UNIT 3

Electrochemistry

Points to Remember

Galvanic cells: A galvanic cell is a device in which chemical energy is converted into electrical energy.e.g. Daniell cell.

- Daniell cell consists of two beakers containing $CuSO_4$ and $ZnSO_4$ solutions. A zinc rod is dipped into $ZnSO_4$ while a copper rod is dipped into $CuS0_4$ solution. In this cell zinc reacts with copper (II) ions and produces metallic copper and zinc (II) ion according to the reaction :

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

  Electrons flow from anode to cathode in the external circuit. The solutions of two beakers are connected by salt bridge.

  Functions of salt bridge :

  (i) It allows the flow of current by completing the electrical circuit.

  (ii) It maintains electrical neutrality of the cell.

  Electrode Potential

  The potential difference that develops between the metal and its electrolyte is known as electrode potential.

  (a) **Oxidation potential:** The tendency of an electrode to lose electrons or to get oxidised is called oxidation potential. For example, $M(s) \longrightarrow M^{n+}(aq) + ne^-$

  (b) **Reduction potential:** The tendency of an electrode to gain electrons or to get reduced is called reduction potential. For example, $M^{n+}(aq) + ne^- \longrightarrow M(s)$

  According to latest IUPAC convention, the half reactions are always written as reduction half reaction and their potentials are represented by reduction potentials

  $$\boxed{E^o_{ox} = - E^o_{red}}$$

  Cell potential of a cell

  The potential difference between the two electrodes of galvanic cell is called the cell potential and is measured in volts.

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

- Half cell potential or electrode potential of M^{n+}/M cannot measured directly because a half cell whether oxidation or reduction half cell cannot work on its own we cannot determine the absolute electrode potential of an electrode. To solve this problem, a reference electrode standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE) is used, its standard electrode potential (oxidation as well as reduction) is arbitrarily taken as zero.

Electrochemical series or e.m.f. series

Arrangement of different electrodes in the order (increasing or decreasing) of their standard electrode potentials.

Applications of the electrochemical series:

1. **To compare the relative oxidising and reducing powers:** substances with higher reduction potentials are stronger oxidising agents.
2. **Calculation of standard emf of electrochemical cell (E^o_{cell})** :
   $E^o_{cell} = E^o_{Cathode} - E^o_{anode}$
3. **Comparison of the reactivity of metals:** A metal with smaller reduction potential has a strong tendency to get oxidised and can displace metals having greater reduction potential from the aqueous solution of their salts.
4. **To predict whether a metal displace hydrogen from acids :** Metals having a negative reduction potential value can displace hydrogen from acid.
5. **To predict the spontaneity of a redox reaction:** E_{cell} should be positive. If emf comes out to be negative, the direct reaction as given cannot take place, the reverse reaction may takes place.

Effect of opposing potential on the cell reaction

Consider a Daniell cell: $Zn_{(s)} | Zn^{2+}_{(aq)} || Cu^{2+}_{(aq)} | Cu$

- When Subscript $E_{ext} < 1.1V$, Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn, the cell acts as electrochemical cell.
- When $E_{ext} > 1.1$ V, flow of current in this case occurs from zinc electrode to copper electrode, the cell now **electrolytic cell.**

NERNST EQUATION FOR SINGLE ELECTRODE

For the electrode reaction $M^{n+}(aq) + ne^- \longrightarrow M(s)$

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF} \ln \frac{[M_{(s)}]}{[M^{n+}_{(aq)}]}$$

Concentration of pure solid [M] should be taken as unity

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{2.303\ RT}{nF} \log \frac{1}{[M^{n+}]} \quad (\text{since } \log_e = 2.303 \log_{10})$$

At 298 K

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]}$$

Calculation of cell potential using Nernst Equation

$$E_{cel} = E^{o}_{cell} - \frac{2.303RT}{nF} \log_{10} \frac{[PRODUCTS]}{[REACTANTS]} \quad \text{At 298K}$$

$$E_{cel} = E^{o}_{cell} - \frac{0.059.}{n} \log_{10} \frac{[PRODUCTS]}{[REACTANTS]}$$

EQUILIBRIUM CONSTANT (Kc) FROM NERNST EQUATION

$$E^{o}_{cell} = \frac{2.303RT}{nF} \log_{10} K_c$$

$$E^{o}_{cell} = \frac{0.059}{n} \log_{10} K_c \quad \text{at 298 K}$$

GIBB'S ENERGY CHANGE AND CELL POTENTIAL

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

$\Delta_r G^{o} = -nF\, E^{o}_{cell}$

$\Rightarrow$ **For cell reaction to be spontaneous, ΔG^{o} must be negative, the value of E^{o}_{cell} must be positive.**

FREE ENERGY CHANGE AND EQUILIBRIUM CONSTANT

$\Delta_r G^{o} = -2.303\, RT \log_{10} K_c$

CONDUCTORS: Substances that allow the flow of electric current through them are called electrical conductors .

Metallic / electronic Conductor

- Flow of electricity due to movement of electrons
- No chemical change as there is no transfer of matter.
- Faraday's law is not followed
- Conduction decreases with temperature because kernels start vibrating faster which interfere in the flow of electrons.

Electrolytic conductor

- Flow of electricity due to movement of ions
- Ions are oxidised or reduced at the electrodes, hence involve transfer of matter .
- Faraday’s law is followed
- Conduction increase with temperature because dissociation increases and viscosity decreases

FACTOR AFFECTING ELECTROLYTIC CONDUCTANCE

1. **Interionic interactions**: Greater the interionic interactions lesser is the mobility of the ions, hence lesser will be conductance.
2. **Solvation of ions:** More the solvation of the ions, the lesser will be the electrical conductivity.
3. **Viscosity of the solvent:** Higher the viscosity of the solvent, lesser is the mobility of ions.
4. **Temperature:** As the temperature of the electrolytic solution is increased, the kinetic energy of the ions in the solution increases, hence their mobility increases. This results in the increase of electrical conductance of the electrolytic solution.
5. **Effect of concentration of solution:** More the concentration of electrolytic solution smaller will be its electrical conductivity.
   - Weak electrolyte ionise to a lesser extent in concentrated solution, on dilution ionisation increases which causes increase in conductivity.
   - Strong electrolyte ionise completely. On dilution interionic attraction decreases, so mobility of ions increases, consequently conductance increases.

Electrolytic conduction

Resistance (R) : A measure of obstruction in the flow of current. Unit: ohm (Ω)

$R \propto \frac{l}{A}$ $R = \rho \frac{l}{A}$

ρ, constant of proportionality, known as specific resistance or resistivity.

Resistivity or specific resistance (ρ) :

$\rho = R \frac{A}{l}$

Resistivity may be defined as the resistance offered by the conductor of 1 m length with area of cross section equal to $1\ m^2$

Unit : ohm. m or Ω. m

Conductance (G): Conductance is a measure of the ease with which current flows through the conductor. It is reciprocal of electrical resistance.

$$G = 1/R$$

Units: ohm^{-1} or Ω^{-1} *i.e.*, Siemen (S), $1S = 1\Omega^{-1}$

Specific conductance or conductivity (κ): conductivity is the reciprocal of resistivity.

$$\kappa = 1/\rho = \frac{1}{R}.\frac{l}{a}$$, l/a is known as cell constant (G*)

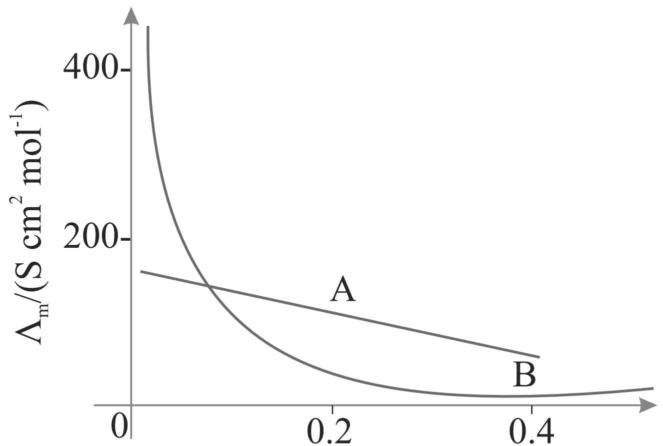
κ = G. G* i.e. $\boxed{\textbf{Conductivity= Conductance x cell constant}}$

Units of k= $ohm^{-1}\,cm^{-1}$ or Sl units are $ohm^{-1}\,m^{-1}$ or $S\,m^{-1}$

- **Molar conductivity (Λ_m) -** of a solution is the conductance of all the ions produced from one mole of the electrolyte dissolved in a given volume of the solution when the electrodes are one cm apart and the area of the electrodes is so large that the whole of the solution is contained between them.

  $\boxed{\Lambda_m = \kappa \times 1000/\text{Molarity}}$, Unit: $ohm^{-1}cm^{2}\,mol^{-1}$ (Scm^2mol^{-1}), Sl unit= Sm^2mol^{-1}
- **Effect of dilution**. Conductance increases (because total no. of ions increase), conductivity decreases (because no. of ions per unit volume decreases), molar conductivity increase with dilution.
- **Variation of molar conductivity with concentration**. For a strong electrolyte, it is given by **Debye - Huckel - Onsager equation**: $\Lambda_m = \Lambda^o_m - A\sqrt{c}$ where A is a constant depending upon the nature of the solvent and temperature. Λ^o_m **is limiting molar conductivity and it is defined as the molar conductivity of electrolyte when concentration appproaches zero i.e. at infinite dilution.**

  Graphical representation of the variation of Λ_m vs $\sqrt{c}$



It can be seen that if we plot Λ_m against $c^{1/2}$, we obtain a straight line with intercept equal to Λ^{O}m and slope equal to '- *A*'.

Reasons for increase of Λ_m with dilution.

- (Molar conductivity of a strong electrolyte increases with dilution because interionic attractions decrease with dilution. Small deviations at higher concentration are due to large interionic attractions.)
- (Molar conductivity of a weak electrolyte increases with dilution because dissociation increases with dilution.)

Inability to determine limiting molar conductivity experimentally for a weak electrolyte. Molar conductivity at infinite dilution for a strong electrolyte can be found by extrapolation to zero concentration but that of weak electrolyte cannot be thus found.

KOHLRAUSCH LAW OF INDEPENDENT MIGRATION OF IONS

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

For e.g. $Al_2(SO_4)_3$ $\Lambda^0_m[Al_2(SO_4)_3] = 2\lambda^0_m(Al^{3+}) + 3\lambda^0_m(SO_4^{2-})$

Applications of Kohlrausch's Law

a) In calculation of limiting molar conductivity of weak electrolyte

b) In calculation of degree of dissociation, i.e., $\alpha = \Lambda_m/\Lambda^0_m$

c) In calculation of dissociation constant (K_α) by using value of α, $K_\alpha = c\alpha^2/ 1-\alpha$

ELECTROLYTIC CELLS : The device in which conversion of electrical energy into chemical energy is done is known as electrolytic cell.

PRODUCTS OF ELECTROLYSIS: If an electrolytic solution consists of more than two ions then during electrolysis all the ions are not discharged simultaneously but certain ions are liberated at the electrode in preference to the others. This is based on the principle of preferential discharged theory which states that the ion which requires least energy is discharged first.

Batteries and Fuel Cells :

Batteries are classified as two types:

Primary: use oxidation-reduction reactions that cannot be reversed very easily

Secondary : reactions of these batteries can be reversed (rechargeable batteries)

Primary Cells :

(i)Dry cell :

Anode(-) $Zn(s) \rightarrow Zn^{2+} + 2e^-$

Cathode(+) $2MnO_{2(s)} + 2NH_4^+ + 2e^- \rightarrow Mn_2O_3 + 2NH_3 + H_2O$

(ii) Mercury Cell :

Anode(-) $Zn(Hg) + 2OH^- \rightarrow ZnO + H_2O + 2e^-$

Cathode(+) $HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$

Overall reaction —$Zn + HgO \rightarrow ZnO + Hg$

Secondary Cells :

(i)Lead storage battery

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

Cathode(+) $PbO_2(s) + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$

Cell reaction- $Pb(s) + PbO_2(s) + 2H_2SO_4 \rightarrow 2PbSO_4 + 2\,H_2O$

On recharging cell reaction is reversed.

(ii)**Nickel — Cadmium cell.**

Anode (-) $Cd + \quad 2\,OH^- \rightarrow Cd(OH)_2 + 2e^-$

Cathode (+) $NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$

Cell reaction — $Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O_{(l)}$

Cell reaction is reversed on recharging.

FUEL CELLS :

It is an electrochemical device used to convert combustion energy produced by burning of fuels into electrical energy. Fuel used are in gaseous state(H_2,CH_4,CO etc) e.g. **H_2- O_2 fuel cell.**

Reactions are

Anode (-) $2[H_{2(g)} + 2OH^-_{(aq)} \rightarrow 2\,H_2O_{(aq)} + 2e^-]$

Cathode(+) $O_2 + 2\,H_2O + 4e^- \rightarrow 4OH^-_{(aq)}$

Cell reaction $2\,H_{2(g)} + O_{2(g)} \rightarrow 2\,H_2O_{(l)}$

Advantages

1) Efficient than any conventional source.

2) No pollution.

3) Electrodes are not affected

CORROSION : It involves the slow destruction of a metal as a result of its reaction with moisture and gases present in atmosphere. More reactive metals corrode more easily. Corrosion of Iron is called rusting.

Mechnism of Rusting

Electrochemical theory of rusting :

Impure surface of iron act as an electrochemical cell. Pure Iron act as anode and impure iron as cathode. Carbonic acid act as the electrolyte(It provide H^+ ion).

(i) $H_2O + CO_2 \longrightarrow H_2CO_3 \leftrightharpoons 2H^+ + CO_3^{2-}$

Setting up of Electrochemical cell on Iron surface

(ii) $Fe(s) \longrightarrow Fe^{2+} + 2e^-$ **(Anode)** $E° = — 0.44\,V$

(iii) $O_2 + 4H^+ + 4e^- \longrightarrow 2\,H_2O$ **(Cathode)** $E° = + 1.23\,V$

$$2Fe(s) + O_2 + 4H^+ \longrightarrow 2Fe^{2+} + 2\,H_2O \quad E_{ce11} = 1.67\,V$$

Cathode is further oxidised by atmospheric oxygen to form rust. $Fe_2O_3.x\,H_2O$

(iv) $4Fe^2 + O_2 + 4H_2O \longrightarrow 2\,Fe_2O_3 + 8\,H^+$

$$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3.xH_2O \text{ (Rust)}$$

Prevention of corrosion :

1) **Barrier protection** — By coating with a suitable material —paint, oil, grease etc

2) Sacrificial protection — Coating with a more reactive metal. The process of coating the surface of iron with Zinc is called Galvanization. More reactive metal act as anode.

3) Alloying with metals that form oxide coats.

4) **Antirust solutions** — Alkaline phosphate or chromate solutions are applied on iron surface to form a heat resistant iron phosphate or chromate coating which prevent corrosion.

4) **Cathodic protection -** Here metal to be protected is set as cathode by attaching a more reactive metal to it. Now the more reactive metal undergo oxidation. for ex. Zn, Al or Mg can be used for cathodic protection.

OBJECTIVE TYPE QUESTIONS

I. MULTIPLE CHOICE QUESTIONS

1. The potential of a hydrogen electrode at pH=10 is :

(a) 0.591 V (b) 0.00 V

(c) -0.591 V (d) -0.059 V

2. How many coulomb are required for the oxidation of 1 mol of H_2O_2 to O_2?

(a) 9.65×10^4C (b) 93000 C

(c) 1.93×10^5C (d) 19.3×10^2C

3. KCl is used in salt bridge because:

(a) It forms a good jelly with agar -agar

(b) It is a strong electrolyte

(c) It is a good conductor of electricity

(d) Migration factor of K^+ and Cl^- ions are almost equal

4. For a spontaneous reaction the ΔG, equilibrium constant (K) and E^0cell will be respectively.

(a) -ve, < 1, - ve (b) - ve, > 1, - ve

(c) - ve, > 1, + ve (d) + ve, > 1, - ve

5. If a salt bridge is removed between the half cells, the voltage:

(a) drops to zero (b) does not change

(c) increase gradually (d) increases rapidly

6. The process in which chemical change occurs on passing electricity is termed :

(a) Ionisation (b) neutralisation

(c) electrolysis (d) hydrolysis

7. The charge required for the reduction of 1 mol of MnO_4^- to MnO_2 is:

(a) 1F (b) 3F

(c) 5F (d) 4F

8. The value of Λ_m^0 for NH_4Cl, NaOH and NaCl are 129.8, 248.1 and 126.4 $Ohm^{-1}cm^2\ mol^{-1}$ respectively. Calculate Λ_m^0 for NH_4OH solution.

(a) 215.5 $Ohm^{-1}cm^2\ mol^{-1}$ (b) 251.5 $Ohm^{-1}cm^2\ mol^{-1}$

(c) 244.7 $Ohm^{-1}cm^2\ mol^{-1}$ (d) 351.5 $Ohm^{-1}cm^2\ mol^{-1}$

9. In a Galvanic cell the electrical work done is equal to :
   (a) Free energy change (b) mechanical work done
   (c) thermodynamic work done (d) all of the above

10. Zn cannot displace following ions from their aqueous solution :
   (a) Al^{3+} (b) Cu^{2+}
   (c) Fe^{2+} (d) Na^{+}

11. Electrical work done is equal to :
   (a) $-nFE^{0}_{cell}$ (b) nFE^{0}_{cell}
   (c) nE^{0}_{cell} (d) None of these

12. Which are not the following decrease with increase in concentration?
   (a) Conductance (b) Molar conductance
   (c) Conductivity (d) All of the above

13. The standard electrode potential values of three metallic cations, X, Y, Z are 0.52,-3.03 and -1.18V, respectively. The order of reducing power of the corresponding metals is
   (a) $Y>Z>X$ (b) $X>Y>Z$
   (c) $Z>Y>X$ (d) $Z>X>Y$

14. How is elctrical conductance of a conductor related with length and area of cross section of the conductor?
   (a) $G=k.l.a^{-1}$ (b) $G=l.a.k^{-1}$
   (c) $G=k.a.l^{-1}$ (d) $G=k.l.a^{-2}$

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

16. The cell constant of a conductivity cell__________________.
   (a) changes with change of electrolyte. (b) changes with change of concentration of electrolyte.
   (c) changes with temperature of electrolyte. (d) remains constant for a cell.

17. An electrochemical cell can behave like an electrolytic cell when
   (a) $E_{cell}=0$ (b) $E_{cell}>E_{ext}$
   (c) $E_{ext}>E_{cell}$ (d) $E_{cell}=E_{ext}$

18. Which of the following statement is not correct about an inert electrode in a cell?
   (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.

19. The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called
    (a) Cell potential
    (b) Cell emf
    (c) Potential difference
    (d) Cell voltage
20. The positive value of the standard electrode potential of Cu^{2+} /Cu indicates that :
    (a) this redox couple is a stronger reducing agent than the H^+/H_2 coupl e.
    (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.

II FILL IN THE BLANKS:

1. The conductance of a solution placed between two opposite faces of a centimetre cube is called...................... .
2. Strong electrolytes give almost a linear plot of Λ_m versus............................ .
3. In a galvanic cell, the electrons flow from .... to...................through connecting wire.
4. The unit of resistivity is ....
5. For the spontaneous cell reaction, E^0 should be........................ .
6. Conductivity of an electrolytic solution.......................with increase in dilution.
7. The unit of cell constant is.......................
8. An aqueous solution of copper nitrate....................be stored in iron vessel.
9. Protection of iron by coating with zinc is called ....
10. To deposit two mol of Ca from $CaCl_2$................................electricity is required .

III ASSERTION REASON TYPE QUESTIONS

(a) Both assertion and reason are correct statements, and reason is the correct explanation of the assertion.

(b) Both assertion and reason are correct statements, but reason is not the correct explanation of the assertion.

(c) Assertion is correct, but reason is wrong statement.

(d) Assertion is wrong, but reason is correct statement.

1. **Assertion:** When aqueous sodium chloride solution is electrolysed, Oxygen gas is produced at the anode.

   Reason : It is due to the overpotential for oxidation of water to oxygen.

2. **Assertion:** Molar conductivity of an electrolyte increases with decrease in concentration.

   Reason: The mobility of ions decrease with increase in concentration.

3. **Assertion:** Reduction of 1 mole of Cu^{2+} ions require 2 faraday of charge.

   Reason: 1 Faraday is equal to the charge of 1 mole of electrons.

4. **Assertion:** Lechlanche cell gives constant voltage throughout its life.

   Reason: The overall reaction of button cell does not involve any ion in solution whose concentration can change during its life time.

5. **Assertion:** Coating iron with zinc prevents rusting.

   Reason: The coating of zinc prevents moist air to come in contact with the metal.

6. **Assertion:** More negative the electrode potential greater is the power to act as oxidising agent .

   Reason: As the electrode potential becomes more negative there is greater tendency to undergo oxidation.

7. **Assertion:** Secondary cells are cells which can be recharged after use.

   Reason: The products are electrolysed back to the initial reactants during recharge of the cell.

8. **Assertion :** Kohlrausch law helps to find the molar conductivity of weak electrolyte at infinite dilution.

   Reason : Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally.

9. **Assertion :** Fluorine is the best oxidising agent.

   Reason : Fluorine has highest reduction potential.

10. **Assertion:** Λ_m for weak electrolytes shows a sharp increase when the electrolyte solution is diluted.

    Reason: For weak electrolytes degree of dissociation increases with dilution of solution.

IV ONE WORD ANSWER TYPE QUESTIONS

1. How much charge in Faraday is required for the reduction of 1 mol Al^{3+} to Al?
2. What is the effect of increase of temperature on ionic conductance?
3. What flows in the internal circuit of a Galvanic cell?
4. Name of the reference electrode in determining the standard electrode potential.
5. Can E^0_{cell} for a cell reaction ever be equal to zero?
6. Name the quantity which is reciprocal of resistivity.
7. How will pH of brine (aqueous NaCl solution) be affected when it is electrolysed?
8. What is the name given to the constant quantity of charge carried by one mole electrons?
9. Name of reference electrode used for determination of E^0 instead of NHE/SHE.
10. What is the effect of presence of salt in water on the rate of rusting of iron?
11. Name the type of cell which was used in Apollo Space Programme for providing electrical power.
12. Under what condition is $E_{cell} = 0$ or $\Delta_r G = 0$?
13. How is equilibrium constant of a reaction related to standard cell potential?
14. Mention the direction of flow of electrons in the following cell:
    $Zn_{(s)} | Zn^{2+}_{(aq)} || Ag^{+}_{(aq)} | Ag_{(s)}$
15. A galvanic cell has electrical potential of 1.1 V. If an opposing potential of 1.1 V is applied to this cell. What will happen to the cell reaction and current flowing through the cell ?

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark Questions)

Q. 1. Why is it not possible to measure single electrode potential ?

Ans. Because the half cell containing single electrode cannot work independently, as charge cannot flow on its own in a single electrode.

Q. 2. Name the factors on which emf of a cell depends.

Ans. Emf of a cell depends on following factors :

(a) Nature of reactants

(b) Concentration of solution in two half cells

(c) Temperature

Q. 3. What is the effect of temperature on the electrical conductance of metal ?

Ans. Temperature increases, electrical conductance decreases.

Q. 4. What is the effect of temperature on the electrical conductance of electrolyte ?

Ans. Temperature increases, electrical conductance increases.

Q. 5. What is the relation between conductance and conductivity ?

Ans. $\Lambda_m^c = \frac{k}{C}$

Q. 6. Reduction potentials of 4 metals A, B, C and D are – 1.66 V, + 0.34 V, + 0.80 V and – 0.76 V. What is the order of their reducing power and reactivity ?

Ans. $A > D > B > C$

Q.7. Why does a dry cell become dead even if it has not been used for a long time?

Ans. NH_4Cl is acidic in nature. It corrodes zinc container

Q.8. Why Na cannot be obtained by the electrolysis of aqueous NaCl solution ?

Ans. Due to low reduction potential, Na^+ ions are not reduced at cathode. Instead, H^+ are reduced and H_2 is obtained.

Q.9. What is the use of platinum foil in the hydrogen electrode ?

Ans. It is used for the in and out flow of electrons.

Q.10. Why $\Lambda_m°$ for CH_3COOH cannot be determined experimentally ?

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

Q.11. Why is it necessary to use a salt bridge in a galvanic cell?

Ans. To complete the inner circuit and to maintain electrical neutrality of the electrolytic solutions of the half cells.

Q.12. Why does mercury cell gives a constant voltage throughout its life?

Ans. This is because the overall cell reaction does not have any ionic concentration in it.

Q.13. What is the role of $ZnCl_2$ in a dry cell ?

Ans. $ZnCl_2$ combines with the NH_3 produced to form a complex salt $[Zn(NH_3)_2]Cl_2$.

Q.14. Why does the conductivity of a solution decrease with dilution ?

Ans. Conductivity of a solution is dependent on the number of ions per unit volume. On dilution, the number of ions per unit volume decreases, hence the conductivity decreases.

Q.15. Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

Ans. Methane and methanol.

Q.16. How does the pH of Aq-NaCl solution be affected when it is electrolysed ?

Ans. When Aq-NaCl solution is electrolysed , H_2 is liberated at cathode, Cl_2 at anode and NaOH is formed in the solution. Hence pH of solution increase.

Q.17. Which reference electrode is used to measure the electrode potential of other electrodes?

Ans. Standard hydrogen electrode (SHE) whose electrode potential is taken as zero.

Q.18. Out of zinc and tin, which one protects iron better even after cracks and why ?

Ans. Zinc protects better because oxidation potential of zinc is greater but that of tin is less than that of iron.

Q.19. Define corrosion. What is the chemical formula of rust ?

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

20. What is the electrolyte used in a dry cell?

Ans. A paste of NH_4Cl

21. How much electricity is required in Coulomb for the oxidation of 1 mole of FeO to Fe_2O_3 ?

Ans. $Fe^{2+} \longrightarrow Fe^{3+} + e^{-1}$

So, $1F = 1F \times 96500C = 96500\,C$

22. Two metals A and B have reduction potential values - 0.76 V and +0.34V respectively. Which of these will liberate H_2 from dil. H_2SO_4 ?

Ans. Metal having higher oxidation potential will liberate H_2 from H_2SO_4. Thus, A will liberate H_2 from H_2SO_4 .

23. How does conc. of sulphuric acid change in lead storage battery when current is drawn from it ?

Ans. Concentration of sulphuric acid decreases.

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

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

Q.25. E^0 values of MnO_4^-, Ce^{4+} and Cl_2 are 1.507, 1.61 and 1.358 V respectively. Arrange these in order of increasing strength as oxidizing agent.

Ans. $Cl_2 < MnO_4^- < Ce^{4+}$

26. Explain Kohlrausch's law of independent migration of ions.

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

$$\Lambda^{\circ}_{Na_2SO_4} = 2\Lambda^{\circ}_{Na^+} + \Lambda^{\circ}_{SO_4^{2-}}$$

27. Give products of electolysis of an equeous solution of $AgNO_3$ with silver electrode.

Ans. At anode: $Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e^-$

At cathode: $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. How can you increase the reduction potential of an electrode for the reaction :

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

Ans. Nernst equation is :

$$E_{M^{n+}/M} = E^{\ominus}_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]} \quad \text{at 298k}$$

$E_{M^{n+}/M}$ can be increased by

(a) Increase in concentration of M^{n+} ions in solution.

(b) By increasing the temperature.

2. Calculate emf of the following cell at 298 K :

$$Mg(s) + 2Ag^+(0.0001M) \rightarrow Mg^{2+}(0.130\,M) + 2Ag(s)$$

[Given : $E^{\theta}_{cell} = 3.17$ V]

The Nernst equation for the cell is :

Ans.

$$E_{cell} = E^{\theta}_{cell} - \frac{0.059}{2}\log\frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$= 3.17 - \frac{0.059}{2}\log\frac{.130}{(.0001)^2}$$

$$= 3.17 - 0.21 = 2.96V$$

Q.3. Suggest a way to determine the $\wedge^{\circ}_{m}$ value of water

Ans. $\wedge^{\circ}_{m}(H_2O) = \Lambda^{\circ}_{m}(H^+) + \Lambda^{\circ}_{m}(OH^-)$

It can be determine from the value of

$\wedge^{\circ}_{m}(HCl)$, $\wedge^{\circ}_{m}(NaOH)$-$\wedge^{\circ}_{m}(NaCl)$. then,

$\wedge^{\circ}_{m}(H_2O) = \wedge^{\circ}_{m}(HCl) + \wedge^{\circ}_{m}(NaOH) - \wedge^{\circ}_{m}(NaCl)$

Q. 4. How much electricity in term of Faraday is required to produce 40 gram of Al from Al_2O_3 ? (Atomic mass of Al = 27 g/mol)

Ans. $Al^{3+} + 3e^- \rightarrow Al$

27 gram of Al require electricity = 3F

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

Q.5. Predict the product of electrolysis of an equeous solution of $CuCl_2$ with an inert electrode.

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

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

At cathode (Reduction): Cu^{2+} will be reduced in preference to H^+ ions.

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

At anode (Oxidation): Cl^- will be reduced in preference to OH- ions.

$$Cl^- \longrightarrow 1/2Cl_2 + 1e^-$$

Q.6. Calculate $\overset{o}{\Lambda}_m$ for $CaCl_2$ and $MgSO_4$ from the following data : $\Lambda^0_m(Ca^{2+})=119.0, Scm^2\ mol^{-1}$, $Mg^{2+}=106.0$, $Cl^- = 76.3$ and $SO_4^{2-} = 160.0 Scm^2\ mol^{-1}$

$$\overset{o}{\Lambda}_{m(CaCl_2)} = \overset{o}{\Lambda}_{m\left(Ca^{2+}\right)} + 2\overset{o}{\Lambda}_{m\left(Cl^-\right)} \quad = 119 + (2 \times 76.3) = 271.6 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\overset{o}{\Lambda}_{m(MgSO_4)} = \overset{o}{\Lambda}_{m\left(Mg^{2+}\right)} + \overset{o}{\Lambda}_{m\left(SO_4^{2-}\right)} \quad = 106 + 160 = 266 \text{ S cm}^2 \text{ mol}^{-1}$$

Q. 7. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Ans. $H^+ + e^- \rightarrow ½H_2 \quad n = 1$

$$E = E^{\Theta} - \frac{0.0591}{n} \log \frac{1}{\left[H^+\right]}$$

$$E = 0 - \frac{0.0591}{1} \times pH$$

$$E = -0.0591 \times 10 \text{ v}$$

$$E = -0.591 \text{ V}$$

Q. 8. If a current of 0.5 amp flows through a metallic wire for 2 hours, how many electrons would flow through the wire ?

Ans. $q = i \times t = 0.5 \times 2 \times 60 \times 60 = 3600$ C

96500 Coulombs are equal to $6.022 \times 10^{23} e^-$

So, 3600 Coulombs $= \dfrac{6.022 \times 10^{23}}{96500} \times 3600 = 2.246 \times 10^{22}$ electrons

Q.9. Calculate the electrode potential of a copper wire dipped in 0.1M $CuSO_4$ solution at 25°C. The standard electrode potential of copper is 0.34 Volt.

Ans. The electrode reaction written as reduction potential is

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

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]} = 0.34 - \frac{0.0591}{2}\log\frac{1}{0.1} = 0.3104 \text{ V}$$

Q.10. The conductivity of a 0.20M solution of KCl at 298K is 0.0248 S cm^{-1}. Calculate molar conductivity.

Ans. Molar conductivity $= \dfrac{k \times 1000}{M} = \dfrac{0.0248 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.2 \text{ mol L}^{-1}}$

$= 124.0 \text{ S cm}^2 \text{ mol}^{-1}$

Q.11. Define conductivity and molar conductivity for a solution of an electrolyte.

Ans. Conductivity is defined as ease with which current flows through electrolyte. It is reciprocal of specific resistance. Molar conductivity is conductance of all the ions produced by one mole of electrolyte when electrodes are at unit distance apart and have sufficient area of cross-section to hold electrolyte.

Q.12. The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is 0.146 × 10^{-3} S cm^{-1} ?

Ans. Cell constant $= k \times R$

$= 0.146 \times 10^{-3} \times 1500$

$= 0.219 \text{ cm}^{-1}$

Q.13. Indicate the reaction which take place at cathode and anode in fuel cell.

Ans. At cathode: $O_2(g)+2H_2O+4e^- \rightarrow 4OH^-(aq)$

At anode: $2H_2(g)+4OH^-(aq) \rightarrow 4H_2O+4e^-$

The overall reaction is : $2H_2(g)+O_2(g) \rightarrow 2H_2O(l)$

Q.14. The standard reduction potential for the Zn^{2+} (aq)/Zn (s) half cell is – 0.76V. Write the reactions occurring at the electrodes when coupled with standard hydrogen electrode (SHE).

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

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

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$$

Q.15. What type of a battery is lead storage cell ? Write the anode and cathode reaction and overall reaction occuring in a lead storage battery during discharging and recharging cell.

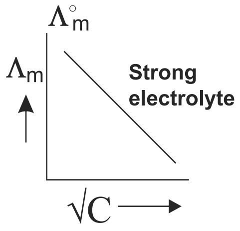
Ans. It is a secondary cell.

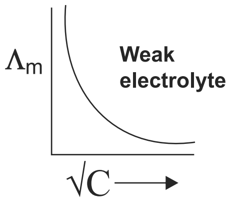
Anode reaction: $Pb+SO_4^{2-} \longrightarrow PbSO_4+2e^-$

Cathode reaction: $PbO_2+4H^+ +SO_4^{2-}+2e^- \longrightarrow PbSO_4+2H_2O$

$Pb(s)+PbO_2(s)+2H_2SO_4 \underset{\text{Recharging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 2PbSO_{4(s)}+2H_2O(l)$

Q.16. Draw a graph between Λ°_m and $\sqrt{C}$ for strong and weak electrolyte.





Q.17. Predict the products of electrolysis in each of the following:

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

(b) An aqueous solution of $Cu\,Cl_2$ with Pt electrodes.

Ans. (a) At Anode (Oxidation)

$4OH^- - 4e^- \longrightarrow 2H_2O+O_2$

At cathode (Reduction)

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

(b) At anode (Oxidation)

$Cl^- \longrightarrow \frac{1}{2}Cl_{(g)} + e^-$

$\frac{1}{2}Cl+Cl \longrightarrow Cl_2$

At cathode (Reduction)

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

Q.18. Determine the values of equilibrium constant K_c and ΔG^θ for the following reaction :

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

Ans.

$$\Delta G^\theta = -nFE^\theta_{cell}$$

$$n = 2,\ E^\theta_{cell} = 1.05\ V$$

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

$$\Delta G^\theta = -2 \times 1.05 \times 96500$$

$$= -202.650\ kJ$$

$$\Delta G^\theta = -RT\ln K_c$$

$$\ln K_c = -\frac{\Delta G^\theta}{RT} = \frac{-202.650 \times 10^3}{8.314 \times 298}$$

$$K_c = 3.32 \times 10^{35}$$

Q.19. The K_{sp} for AgCl at 298 K is 1.0×10^{-10}. Calculate the electrode potential for Ag^+/Ag electrode immersed in 1.0M KCl solution. Given $E^\circ Ag^+/Ag = 0.80$ V.

Ans.

$$AgCl\,(s) \rightleftharpoons Ag^+ + Cl^-$$

$$K_{sp} = [Ag^+][Cl^-]$$

$$[Cl^-] = 1.0\ M$$

$$[Ag^+] = \frac{K_{sp}}{\left[Cl^-\right]} = \frac{1 \times 10^{-10}}{1} = 1 \times 10^{-10}\ M$$

Now, $Ag^+ + e^- \rightarrow Ag\,(s)$

$$E = E^\theta - \frac{0.059}{1}\log\frac{1}{\left[Ag^+\right]} = 0.80 - \frac{0.059}{1}\log\frac{1}{10^{-10}}$$

$$= 0.80 - 0.059 \times 10 = 0.21\ V$$

Q.20. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The free energy change for the decomposition reaction :

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2 \text{ is } \Delta G = +960 \text{ kJ}, F = 96500 \text{ C mol}^{-1}.$$

Ans.

$$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$$

$$n = \frac{6\times 2}{3} = 4e^-$$

$$\Delta G = -nFE$$

$$\Delta G = 960 \times 10^3 \text{ J}, n = 4, F = 96500 \text{ C mol}^{-1}$$

$$960 \times 10^3 = -4 \times 96500 \times E$$

$$E = -2.487 \text{ V}$$

Minimum potential difference needed to reduce $Al_2O_3 = -2.487$ V.

Q.21. Two electrolytic cells containing silver nitrate solution and copper sulphate solution are connected in series. A steady current of 2.5 amp was passed through them till 1.078 g of Ag were deposited . How long did the current flow ? What weight of copper will be deposited ? (Ag = 107.8 u, Cu = 63.5 u)

Ans. $W = z \times i \times t$

$$t = \frac{w}{z \times i}$$

$$t = \frac{1.078 \times 1 \times 96500}{107.8 \times 2.5} = 386 \text{ Seconds}$$

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

$$w = \frac{63.5}{2x96500} \text{ x } 2.5x386 = 0.3175 \text{ gram}$$

Q.22. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 amp for 20 minutes . What mass of the nickel will be deposited at the cathode ? (Ni = 58.7u)

Ans. $W = z \times i \times t$

$$z = \frac{58.7}{2 \text{ x } 96500}$$

$$w = 1.825 \text{ gram}$$

Q.23. The cell in which the following reaction occurs :

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

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

Ans.

$$n = 2$$

$$\Delta G^o = -nFE^0_{cell} = -2 \times 96500 \times 0.236 \text{ J} = -45.55 \text{ kJ/mol}$$

$$\Delta G^o = -2.303 \text{ RT} \log K_c$$

$$\log K_c = \frac{\Delta G^o}{-2.303RT} = \frac{45.55 \times 10^3}{2.303 \times 8.314 \times 298} = 7.983$$

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

Q.24. The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}. Calculate its degree of dissociation and dissociation constant. Given $\Lambda^o(H^+)$ = 349.6 S cm^2 mol^{-1}, $\Lambda^o(HCOO^-)$ = 54.6 S cm^2 mol^{-1}.

Ans.

$$\Lambda^o_m(HCOOH) = \Lambda^o_m(H^+) + \Lambda^o_m(HCOO^-)$$

$$= 349.6 + 54.6 \text{ S cm}^2 \text{ mol}^{-1} = 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda^o_m = 46.1 \text{ S cm}^2 \text{ mol}^{-1}$$

$$HCOOH \rightleftharpoons HCOO^- + H^+$$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{46.1}{404.2} = 0.114$$

	$HCOOH \rightleftharpoons$	$HCOO^-$ +	H^+
Initial conc.	C mol L^{-1}	0	0
At equil.	C(1 – α)	Cα	Cα

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.025 \times (0.114)^2}{1-0.114}$$

$$= 3.67 \times 10^{-4}$$

Q.25. **Calculate the standard cell potentials of galvanic cells in which the following reaction take place:**

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

Also calculate ΔG^o and equilibrium constant of the reaction.

Ans.

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

$$= 0.40-(-0.74) = 0.34V$$

$$\Delta \mathbf{G}^o = -nFE^0_{cell} = -6x96500x0.34 = -196860$$

$$= -196860\ j\ mol^{-1} = -196.86kJ/mol$$

$$-\Delta \mathbf{G}^o = 2.303XRT \log K_c$$

$$196860 = 2.303 \times 8.314 \times 298 \log K_c$$

or

$$\log K_c = 34.5014$$

$$K_c = \text{antilog } 34.5014 = 3.193 \times 10^{34}$$

Q.26. **Calculate the potential of the following cell**:

Sn^{4+} (1.5 M) + Zn → Sn^{2+} (0.5) + Zn^{2+} (2M).

Given : $E^0_{Sn^{4+}/Sn^{2+}} = 0.13V, E^0_{Zn^{2+}/Zn} = -0.76V$

Will the cell potential increase or decrease, if the concentration of Sn^{4+} is increased?

Ans.

$$E_{cell} = E^{\theta}_{cell} - \frac{0.0591}{n} \log \frac{[Sn^{2+}][Zn^{2+}]}{[Sn^{4+}][Zn]}$$

$$= 0.89 - \frac{0.0591}{2} \log \frac{0.5 \times 2}{1.5 \times 1} \quad = 0.89 - \frac{0.0591}{2} \log \frac{1}{1.5} \quad = 0.895\ V$$

On increasing the concentration of Sn^{4+}, EMF of the cell will increase.

Q.27. **E° (Cu^{2+}/Cu) and E° (Ag^+/Ag) is + 0.337 V and + 0.799 V respectively. Make a cell whose EMF is +ve. If the concentration of Cu^{2+} is 0.01M and E_{cell} at 25°C is zero, calculate the concentration of Ag^+.**

Ans. Cu is more reactive than silver, so that the cell is as $Cu|Cu^{2+}$ (0.01M) || $Ag^+(C)|Ag$ or cell reaction

$$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$$

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

$$= E^\circ_{cell} - \frac{0.0591}{n}\log\frac{(0.01)\times 1^2}{1\times[Ag^+]^2}$$

Or $[Ag^+] = 1.47 \times 10^{-9}$ M

Q.28. Calculate the potential of the cell at 298 K :

$Cd \mid Cd^{2+}$ (0.1M) $\parallel H^+$ (0.2M) $\mid$ Pt, H_2 (0.5 atm)

Given E° for Cd^{2+}/Cd = – 0.403 V, R = 8.314 J^{-1} mol^{-1}, F = 96500 C mol^{-1}.

Ans. The cell reaction is $Cd + 2H^+ (0.2M) \rightarrow Cd^{2+} (0.1M) + H_2$ (0.5 atm)

$$E^\circ_{cell} = 0 - (-0.403) = +0.403 \text{ V}$$

$$E_{cell} = 0.403 - \frac{2.303RT}{nF}\log\frac{[Cd^{2+}]\times P_{H_2}}{[Cd][H^+]^2}$$

$$= 0.403 - \frac{2.303\times 8.314\times 298}{2\times 96500}\log\frac{0.1\times 0.5}{(0.2)^2}$$

$$E_{cell} = 0.403 - 0.003 = 0.40 \text{ V}$$

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

Ans. Diameter = 1 cm, radius = 0.5 cm

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

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

$$\text{Conductivity (k)} = \frac{1}{\rho} = \frac{1}{87.135} = 0.01148 \text{ ohm}^{-1}\text{ cm}^{-1} = 0.01148 \text{ ohm cm}$$

$$\text{Molar conductivity } \Lambda^c_m = \frac{k\times 1000}{M} = \frac{0.01148\times 1000}{0.05} = 29.6 \text{ S cm}^2\text{ mol}^{-1}$$

Q.30. Name the cell which:

- **(a) was used in Apollo Space programme.**
- **(b) is used in automobiles and inverters.**
- **(c) is suitable for hearing aids and watches.**
- **(d) does not give a steady potential and is used in transistors.**

Ans. (a) Fuel cell

(b) Lead storage cell

(c) Mercury cell

(d) Dry cell

LONG ANSWER TYPE QUESTIONS (5 Marks)

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

Ans.

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

$$= \frac{7.896 \times 10^{-5}\ \text{S cm}^{-1} \times 1000\ \text{cm}^3\ \text{L}^{-1}}{0.00241\ \text{mol L}^{-1}} = 32.76\ \text{S cm}^2\ \text{mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda^o_m} = \frac{32.76}{390.5} = 8.39 \times 10^{-2}$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.00241 \times \left(8.39 \times 10^{-2}\right)^3}{1 - 8.39 \times 10^{-2}} = 1.86 \times 10^{-5}$$

Q.2. Three electrolytic cells A, B, C containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ respectively all connected in series. A Steady current of 1.5 amperes was passed through then until 1.45g of silver deposited at the cathode of cell B How long did the current flow? What mass of copper and of zinc were deposited ?

Ans. 108 g of silver is deposited by $Ag^+ + e^- \longrightarrow Ag_{(s)}$ is 96500C.

1.45 g silver is deposited by $= \frac{96500 \times 1.45}{108} = 1295.6C$

$$Q = I \times t$$
$$1295.6 = 1.5xt$$
$$t = \frac{12956}{1.5} = 863\ s$$

In cell A, the electrode reaction is

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

2F of electricity deposit Zn = 65.3 g

In cell A, the electrode reaction is

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

2F of electricity deposit Zn=65.3g

$$1295.6 \text{ of electricity deposit Zn} = \frac{65.3 \times 1295.6}{2 \times 96500}$$

$= 0.438$ g

In cell C, the electrode reaction is

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

2F of electricity deposit Cu = 63.5g

$$1295.6 \text{ of electricity deposit Cu} = \frac{63.5 \times 1295.6}{2 \times 96500}$$

$= 0.426$g

Q. 3. (a) State Kohlraush's law.

(b) Suggest a way to determine the Λ°_m for CH_3COOH.

(c) The Λ°_m for sodium acetate, HCl, NaCl are 91.0, 425.9 and 126.4 S cm^2 mol^{-1} respectively at 298 K. Calculate Λ°_m for CH_3COOH.

Ans. (a) The molar conductivity at a infinite dilution for a given salt can be expressed as the sum of the individual contribution from the ions of electrolyte.

(b) $\Lambda^\circ\ CH_3COOH = ?$

$$\lambda^\circ\ CH_3COO^- + \lambda^\circ\ H^+ = \lambda^\circ\ CH_3COO^- + \lambda^\circ\ Na^+ + \lambda^\circ\ H^+ + \lambda^\circ\ Cl^- - \lambda^\circ\ Na^+ - \lambda^\circ\ Cl^- \quad ...(i)$$

$$\Lambda^\circ_m\ CH_3COOH = \Lambda^\circ\ CH_3COONa + \Lambda^\circ\ HCl - \Lambda^\circ\ NaCl$$

(c) $\Lambda^\circ_m\ CH_3COOH = \Lambda^\circ\ CH_3COONa + \Lambda^\circ\ HCl - \Lambda^\circ\ NaCl$

$= 91.0 + 425.9 - 126.4$

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

Q.4. **(a) Define weak and strong electrolytes**

(b) The E^0 values corresponding to the following two reduction electrode processes are:

(i) $Cu^+/Cu = 0.52V$ (ii) $Cu^{2+}/Cu^+ = 0.16V$

Formulate the galvanic cell for their combination . Calculate the cell potential and ΔG^o for the cell reaction.

Ans. (a) Weak electrolyte: the substance which partially ionized in solution is known as weak electrolyte. Example: NH_4OH

Strong electrolyte: The substance which completely ionized in solution is known as strong electrolyte. Example: NaCl.

(b) $Cu^{+} + e^{-} \rightarrow Cu$

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

Overall cell reaction: $2Cu^{+} \longrightarrow Cu + Cu^{2+}$

$Cu^{+}|Cu^{2+}||Cu^{+}|Cu$

$E^{\theta}cell = 0.52 - 0.16 = 0.36V$

$\Delta G^{o} = -nFE^{\theta}_{Cell}$

$= -1 \times 96500 x 0.36$

$= -34740 \ J \ mol^{-1}$

Q.5. **Calculate emf and ΔG^{o} for the following cell at 298K.**
$Mg(s) \mid Mg^{2+}(10^{-3} M) \parallel Cu^{2+}(10^{-4} M) \mid Cu(s)$
[Given : E^{o} $Mg^{2+}/Mg = -2.36$ V; E^{o} $Cu^{2+}/Cu = 0.34$ V; I F = 96500 C mol^{-1}]

Ans. $E_{cell} = E^{\theta}_{cell} - \frac{0.059}{2} \log \frac{[Mg^{2+}]}{[Cu^{2+}]}$

$E_{cell} = 0.34 - (-2.36) - \frac{0.059}{2} \log \frac{10^{-3}}{10^{-4}}$

$= 2.70 - 0.02655 = 2.67V$

$\Delta G^{o} = -nF E^{\theta}_{cell} = -2X96500X2.71$

$= -5.23X10^{2} \ kJ \ mol^{-1}$

Q.6. **(a) Give the units of conductivity and molar conductivity**
(b) Write down Nernst equation and calculate the emf of the following cell at 298 K:
$Cu(s) \mid Cu^{2+}(0.13 M) \parallel Ag^{+}(10^{-4} M) \mid Ag(s)$
Given: $E^{o}(Cu^{2+}/Cu) = +0.34$ V and $E^{o}(Ag^{+}/Ag) = +0.80$ v.

Hint: (a) Conductivity Scm^{-1} cm, Molar conductivity $Scm^{-2} mol^{-1}$

(b) $Q = \frac{[Cu^{2+}][Ag]^{2}}{[Cu][Ag^{+}]^{2}} \quad \frac{0.13 \times 1^{2}}{1 \times (10^{-4})^{2}} = 0.13 X 10^{8}$

$E = E^{o} - \frac{0.0591}{n} \log_{10}Q$

$= 0.46 - \frac{0.0591}{2} \log_{10}(0.13 \times 10^{8}) = 0.25V$

Q.7. **(a) Calculate the emf of the following concentration cell:**
$Zn_{(s)} \mid ZnSO_4(0.001 M) \parallel ZnSO_4(0.01 M) \mid Zn(s)$
(b) How can the reduction potential of an electrode be increased ?

Hint: (a)

$E = E^{\circ} - \frac{0.0591}{n} \log_{10}Q$

$= 0 - \frac{0.0591}{n} \log 10 = 0.0295 \text{ Volt}$

(b) $M^{n+} \ ne^{-} \longrightarrow M$

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

or

$E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} + \frac{2.303 \ RT}{nF} \log [M^{n+}]$

From the above relation it is clear that the reduction potential can be increased either by increasing temperature or by increasing the concentration of metal ion.

Q.8. (i) The conductivity of 0.02M solution of NaCl is 2.6×10^{-2} S cm^{-1}. What is its molar conductivity ?

(ii) Give reasons:

(a) Rusting of iron pipe can be prevented by joining it with a piece of magnesium.

(b) Dry cell become dead after a long time, even if it has not been used?

Ans.

$K = 2.6 \times 10^{-2}$ S cm^{-1}

C = 0.02M

$$\Lambda m = \frac{k \times 1000}{C(M)}$$

$$= \frac{2.6 \times 10^{-2} \times 1000}{0.02}$$

$$= \frac{26 \times 100}{0.02 \times 100} = \frac{26 \times 10^{2}}{2}$$

$$= 13 \times 10^{2} \text{ S cm mol}^{-1}$$

(ii) (a) It is due to cathodic protection in which magnesium metal is oxidised in preference to iron and acts as the anode.

(b) A dry cell becomes dead after a long time because the acidic NH_4Cl corrodes with the zinc container of dry cell.

Q.9. (i) Depict the galvanic cell in which the reaction

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

take place. Further show :

(a) Which of the electrode is negatively charged?

(b) The carriers of the current in the cell.

(c) Individual reaction at each electrode?

(ii) A solution of $CuSO_4$ is electrolysed for 10 mins. With a current of 1.5 amperes. What is the mass of copper deposited at the cathode ?

Ans. (i) $Zn_{(s)} | Zn^{2+}_{(aq)} \| Ag^{+}_{(aq)} | Ag_{(s)}$

(a) Zn electrode (anode)

(b) Ions are carriers of the current in the cell.

(c) At anode:

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

At cathode:

$Ag^{+} + e^{-} \rightarrow Ag(s)$

(ii) I = 1.5 Ampere

Time: $10 \times 60s = 600s$

$Q = I \times t = 1.5 \times 600 = 900$ C

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

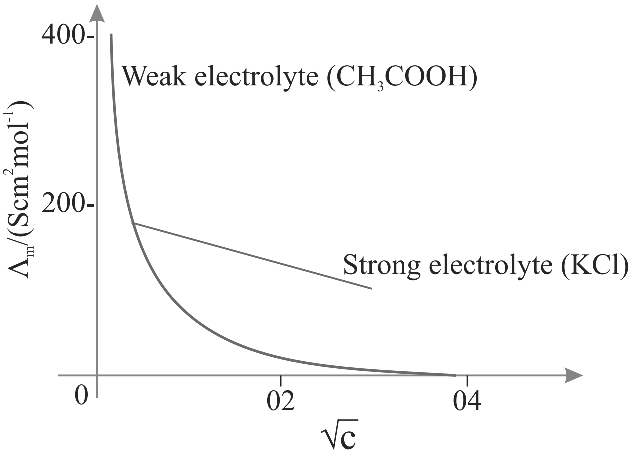
2F amount of electricity deposit copper = 63.5g

900 C amount of electricity deposit copper = $\frac{63.5 \times 900}{2 \times 96500} = 0.296g$

CASE STUDY BASED QUESTIONS

1. **Read the passage given below and answer the questions that follow:**

The study of the conductivity of electrolyte solution is important for the development of electrochemical devices, for the characterisation of the dissociation equilibrium of weak electrolytes and for the understanding of charge transport by ions. The conductivity of electrolyte is measured for electrolyte solution with concentration in the range of 10^{-3} to 10^{-4}mol/L, as solution in this concentration range can be easily prepared. The variation in molar conductivity (Λ_m) of strong electrolyte with concentration is given by equation $\Lambda_m = \Lambda^0_{m} - A\sqrt{C}$ Where Λ^0_m is the molar conductivity at infinite dilution and Cis the concentration for solution. Following graph shows the, variation of molar conductivity with concentration for both weak and strong electrolytes.



Limiting molar conductivity cannot be determined by extrapolation of Λ_m versus$\sqrt{C}$ curve. Molar conductivity at infinite dilution can be calculated by sum of contributions of each ion. $\Lambda^0_m = v^+\lambda_0^+ + v\lambda_0^-$

Where λ_0^+ and λ_0^- are the limiting ionic conductivities of positive and negative ions respectively and v^+ and v^- are their stoichiometric coefficients in the salt molecular formula.

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

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

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

(A) **ASSERTION**: For CH_3COOH Λ^0_m cannot be determined experimentally.

REASON: CH_3COOH is a weak acid and Debye Huckel Onsager equation cannot be used. Extrapolation method cannot be employed.

(B) **ASSERTION** : The ratio of conductivity to the observed conductance does not depend upon the concentration of the solution taken in the conductivity cell.

REASON : Conductivity of solution decreases with dilution whereas observed conductance increases with dilution.

(C) **ASSERTION** : Molar conductance of all electrolytes decrease with increasing concentration.

REASON : Lesser no. of ions are available per unit volume of solution at higher concentration.

(D) **ASSERTION** : 0.1 M NH_4OH at 25°C has lesser conductance than at 50 °C.

REASON : Conductance of a weak electrolyte decreases with increase in temperature.

2. **Read the passage given below and answer the questions that follow:**

In the Daniell cell, the copper electrode is the anode. The electrons leave the cell from the zinc and enter into the copper electrode. To complete the circuit a salt bridge (an inverted U-tube) is used. Salt bridge consists of a concentrated solution of agar-agar + KCl/ KNO_3/NH_4NO_3. The mobility of cations and anions are the same. The maximum electrical work is given by $W_{max} = -\Delta G$. This ΔG is related to emf as $\Delta G = -nFE$. The extent of reaction is measured by ΔG. The emf of a cell is determined by the Nernst equation,

$$E = E^0 - \frac{0.0591}{n} \log Q.$$

The Nernst equation is also used to calculate the emf of concentration cell.

$M|M^+_{(aq)} || M^+_{(aq)}|M$. When a given cell is at equilibrium, $Q = K_{eq}$.

To calculate the standard electrode potential of a half cell like Ag/Ag^+, Cu/Cu^{2+}, one has to complete it with SHE e.g.

$Pt/H_2(g)/H^+_{(aq)}$ its $E^0 = 0$ (by convention). From the emf study, we can calculate E^0, pH, valency, K_{eq}, K_s, thermodynamic parameters, etc.

(A) An electrochemical cell stops working after some time because

(a) Electrode potential of both the electrodes becomes zero.

(b) Electrode potential of both the electrodes becomes equal.

(c) One of the electrode is eaten away.

(d) The reaction start s proceeding in opposite direction.

(B) **Which of the following statements is correct for a galvanic cell?**

(a) Reduction occurs at cathode. (b) Oxidation occurs at anode.

(c) Electrons flow from anode to cathode. (d) All statements are correct.

(C) **What is correct when net cell reaction is spontaneous?**

(a) $E°_{cell}$ is negative (b) $E_{cell} > 0$

(c) $E_{cell} = E^0_{cell}$ (d) $\Delta G < 0$

(D) **The function of salt bridge is to:**

(a) allow ions to move from anode to cathode

(b) allow solutions from one half cell to the other half cell

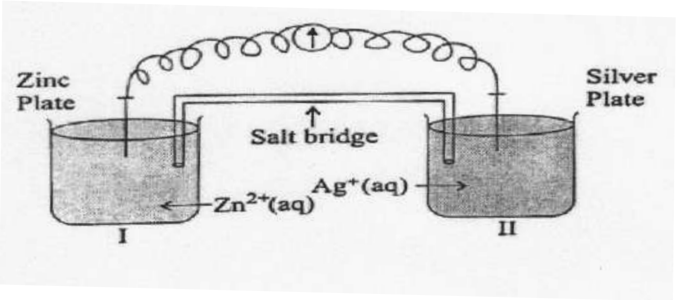
(c) allow the current to flow through the cell and keep the solutions electrically neutral

(d) keep the level of solutions same.

3. Read the passage given below and answer the questions that follow:

Oxidation-reduction reactions are commonly known as redox reactions. They involve transfer of electrons from one species to another. In a spontaneous reaction, energy is released which can be used to do useful work. The reaction is split into two half reactions. Two different containers are used and a wire is used to drive the electrons from one side to the other and a Voltaic/Galvanic cell is created. It is an electrochemical cell that uses spontaneous redox reactions to generate electricity. A salt bridge also connects to the half cells. The reading of the voltmeter gives the cell voltage or cell potential or electromotive force. If E^0cell is positive the reaction is spontaneous and if it is negative the reaction is non-spontaneous and is referred to as electrolytic cell. Electrolysis refers to the decomposition of a substance by an electric current. One mole of electric charge when passed through a cell will discharge half a mole of a divalent metal ion such as Cu^{2+}. This was first formulated by Faraday in the form of laws of electrolysis.

The conductance of material is the property of materials due to which a material allows the flow of ions through itself and thus conducts electricity. Conductivity is represented by k and it depends upon nature and concentration of electrolyte, temperature etc. A more common term molar conductivity of a solution at a given concentration is conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with the unit area of cross-section and distance of unit length. Limiting molar conductivity of weak electrolytes cannot be obtained graphically.



(A) Which plate zinc or silver is going to act as cathode of the cell?

(B) What will happen if the salt bridge is removed?

(C) When does electrochemical cell behaves like an electrolytic cell?

(D) (i) What will happen to the concentration of Zn^{2+} and Ag^{+} when $E_{cell}=0$

(ii) Why does conductivity of a solution decreases with dilution?

OR

(D) 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.

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. c 2. c 3. d 4. c 5. a 6. c 7. b 8. b 9. a 10. a, d
11. a 12. a,b 13. a 14. a 15. a, b 16. d 17. c 18. d 19. b 20. b,d

II FILL IN THE BLANKS

1. Conductivity 2. $c^{1/2}$ 3. Anode to cathode
4. ohm metre 5. positive 6. decreases
7. m^{-1} 8. cannot 9. galvanisation
10. 4F

III ASSERTION REASON TYPE QUESTIONS

1. a 2. a 3. a. 4. d 5. c.
6. d. 7. a 8. a 9. a 10. a

IV ONE WORD ANSWER TYPE QUESTIONS

1. 3F 2. Increases 3. ions
4. Standard hydrogen electrode 5. No 6. Conductivity
7. increases 8. Faraday constant
9. Calomal electrode 10. increases 11. Fuel Cell
12. At equilibrium 13. $E^0\text{cell} = \frac{0.0591}{n} \log K_c$
14. From Zinc to Silver 15. Equilibrium state is attained

CASE STUDY BASED QUESTIONS

1: (A) a (B) b (C) c (D) c
2: (A) b (B) d (C) b,d (D) c
3: (A) Cathode (B) voltage will drop to zero (C) When $E_{ext} > E_{cell}$
(D) (i) Increasing concentration of Zn^{2+} and decreasing concentration of Ag^{+} reaches to an equilibrium
(ii) Due to decrease in no. of ions per unit volume.

OR

(D) $\Lambda_m = K \times \frac{1000}{M}$

$138.9 = K \times \frac{1000}{1.5}$

$K = 0.208\ \text{ohm}^{-1}\,\text{cm}^{-1}$

UNIT TEST-1

CHAPTER-3

ELECTROCHEMISTRY

TIME ALLOWED : 1 HR. **M.M. 20**

1. What does the negative sign in the expression $E^0_{(Zn^{2+}/2n)} = -0.76$ V mean? 1
2. Write unit of molar conductivity. 1
3. Suggest a way to determine the Λ_m^o value of water. 1
4. Write the nernst equation of the following cell

   $Mg(s)|Mg^{2+}(0.001M) \| Cu^{2+}(0.001M)|Cu(s)$ 1
5. Why is it not possible to measure single electrode potential? 1
6. Calculate emf of the following cell 2

   $Cd|Cd^{2+}(0.10M) \| H^+(0.20M)|H_2(0.5\ atm)/Pt$

   (Given E^0 for $Cd^{2+}/Cd = -0.403V$)
7. Why on dilution Λ_m of CH_3COOH increases drastically while that of CH_3COONa increases gradually? 2
8. Conductivity of 2.5×10^{-4} M methanoic acid (HCOOH) is 5.25×10^{-5} Scm^{-1}. Calculate its molar conductivity and degree of dissociation. 3

   Given: $\lambda^0(H^+) = 349.5\ Scm^2mol^{-1}$ and $\lambda^0(HCOO^-) = 50.5\ Scm^2mol^{-1}$.
9. (i) The conductivity of an aqueous solution of NaCl in a cell is 92 ohm^{-1}, the resistance offered by the cell is 247.8 ohm. Calculate the cell constant. 3

   (ii) What is the effect of dilution on the conductivity of an electrolytic solution?
10. Calculate EMF and ΔG for the following cell at 298K:

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

    Given : $E^0_{(Mg^{2+}/Mg)} = -2.37V$, $E^0_{(Ag^+/Ag)} = +0.80V$ 5

UNIT TEST-2

CHAPTER-3

ELECTROCHEMISTRY

TIME ALLOWED :1 HR. **M.M. 20**

1. Express the relation between conductivity and molar conductivity of the solution. 1
2. Name any two metals which can be used for cathodic protection of iron. 1
3. Name a battery used in Apollo space programme. 1
4. Write the correct representation of the cell: 2

   $2Cr_{(s)} + 3Cd^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3Cd_{(s)}$
5. How many Faradays of charge are required to convert 1 mole of Fe^{2+} to Fe? 1
6. How does molar conductivity vary with dilution for 2

   (i) weak electrolyte and for

   (ii) strong electrolyte? Give reasons for these variations.
7. The conductivity of 0.2 M solution of KCl at 298 K is 0.025 S cm^{-1}. Calculate the molar conductivity. 2
8. Account for the following: 2

   (i) Alkaline medium inhibits the rusting of iron.

   (ii) Iron does not rust even if the zinc coating is broken in a galvanised iron pipe.
9. Calculate the emf for the given cell at 25°C. 3

   Cr I Cr^{3+}(0.1M) II Fe^{2+}(0.01M) I Fe

   [Given: $E^0_{Cr^{3+}/Cr} = -0.74$ V, $E^0_{Fe^{2+}/Fe} = -0.44$ V]
10. (a) Write the cell reactions which occur in lead storage battery 3

    (i) When the battery is in use and

    (ii) When the battery is on charging.

    (b) Mention two advantages of fuel cells.
11. Molar conductivities at infnite dilution for NH_4Cl, NaOH and NaCl solutions at 298 K are respectively 129.8, 217.4 and 108.9 S cm^2 mol^{-1} and the molar conductivity of a 10^{-2} M solution of NH_4OH is 9.33 S cm^2 mol^{-1} Calculate the degree of dissociation (α) of NH_4OH in the above mentioned solution. 3