Electrochemistry

(Q.) Give the relationship between free energy change and EMF of a cell. (1 Mark)

(Ans) $-\Delta_r G = n\,FE_{cell}$ $\Delta_r G$ = Free energy changes
n = moles of electrons F = 96500 Coulomb
E_{cell} = EMF of a cell

(Q.) How much amount of a substance is deposited by 1 coulomb? (1 Mark)

(Ans) 1 Coulomb deposits Eq .Wt. / 96500 gram. This is known as electrochemical equivalent of the substance.

(Q.) Write the relationship between molar conductivity & specific conductivity.(1 Mark)

(Ans)

$\Lambda_m = \kappa \times \frac{1000}{C}$ (κ = Specific conductivity & Λ_m is the molar conductivity

C = molar concentration

(Q.) What is the reference electrode in determining the standard electrode potential? (1 Mark)

(Ans) Normal hydrogen electrode (NHE)

(Q.) Write the use of platinum foil in the hydrogen electrode. (1 Mark)

(Ans) Platinum foil is used for the inflow and out flow of electrons.

(Q.) How will you identify whether given electrolyte is a strong or a weak electrolyte? (1 Mark)

(Ans) A strong electrolyte conducts electricity to a large extent in an aqueous solution of the electrolyte whereas a weak electrolyte conducts electricity to a small extent.

(Q.) What flows in the internal circuit of a galvanic cell? (1 Mark)

(Ans) Ions

(Q.) Which electrolyte is used in a dry cell? (1 Mark)

(Ans) A paste of NH_4Cl, MnO_2 and carbon.

(Q.) Name the metal that can be used in cathodic protection of iron against rusting.(1 Mark)

(Ans) A metal which is more electropositive than iron e.g Al, Zn, Mg etc.

(Q.) Why a dry cell becomes dead after some time even it has not been used?(1 Mark)

(Ans) The acidic NH_4Cl corrodes the zinc container. So a dry cell becomes dead after a long time.

(Q.) Why in a concentrated solution, a strong electrolyte shows deviations from Debye – Huckel –Onsager equation? (1 Mark)

(Ans) The inter ionic forces of attraction are large in a concentrated solution of a strong electrolyte. Hence, it shows deviations from Debye – Huckel Onsager equation.

(Q.) What do you understand by EMF of the cell? (1 Mark)

(Ans) The difference between the electrode potentials of the two half cells is called EMF of the cell.

(Q.) Which cells were used in the Apollo space program? (1 Mark)

(Ans) $H_2 – O_2$ fuel cell

(Q.) How can you increase the reduction potential of an electrode? (1 Mark)

(Ans) By increasing the concentration of the ions.

(Q.) Which electrolyte is used in mercury cell and fuel cell? (1 Mark)

(Ans) In mercury cell, moist mercuric oxide mixed with KOH and in fuel cell concentrated aqueous KOH or NaOH solution are used.

(Q.) What are the units of molar conductivity? (1 Mark)

(Ans) $Ohm^{-1}cm^2mol^{-1}$ or $S\ cm^2\ mol^{-1}$

(Q.) Which allotrope of carbon is used for making electrodes? (1 Mark)

(Ans) Graphite

(Q.) Why it is necessary to use a salt bridge in a galvanic cell? (1 Mark)

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

(Q.) Define (i) Faraday's constant (ii) Electrochemical equivalent (2 Marks)

(Ans) (i) Faraday's constant is equal to charge on 1 mol of electrons. Its value is 96500 C mol^{-1}.
(ii) Electrochemical equivalent is amount of substance deposited when 1 ampere current is passed for 1 second (or when 1 C of charge is passed.) Its unit is gC^{-1}.

(Q.) (i) What is corrosion? (ii) What is Galvanisation ? (2 Marks)

(Ans) (i)Corrosion is the process of transformation of the metal into its oxides, sulphides,carbonates and sulphates by the atmospheric gases on the surface of the metal and oxygen.
(ii) Galvanisation is a process of coating iron with zinc. It protects iron from rusting.

(Q.) Define Kohlrausch's law. Calculate limiting molar conductivity of A_xB_y. (2 Marks)

(Ans) According to Kohlrausch's law, molar conductivity of an electrolyte at infinite dilution is sum of the limiting ionic conductivities of the cation and the anion each multiplied with the number of ions present in one formula unit of the electrolyte.

Limiting molar conductivity of A_xB_y = $x\lambda^o_+ + y\lambda^o_-$

(Q.)Calculate molar conductivity of solution of $MgCl_2$ at infinite dilution from the given data.

$\lambda Mg^{2+} = 107.12\ ohm^{-1}cm^2mol^{-1}$

$\lambda Cl^- = 76.34\ ohm^{-1}cm^2mol^{-1}$ **(2 Marks)**

(Ans)

$MgCl_2 \rightarrow Mg^{2+} + 2Cl^-$

$$\lambda_m^\infty(MgCl_2) = \lambda^\infty(Mg^{2+}) + 2\lambda^\infty Cl^-$$
$$= 107.12 + 2 \times 76.34$$
$$= 107.12 + 152.68$$
$$= 259.8\ ohm^{-1}cm^2mol^{-1}$$

(Q.) When 3 ampere of electricity is passed for 45 minutes 2.0 g of metal is deposited. Find equivalent weight of metal. (2 Marks)

(Ans) Q = I X t
= 3 X 45 X 60= 8100 C

8100 C of electricity deposits 2.0 g of metal

∴ 96500 C of electricity deposits = (2.0/8100) X 96500
= 23.82 g of metal

∴ Eq. Wt. of metal is 23.82 g.

(Q.)Find the value of equilibrium constant from the following data-

$E^\circ_{cell} = 0.295V,\ T = 25^0C,\ n = 2$ **(2 Marks)**

(Ans)

$$E^\circ_{cell} = \frac{0.0591}{n}\log K$$

Or $0.295 = \frac{0.0591}{2}\log K$

$\log\ K = \frac{0.295}{0.0295} = 10$

$K = 10^{10}$

(Q.) How many grams of oxygen will be produced at STP on passing 1 F of electricity from water? (2 Marks)

(Ans) $2H_2O \rightarrow 2O_2 + 4H^+ + 4e^-$

∴ 4 F of electricity produced O_2 = 32

∴ 1 F of electricity produced O_2 = 32/4 = 8

(Q.)Find emf of H_2–O_2 fuel cell from the following data -

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$

$\Delta G_f^\circ H_2O = -235 kJ\ mol^{-1}$ **(2 Marks)**

(Ans)

$\Delta G_f^\circ = -235\ kJ\ mol^{-1} = -235\times10^3 mol^{-1}$

$= \Delta G_f^\circ = -nFE_{cell}^\circ$

$E_{cell}^\circ = \dfrac{\Delta G^\circ}{-nF} = \dfrac{-235\times10^3}{-2\times96500}$

$= 1.218\ V$

(Q.) The emf of Zn – Cu cell is 1.1 V at 298 K. Calculate equilibrium constant of reaction.(2 Marks)

(Ans)

$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

$\therefore\ n = 2$

$E^\circ = \dfrac{0.0591}{n}\log K$

or, $1.1 = \dfrac{0.0591}{2}\log K$

or $\log K = \dfrac{1.1\times2}{0.0591} = 37.22$

$K = \text{Antilog } 37.22 = 1.68\times10^{37}$

(Q.)Calculate standard free energy change for the following chemical reaction –

$2\ Ag^+ + Cd \longrightarrow 2\ Ag + Cd^{2+}$

$Cd^{2+}/Cd = E^\circ = -0.40V,\ Ag^+/Ag = 0.80\,V$ **(2 Marks)**

(Ans)

It is clear from E° data that Ag is anode and Cu is Cathode.

$E_{cell}^\circ = E_c^\circ - E_A^\circ$

$= 0.80 - (-0.40)$

$= 1.20\ V$

$n = 2$

$\Delta G = -nE^\circ F$

$= -2\times1.20\times96500$

$= 231600\ J = 231.6\ kJ$

(Q.) Calculate mass of copper deposited when a current of 0.3 ampere is passed in aq solution of copper sulphate for two hour. **(2 Marks)**

(Ans) Equivalent wt. of Cu = At.Wt./Valency

$= 63.5 / 2 \Rightarrow 31.75$

Z for Cu $= 31.75/96500$

$= 3.29 \times 10^{-4}\ gC^{-1}$

$W = ZI\,t = 3.29\times10^{-4}\times0.3\times2\times3600 = 0.7106\ g.$

(Q.) Calculate the number of coulombs required to deposite 7.25g of Al. **(2 Marks)**

(Ans)

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

27g (= 1 mole) of Al is deposited by $= 3$ moles of e^-

Charge required to deposit 27g of Al $= 3\times96500\ C$

$\therefore$Charge required to deposit 7.25g of Al $= \dfrac{3\times96500}{27}\times7.25$

$= 77736.11\ C.$

(Q.)Represent the following cell reactions as galvanic cell -

(i) Cu (s) + 2Ag$^+$ (aq) → Cu^{2+} (aq) + 2 Ag (s)

(ii) Co (s) + Pd^{2+} (aq) → Co^{2+} (aq) + Pd (s) **(2 Marks)**

(Ans) (i) In this reaction copper is oxidized to Cu^{2+}

. Cu will act as anode. Ag^+ is reduced to Ag during reaction. . Ag will act as cathode.

Cu (s) / Cu^{2+} (aq) || Ag^+ (aq) / Ag (s)

(ii) In this reaction cobalt is oxidized and Pd is reduced. So, Co acts as anode and Pd acts as cathode.

Co (s) / Co^{2+} (aq) || Pd^+ (aq) / Pd (s)

(Q.) Write the half cell reaction and net cell reaction for following electrodes -

(i) Ni / Ni^{2+} || Ag^+ / Ag (ii) Cr / Cr^{3+} || Pb^{2+} / Pb (2 Marks)

(Ans) (i)

$Ni - 2e^- \longrightarrow Ni^{2+}$ Oxidation half reaction

$2Ag^+ + 2e^- \longrightarrow 2Ag$ Reduction half reaction

$Ni + 2Ag^+ \longrightarrow Ni^{2+} + 2Ag$

(ii)

$2Cr - 6e^- \longrightarrow 2Cr^{3+}$ Oxidation half reaction

$3Pb^{2+} + 6e^- \longrightarrow 2Pb$ Reduction half reaction

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

(Q.) Define and give one example of each of the following-

(i) Primary Cells (ii) Secondary Cells (iii) Fuel Cell (3 Marks)

(Ans) (i)**Primary cells** are those which produce electrical energy from chemical energy.They cannot berecharged. *e.g.* Dry cell.

(ii)**Secondary cells** are used for storing electricity. They can be recharged. *e.g.* Lead storage battery.

(iii)**Fuel cells** are used to convert energy from combustion of fuels into electrical energy are called fuel cells. *e.g.* H_2-O_2fuel cell.

(Q.) Write the reactions taking place at cathode, at anode and cell reaction in lead storage cell. (3 Marks)

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

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

Cell reaction Pb (s) + PbO_2 (s) + $2H_2SO_4 \rightarrow 2PbSO_4$ (s) + $2H_2O$ (*l*)

(Q.) What is Nernst equation? Write its expression for single electrode & cell.(3 Marks)

(Ans) Nernst equation is relationship between temperature, concentration of electrolyte at electrode and electrode potential.

For reaction : $M^{n+} + ne^- \longrightarrow M_{(s)}$

$$E_{M^{n+}/M_{(s)}} = E^\circ_{M^{n+}/M_{(s)}} - \frac{2.303RT}{nF}\log\left[\frac{M_s}{M^{n+}}\right]$$

Where,

$E_{M^{n+}/M}$ = Reduction potential

$E^\circ_{M^{n+}/M}$ = Standard reduction potential

T = Temperature in K

n = No. of e^-in balanced cell reaction

F = 96500 C

For cell

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log\left[\frac{\text{Product}}{\text{Reactant}}\right]$$

(Q.) The resistance of 1N solution of CH_3COOH is 250 ohm. The cell constant is 1.15 cm^{-1}. Calculate the equivalent conductance of solution. (3 Marks)

(Ans)

$$\text{Conductivity} = \frac{1}{R} \times \text{cell constant}$$

$$= \frac{1}{250} \times 1.15 = 4.6 \times 10^{-3}$$

$$\Lambda eq = \frac{\text{conductivity} \times 1000}{N}$$

$$= \frac{4.6 \times 10^{-3} \times 1000}{1.0}$$

$$= 46 \times ohm^{-1}\, cm^2\, eq^{-1}$$

(Q.)

Find the *emf* of following cell -

$$Zn/Zn^{2+}_{(0.1M)} \,||\, Pb^{2+}_{(1M)}/Pb$$

$$E^0_{Zn/Zn^{2+}} = -0.76V \text{ and } E^0_{Pb^{2+}/Zn} = 0.12V$$

(3 Marks)

(Ans) From the cell representation it is clear that zinc is anode and Pb is cathode

$$E^\circ_{cell} = E^\circ_C - E^\circ_A$$

$$= -0.12 - (-0.76)$$

$$= -0.12 + 0.76$$

$$= +0.64\ V$$

$$\text{Given} [Zn^{2+}] = 0.1M,\ [Pb^{2+}] = 1.0V,\ n = 2$$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \left[\frac{Zn^{2+}}{Pb^{2+}}\right]$$

$$E_{cell} = 0.64 - \frac{0.0591}{2} \log \left[\frac{0.1}{1.0}\right]$$

$$= 0.64 - 0.02955 \times 1$$

$$= 0.64 + 0.02955$$

$$= 0.669\ V$$

(Q.)The resistance of 0.5 M CH_3COOH solution is 100 ohm. The cell constant is 0.035 cm^{-1}. Calculate molar conductivity of solution. (3 Marks)

(Ans)

$$\text{Electrolytic Conductance} = \frac{1}{R} \times \textit{cell constant}$$

$$= \frac{1}{100} \times 0.035$$

$$= 3.5 \times 10^{-4} ohm^{-1} cm^{-1}$$

$$\text{Molar Conductance} = \frac{1000 \times \textit{Electrolytic Conductance}}{\textit{Concentration}}$$

$$= \frac{1000 \times 3.5 \times 10^{-4}}{0.5}$$

$$= 7.0\ ohm^{-1}\, cm^2\, mol^{-1}$$

(Q.) An unknown metal M displaces Ni from $NiCl_2$ solution but it dont displace Mn from $MnCl_2$ solution. Arrange metal M, Ni &Mn in correct order of reducing power.(3 Marks)

(Ans) (i) Oxidation potential of M is more than Ni because M displaces Ni^{2+} from $NiCl_2$.

(ii) Oxidation potential of M is less than Mn^{2+} because M cannot displace Mn^{2+} from $MnCl_2$.Order of oxidation potential is Ni < M <Mn. More the oxidation potential means stronger reducing power. Correct order of reducing powers is Mn> M > Ni

(Q.)Chromium metal can be plated out from acidic solution containing CrO_3 according to following reaction-

$$CrO_3 + 6H^+ + 6e^- \rightarrow Cr + 3H_2O$$

Calculate the mass of chromium that will be plated out by 12000 C of charge.(3 Marks)

(Ans)

$$CrO_3 + 6H^+ + 6e^- \longrightarrow Cr_{(s)} + 3H_2O$$

$$\therefore 6 \text{ mole of } e^- \text{deposit} \quad = 1 \text{ mole of } Cr \quad = \quad 52g \text{ of } Cr$$

$$\text{Quantity of electricity on 6 moles of } e^- \quad = 6 \times 96500 = \ 579000C$$

$$\therefore \ 12{,}000 \ C \text{ of charge deposits} \qquad = \frac{52}{579000} \times 12000$$

$$= 1.077g \text{ of } Cr$$

(Q.)Predict if the following reaction is feasible or not ,

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

Given $E^\circ_{Cu^{2+}/Cu} = 0.34$ V and $E^\circ_{Ag^+/Ag} = +0.80$V **(3 Marks)**

(Ans) E°_{cell} must be positive for cell reaction to be feasible. In the given reaction,Ag is oxidized. So, it is acting as anode and Cu is reduced so, it is acting as cathode.

$$E^\circ_{cell} = E^\circ_{(C)} - E^\circ_{(A)}$$

$$= (+0.34V) - (+0.80V)$$

$$= 0.34 \text{ V} - 0.80 \text{ V}$$

$$= -0.46 \text{ V}$$

Since E°_{cell} is having negative value, so the reaction is not feasible.

(Q.)(i) Define corrosion. (ii) What is rust? (iii)Write three factors which promote corrosion. (5 Marks)

(Ans) (i) The process of slowly eating away of the metal due to attack of the atmospheric gases on the surface of the metal resulting into the formation of compounds such as oxides, sulphidesetc is called **corrosion**.

(ii) Rust is hydrated ferric oxide, $Fe_2O_3.xH_2O$.

(iii) **Reactivity of the metal**: More active metals are readily corroded.

Presence of air and moisture: Air and moisture accelerate corrosion.

Presence of electrolytes: Iron rusts faster in saline water than in pure water.

(Q.)(i) State Faraday' first and second law of electrolysis.

(ii) If resistance of a solution is 20 ohms, what will be the conductance of the same solution?

(iii) For a weak electrolyte there is a very large increase in conductance with dilution near infinite dilution, why?

(iv) How will you calculate the dissociation constant of a weak electrolyte? (5 Marks)

(Ans)(i) **Faraday' first law of electrolysis**

Mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolyte

Faraday'second law of electrolysis

When same quantity of electricity is passed through solutions of different electrolytes connected in series, the weights of the substances produced at the electrodes are directly proportional to their equivalent weights.

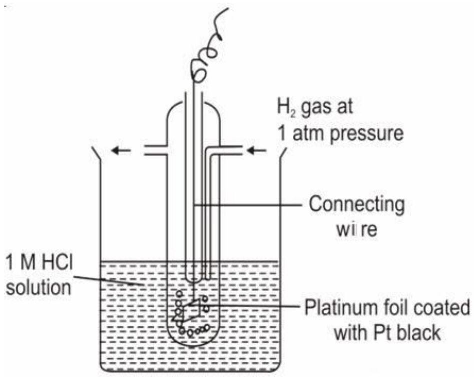
(ii) conductance is reciprocal of resistance, so conductance of the solution = 1/20 = 0.05 ohm^{-1}.

(Q.) (i) Why is the salt bridge used in electrochemical cell?
(ii) Name an electrode which is used as a reference electrode? Give its diagram and working.
(iii) How does electrochemical series help in the following:
(a) Comparing the relative oxidizing or reducing properties of elements.
(b) Predicting the reactivity of a metal with acid. **(5 Marks)**

(Ans) **(i)** In an electrochemical cell, salt bridge is used to maintain the electrical neutrality of the solutions in two half cells. It completes the electrical circuit by allowing the ions to flow from one solution to other without mixing the two solutions.

(ii) The absolute value of the electrode potential of a single electrode cannot be measured because oxidation and reduction half cell cannot take place alone. To overcome this difficulty, we use a reference electrode whose electrode potential is arbitrarily assigned a value.

Example: Standard or Normal Hydrogen Electrode (SHE or NHE). Its electrode potential is taken as 0.00 V at zero Kelvin.



Standard Hydrogen Electrode

To determine the electrode potential of any electrode, a cell is set up with SHE as one of the electrodes. Since, the EMF of the SHE electrode isarbitrarily taken as 0.00 V, the EMF of the cell will directly give the electrode potential value of the other electrode.

(iii) The arrangement of various elements in order of their increasing values of electrode potentials is known as electrochemical series.

(a) Positive sign of electrode potential value represents the reduction potential. This indicates that greater the value of reduction potential, more easily the substance is reduced. It is said to be a stronger oxidising agent.

Thus, according to electrochemical series, F_2 has the highest reduction potential (strongest oxidising agent) and Li^+ ion has the lowest reduction potential, thus it is the weakest oxidizing agent in the series.

(b) A metal with greater oxidation potential can displace metals with lower oxidation potential from their salt solution.

For example: Decreasing order of oxidation potentials of these metals are:

Mg ☐ Zn ☐ Fe ☐ Cu ☐ Ag

Hence, each metal can displace metals on its right from the salt solutions.

(Q.) Write the relationship between molar conductivity and specific conductivity.

(Ans)

$$\lambda_m = \kappa \times \frac{1000}{C} \quad (\kappa = \text{Specific conductivity \& } \Lambda_m \text{ is the molar conductivity})$$

C = molar concentration

(Q.) How will you identify whether the given electrolyte is a strong or a weak electrolyte?

(Ans) A strong electrolyte conducts electricity to a large extent in an aqueous solution of the electrolyte whereas a weak electrolyte conducts electricity to a small extent.

(Q.) The resistance of 0.5 M CH_3COOH solution is 100 ohm. The cell constant is 0.035 cm^{-1}. Calculate molar conductivity of solution.

(Ans)

$$\text{Electrolyte Conductivity} = \frac{1}{R} \times \text{cell constant}$$
$$= \frac{1}{100} \times 0.035$$
$$= 3.5\times10^{-4} ohm^{-1}cm^{-1}$$
$$\text{Molar Conductivity} = \frac{1000\times\text{Electrolyte Conductivity}}{\text{Concentration}}$$
$$= \frac{1000\times3.5\times10^{-4}}{0.5}$$
$$= 7.0\ ohm^{-1}\,cm^2\,mol^{-1}$$

(Q.) Calculate the equivalent conductivity of 1 m H_3PO_4 solution whose conducting is 25 x 15^2 Scm^{-1}.

(Ans)

$$\kappa = 26 x 10^{-2}\,S\,cm^{-1}$$
$$1M\ H_3PO_4 = 98\,gL^{-1}$$
$$\text{Equivalent wt.} = \frac{98}{3} = 32.67$$
$$\lambda_{eq} = \frac{\kappa \,x\, 1000}{N}$$
$$= \frac{26\ x\ 10^{-2}\ x\ 1000}{32.67}$$
$$= 8.66\ x\ 10$$
$$= 86.6\ S\ cm^2\,equiv^{-1}$$

(Q.)Calculate the resistance of 0.01N solution of an electrolyte whose equivalent conductivity is 328 ohm^{-1} $cm^2 equiv^{-1}$.(The cell constant of the cell is 0.88 cm^{-1})

(Ans)

$$\lambda_{eq} = 328\ ohm^{-1}\,cm^2\,equiv^{-1}$$
$$\text{Cell constant}, \frac{l}{A} = 0.88cm^{-1}$$
$$\lambda_{eq} = \frac{\kappa\ x\ 1000}{N}$$
$$\Rightarrow 328\,ohm^{-1}\,cm^2\,equiv^{-1} = \frac{\kappa\ x\ 1000}{0.01}$$
$$\Rightarrow \kappa = 0.00328\ ohm^{-1}cm^{-1}$$

As we know

$$\kappa = \frac{1}{R}\ x\ \frac{l}{A}$$
$$\Rightarrow 0.00328 = \frac{1}{R}\ x\ 0.88$$
$$\Rightarrow R = 268\,ohm$$

(Q.) What are the factors which influences the electronic conductance.

(Ans) The nature and structure of the metal

The density of metal Temperature The number of valance electron per atom

(Q.) The potential difference of 20 V applied to an end of column of 0.1 M $AgNO_3$ solution, 4 cm in diameter and 12 cm in length gave a current of 0.20 A. Calculate molar conductance of the solution.

(Ans)

$$R = \frac{V}{I}$$

$$R = \frac{20}{0.20} = 100 \text{ ohm}$$

$$\text{Radius of column} = \frac{4}{2} = 2 \text{ cm}$$

$$\text{Area of cross section} = \pi \times (2)^2 = 12.57 \text{cm}^2$$

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

$$= \frac{1}{100} \times \frac{12}{12.57}$$

$$\lambda_m = \frac{0.01 \times 12 \times 1000}{12.07 \times 0.1} = 95.5 \text{ S cm}^2\text{mol}^{-1}$$

(Q.) Deduce the units of resistance based on the S.I. convention.

(Ans)

$$R = \frac{V}{I}$$

$$= \frac{\text{Work per unit charge}}{A}$$

$$= \frac{\text{Work}}{\text{Charge}} \times \frac{1}{A}$$

$$= \frac{\text{Force x length}}{\text{Charge x A}}$$

$$= \frac{[\text{kg m s}^{-2}][\text{m}]}{(\text{A x s}) \text{x A}}$$

$$\Rightarrow \frac{\text{kg m}^2}{\text{s}^3 \text{A}^2} = 1\Omega$$

(Q.) Establish a relationship between λ_m and λ_{eq}.

(Ans) As we know

$$\lambda_m = \frac{\kappa \times 1000}{M} \text{...........(i)}$$

$$\lambda_{eq} = \frac{\kappa \times 1000}{N} \text{...........(ii)}$$

On dividing eq (i) by (ii)

$$\frac{\lambda_m}{\lambda_{eq}} = \frac{N}{M}$$

$$\lambda_m = \frac{N}{M} \times \lambda_{eq}$$

(Q.) An N/50 solution of a weak monobasic and has a resistivity of 2.16×10^3 ohm at 18^0C. Calculate the molar conductance of the solution.

(Ans)

$$\rho = 2.16 \times 10^3 \text{ ohm}$$

Since acid is monobasic

Normality of solution = molarity of solution

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

$$= \frac{1 \times 1000 \times 50}{2.16 \times 10^3 \times 1} = 23.15 \text{ S cm}^2 \text{ mol}^{-1}$$

(Q.) A solution containing 2 g of anhydrous $BaCl_2$ in 400cm^3 of water has a conductivity of 0.0058 S cm^{-1}. Calculate the molar & equivalent conductivity of this solution.

(Ans) Molar mass of $BaCl_2$ = 137 + 2 x 35.5 = 208 g mol^{-1}

$$\text{No. of mole} = \frac{2}{208} = 9.61 \times 10^{-3}$$

$$\lambda = \frac{\kappa \times 1000}{M}$$

$$= \frac{0.0058 \times 1000}{\frac{9.61 \times 10^{-3} \times 1000}{400}}$$

$$= \frac{0.0058 \times 400}{9.61 \times 10^{-3}} = 241.41\ S\,cm^2\,mol^{-1}$$

$$\text{Eq. mass of } BaCl_2 = \frac{1}{2} \times \text{Molar mass of } BaCl_2 = \frac{208}{2}$$

$$\lambda_{eq} = \frac{\text{Eq. mass}}{\text{molar mass}} \times \lambda_m$$

$$= \frac{104}{208} \times 241.67$$

$$= 120.83\ S\,cm^2 eq^{-1}$$

(Q.) How does temperature affect the electrolytic conduction of a electrolyte?

(Ans) As the temperature increase the Inter-ionic attraction, Solute-solvent and solvent-solvent interaction decreases. As a resect more ions are free to move & available for electrical conductivities.

(Q.) A 0.05 M KOH solution offered a resistance of 31.6 ohm in a conductivity cell. If the cell constant of cell is 0.367 cm^{-1}. Calculate the molar conductance.

(Ans)

$$\kappa = \frac{1}{R} \times \frac{1}{A}$$

$$= \frac{1}{31.6} \times 0.367 = 1.16 \times 10^{-2}\ S\ cm^{-1}$$

$$\lambda_m = \frac{1.16 \times 10^{-2} \times 1000}{0.05} = 232\ S\ cm^2\ mol^{-1}$$

(Q.) Why in a concentrated solution, a strong electrolyte shows deviations from Debye – Huckel-Onsager equation?

(Ans) The interionic forces of attraction are large in a concentrated solution of a strong electrolyte. Hence it shows deviations from **Debye – Huckel Onsager** equation.

(Q.) Define Kohlrausch's law

(Ans)

According to Kohlrausch's law molar conductivity of an electrolyte at infinite dilution is sum of contributions from its individual ions if the molar conductivity of cations is represented as λ_+^∞ and that of anions as λ_-^∞, then

$$\therefore \qquad \wedge_m^\infty = \upsilon_+ \lambda_+^\infty + \upsilon_- \lambda_-^\infty$$

Where,

υ_+ and υ_- are no. of cations and anions in formula of electrolyte.

(Q.) The value of Molar conductance at infinite dilution forHCl, NaCl& CH_3COONa are 426.1,126.5 & 91.0 S cm^2 mol^{-1}respectively. Calculate the molar conductivity of acetic acid at infinite dilution

(Ans)

$\lambda_m^0(HCl) = \lambda_{H^+}^0 + \lambda_{Cl^-}^0$ ---------(i)

$\lambda_m^0(CH_3COONa) = \lambda_{CH_3COO^-}^0 + \lambda_{Na^+}^0$ ---------(ii)

$\lambda_m^0(NaCl) = \lambda_{Na^+}^0 + \lambda_{Cl^-}^0$ ---------------(iii)

On Adding (i) & (ii) & subtract from them equation (iii)

$$\lambda_m^0(HCl) + \lambda_m^0(CH_3COONa) - \lambda_m^0(NaCl)$$
$$= \lambda_{H^+}^0 + \lambda_{Cl^-}^0 + \lambda_{CH_3COO^-}^0 + \lambda_{Na^+}^0 - \lambda_{Na^+}^0 - \lambda_{Cl^-}^0$$
$$= \lambda_{H^+}^0 + \lambda_{CH_3COO^-}^0$$

$$\lambda_m^0(CH_3COOH) = 426.1 + 91.0 - 126.5$$
$$= 390.6\ S\ cm^2\ mol^{-1}$$

(Q.) The specific conductivity of 0.1 M NH_4OH is 3.6×10^{-4} S cm^{-1}.The molar conductance at infinite dilution for NH_4^+ ions & OH^- ions are 53.0 & 198.0 S cm^2 mol^{-1} respectively. Calculate the degree of dissociation of 0.1 M NH_4OH.

(Ans)

$$\lambda_m = \frac{\kappa \times 1000}{M}$$
$$= \frac{3.6 \times 10^{-4} \times 1000}{0.1}$$
$$= 3.6\ S cm^2\ mol^{-1}$$

$$\lambda_m^0(NH_4OH) = \lambda_m^0(NH_4^+) + \lambda_m^0(OH^-)$$
$$= 53 + 198$$
$$= 251\ S cm^2\ mol^{-1}$$

Thus,

$$\text{Degree of dissociation}, \alpha = \frac{\lambda_m}{\lambda_m^0}$$
$$= \frac{3.6}{251}$$
$$= 0.014$$

(Q.)How does molar conductivity of a weak electrolyte vary with its concentration in solution?

(Ans) Weak electrolyte have lower degree of dissociation at higher concentration and hence for such electrolyte the change in molar conductivity is due to increase in the degree of dissociation. In such cases molar conductivity increases steeply on dilution.

(Q.)Why does the conductivity of an electrolyte decreases with dilution whereas molar conductivity increases?

(Ans) Since conductivity is the conductance of 1 cm^3 of the solution .On diluting the concentration of ions per cm^3 decreases as a result the conductivity decreases .But in case of molar conductivity, we have two terms

$$\lambda_m = \kappa \times V$$

On diluting the volume containing 1 mole of electrolyte increases as a result the product of and V also increases.

(Q.) At 25 ^{0}C, the conductivity of saturated solution of AgCl is 3.41×10^{-6} S cm^{-1} and that of water is 1.61×10^{-6} S cm^{-1}. The λ^0 for Ag^+ and Cl^- ions are 61.92 & 76.34 S cm^2 mol^{-1} respectively. Calculate the solubility of AgCl in gram per litre at given temperature.

(Ans)

$\lambda^0_{Ag^+} = 61.92\ S\,cm^2 mol^{-1}$

$\lambda^0_{Cl^+} = 76.34\ S\,cm^2 mol^{-1}$

Since AgCl is sparingly soluble salt, its saturated solution may be regarded as an infinitly dilute solution.

$\lambda^{sat}_m = \lambda^0_m = \lambda^0_{Ag^+} + \lambda^0_{Cl^-}$

$\lambda^{sat}_m = 61.92 + 76.34$

$= 138.26\ S\,cm^2\ mol^{-1}$

Since,

$\kappa_{salt} = \kappa_{sat} - \kappa_{water}$

$= 3.41\times10^{-6} - 1.61\times10^{-6}$

$= 1.80\times10^{-6}$

$\lambda^{sat}_m = \dfrac{\kappa_{salt}\times1000}{M}$

$M = \dfrac{1.80\times10^{-6}\times1000}{138.26}$

$= 1.3\times10^{-5} mol L^{-1}$

Solubility of AgCl = Molarity × molar mass of AgCl

$= 1.3\times10^{-5}\times 143.5$

$= 1.86\times10^{-3}\ gL^{-1}$

(Q.) The molar conductance at infinite dilution of $Al_2(SO_4)_3$ is 858 S cm^2mol^{-1}.Calculate the molar conductance at infinite dilution of Al^{3+} ion if that of SO_4^{2-} is 160 S cm^2mol^{-1}

(Ans)

$\lambda^0\{Al_2(SO_4)_3\} = 2\lambda^0_{Al^{3+}} + 3\lambda^0_{SO_4^{2-}}$

$858 = 2\lambda^0_{Al^{3+}} + 3\times160$

$\lambda^0_{Al^{3+}} = \dfrac{858 - 480}{2}$

$= 189\ S\,cm^2\ mol^{-1}$

(Q.) The conductivity of $BaSO_4$ was found to be 3.6 x 10^{-6} S cm^{-1} and that of water is 1.25 x 10^{-6} S cm^{-1}. The λ^0 for Ba^{2+} and SO_4^{2-} ions are 110 & 136.6 S cm^2 mol^{-1} respectively. Calculate the solubility of $BaSO_4$ in gram per litre. (Atomic mass of Ba=137, S=32,O=16).

(Ans)

$\lambda^0_{Ba^{2+}} = 110\ S\,cm^2 mol^{-1}$

$\lambda^0_{SO_4^{2-}} = 136.6\ S\,cm^2 mol^{-1}$

Since $BaSO_4$ is sparingly soluble salt, its saturated solution may be regarded as an infinitly dilute solution.

$\lambda^{sat}_m = \lambda^0_m = \lambda^0_{Ba^{2+}} + \lambda^0_{SO_4^{2-}}$

$\lambda^{sat}_m = 110 + 136.6$

$= 246.6\ S\,cm^2\ mol^{-1}$

Since,

$\kappa_{salt} = \kappa_{sat} - \kappa_{water}$

$= 3.6\times10^{-6} - 1.25\times10^{-6}$

$= 2.35\times10^{-6}$

$\lambda^{sat}_m = \dfrac{\kappa_{salt}\times1000}{M}$

$M = \dfrac{2.35\times10^{-6}\times1000}{246.6}$

$= 9.52\times10^{-6} mol L^{-1}$

Solubility of $BaSO_4$ = Molarity × molar mass of AgCl

$= 9.52\times10^{-6}\times(137+32+48)$

$= 2.218\times10^{-3}\ gL^{-1}$

(Q.) The conductivity of 10^{-3} M acetic acid is 4.95×10^{-5} S cm^{-1}. Calculate its degree of dissociation if λ° of CH_3COOH is 390.5 S cm^2 mol^{-1}.

(Ans)

$$\lambda_m = \frac{4.95 \times 10^{-5} \times 1000}{10^{-3}}$$

$$= 49.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\lambda_m^c}{\lambda_m^0}$$

$$= \frac{49.5}{390.5}$$

$$= 0.126$$

(Q.) How much amount of a substance is deposited by 1 coulomb?

(Ans) 1 Coulomb deposits Eq .Wt. / 96500 gram. This is known as electrochemical equivalent of the substance.

(Q.) Why a dry cell becomes dead after a long time even it has not been used?

(Ans) The acidic NH_4Cl corrodes the zinc container. That is why a dry cell becomes dead after a long time.

(Q.) Name the metal that can be used in cathodic protection of iron against rusting.

(Ans) A metal which is more electropositive than iron e.g Al, Zn, Mg etc.

(Q.) Give the relationship between free energy change and EMF of a cell.

(Ans) $-\Delta_r G = n FE_{cell}$

$\Delta_r G$ = Free energy changes

n = moles of electrons

F = 96500 Coulomb

E_{cell} = EMF of a cell

(Q.) Which cells were used in the Apollo space program?

(Ans) H_2–O_2 fuel cell.

(Q.) How can you increase the reduction potential of an electrode ?

(Ans) By increasing the concentration of the ions.

(Q.) Which electrolyte is used in mercury cell and fuel cell?

(Ans) In mercury cell , moist mercuric oxide mixed with KOH and in fuel cell concentrated aqueous KOH or NaOH solution are used as electrolyte.

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

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

(Q.) Write the half cell reaction and net cell reaction for the following electrodes

(i) $Ni / Ni^{2+} \,||\, Ag^{+} / Ag$ (ii) $Cr / Cr^{3+} \,||\, Pb^{2+} / Pb$

(Ans)

(i)

Oxidation half reaction:-

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

Reduction half reaction:-

$2Ag^+ + 2e^- \longrightarrow 2Ag$

Over all net cell reaction:-

$Ni + 2Ag^+ \longrightarrow Ni^{2+} + 2Ag$

(ii)

Oxidation half reaction:-

$2Cr \longrightarrow 2Cr^{3+} + 6e^-$

Reduction half reaction:-

$3Pb^{2+} + 6e^- \longrightarrow 3Pb$

Over all net cell reaction:-

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

(Q.) Find emf of H_2–O_2 fuel cell from the following data

$2H_2 + O_2 \longrightarrow 2H_2O$

$\Delta G_f^\circ(H_2O) = -235 \text{kJ mol}^{-1}$

(Ans)

$$\Delta G_f^\circ(H_2O) = -235 \text{kJ mol}^{-1}$$
$$= -235\times10^3 \text{ Jmol}^{-1}$$
$$\Delta G_f^\circ = -nFE_{cell}^\circ$$
$$E_{cell}^\circ = \frac{\Delta G^\circ}{-nF} = \frac{-235\times10^3}{-2\times96500}$$
$$= 1.218 \text{ V}$$

(Q.) Calculate electrode potential of hydrogen electrode having a pH = 10.

(Ans) For hydrogen electrode

$E^\circ = 0$ and $n = 1$

$$pH = -\log[H^+]$$
$$10 = -\log[H^+]$$
$$\therefore [H^+] = 10^{-10}$$
$$E = E^\circ + \frac{0.0591}{n}\log[H^+]$$
$$= 0 + \frac{0.0591}{1}\log 10^{-10}$$
$$= -0.59 \text{ V}$$

(Q.) How many grams of oxygen will be produced at STP on passing 1 F of electricity.

(Ans)

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

$\because$ 4 F of electricity produced $O_2 = 32$ g

$\therefore$ 1 F of electricity produced $O_2 = \frac{32}{4} = 8$g

(Q.) Find the *emf* of following cell

$Zn/Zn^{2+}(0.1M) \,||\, Pb^{2+}(1M)/Pb$

$E^\circ(Zn^+/Zn) = -0.76$V and $E^\circ(Pb^{2+}/Pb) = -0.12$V

(Ans) From the cell representation it is clear that the *Zn* is anode and *Pb* is cathode.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= -0.12-(-0.76)$$
$$= +0.64\ V$$

Given that $[Zn^{2+}]=0.1M$, $[Pb^{2+}]=1.0M$, $n=2$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\left[\frac{Zn^{2+}}{Pb^{2+}}\right]$$

$$E_{cell} = 0.64 - \frac{0.0591}{2}\log\left[\frac{0.1}{1.0}\right]$$

$$= 0.64 - \frac{0.0591}{2} - \log 10$$
$$= 0.64 + 0.02955 \times 1$$
$$= 0.669\ V$$

(Q.) Calculate molar conductivity of solution of $MgCl_2$ at infinite dilution from the given data.

$$\lambda_{Mg^{2+}} = 107.12\ ohm^{-1}cm^2mol^{-1}$$

$$\lambda_{Cl^-} = 76.34\ ohm^{-1}cm^2mol^{-1}$$

(Ans)

$$MgCl_2 \longrightarrow Mg^{2+} + 2Cl^-$$

$$\lambda^\infty_{MgCl_2} = \lambda^\infty_{Mg^{2+}} + 2\lambda^\infty_{Cl^-}$$
$$= 107.12 + (2 \times 76.34)$$
$$= 259.8\ ohm^{-1}\ cm^2\ mol^{-1}$$

(Q.) When 3 ampere of electricity is passed for 45 minutes to the metal, 2.0 g of metal is deposited. Find equivalent weight of metal.

(Ans)

$$Q = i \times t$$
$$= 3 \times 45 \times 60 = 8100C$$

$\because$ 8100 C of electricity deposits metal $= 2g$

$\therefore$ 96500C of electricity deposits metal $= \frac{2g}{8100C} \times 96500C$

$$= 23.82g$$

$\therefore$ Eq. wt of metal is $= 23.82g$