UNIT – 9 – ELECTRO CHEMISTRY

II. Answer the following questions:

1. Define anode and cathode

Anode is the electrode at which oxidation occurs. It sends electrons into the outer circuit. It has a negative charge and in shown as (-) in cell diagram.

Cathode is the electrode at which reduction occurs. It receives electrons from the outer circuit. It has a positive charge and is shown as (+) in cell diagram.

2. Why does conductivity of a solution decrease on dilution of the solution

The conductivity of solution is directly proportional to the number of ions present in unit volume of the solution. On dilution, the ion concentration decreases per unit volume and hence conductivity decreases.

3. State Kohlrausch Law. [JUN-25] How is it useful to determine the molar conductivity of weak electrolyte at infinite dilution? [GMQ-19, JUN-20]

Kohlrausch's Law: At infinite dilution, the limiting molar conductivity of an electrolyte is equal to the some of the limiting molar conductivities of its constituent ions.

Calculation of molar conductance at infinite dilution of a weak electrolyte:

It is impossible to determine the molar conductance at infinite dilution for weak electrolytes experimentally. However, the same can be calculated using Kohlrausch's Law.

For example, the molar conductance of CH_3COOH, can be calculated using the experimentally determined molar conductivities of strong electrolytes HCl, NaCl and CH_3COONa.

$\Lambda^\circ_{CH_3COONa} = \lambda^\circ_{Na^+} + \lambda^\circ_{CH_3COO^-}$ ----------(1)

$\Lambda^\circ_{HCl} = \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}$ ----------(2)

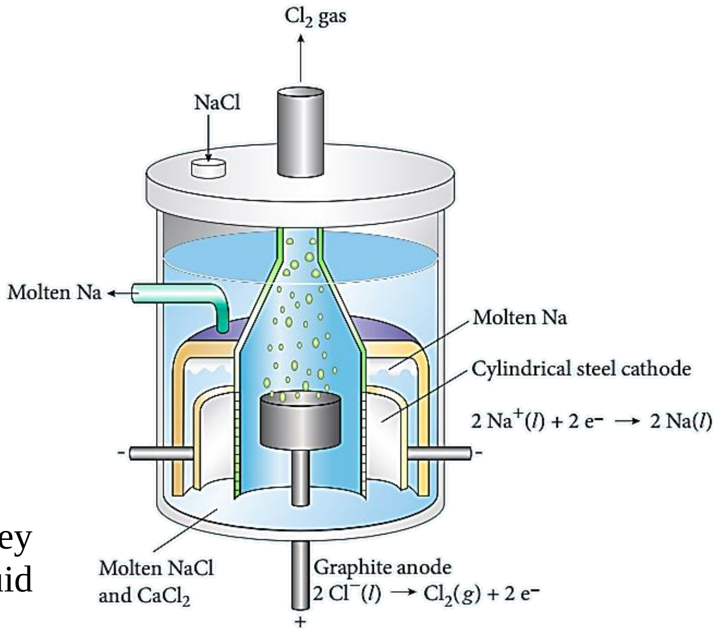
$\Lambda^\circ_{NaCl} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$ ----------(3)

Equation (1) + Equation (2) – Equation (3) gives.

$(\Lambda^\circ_{CH_3COONa}) + (\Lambda^\circ_{HCl}) - (\Lambda^\circ_{NaCl}) = \lambda^\circ_{H^+} + \lambda^\circ_{CH_3COO^-} = \Lambda^\circ_{CH_3COOH}$

4. Describe the electrolysis of molten NaCl using inert electrodes

The electrolytic cell consists of two iron electrodes dipped in molten sodium chloride and they are connected to an external DC power supply via a key as shown in the figure. The electrode which is attached to the negative end of the power supply is called the cathode, and the one which attached to the positive end is called the anode. Once the key is closed, the external DC power supply drives the electrons to the cathode and at the same time pull the electrons from the anode.



Cell reactions:

Na^+ ions are attracted towards cathode, where they combine with the electrons and reduced to liquid sodium.

Cathode (reduction) $Na^+_{(l)} + e^- \rightarrow Na_{(l)}$ $E^o = -2\ 71V.$

Similarly, Cl^- ions are attracted towards anode where they lose their electrons and oxidised to chlorine gas.

Anode (oxidation) $2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e^-$ $E^o = -1.36V$

The overall reaction is, $2Na^+_{(l)} + 2Cl^-_{(l)} \rightarrow 2Na_{(l)} + Cl_{2(g)}$ $E^o = -4.07V$

The negative Eo value shows that the above reaction is a non spontaneous one. Hence, we have to supply a voltage greater than 4.07V to cause the electrolysis of molten NaCl.

In electrolytic cell, oxidation occurs at the anode and reduction occur at the cathode as in a galvanic cell, but the sign of the electrodes is the reverse i.e., in the electrolytic cell cathode is –ve and anode is +ve.

5. State Faraday's Laws of electrolysis [GMQ,HY-19, AUG-21, APR-23, JUN-25]

First Law: The mass of the substance (m) liberated at an electrode during electrolysis is directly proportional to the quantity of charge (Q) passed through the cell.

$$\text{i.e } m \,\alpha\, Q$$

We know that the charge is related to the current by the equation $I = \frac{Q}{t} \Rightarrow Q = It$

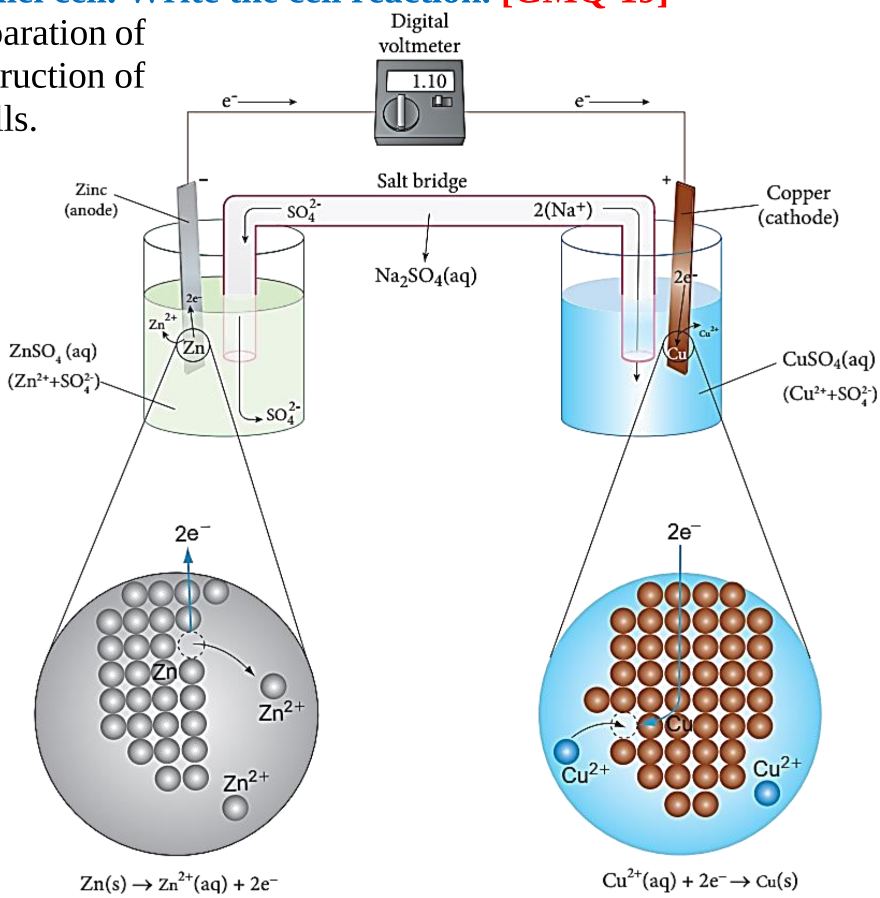
$$\therefore m \propto It \qquad \text{(or)} \qquad m = Z\,It$$

Where is Z is known as the electro chemical equivalent of the substance produced of the electrode.

Second Law: When the same quantity of charge is passed through the solutions of different electrolytes, the amount of substances liberated at the respective electrodes are directly proportional to their electrochemical equivalents.

6. Describe the construction of Daniel cell. Write the cell reaction. [GMQ-19]

Construction of Daniel cell: The separation of half reaction is the basis for the construction of Daniel cell. It consists of two half cells.



Oxidation half cell: A metallic zinc strip that dips into an aqueous solution of zinc sulphate taken in a beaker.

Reduction half cell: A copper strip that dips into an aqueous solution of copper sulphate taken in a beaker.

Joining the half cells: The zinc and copper strips are externally connected using a wire through a switch (k) and a load (example: volt meter). The electrolytic solution present in the cathodic and anodic compartment are connected using an inverted U tube containing a agar-agar gel mixed with an inert electrolytes such as KCl, Na_2SO_4 etc., The ions of inert electrolyte do not react with other ions present in the half cells and they are not either oxidised (or) reduced at the electrodes. The solution in the salt bridge cannot get poured out, but through which the ions can move into (or) out of the half cells.

When the switch (k) closes the circuit, the electrons flows from zinc strip to copper strip. This is due to the following redox reactions which are taking place at the respective electrodes.

Cell reaction:

Anodic oxidation: The electrode at which the oxidation occurs is called the anode. In Daniel cell, the oxidation take place at zinc electrode, i.e., zinc is oxidised to Zn^{2+} ions by loosing its electrons. The Zn^{2+} ions enter the solution and the electrons enter the zinc metal, then flow through the external wire and then enter the copper strip. Electrons are liberated at zinc electrode and hence it is negative (-ve).

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ (loss of electron-oxidation)

Cathodic reduction: As discussed earlier, the electrons flow through the circuit from zinc to copper, where the Cu^{2+} ions in the solution accept the electrons, get reduced to copper and the same get deposited on the electrode. Here, the electrons are consumed and hence it is positive (+ve).

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ (gain of electron-reduction)

Salt bridge: The electrolytes present in two half cells are connected using a salt bridge. We have learnt that the anodic oxidation of zinc electrodes results in the increase in concentration of Zn^{2+} in solution. i.e., the solution contains more number of Zn^{2+} ions as compared to SO_4^{2-} and hence the solution in the anodic compartment would become positively charged. Similarly, the solution in the cathodic compartment would become negatively charged as the Cu^{2+} ions are reduced to copper i.e., the cathodic solution contain more number of SO_4^{2-} ions compared to Cu^{2+}.

To maintain the electrical neutrality in both the compartments, the non reactive anions Cl^-(from KCl taken in the salt bridge) move from the salt bridge and enter into the anodic compartment, at the same time some of the K^+ ions move from the salt bridge into the cathodic compartment.

Completion of circuit: Electrons flow from the negatively charged zinc anode into the positively charged copper cathode through the external wire, at the same time, anions move towards anode and cations are move towards the cathode compartment. This completes the circuit.

Consumption of Electrodes: As the Daniel cell operates, the mass of zinc electrode gradually decreases while the mass of the copper electrode increases and hence the cell will function until the entire metallic zinc electrode is converted in to Zn^{2+} or the entire Cu^{2+} ions are converted in to metallic copper.

Unlike Daniel cell, in certain cases, the reactants (or) products cannot serve as electrodes and in such cases inert electrode such as graphite (or) platinum is used which conducts current in the external circuit.

7. Why is anode in galvanic cell considered to be negative and cathode positive electrode?

- A galvanic cell works basically in reverse to an electrolytic cell. The anode is the electrode where oxidation takes place, in a galvanic cell, it is the negative electrode, as when oxidation occurs, electrons are left behind on the electrode.
- The anode is also the electrode where metal atoms give up their electrons to the metal and go into solution. The electron left behind on it renders it effectively negative and the electron flow goes from it through the wire to the cathode.
- Positive aqueous ions in the solution are reduced by the incoming electrons on the cathode. This why the cathode is a positive electrode, because positive ions are reduced to metal atoms there.

8. The conductivity of a 0.01M solution of a 1:1 weak electrolyte at 298K is 1.5×10^{-4} S cm^{-1}. (i) molar conductivity of the solution, (ii) degree of dissociation and the dissociation constant of the weak electrolyte Given that $\lambda°_{cation}$ = 248.2 S cm^2 mol^{-1}, $\lambda°_{anion}$ = 51 8 S cm^2 mol^{-1}

C = 0.01M; $\lambda°_{cation}$ = 248.2 S cm^2 mol^{-1}; K = 1.5 x 10^{-4} S cm^{-1}; $\lambda°_{anion}$ = 51.8 S cm^2 mol^{-1}

(i) Molar conductivity: K = 1.5 x 10-4 S cm-1 [$\because$ $1 cm^{-1} = 1 \times 10^2 m^{-1}$]

$\Lambda^{\circ}_{m} = \frac{K(sm^{-1})\times10^{-3}}{C(in\ M)}$ mol^{-1} m^{3} = $\frac{1.5\times10^{-4}\times10^{2}\times10^{-3}}{0.01}$ S mol^{-1} m^{2} = 1.5×10^{-3} S mol^{-1} m^{2}

(ii) Degree of dissociation $\alpha = \frac{\Lambda^{o}}{\Lambda^{o}_{\infty}}$

$\Lambda^{o}_{\infty} = \lambda^{o}_{cation} + \lambda^{o}_{anion}$ = (248.2 + 51.8) S cm^{2} mol^{-1} = **300 S cm^{2} mol^{-1}**

$\alpha = \frac{\Lambda^{o}}{\Lambda^{o}_{\infty}} = \frac{1.5\times10^{-3}\ Sm^{2}\ mol^{-1}}{300\times10^{-4}\ Sm^{2}\ mol^{-1}}$ = **0.05**

Dissociation constant of a weak acid,

$K_a = \frac{\alpha^{2}C}{1-C} = \frac{(0.05)^{2}(0.01)}{1-0.05} = \frac{25\times10^{-4}\times10^{-2}}{95\times10^{-2}}$ = 0.26×10^{-4} = **2.6×10^{-5}**

9. Which of 0.1M HCl and 0.1M KCl do you expect to have greater Λ°_{m} and why? [FUT23]

The concentration of HCl and KCl are same but molar conductivity of HCl is higher.

Molar conductance of 0.1M HCl = 39.132×10^{-3} S cm^{2} mol^{-1}

Molar conductance of 0.1M KCl = 12.896×10^{-3} S cm^{2} mol^{-1}

Since smaller the cation higher the molar conductivity. H^{+} ions are smaller when compared to K^{+} ions. ∴ 0.1M HCl will have greater molar conductivity (Λ_{m}).

10. Arrange the following solution in the decreasing order of specific conductance.
(i) 0.01M KCl (ii) 0.005M KCl (iii) 0.1M KCl (iv) 0.25M KCl (v) 0.5M KCl

Specific conductivity decreases with decrease in concentration of the solution. So the decreasing order of specific conductance is,

0.5M KCl > 0.25M KCl > 0.1M KCl > 0.01M KCl > 0.005M KCl

11. Why is AC current used instead of DC in measuring the electrolytic conductance? [PTA-5]

If we apply DC current through the conductivity cell, it will lead to the electrolysis of the solution taken in the cell. AC current is used for this measurement to prevent electrolysis.

12. 0.1 M NaCl solution is placed in two different cells having cell constant 0.5 and 0.25 cm^{-1} respectively. Which of the two will have greater value of specific conductance?

Specific conductance, $K = \frac{1}{R}\frac{l}{A}$

Specific conductance, K is directly proportional to cell constant $\frac{l}{A}$

∴ The cell with higher cell constant has greater value of specific conductance. i.e., The cell with 0.5cm^{-1} cell constant will have greater value of specific conductance.

13. A current of 1.608A is passed through 250ml of 0.5M solution of copper sulphate for 50 minutes. Calculate the strength of Cu^{2+} after electrolysis assuming volume to be constant and the current efficiency is 100%.

I = 1.608A; t = 50min = 50 × 60 = 3000s; V = 250ml; C = 0.5M; η = 100%

Calculate the number of faradays of electricity passed through the $CuSO_4$ solution,

⟹ Q = It = 1.608 × 3000 = 4824 C; ∴ Number of Faradays of electricity = $\frac{4824\ C}{96500\ C}$ = 0.05F

Electrolysis of $CuSO_4$, $Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}$

The above equation shows that 2F electricity will deposit 1 mole of Cu^{2+} to Cu.

∴ 0.05F electricity will deposit = $\frac{1\ mol}{2F}\times 0.05F$ = 0.025 mol

Initial number of molar of Cu^{2+} in 250 ml of solution = $\frac{0.5}{1000\ ml}$ × 250ml = 0.125 mol

∴ Number of moles of Cu^{2+} after electrolysis = 0.125 – 0.025 = 0.1 mol

∴ Concentration of Cu^{2+} = $\frac{0.1\ mol}{250\ ml}$ × 1000ml = **0.4M**

14. Can Fe^{3+} oxidises Bromide to bromine under standard conditions?
Given: $E^{\circ}_{\frac{Fe^{3+}}{Fe^{2+}}}$ = 0.771V; $E^{\circ}_{\frac{Br_2}{Br^-}}$ = 1.09V [MAR-24]

Required half-cell reaction,

$2Br^- \longrightarrow Br_2 + 2e^-$ (E°_{ox}) = -1.09V

$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$ (E°_{red}) = +0.771V

$2Fe^{3+} + 2Br^- \longrightarrow 2Fe^{2+} + Br_2$ (E°_{cell}) = ?

$(E^{\circ}_{cell}) = (E^{\circ}_{ox}) + (E^{\circ}_{red})$ = -1.09 + 0.771 = -0.319V

E°_{cell} is –ve; ΔG is +ve and the cell reaction is non-spontaneous. Hence Fe^{3+} cannot oxidises Br^- to Br_2.

15. Is it possible to store copper sulphate in an iron vessel for a long time?
Given: $E^{\circ}_{\frac{Cu^{2+}}{Cu}}$ = 0.34V; $E^{\circ}_{\frac{Fe^{2+}}{Fe}}$ = -0.44V [PTA-4, HY-19, SRT-22, HY-24, JUN-25]

$(E^{\circ}_{ox})_{\frac{Fe}{Fe^{2+}}}$ = 0.44V and $(E^{\circ}_{red})_{\frac{Cu^{2+}}{Cu}}$ = 0.34V

These +ve emf values shows that iron will oxidise and copper will get reduced i.e., the vessel will dissolve. Hence it is not possible to store copper sulphate in an iron vessel.

16. Two metals M_1 and M_2 have reduction potential values of –*x*V and +*y*V respectively. Which will liberate H_2 and H_2SO_4?

Metals having higher oxidation potential will liberate H_2 and H_2SO_4. Hence, the metal M_1 having +*x*V, oxidation potential will liberate H_2 from H_2SO_4.

17. Reduction potential of two metals M_1 and M_2 are $E^{\circ}_{\frac{M_1^{2+}}{M_1}}$ = -2.3V and $E^{\circ}_{\frac{M_2^{2+}}{M_2}}$ = 0.2V. Predict which one is better for coating the surface of iron. Given: $E^{\circ}_{\frac{Fe^{2+}}{Fe}}$ = -0.44V [PTA4, JUN23]

Oxidation potential of M_1 is more +ve than the oxidation potential of Fe which indicates that it will prevent iron from rusting.

18. Calculate the standard emf of the cell: $Cd|Cd^{2+}||Cu^{2+}|Cu$ and determine the cell reaction. The standard reduction potentials of $Cu^{2+}|Cu$ and $Cd^{2+}|Cd$ are 0.34V and -0.40V respectively. Predict the feasibility of the cell reaction.

Cell reactions:

Oxidation at anode: $Cd_{(s)} \longrightarrow Cd^{2+}_{(aq)} + 2e^-$ $(E^{\circ}_{ox})_{\frac{Cd}{Cd^{2+}}}$ = 0.4V

Redution at cathode: $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ $(E^{\circ}_{red})_{\frac{Cu^{2+}}{Cu}}$ = 0.34V

$(E^{\circ}_{cell}) = (E^{\circ}_{ox}) + (E^{\circ}_{red})$ = 0.4 + 0.34 = 0.74V.

emf is +ve, so ΔG is (-)ve, the reaction is feasible.

19. In fuel cell H_2 and O_2 react to produce electricity. In the process, H_2 gas is oxidised at the anode and O_2 gas is reduced at cathode. If 44.8 litre of H_2 at 25°C and 1atm pressure reacts in 10minutes, what is average current produced? If the entire current is used for electro deposition of Cu from Cu^{2+}, how many grams of Cu deposited?

Oxidation at anode: $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$

1 mole of hydrogen gas produces 2 moles of electrons at 25°C and 1 atm pressure, 1 mole of hydrogen gas occupies = 22.4litres.

∴ no. of moles of hydrogen gas produced = $\frac{1\ mole}{22.4\ litres} \times 44.8\ litres$ = 2 moles of hydrogen

∴ 2 of moles of hydrogen produces 4 moles of electron i.e., 4F charge

We know that Q = It

I = $\frac{Q}{t} = \frac{4F}{10\ mins} = \frac{4 \times 96500\ C}{10 \times 60\ s}$ = **643.33A**

Electro deposition of copper, $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

2F charge is required to deposit 1 mole of copper i.e., 63.5g

If the entire current produced in the fuel cell i.e., 4F is utilised for electrolysis, then 2 × 63.5 i.e., 127.0g copper will be deposited at cathode.

20.The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate and chromium nitrate respectively. If 2.935g of Ni was deposited in the first cell. The amount of Cr deposited in the another cell? Given: molar mass of Nickel and chromium are 58.74 and 52gm^{-1} respectively.

m_{Ni} = 2.935g; m_{Cr} = ?

$e_{Ni^{2+}} = \frac{Atomic\ mass}{Valency} = \frac{58.74}{2} = 29.37$

$e_{Cr^{3+}} = \frac{Atomic\ mass}{Valency} = \frac{52}{2} = 17.33$

According to Faraday's Second law, $\frac{m_{Cr}}{m_{Ni}} = \frac{e_{Cr^{3+}}}{e_{Ni^{2+}}}$;

$m_{Cr} = \frac{e_{Cr^{3+}}}{e_{Ni^{2+}}} \times m_{Ni} = \frac{17.33 \times 2.935}{29.37} = 1.732$g

21.A copper electrode is dipped in 0.1M copper sulphate solution at 25°C. Calculate the electrode potential of copper. [Given: $E°_{Cu^{2+}|Cu}$ = 0.34V]

$[Cu^{2+}]$ = 0.1M; $E°_{Cu^{2+}|Cu}$= 0.34V; E_{cell} = ?

Cell reaction is, $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

$E_{cell} = E° - \frac{0.0591}{n}\log\frac{[Cu]}{[Cu^{2+}]} = 0.34 - \frac{0.0591}{2}\log\frac{1}{0.1}$ = 0.34 – 0.0296 = **0.31V**

22.For the cell $Mg_{(s)}|Mg^{2+}_{(aq)}||Ag^{+}_{(aq)}|Ag_{(s)}$, calculate the equilibrium constant at 25°C and maximum work that can be obtained during operation of cell. Given: $E°_{Mg^{2+}|Mg}$= -2.37V and $E°_{Ag^{+}|Ag}$= 0.80V.

Oxidation at anode: $Mg \longrightarrow Mg^{2+} + 2e^-$ (E°_{ox})= 2.37V ⇢ (1)

Reduction at cathode: $Ag^+ + e^- \longrightarrow Ag$ (E°_{red})= 0.80V ⇢ (2)

∴ $E^{\circ}_{cell} = (E^{\circ}_{ox})_{anode} + (E^{\circ}_{red})_{cathode}$ = 2.37 + 0.80 = $\mathbf{3.17V}$

Overall reaction, Equation (1) + 2 × equation (2) ⟹ $Mg + 2Ag^+ + e^- \longrightarrow Mg^{2+} + 2Ag$

$\Delta G° = -nFE°$ = – 2 × 96500 × 3.17 = – 611810 KJ = **– 6.12 × 10^5 J**

W = 6.12 × 10^5 J; log $K_c = \frac{6.12 \times 10^5}{2.803 \times 8.314 \times 298}$; **$K_c$** = Antilog of (107.2) = **1.5849**

23.9.2 ×10^{12} litres of water is available in a lake. A power reactor using the electrolysis of water in the lake produces electricity at the rate of 2 × 10^6 Cs^{-1} at an appropriate voltage. How many years would it like to completely electrolyse the water in the lake. Assume that there is no loss of water except due to electrolysis.

At anode: $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$ ⇢ (1)

At cathode: $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ ⇢ (2)

Overall reaction: $6H_2O \longrightarrow 4H^+ + 4OH^- + 2H_2 + O_2$

Equation (1) + (2) × 2 ⟹ $4H_2O \longrightarrow 2H_2 + O_2$

∴ According to Faradays Law of electrolysis, to electrolyse two mole of Water (36g ≃ 36mL of H_2O), 4F charge is required alternatively, when 36mL of water is electrolysed, the charge generated = 4 × 96500C.

∴ When the whole water which is available on the lake is completely electrolysed the amount of charge generated is equal to

$= \frac{4 \times 96500\ C}{36\ mL} \times 9 \times 10^{12}$ L $= \frac{4 \times 96500 \times 9 \times 10^{12}}{36 \times 10^{-3}}$ C = **96500 × 10^{15} C**

∴ Given that in 1 second, 2 × 10^6 C is generated therefore, the time required to generate 96500 × 10^{15}C is $= \frac{1S}{2 \times 10^6 \times C} \times 96500 \times 10^{15}C$ = **48250 × 10^9S**

∴ Number of years $= \frac{48250 \times 10^9}{365 \times 24 \times 60 \times 60}$ = **1.5299 × 10^6 years** [1 years = 365 × 24 × 60 × 60 sec]

24.Derive an expression for Nernst equation. [SEP-20, SRT,MAY,JUL,SEP-22, MAR-25]

Nernst equation is the one which relates the cell potential and the concentration of the species involved in an electrochemical reaction. Let us consider an electrochemical cell for which the overall redox reaction is,

$$xA + yB \rightleftharpoons lC + mD$$

The reaction quotient Q for the above reaction is given below

$Q = \frac{[C]^l[D]^m}{[A]^x[B]^y}$ ---------------→(1)

We have already learnt that, $\Delta G = \Delta G° + RT \ln Q$ ---------------→(2)

The Gibbs free energy can be related to the cell emf as follows

$\Delta G = -nFE_{cell}$; $G° = -nFE°_{cell}$

Substitute these values and Q from (1) in the equation (2)

(2) ⟹ $-nFE_{cell} = -nFE°_{cell} + RT \ln \frac{[C]^l[D]^m}{[A]^x[B]^y}$ ---------------→(3)

Divide the whole equation (3) by (-nF)

(3) ⟹ $E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{[C]^l[D]^m}{[A]^x[B]^y}$

(or) $E_{cell} = E^{\circ}_{cell} - \frac{2.303\ RT}{nF} \log \frac{[C]^l[D]^m}{[A]^x[B]^y}$ ---------------→(4)

The above equation (4) is called the Nernst equation.

At 25°C (298K), the above equation (4) becomes,

$E_{cell} = E^{\circ}_{cell} - \frac{2.303 \times 8.314 \times 298}{n\ (96500)} \log \frac{[C]^l[D]^m}{[A]^x[B]^y}$

$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[C]^l[D]^m}{[A]^x[B]^y}$ ---------------→(5)

25.Write a note on sacrificial protection.

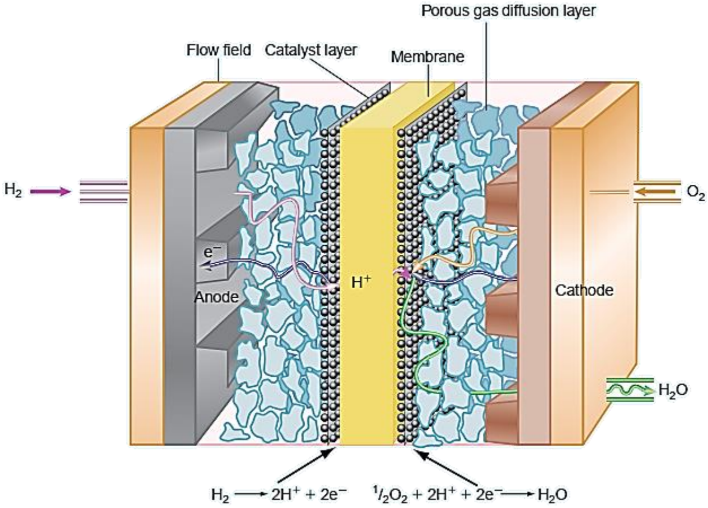
- Unlike galvanising the entire surface of the metal to be protected need not be covered with a protecting metal.
- Instead, metals such as Mg or zinc which is corroded more easily than iron can be used as a sacrificial anode and the iron material acts as a cathode.
- So iron is protected, but Mg or Zn is corroded. This process is called as sacrificial protection.

26.Explain the function of H_2 – O_2 fuel cell.

- The galvanic cell in which the energy of combustion of fuels is directly converted into electrical energy is called the fuel cell.
- It requires a continuous supply of reactant to keep functioning.
- The general representation of a fuel cell is follows
  Fuel | Electrode | Electrolyte | Electrode | Oxidant
- Let us understand the function of fuel cell by considering hydrogen – oxygen fuel cell.
- In this case, hydrogen act as a fuel and oxygen as an oxidant and the electrolyte is aqueous KOH maintained at 200°C and 20 – 40 atm.

- Porous graphite electrode containing Ni and NiO serves as the inert electrodes.
- Hydrogen and oxygen gases are bubbled through the anode and cathode, respectively.

Oxidation occurs at the anode:
$2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$
Reduction occurs at the cathode:
$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$
The overall reaction is $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$
The above reaction is the same as the hydrogen combustion reaction, however, they do not react directly ie., the oxidation and reduction reactions take place separately at the anode and cathode respectively like H_2 - O_2 fuel cell. Other fuel cells like propane – O_2 and methane O_2 have also been developed.



27. Ionic conductance at infinite dilution of Al^{3+} & SO_4^{2-} are 189 and 160mho cm² equiv⁻¹. Calculate the equivalent and molar conductance of the electrolyte $Al_2(SO_4)_3$ at infinite dilution.

$\lambda^\circ_{Al^{3+}}$ = 189 mho cm² equiv⁻¹; $\lambda^\circ_{SO_4^{2-}}$ = 160 mho cm² equiv⁻¹; λ°_m = ? ; λ° = ?

$$Al_2(SO_4)_3 \longrightarrow 2Al^{3+} + 3SO_4^{2-}$$

Equivalent conductance

$(\Lambda^\circ)_{Al_2(SO_4)_3} = \frac{1}{3}\lambda^\circ_{Al^{3+}} + \frac{1}{2}\lambda^\circ_{SO_4^{2-}} = \left(\frac{1}{3} \times 189\right) + \left(\frac{1}{2} \times 160\right)$ = 63+80 = **143 mho cm² equiv⁻¹**

Molar conductance

$(\Lambda^\circ_m)_{Al_2(SO_4)_3} = 2\lambda^\circ_{Al^{3+}} + 3\lambda^\circ_{SO_4^{2-}}$ = (2 × 189) + (3 × 160) = 378+480 = **858 mho cm² equiv⁻¹**

EVALUATE YOURSELF

1. Calculate the molar conductance of 0.01M aqueous KCl solution at 25°C. The specific conductance of KCl at 25°C is 14.114 × 10⁻² Sm⁻¹.

Molar conductance, $\Lambda_m = \frac{K \times 10^{-3}}{M}$ mol⁻¹ m³

Specific conductance, K = 14.114 × 10⁻² Sm⁻¹

Molar conductance, $\Lambda_m = \frac{14.114 \times 10^{-2} \times 10^{-3}}{0.01}$ = **14.114 × 10⁻³ Sm² mol⁻¹**

2. The resistance of 0.15N solution of an electrolyte is 50 Ω. The specific conductance of the solution is 2.4 Sm⁻¹, The resistance of 0.5 N solution of the same electrolyte measured using the same conductivity cell is 480 Ω. Find the equivalent conductivity of 0.5 N solution of the electrolyte.

R_1 = 50Ω; R_2 = 480Ω; κ_1 = 2.4Sm⁻¹; κ_2 = **?** Sm⁻¹; N_1 = 0.15N; N_2 = 0.5N;

We know that,

$\kappa = \frac{Cell\ Constant}{R}$; $\therefore \frac{\kappa_2}{\kappa_1} = \frac{R_1}{R_2}$ $\Rightarrow \boldsymbol{\kappa_2} = \kappa_1 \times \frac{R_1}{R_2} = 2.4Sm^{-1} \times \frac{50\Omega}{480\Omega}$ = **0.25Sm⁻¹**

3. The emf of the following cell at 25°C is equal to 0.34v. Calculate the reduction potential of copper electrode.

Pt (s) | H_2 (g, 1atm) | H^+ (aq, 1M) ‖ Cu^{2+} (aq, 1M) | Cu (s)

E°_{cell} = 0.34V

$E^\circ_{cell} = E^\circ_{anode} + E^\circ_{cathode}$

$E^\circ_{cell} = (E^\circ_{ox})_{SHE} + (E^\circ_{red})_{Cu^{2+}|Cu}$

$0.34V = 0 + (E^\circ_{red})_{Cu^{2+}|Cu}$ $\Rightarrow$ $\therefore (E^\circ_{red})_{Cu^{2+}|Cu}$ = **0.34V**

4. **Using the calculated emf value of zinc and copper electrode, calculate the emf of the following cell at 25°C.**
   Zn (s) | Zn^{2+} (aq, 1M) ‖ Cu^{2+} (aq, 1M) | Cu (s)

$E°_{Zn|Zn^{2+}}$ = 0.76V ; $E°_{Cu^{2+}|Cu}$ = 0.34V

$E°_{cell} = E°_{ox} + E°_{red}$ = 0.76V + 0.34V = 1.10V

∴ $E°_{cell}$ = **1.10V**

5. **Write the overall redox reaction which takes place in the galvanic cell,**
   Pt (s) | Fe^{2+} (aq), Fe^{3+} (aq) ‖ MnO_4^- (aq), H^+ (aq), Mn^{2+} (aq) | Pt (s)

Oxidation at anode, $Fe^{2+} \rightarrow Fe^{3+} + e^-$ - - - - - (1)

Reduction at cathode, $MnO_4^- + H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ - - - - - (2)

To balance multiply equation (1) × 5 and equation (2) × 1

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

Overall Redox reaction is, $\mathbf{5Fe^{2+}_{(aq)} + MnO^-_{4(aq)} + 8H^+_{(aq)} \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}_{(aq)}}$

6. **The electrochemical cell reaction of the Daniel cell is, $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(aq)}$ What is the change in the cell voltage on increasing the ion concentration in the anode compartment by a factor 10?**

$\mathbf{Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(aq)}}$

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

If the concentration of Zn^{2+} is increased, the second term on the RHS becomes more negative. This lowers the value of E_{cell}, so E_{cell} value will decrease if the ion concentration in the anode compartment is increased.

7. **A solution of a salt of metal was electrolysed for 15 minutes with a current of 0.15 amperes. The mass of the metal deposited at the cathode is 0.783g. Calculate the equivalent mass of the metal.**

I = 0.15 amperes; t = 15 mins = 15 × 60 = 900 s

Q = It = 0.15 × 900s = 135 Coulombs

Hence, 135 Coulombs of electricity deposit is equal to 0.783g of metal.

∴ 96500 coulombs of electricity deposit is equal to = $\frac{0.783 \times 96500}{135}$ = 559.7g of metal.

Hence equivalent mass of the metal is **559.7**

GOVERNMENT EXAM QUESTION PAPER

1. **A conductivity cell has two platinum electrodes separated by a distance 1.5 cm and the cross sectional area of each electrode is 4.5 sq cm. Using this cell, the resistance of 0.5 N electrolytic solution was measured as 15 Ω . Find the specific conductance of the solution. [PTA-1, MAR-20]**

l = 1.5 cm = 1.5 × 10^{-2} m;

A = 4.5 sq cm = 4.5 cm^2 = 4.5 × 10^{-4} m^2;

R = 15Ω

$K = \frac{1}{R}\left(\frac{l}{A}\right) = \frac{1}{15\Omega} \times \frac{1.5 \times 10^{-2}\, m}{4.5 \times 10^{-4}\, m^2} = \mathbf{2.22\ Sm^{-1}}$

2. **How cathodic production helps to protect the metal from correction? [PTA-6, MAR20]**

In this technique, unlike galvanising the entire surface of the metal to be protected need not be covered with a protecting metal. Instead, metals such as Mg or zinc which is corroded more easily than iron can be used as a sacrificial anode and the iron material acts as a cathode. So iron is protected, but Mg or Zn is corroded.

3. Define molar conductance and specific conductance. How they are related? [PTA-4, SRT-22]

Specific conductance: The specific conductance is defined as the conductance of a cube of an electrolytic solution of unit dimensions. The SI unit of specific conductance is Sm^{-1}.

Molar conductance: The conductivity cell in which the electrodes are separated by 1m and having V m^3 of electrolytic solution which contains 1 mole of electrolyte. The conductance of such a system is called the molar conductance (Λ_m).

$$\Lambda_m = \frac{K\,(Sm^{-1})\ \times 10^{-3}}{M}\ mol^{-1}\,m^3$$

4. What are the conventions used in Galvanic cell notation. [PTA-1, SRT-22, MAR-24]

- The galvanic cell is represented by a cell diagram, for example, Daniel cell is represented as

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

- In the above notation, a single vertical bar (|) represents a phase boundary and the double vertical bar (||) represents the salt bridge.
- The anode half cell is written on the left side of the salt bridge and the cathode half cell on the right side.
- The anode and cathode are written on the extreme left and extreme right, respectively.
- The emf of the cell is written on the right side after cell diagram.

5. Write the Factors affecting electrolytic conductance. [HY-19, AUG-21, SRT,MAY- 22]

- If the interionic attraction between the oppositely charged ions of solutes increases, the conductance will decrease.
- Solvent of higher dielectric constant show high conductance in solution.
- Conductance is inversely proportional to the Viscosity of the medium. i.e., conductivity increases with the decrease in viscosity.
- If the temperature of the electrolytic solution increases, conductance also increases. Increase in temperature increases the kinetic energy of the ions and decreases the attractive force between the oppositely charged ions and hence conductivity increases.
- Molar conductance of a solution increases with increase in dilution. This is because, for a strong electrolyte, interionic forces of attraction decrease with dilution. For a weak electrolyte, degree of dissociation increases with dilution.

6. A solution of silver nitrate is electrolysed for 20 minutes with a current of 2 amperes. Calculate the mass of silver deposited at the cathode. [SEP- 20, SEP-22]

Electrochemical reaction at cathode is $Ag^+ + e^- \rightarrow Ag$ (reduction)

m = ZIt

Z = $\frac{molar\ mass\ of\ Ag}{96500} = \frac{108}{1 \times 96500}$; I = 2A; t = 20m = 20 × 60s = 1200s;

It = 2A × 1800s = 3600C

m = $\frac{108\ g\ mol^{-1}}{96500\ C\ mol^{-1}} \times 3600C$

m = 4.03g

7. Define equivalent conductance. [AUG-21]

Equivalent conductance is defined as the conductance of 'V' m3 of electrolytic solution containing one gram equivalent of electrolyte in a conductivity cell in which the electrodes are one metre apart.

$$\Lambda = \frac{K\,(Sm^{-1})\ \times 10^{-3}\ (gram\ equivalent)^{-1}\,m^3}{N}$$

8. Mention the three Applications of Kohlraush's Law. [SRT-22]

Applications of Kohlrausch's Law

- Calculation of molar conductance at infinite dilution of a weak electrolyte.
- Calculation of degree of dissociation of weak electrolytes.
- Calculation of solubility of sparingly soluble salts.

9. Calculate the molar conductance of 0.025M aqueous solution of calcium chloride at 25°C. The specific conductance of calcium chloride is 12.04×10^{-2} Sm^{-1}. [SRT-22]

Molar cunductance $\Lambda_m = \frac{K\,(Sm^{-1}) \times 10^{-3}}{M}\, mol^{-1}\, m^3$

$\Lambda_m = \frac{12.04 \times 10^{-2}\ Sm^{-1} \times 10^{-3}}{0.025}\, mol^{-1}\, m^3$ = $\mathbf{481.6 \times 10^{-5}\ Sm^2\ mol^{-1}}$