18. **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. 19. **Why on dilution the Λ_m 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.

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

Q. 20. **How much charge is required for the reduction of 1 mol of Zn^{2+} to Zn?** [*CBSE Patna 2015*]

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

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

Q. 21. **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. 22. **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. 23. **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. 24. **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. 25. **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 $[Zn(NH_3)_2 Cl_2]$ otherwise the pressure developed due to NH_3 would crack the seal of the cell.

Q. 26. **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. 27. **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. 28. **What is the overall electrochemical reaction taking place in rusting?**

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

Q. 29. **Write the chemical formula of rust.**

Ans. $Fe_2O_3 \cdot xH_2O$

Q. 30. **What is galvanization?**

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

Q. 31. **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.

Electrochemistry

Q. 32. **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. 33. **Using the E^o values of X and Y, predict which is better for coating the surface of iron to prevent rust and why?**

Given:$[E^o_{(Fe^{2+}/Fe)} = -0.44 \text{ V}]$, $[E^o_{(X^{2+}/X)} = -2.36 \text{ V}]$, $[E^o_{(Y^{2+}/Y)} = -0.14 \text{ V}]$ *[CBSE 2019 (56/4/3)]*

Ans. X, as its standard reduction potential is less than Y. Therefore, it will undergo oxidation more easily than Y.

Q. 34. **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 and therefore when coating is broken, rusting will take place faster.

Short Answer Questions–I [2 marks]

Q. 1. **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. $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

Applying Nernst equation,

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

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

$$-0.118 = 0.059 \log [H^+]$$

or $\qquad -0.118 = -0.059 \text{ pH}$

$$\text{pH} = \mathbf{2}$$

Q. 2. **Calculate $\Delta_r G^o$ and log K_c for the following reaction:** *[CBSE 2019 (56/4/1)]*

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

Given: $E^o_{Cd^{2+}/Cd} = -0.403 \text{ V}, E^o_{Zn^{2+}/Zn} = -0.763 \text{ V}$

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

Here, $\qquad E^o_{cell} = E^o_{cathode} - E^o_{anode}$

$$= E^o_{Cd^{2+}/Cd} - E^o_{Zn^{2+}/Zn}$$

$$= -0.403 \text{ V} - (-0.763 \text{ V})$$

$$= 0.360 \text{ V}$$

$E^o_{cell} = 0.360 \text{ V}; n = 2$

$\Delta_r G^o = -nFE^o_{cell}$

$$= -2 \times 96500 \text{ mol}^{-1} \times 0.36 \text{ V}$$

$$= 69480 \text{ CV mol}^{-1}$$

$$= 69480 \text{ J mol}^{-1}$$

$$= \mathbf{69.48 \text{ kJ mol}^{-1}}$$

$$\log K_c = \frac{n}{0.059} E^o_{cell}$$

$$= \frac{2}{0.059} \times 0.36$$

$$\log K_c = \mathbf{12.20}$$

Q. 3. 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. $\Lambda_m = \dfrac{\kappa \times 1000}{C} = \dfrac{0.025 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.2 \text{ mol L}^{-1}} = \mathbf{125 \text{ S cm}^2 \text{ mol}^{-1}}$

Q. 4. 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. $\Lambda_m = \dfrac{\kappa \times 1000}{M}$

$\kappa = \dfrac{\Lambda_m \times M}{1000}$

$\kappa = \dfrac{138.95 \text{ S cm}^2 \text{mol}^{-1} \times 1.5 \text{ mol L}^{-1}}{1000 \text{ cm}^3 \text{ L}^{-1}} = \mathbf{0.208455 \text{ cm}^{-1}}$

Q. 5. The following curve is obtained when molar conductivity (Λ_m) 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 (Λ^o_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 (Λ^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.
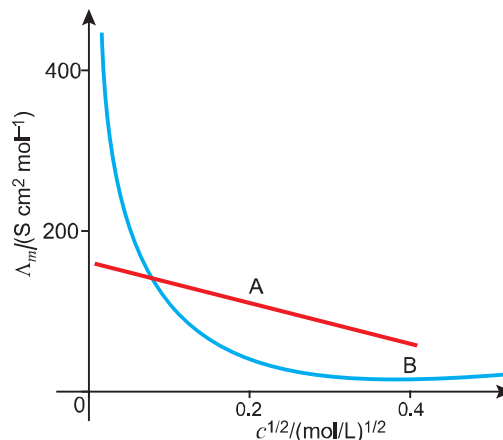
Q. 6. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? *[CBSE (AI) 2014]*

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 ν_+ cations and ν_- anions then its limiting molar conductivity is given by

$$\Lambda^o_m = \nu_+ \lambda^o_+ + \nu_- \lambda^o_-$$

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.

Electrochemistry

Q. 7. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is 39.05 S cm^2 mol^{-1}. Given $\lambda^o_{(H^+)}$ = 349.6 S cm^2 mol^{-1} and $\lambda^o_{(CH_3COO^-)}$ = 40.9 S cm^2 mol^{-1} **[CBSE Delhi 2017]**

Ans.

$$\Lambda^o_{(CH_3COOH)} = \lambda^o_{(CH_3COO^-)} + \lambda^o_{(H^+)}$$
$$= (40.9 + 349.6) \text{ S cm}^2 \text{ mol}^{-1}$$
$$= 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$
$$\alpha = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{39.05 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.1$$

$\Rightarrow$ **α = 10%**

Q. 8. 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. $Cu^{2+} + 2e^- \longrightarrow Cu$

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

∴ 1.27 g of copper will be deposited by $\frac{2 \times 96500 \times 1.27}{63.5}$ C = 3860 C

I = 2 A, Q = 3860 C

∴ $t = \frac{Q}{I} = \frac{3860}{2}$ = **1930 s**

Q. 9. How many moles of mercury will be produced by electrolysing 1.0 M Hg(NO$_3$)$_2$ solution with a current of 2.00 A for 3 hours? **[CBSE (AI) 2011]**

Ans. Mass of mercury produced at the cathode,

$$m = Z \times I \times t = \frac{M \times I \times t}{n \times F}$$

$$m = \frac{M \text{ g mol}^{-1} \times 2A \times 3 \times 60 \times 60 \text{ s}}{2 \times 96500 \text{ C mol}^{-1}}$$

$$= 0.1119 \times M \text{ g} = 0.119 \times M \text{ g}$$

No. of moles of mercury produced = $\dfrac{0.119 \times M \text{ g}}{M \text{ g mol}^{-1}}$ = **0.119 mol**

Q. 10. 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. $W = Z \times I \times t$

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

M = **63.3 g/mol**

Q. 11. How many molecules of chlorine should be deposited from molten sodium chloride in one minute by a current of 300 milliampere?

Ans. $Q = I \times t$

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

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

2 × 96500 C deposit Cl$_2$ = 1 mol

∴ 18 C will deposit Cl$_2$ = $\dfrac{1 \text{ mol} \times 18 \text{ C} \times 6.022 \times 10^{23}}{2 \times 96500 \text{ C}}$ molecules

= **5.616 × 10^{19} molecules**

Q. 12 Chromium metal is electroplated using an acidic solution containing CrO_3 according to the following equation:

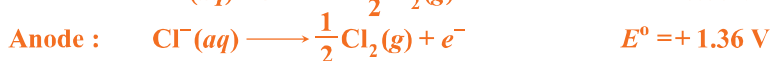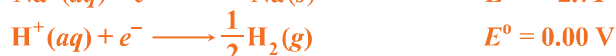$$CrO_3(aq) + 6H^+ + 6e^- \longrightarrow Cr(s) + 3H_2O$$

Calculate how many grams of chromium will be electroplated by 24,000 coulombs. How long will it take to electroplate 1.5 g chromium using 12.5 A current?

[Atomic mass of Cr = 52 g mol^{-1}, 1 F = 96500 C mol^{-1}]

Ans. 6×96500 C deposit Cr = 52 g

$\therefore$ 24,000 C will deposit Cr = $\dfrac{52 \text{ g}}{6 \times 96500 \text{ C}} \times 24,000$ C = **2.155 g**

52 g of Cr is deposited by 6×96500 C.

$\therefore$ 1.5 g of Cr require = $\dfrac{6 \times 96500 \text{ C}}{52 \text{ g}} \times 1.5$ g = 16701.9 C

$$Q = I \times t \qquad \Longrightarrow \qquad t = \dfrac{Q}{I}$$

$\therefore$ Time for which the current is passed = $\dfrac{16701.9 \text{ C}}{12.5 \text{ A}}$ = **1336.15 s**

Q. 13. Following reactions may occur at cathode and anode during electrolysis of aqueous sodium chloride. What products will be held at anode and cathode? Use given E^o values to justify your answer.

Cathode : $\quad Na^+(aq) + e^- \longrightarrow Na(s) \qquad\qquad E^o = -2.71$ V

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

Anode : $\quad Cl^-(aq) \longrightarrow \dfrac{1}{2}Cl_2(g) + e^- \qquad\qquad E^o = +1.36$ V

$\qquad\qquad 2H_2O(aq) \longrightarrow O_2(g) + 4H^+ + 4e^- \qquad E^o = +1.23$ V $\qquad$ *[CBSE 2019 (56/5/2)]*

Ans. $H_2(g)$ is produced due to greater E^o value of H^+ ion and $Cl_2(g)$ is produced due to over-potential of oxygen.

Q. 14. Define the following terms:

    (i) **Molar conductivity (Λ_m)**   (ii) **Secondary batteries**   *[CBSE (AI) 2014]*

Ans. (i) 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.

$$\Lambda_m = \kappa \times V \quad or \quad \Lambda_m = \dfrac{\kappa \times 1000}{\text{Molarity}}$$

where, κ is the conductivity and V is the volume of the solution containing 1 mole of the electrolyte.

(ii) 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. 15. 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?   *[CBSE 2020 (56/3/1)]*
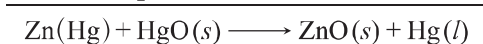
    (iii) Which cell is used in automobiles and inverters?

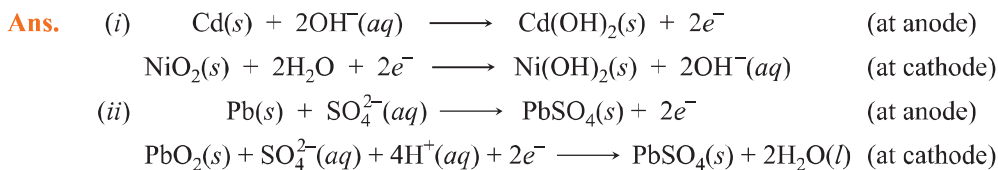   (iv) Which cell does not have long life?   *[CBSE Delhi 2016; South 2016]*

Ans. (i) Mercury cell   (ii) Fuel cell

    (iii) Lead storage cell   (iv) Dry cell

Q. 16. 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]*
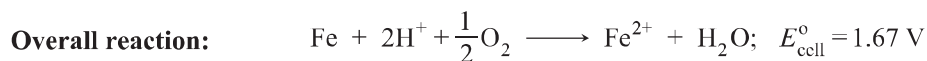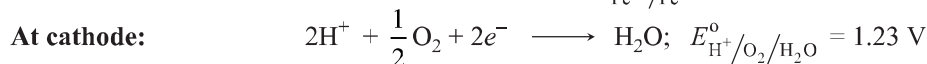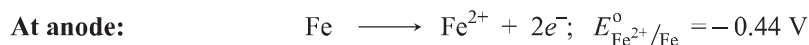
Ans. Mercury cell

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

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

$$\overline{\quad Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l) \quad}$$

Electrochemistry

Q. 17. Write electrode reactions taking place in (*i*) Ni–Cd cell, (*ii*) Lead Acid Accumulator.

Ans. (*i*) $Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$ (at anode)

$NiO_2(s) + 2H_2O + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$ (at cathode)

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

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

Q. 18. 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: $Fe \longrightarrow Fe^{2+} + 2e^-;\ E^o_{Fe^{2+}/Fe} = -0.44\ V$

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

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

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).

$$2Fe^{2+} + \dfrac{1}{2}O_2 + 2H_2O \longrightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3 \cdot xH_2O\ (Rust)$$
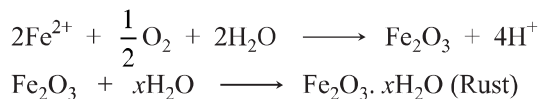
Short Answer Questions–II [3 marks]

Q. 1. 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.

(Given: $E^o_{Zn^{2+}/Zn} = -0.763\ V$, $E^o_{Ag^+/Ag} = +0.80\ V$) **[CBSE (F) 2010]**

Ans. Electrochemical cell

$$Zn(s)\,|\,Zn^{2+}\,(0.10\ M)\,||\,Ag^+\,(conc.)\,|\,Ag(s)$$
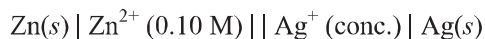
$$E^o_{cell} = E^o_R - E^o_L = E^o_{Ag^+/Ag} - E^o_{Zn^{2+}/Zn}$$

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

We know that,

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

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

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

Or

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

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

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

Q. 2. 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 ($E^o_{Zn^{2+}/Zn} = -0.76$ V).

Ans. The electrode reaction written as reduction reaction is

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

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,

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

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

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

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

Q. 3. A strip of nickel metal is placed in a 1 molar solution of $Ni(NO_3)_2$ and a strip of silver metal is placed in a 1 molar solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter.

   (*i*) Write the balanced equation for the overall reaction occurring in the cell and calculate the cell potential.

  (*ii*) Calculate the cell potential, E, at 25°C for the cell if the initial concentration of $Ni(NO_3)_2$ is 0.100 molar and the initial concentration of $AgNO_3$ is 1.00 molar.

$[E^o_{Ni^{2+}/Ni} = -0.25$ V; $E^o_{Ag^+/Ag} = 0.80$ V, $\log 10^{-1} = -1]$ **[CBSE (F) 2012]**

Ans. (*i*) **At anode:** $Ni \longrightarrow Ni^{2+} + 2e^-$

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

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

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$= E^o_{Ag^+/Ag} - E^o_{Ni^{2+}/Ni}$$

$$= 0.80 \text{ V} - (-0.25 \text{ V})$$

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

     (*ii*) $E_{cell} = E^o_{cell} - \frac{0.059}{n} \log \frac{[Ni^{2+}]}{[Ag^+]^2}$

Here, $n = 2$, $E^o_{cell} = 1.05$ V, $[Ni^{2+}] = 0.1$ M, $[Ag^+] = 1.0$ M

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

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

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

Q. 4. The emf of a cell corresponding to the reaction.

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

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

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

Cell reaction: $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$

Electrochemistry

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

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

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

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

$$2 pH - 1 = 16.244$$

$$pH = \textbf{8.62}$$

Q. 5. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The free energy change for the decomposition reaction

$$\frac{2}{3} Al_2O_3 \longrightarrow \frac{4}{3} Al + O_2 \text{ is 960 kJ } (F = 96,500 \text{ C mol}^{-1}). \qquad\qquad \textbf{\textit{[HOTS]}}$$

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

$\therefore \qquad\qquad \frac{2}{3} Al_2O_3 \longrightarrow \frac{4}{3} Al + O_2, n = \frac{2}{3} \times 6e^- = 4e^-$
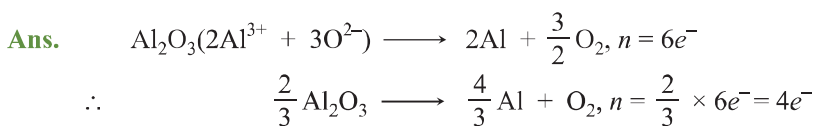
$$\Delta_r G = 960 \times 1000 = 960000 \text{ J}$$

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

$\Rightarrow \qquad\qquad E_{cell} = -\dfrac{\Delta_r G}{nF} = \dfrac{-960000}{4 \times 96500} = \textbf{-2.487 V}$

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

Q. 6. Calculate $\Delta_r G^\circ$ and $\log K_c$ for the following reaction at 298 K:

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

Given: $E^o_{cell} = 0.30$ V $\qquad\qquad\qquad\qquad\qquad\qquad \textbf{\textit{[CBSE (F) 2016]}}$

Ans.
$$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-] \times 2$$
$$\underline{Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s) \qquad\qquad] \times 3}$$
$$\underline{2Cr(s) + 3Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Fe(s), \quad n = 6}$$
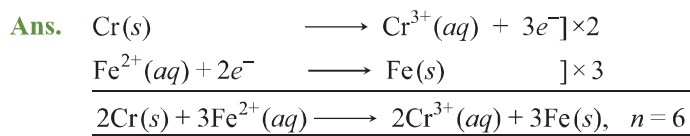
Here, $n = 6$, $E^o_{cell} = 0.30$ V

Substituting the values in the expression, $\log K_c = \dfrac{n}{0.059} E^o_{cell}$, we get

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

or $\qquad\qquad \log K_c = 30.5084$

$$K_c = \text{Antilog } (30.5084)$$

or $\qquad\qquad K_c = \textbf{3.224} \times \textbf{10}^{30}$

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

$$= -6 \times 96500 \times 0.30$$

$$= -173700 \text{ J mol}^{-1}$$

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

Q. 7. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.   **[CBSE (AI) 2012]**

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

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

Conductivity, $\kappa = \dfrac{1}{\rho} = \dfrac{1}{87.135 \ ohm \ cm} = \mathbf{0.01148 \ S \ cm^{-1}}$

Molar Conductivity, $\Lambda_m = \dfrac{\kappa \times 1000}{M}$

$= \dfrac{0.01148 \ S \ cm^{-1} \times 1000 \ cm^3 \ L^{-1}}{0.05 \ mol \ L^{-1}}$

$= \mathbf{229.6 \ S \ cm^2 \ mol^{-1}}$

Q. 8. From the following molar conductivities at infinite dilution, calculate Λ_m^o for NH_4OH.

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

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

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

Ans. $\Lambda_{m(NH_4OH)}^o = \lambda_{NH_4^+}^o + \lambda_{OH^-}^o$

$= (\lambda_{NH_4^+}^o + \lambda_{Cl^-}^o) + \dfrac{1}{2}(\lambda_{Ba^{2+}}^o + 2\lambda_{OH^-}^o) - \dfrac{1}{2}(\lambda_{Ba^{2+}}^o + 2\lambda_{Cl^-}^o)$

$= \Lambda_{m(NH_4Cl)}^o + \dfrac{1}{2}[\Lambda_{m(Ba(OH)_2)}^o] - \dfrac{1}{2}[\Lambda_{m(BaCl_2)}^o]$

$= 129.8 + \dfrac{1}{2} \times 457.6 - \dfrac{1}{2} \times 240.6$

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

Q. 9. 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. $\Lambda_m^c = \dfrac{\kappa \times 1000}{M}$

$\Lambda_m^c = \dfrac{5.25 \times 10^{-5} \ S \ cm^{-1} \times 1000 \ cm^3 \ L^{-1}}{2.5 \times 10^{-4} \ mol \ L^{-1}}$

$\Lambda_m^c = \mathbf{210 \ S \ cm^2 \ mol^{-1}}$

$\Lambda_m^o (HCOOH) = \Lambda_{HCOO^-}^o + \Lambda_{H^+}^o$

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

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

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

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

Q. 10.   (*i*) 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?

(*ii*) Write the reactions taking place at the anode and cathode in the above cell.

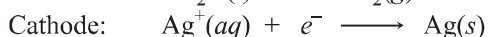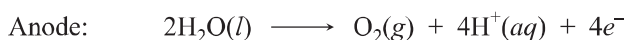(*iii*) Give reactions taking place at the two electrodes if these are made up of Ag.

Electrochemistry

Ans. (i) $Ag^+ + e^- \longrightarrow Ag$
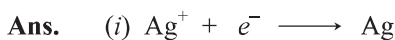
Quantity of charge required to deposit 108 g of silver = 96500 C

$\therefore$ Quantity of charge required to deposit 1.50 g of silver = $\dfrac{96500}{108} \times 1.50 = 1340.28$ C
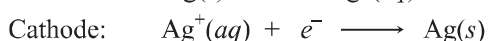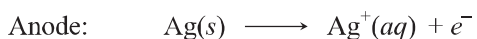
$$t = \dfrac{Q}{I}$$

$\therefore$ Time taken = $\dfrac{1340.28}{1.50} = \mathbf{893.52\ s}$

(ii) Inert electrodes

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

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

(iii) Ag electrodes

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

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

Q. 11. (i) **Calculate $\Delta_r G^\circ$ for the reaction**

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

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

(ii) **Name the type of cell which was used in Apollo space programme for providing electrical power.** [*CBSE (AI) 2014*]

Ans. (i) $Mg(s) + Cu^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cu(s)$
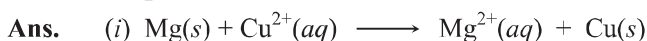
$$\Delta_r G^\circ = -nFE^o_{cell}$$

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

$\therefore \qquad \Delta_r G^\circ = -2 \times 96500$ C mol$^{-1} \times 2.71$ V

$$= -523030 \text{ J mol}^{-1}$$

$$= \mathbf{-523.03\ kJ\ mol^{-1}}$$

(ii) H_2—O_2 fuel cell

Long Answer Questions [5 marks]

Q. 1. **The electrochemical cell given alongside converts the chemical energy released during the redox reaction**

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

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.
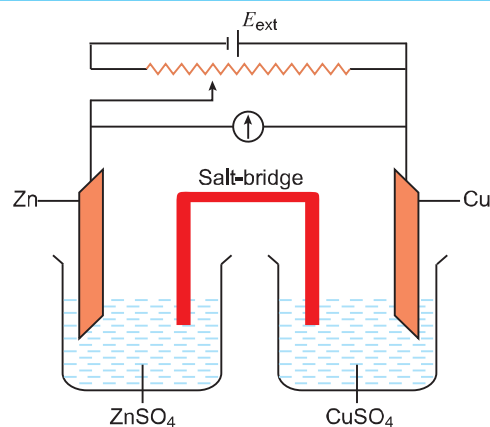
(*ii*) The reaction stops and no current flows.

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. 2. **Consider the figure given below and answer the questions (*i*) to (*vi*):**
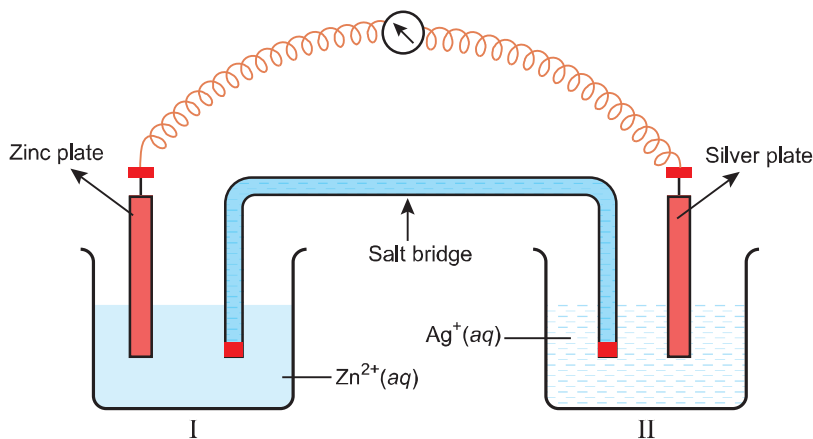
(*i*) **Write the direction of electron flow.**

(*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 $E_{cell} = 0$.

(*v*) Concentration of Zn^{2+} ions will increase and concentration of Ag^+ ions will decrease.

(*vi*) When $E_{cell} = 0$, equilibrium is reached and concentration of Zn^{2+} ions and Ag^+ ions will not change.

Q. 3. **Calculate e.m.f and ΔG for the following cell at 298 K:**

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

Given: [$E^o_{Mg^{2+}/Mg} = -2.37$ V, $E^o_{Ag^+/Ag} = +0.80$ V] [*CBSE Guwahati 2015*]

Ans. At anode : $\qquad\qquad\qquad Mg \longrightarrow Mg^{2+} + 2e^-$

At cathode: $\qquad\qquad [Ag^+ + e^- \longrightarrow Ag] \times 2$

$$\overline{Mg + 2Ag^+ \longrightarrow Mg^{2+} + 2Ag;\ \ n = 2}$$

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

$$= E^o_{Ag^+/Ag} - E^o_{Mg^{2+}/Mg}$$

$$= 0.80 \text{ V} - (-2.37 \text{ V})$$

$$= 3.17 \text{ V}$$

Electrochemistry

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

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

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

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

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

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

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

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

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

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

$$= \mathbf{-577.649 \text{ kJ mol}^{-1}}$$

Q. 4. **(i) Calculate the standard free energy change for the following reaction at 25°C.**

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

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

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

(ii) 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: [*HOTS*]

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

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

Ans. **(i)**
$$E^o_{cell} = E^o_{Ca^{2+}/Ca} - E^o_{Au^{3+}/Au}$$

$$= (-2.87 \text{ V}) - (1.50 \text{ V})$$

$$= -4.37 \text{ V}$$

$$\Delta_r G^o_{cell} = -nFE^o_{cell}$$

$$= -6 \times 96500 \times (-4.37 \text{ V})$$

$$= \mathbf{+2530.230 \text{ kJ/mol}}$$

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.

(ii) E^o_{cell} for reaction of tarnished silver ware with aluminium pan is

$$(-0.71 \text{ V}) - (-1.66 \text{ V}) \quad i.e., \quad +\mathbf{0.95 \text{ V}}$$

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

Q. 5. **(i) Write the cell reaction and calculate the e.m.f. of the following cell at 298 K:**
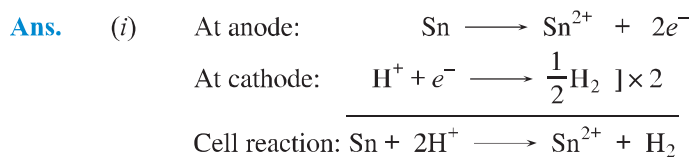
$$Sn(s) \mid Sn^{2+} (0.004 \text{ M}) \parallel H^+ (0.020 \text{ M}) \mid H_2(g) (1 \text{ bar}) \mid Pt(s)$$

(Given : $E^o_{Sn^{2+}/Sn} = -0.14$ V)

(ii) Give reasons:

(a) On the basis of E^o values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl.

(b) Conductivity of CH_3COOH decreases on dilution.

Ans. (*i*) At anode: $Sn \longrightarrow Sn^{2+} + 2e^-$

At cathode: $H^+ + e^- \longrightarrow \dfrac{1}{2} H_2 \;] \times 2$

Cell reaction: $\underline{Sn + 2H^+ \longrightarrow Sn^{2+} + H_2}$

$E^o_{cell} = E^o_{cathode} - E^o_{anode} = E^o_{H^+/H_2} - E^o_{Sn^{2+}/Sn} = 0.00\ V - (-0.14\ V) = 0.14\ V$

$[Sn^{2+}] = 4 \times 10^{-3}\ M;\ \ [H^+] = 2 \times 10^{-2}\ M;\ \ n = 2$

Substituting these values in the Nernst equation for above cell reaction

$$E_{cell} = E^o_{cell} - \frac{0.059}{n} \log \frac{[Sn^{2+}]}{[H^+]^2}, \text{ we get}$$

$$E_{cell} = 0.14 - \frac{0.059}{2} \log \frac{4 \times 10^{-3}}{(2 \times 10^{-2})^2}$$

or $E_{cell} = 0.14 - 0.0295 \log 10$

$E_{cell} = 0.1400 - 0.0295 = \mathbf{0.1105\ V}$

(*ii*) (*a*) Due to the oxygen overpotential, liberation of chlorine gas is preferred.

(*b*) As number of ions per unit volume that carry the current in the solution decreases on dilution and therefore conductivity of CH_3COOH decreases on dilution.

Q. 6. (***i***) **Represent the cell in which the following reaction takes place:**

$2Al(s) + 3Ni^{2+}(0.1\ M) \longrightarrow 2Al^{3+}(0.01\ M) + 3Ni(s)$

Calculate the emf if $E^o_{cell} = 1.41\ V$.

(***ii***) **How does molar conductivity vary with increase in concentration for strong electrolyte and weak electrolyte? How can you obtain limiting molar conductivity (Λ^o_m) for weak electrolyte?** [***CBSE 2019 (56/2/2)***]

Ans. (*i*) $2Al(s) + 3Ni^{2+}(0.1\ M) \longrightarrow 2Al^{3+}(0.01\ M) + 3Ni(s), n = 6$
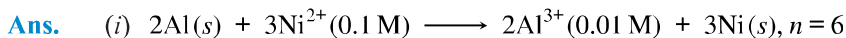
Cell representation: $Al(s) \,|\, Al^{3+}(0.01\ M) \,\|\, Ni^{2+}(0.1\ M)\,|\, Ni(s)$

Here, $n = 6$, $E^o_{cell} = 1.41\ V$, $[Ni^{2+}] = 0.1\ M$, $[Al^{3+}] = 1 \times 10^{-2}\ M$

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

$$E_{cell} = 1.41 - \frac{0.0591}{6} \log \frac{(10^{-2})^2}{(0.1)^3}$$

$$= 1.41 - 0.00985 \log 10^{-1}$$

$$= 1.41 + 0.00985 = 1.41985\ V$$

$E_{cell} = \mathbf{1.42\ V}$

(*ii*) With increase in concentration, the greater interionic attraction retard the motion of the ions and therefore, the molar conductivity falls for both with increasing concentration. The limiting molar conductivity (Λ^o_m) for weak electrolyte can be calculated by using Kohlrausch's law.

Q. 7. **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 cm^2 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^o_m for $NH_4Cl = 129.8$ S cm^2 mol^{-1}

Λ^o_m for $NaOH = 217.4$ S cm^2 mol^{-1}

Λ^o_m for $NaCl = 108.9$ S cm^2 mol^{-1}

Electrochemistry

By Kohlrausch's law,

$$\Lambda^o_m \text{ for } NH_4OH = \lambda^o_{NH_4^+} + \lambda^o_{OH^-}$$

$$= \Lambda^o_m(NH_4Cl) + \Lambda^o_m(NaOH) - \Lambda^o_m(NaCl)$$

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

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

$$\Lambda^c_m = 9.33 \text{ S cm}^2 \text{ mol}^{-1} \text{ (Given)}$$

$$\therefore \quad \text{Degree of dissociation } (\alpha) = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{9.33}{238.3} = 0.0392$$

or   Percentage dissociation $= 0.0392 \times 100 = \textbf{3.92\%}$

Calculation of dissociation constant

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Initial conc. c 0   0

Equilibrium conc. $c - c\alpha$ $c\alpha$ $c\alpha$

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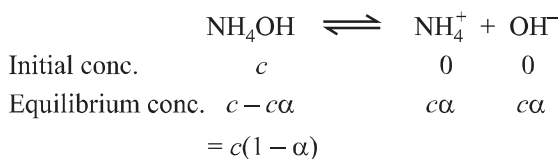
$$K = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1 - \alpha}$$

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

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

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

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

Q. 8. **(i) State Kohlrausch law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch law.**

(ii) Calculate Λ^o_m for acetic acid.
Given that Λ^o_m (HCl) = 426 S cm^2 mol^{-1}, Λ^o_m (NaCl) = 126 S cm^2 mol^{-1}
Λ^o_m (CH$_3$COONa) = 91 S cm^2 mol^{-1}   *[CBSE Delhi 2010]*

Ans. (i) For definition refer to Basic Concepts Point 12.

Expression for the molar conductivity of acetic acid: $\Lambda^o_m(CH_3COOH) = \Lambda^o_{CH_3COO^-} + \Lambda^o_{H^+}$

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

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

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

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

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

Q. 9. **(i) What type of a battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery.**

(ii) Calculate the potential for half-cell containing 0.10M K$_2$Cr$_2$O$_7$ (aq), 0.20 M Cr^{3+}(aq) and 1.0×10^{-4} M H$^+$(aq). The half cell reaction is
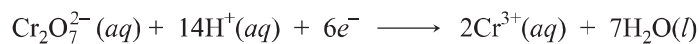**$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$**
and the standard electrode potential is given as $E^o = 1.33$V.   *[CBSE (AI) 2011]*

Ans. (i) Refer to Basic Concepts Point 26(b).

(ii) For half cell reaction

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

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

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

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

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

$$= 1.33 \text{ V} - \frac{0.0591}{6}\ [\log 4 + \log 10^{55}]$$

$$= 1.33 \text{ V} - \frac{0.0591}{6}\ [2\log 2 + 55\log 10]$$

$$= 1.33 \text{ V} - \frac{0.0591}{6}\ [2 \times 0.3010 + 55]$$

$$= 1.33 \text{ V} - 0.548 \text{ V} = \textbf{0.782 V}$$

Q. 10. **(i) Define the following terms:** [*CBSE (AI) 2014*]

  (a) Limiting molar conductivity

  (b) Fuel cell

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

Ans. (i) (a) The limiting value of 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.

(ii) For 0.1 mol L^{-1} KCl solution,

Conductivity, $\kappa = 1.29 \times 10^{-2}$ Ω^{-1} cm^{-1}, Resistance, $R = 100$ Ω

  Cell constant = Conductivity × resistance

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

For 0.02 mol L^{-1} solution,

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

  Conductivity, $\kappa = \dfrac{\text{Cell constant}}{\text{Resistance}}$

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

Molar conductivity, $\Lambda_m = \dfrac{\text{Conductivity }(\kappa) \times 1000\ cm^3\ L^{-1}}{\text{Molarity}}$

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

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

Electrochemistry

Q. 11. **(i)** State two advantages of H_2—O_2 fuel cell over ordinary cell. **[CBSE 2020 (56/1/1)]**

(ii) Silver is electrodeposited on a metallic vessel of total surface area 500 cm² 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. **(i)** **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*)

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

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

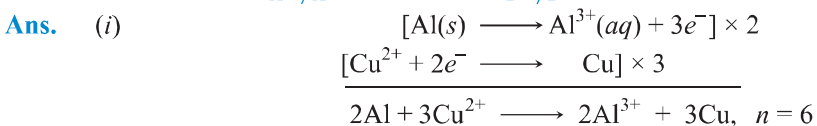$$V = \frac{4.029 \text{ g}}{10.5 \text{ g cm}^{-3}} = 0.3837 \text{ cm}^3$$

Let the thickness of silver deposited be x cm.

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

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

Q. 12. **(i)** Calculate E^o_{cell} for the following reaction at 298 K:

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

Given: $E_{cell} = 1.98$ V

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

Given: $[\,E^o_{A^{2+}/A} = -2.37 \text{ V}, \ E^o_{B^{2+}/B} = -0.14 \text{ V}]$ **[CBSE Central 2016]**

Ans. **(i)**
$$[Al(s) \longrightarrow Al^{3+}(aq) + 3e^-] \times 2$$
$$\underline{[Cu^{2+} + 2e^- \longrightarrow Cu] \times 3}$$
$$2Al + 3Cu^{2+} \longrightarrow 2Al^{3+} + 3Cu, \quad n = 6$$

Here, $n = 6$, $E_{cell} = 1.98$ V, $[Al^{3+}] = 1 \times 10^{-2}$ M, $[Cu^{2+}] = 1 \times 10^{-2}$ M

Substituting these values in the Nernst equation for above electrochemical change,

$$E_{cell} = E^o_{cell} - \frac{0.059}{n} \log \frac{[Al^{3+}]^2}{[Cu^{2+}]^3} \quad \text{we get}$$

$$1.98 = E^o_{cell} - \frac{0.059}{6} \log \frac{(10^{-2})^2}{(10^{-2})^3}$$

$$1.98 = E^o_{cell} - \frac{0.059}{6} \log 10^2$$

$$E^o_{cell} = 1.98 + \frac{0.059}{6} \times 2 \log 10$$

$$= 1.98 + 0.0197 = \textbf{1.9997 V}$$

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

Time allowed: 1 hour   **Max. marks: 30**

Choose and write the correct answer for each of the following.   **(3 × 1 = 3)**

1. **While charging the lead storage battery _____.**

    (*a*) $PbSO_4$ anode is reduced to Pb.   (*b*) $PbSO_4$ cathode is reduced to Pb.

    (*c*) $PbSO_4$ cathode is oxidised to Pb.   (*d*) $PbSO_4$ anode is oxidised to PbO_2.

2. **When 0.1 mole of MnO_4^{2-} is oxidised, the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^{-} is**

    (*a*) 96500 C   (*b*) 9650 C

    (*c*) 96.50 C   (*d*) 2 × 96500 C

3. **Which of the following statement is correct?**

    (*a*) E_{cell} and $\Delta_r G$ of cell reaction both are extensive properties.

    (*b*) E_{cell} and $\Delta_r G$ of cell reaction both are intensive properties.

    (*c*) E_{cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive property.

    (*d*) E_{cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property.
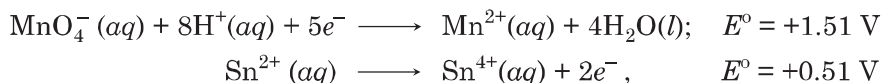
In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

   (*a*) *Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).*

   (*b*) *Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).*

   (*c*) *Assertion (A) is correct, but Reason (R) is incorrect statement.*

   (*d*) *Assertion (A) is incorrect, but Reason (R) is correct statement.*   **(3 × 1 = 3)**

4. **Assertion** (*A*) **:** Rusting of iron is quicker in saline water than in ordinary water.

    Reason   (*R*) **:** Salt water helps in flow of current in the miniature cell developed on the iron surface.

5. **Assertion** (*A*) **:** An electrochemical cell can be set up only if the redox reaction is spontaneous.

    Reason   (*R*) **:** A reaction is spontaneous if free energy change is negative.

6. **Assertion** (*A*) **:** If $\lambda^o_{Na^+}$ and $\lambda^o_{Cl^-}$ are molar limiting conductivity of sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation: $\lambda^o_{NaCl} = \lambda^o_{Na^+} + \lambda^o_{Cl^-}$

    Reason   (*R*) **:** This is according to Kohlrausch law of independent migration of ions.

Answer the following questions:

7. What does the negative sign in the expression $E^o_{Zn^{2+}/Zn} = -0.76\,V$ mean?   **(1)**

8. What is the value of K_c, when $E^o = 0\,V$?   **(1)**

9. (*i*) For a weak electrolyte, molar conductance in dilute solution increases sharply as its concentration in solution is decreased. Give reason.

    (*ii*) Write overall cell reaction for lead storage battery when the battery is being charged. **(2)**

Electrochemistry

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

$$MnO_4^- \ (aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l); \quad E^o = +1.51 \text{ V}$$
$$Sn^{2+} \ (aq) \longrightarrow Sn^{4+}(aq) + 2e^-, \quad E^o = +0.51 \text{ V}$$

Construct the redox equation from the standard potential of the cell and predict if the reaction is reactant favoured or product favoured. **(2)**

11. Determine the values of equilibrium constant (K_c) and ΔG^o for the following reaction:

$$Ni(s) + 2Ag^+(aq) \longrightarrow Ni^{2+}(s) + 2Ag(s), E^o = 1.05 \text{ V}$$
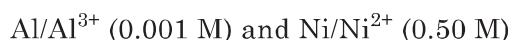
(1 F = 96500 C mol^{-1}) **(2)**

12. 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. **(2)**

13. 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.

$E^o_{Ni^{2+}/Ni} = -0.25 \text{ V}; \ E^o_{Al^{3+}/Al} = -1.66 \text{ V (log } 8 \times 10^{-6} = -5.097)$ **(3)**

14. The conductivity of 0.001028 mol L^{-1} acetic acid is 4.95×10^{-5} S cm^{-1}. Calculate its dissociation constant if Λ^o_m for acetic acid is 390.5 S cm^2 mol^{-1}. **(3)**

15. Give three point of differences between electrochemical cell and electrolytic cell. **(3)**

16. Consider the figure given below and answer the following questions.
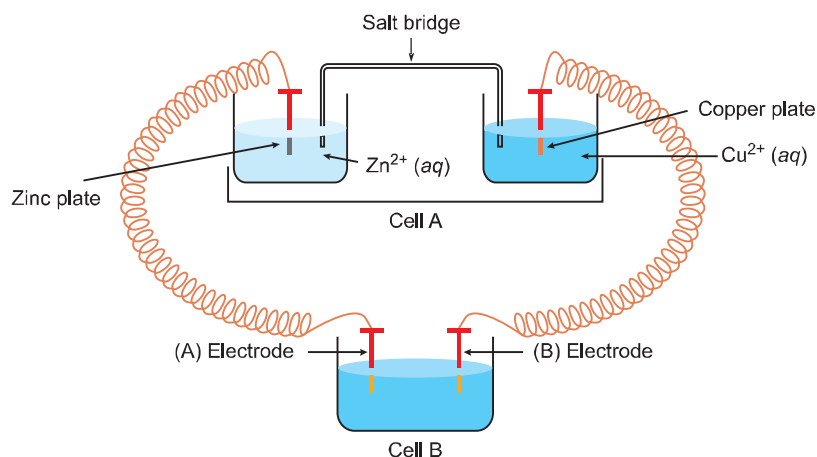
(i) Cell 'A' has $E_{cell} = 2$ V and Cell 'B' has $E_{cell} = 1.1$ V. Which of the two cells 'A' or 'B' will act as an electrolytic cell? Which electrode reactions will occurs in this cell?

(ii) In cell 'A' has $E_{cell} = 0.5$ V and cell 'B' has $E_{cell} = 1.1$ V then what will be the reactions at anode and cathode? **(5)**

Answers

1. (a)   2. (b)   3. (c)   4. (a)   5. (b)   6. (a)   10. 0.3105 V
11. 3.92×10^{39}; –202.65 kJ   13. 1.4602 V   14. 1.77×10^{-5} mol L^{-1}