Chapter – ElectroChemistry

Very Short Answer Questions   **1 Mark**

1. What is the effect of temperature on molar conductivity?
Ans: Molar conductivity of an electrolyte increases with an increase in temperature.

2. Why is it not possible to measure single electrode potential?
Ans: It is not possible to measure single electrode potential because the half cell containing a single electrode cannot exist independently, as charge cannot flow on its own in a single electrode.

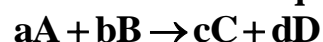## 3. Name the factor on which emf of a cell depends:
Ans: Emf of a cell depends on the following factors
a. Nature of reactants.
b. Concentration of solution in two half cells.
c. Temperature
d. Pressure of gas.

4. What are the units of molar conductivity?
Ans: $cm^2 ohm^{-1} mol^{-1}$ or $Scm^2 mol^{-1}$

5. Write Nernst equation or the general cell reaction
$$aA + bB \rightarrow cC + dD$$

Ans: $Ecell = E^0 cell - RT \ln \dfrac{[C]^c [D]^d}{nF[A]^a [B]^b}$

6. What is the EMF of the cell when the cell reaction attains equilibrium?
Ans: Zero

7. What is the electrolyte used in a dry cell?
Ans: A paste of NH_4Cl , MnO_2 and Carbon.

8. How is cell constant calculated from conductance values?

Ans: $\text{Cell Constant} = \dfrac{\text{specific conductance}}{\text{observed conductance}}$

9. What flows in the internal circuit of a galvanic cell?
Ans: Ions

10. Define electrochemical series.
Ans: The arrangement of various electrodes in the decreasing or increasing order of their standard reduction potentials is called electrochemical series.

11. Why in a concentrated solution, a strong electrolyte shows deviations from Debye-Huckle- Onsagar equation?
Ans: Because interionic forces of attractions are large.

12. What is the use of Platinum foil in the hydrogen electrode?
Ans: It is used for inflow and outflow of electrons.

13. Corrosion of motor cars is of greater problem in winter when salts are spread on roads to melt ice and snow. Why?
Ans: It is used for inflow and outflow of electrons.

14. Is it safe to stir AgNO₃ solution with a copper spoon?
$\left(E^0_{Ag+/\,Ag} = 0.80 \text{ Volt}; \ E^0_{Cu+2/\,Cu} = 0.34 \text{ Volt}\right)$

Ans: No it is not safe because reacts with $AgNO_3$ Solution (Emf will be positive.)

15. 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 solution.

Short Answer Questions   **2 Marks**

1. How can you increase the reduction potential of an electrode? For the reaction?
$M^{n+}(aq) + ne^{-1} \rightarrow M(s)$

Ans: Nernst equation is:

$E^0_{\frac{M^{n+}}{M}} = E_{\frac{M^{n+}}{M}} - \dfrac{2.303RT}{nF}\log\dfrac{1}{[M^{n+}]}$

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

a. increase in concentration of M^{n+} ions in solution

b. By increasing the temperature.

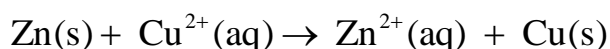**2. Calculate emf of the following cell at 298K.**

$$Zn / Zn^{2+}(10^{-4}M) \| Cu^{2+}(10^{-2}M) / Cu$$

Given $E^0_{Zn^{2+}/Zn} = -0.76V$

$\quad\quad E^0_{Cu^{2+}/Cu} = +0.34V$

Ans: Cell reaction is as follows.

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

$n = 2$ and $T = 298$ K

$$E_{cell} = \left(E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}\right) - \frac{0.0591}{n} \log \frac{\left[Zn^{2+}(aq)\right]}{\left[Cu^{+2}(aq)\right]}$$

$$E_{cell} = 0.34V - (-0.76) - \frac{0.0591}{2} \log \frac{10^{-4}}{10^{-2}}$$

$$E_{cell} = 1.10 - 0.02955 \log 10^{-2}$$

$$= 1.10 + 2 \times 0.02955$$

$$\therefore E_{cell} = +1.1591V$$

3. Electrolysis of KBr(aq) gives Br_2 at anode but does not give F_2 . Give a reason.

Ans: Oxidation takes place at anode. Now higher the oxidation Potential, easier to oxidize. Oxidation potential of Br^- , H_2O ,F^- are in the following order.

$Br^- > H_2O > F^-$.

Therefore in aq Solution of KBr. Br^- ions are oxidized to Br_2 in preference to H_2O . On the other hand, in aqueous solution of KF, H_2O is oxidized in preference to F^- . Thus in this case oxidation of H_2O at anode gives O_2 and no F_2 is produced.

4. What happens when a piece of copper is added to

a. An aqueous solution of $FeSO_4$?

Ans: Nothing will happen when the piece of copper is added to $FeSo_4$ because reduction potential $E^0_{Cu^{+2}/Cu}$ $(-0.34V)$ is more than the reduction potential $E^0_{(Fe^{2+}/Fe)}(-0.44V)$

b. An aqueous solution of $FeCl_3$?

Ans: copper will dissolve in an aq solution of $FeCl_3$ because reduction potential $E^0_{(Fe^{3+}/Fe^{2+})}$ $(+0.77V)$ is more than the reduction potential $E^0_{Cu^{+2}/Cu}$ $(-0.34V)$.

$$Cu(s) + 2FeCl_3 (aq) \rightarrow Cu^{+2}(aq) + 2 FeCl_2(aq)$$
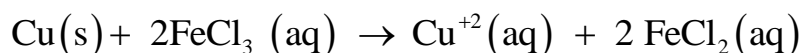
5. Define corrosion. Write the chemical formula of rust.
Ans: Corrosion is a process of determination of metal as a result of its reaction with air and water surrounding it. It is due to the formulation of sulphides, oxides, carbonates, hydroxides, etc.
Formula of rust- $Fe_2O_3.xH_2O$

6. Write short notes on reduction and oxidation potentials.
Ans: oxidation potential: this is a measure of the tendency of a chemical species to acquire electrons loose or to get oxidized at an electrode.
Reduction potential: this is a measure of the tendency of a chemical species to acquire electrons gain or to get reduced at an electrode.

7. How are standard electrode potentials measured?
Ans: the standard electrode potential is measured by a galvanic cell which is constructed with a standard hydrogen electrode on one side and an unknown half cell on the other side.

8. What is cell constant? How is it determined?
Ans: cell constant is defined as the ratio of distance between the electrodes which is divided by the area of the cross-sectional of the electrode.
Calculating the resistance of a cell containing a known conductivity solution is the process of determining cell constant experimentally.

9. What is conductivity water?
Ans: Conductivity water is a measure of the ability of water to pass an electric current.

10. Why is it necessary to platinumize the electrodes of a conductivity cell before it is used for conductance measurement?
Ans: Because platinization will increase the surface area of the electrode on which the hydrogen gas can be contacted with hydrogen ions. Due to this the reactions happen faster and lead to better conduction measurement.

## 11. Why does mercury cell give constant voltage?
Ans: Due to The overall cell reaction does not include any ion in the solution whose concentration changes during its life time.

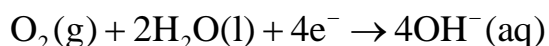**12. What is a fuel cell? Write reaction involved in $H_2 - O_2$ fuel cell.**

Ans: An electrochemical cell in which chemical energy of fuel is directly converted into electrical energy is known as Fuel cell.

The Half cell reactions in Hydrogen-oxygen fuel cell as follows:

Oxidation at anode:

$$2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$$
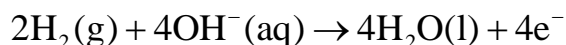
Reduction at cathode:

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

13. Why is Li the best reducing agent whereas Fluorine is the best oxidizing agent? but not to E_{cell} . Explain.

Ans: according to the electrochemical series, Li ion has the lowest reduction potential which means it acts as the best reducing agent. Similarly, F has the highest reduction potential, thus fluorine oxidizes another substance readily. So, F is the best oxidizing agent.

14. Why sodium metal is not obtained at cathode when NaCl is electrolysed with Pt electrodes but obtained when molten NaCl is electrolysed?

Ans: Because the reduction potential of Na^+ , $E^0_{Na^+/Na} = -2.7V$ is energetically more difficult than the reduction of water.

15. Zn rod weighing 25g was kept in 100mL of 1 M copper sulphate solution. After certain time interval, the molarity of Cu^{2+} was found to be 0.8M . What is the molarity of SO_4^{-2} in the resulting solution and what should be the mass of Zn rod after cleaning and drying?

Ans: weight of Zn rod $= 25g$

Number of moles that are required by Cu^{2+} to Cu $=$ Molarity $\times$ volume

$$= (1 - 0.8) \times \frac{100L}{1000} = 0.2 \times 0.1 = 0.02 mole$$

Molar mass of Zinc $= 64.5g/mol$

The zinc gets oxidized $= 0.02 \times 65.4 = 1.308g$

Hence, weight of Zn rod left will be $= 25 - 1.308 = 23.69gm$

16. Which will have greater molar conductivity and why? Sol A. 1 mol KCl dissolved in 200cc of the solution or Sol B. 1 mol KCl dissolved in 500cc of the solution.

Ans: Sol B: 1 mol KCl has dissolved in 500c of the solution has greater molar conductivity. Because, the number of ions in Sol B is greater than Sol A.

Molar conductivity is the conduction of all moles produced from 1mole of KCl and which increases with dilution.

Short Answer Questions   **2 Marks**

1. Write any three differences between potential difference and e.m.f.
Ans:

| E.M.F	POTENTIAL DIFFERENCE
1. It is the difference between the electrode potential of two electrodes when no current is flowing through the circuit.	1. It is the difference of potential between the electrodes in a closed circuit.
2. It is the maximum voltage obtained from a cell.	2. It is less than the maximum voltage obtained from a cell.
3. It is responsible for the steady flow of current.	3. It is not responsible for the steady flow of current.

2. Why does an electrochemical cell stop working after some time?
Ans: The reduction potential of an electrode depends upon the concentration of solution with which it is in contact.

As the cell works, the concentration of reactants decreases. Then according to Le Chatelier's principle, it will shift the equilibrium in the backward direction. On the other hand, if the concentration is more on the reactant side then it will shift the equilibrium in the forward direction. When cell works concentration in an anodic compartment in cathodic compartment decreases and hence $E^0_{cathode}$ cathode will decrease. Now EMF of the cell is $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

A decrease in $E^0_{cathode}$ and a corresponding increase in E^0_{anode} wil mean that EMF of the cell will decrease and will ultimately become zero i.e., cell stops working after some time.

3. For the standard cell,

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

   $E^0_{Cu^{2+}/cu} = +0.34V$
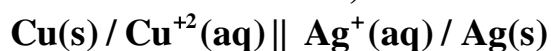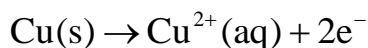
$E^0_{Ag^+/Ag} = +0.80 \ V$

i) Identify the cathode and the anode as the current is drawn from the cell.

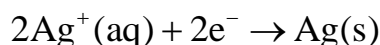**Ans:** From the cell representation, Ag / Ag^+ electrode is cathode and Cu / Cu^+ an electrode is anode.

ii)Write the reaction taking place at the electrodes.
Ans:

At anode:

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

At cathode:

$$2Ag^+(aq) + 2e^- \rightarrow Ag(s)$$

iii) Calculate the standard cell potential.
Ans:

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

$$E^0_{cell} = E^0_{Ag^+/Ag} - E^0_{Cu^{2+}/Cu}$$

The standard cell potential, $E^0_{cell} = +0.80V - (+0.34V) = +0.46V$

4. Can we store copper sulphate in Zinc vessels and silver vessels? Give reasons.
Given

$$E^0_{Cu^{2+}/Cu} = +0.34V; E^0_{Zn^{2+}/Zn} = -0.76V; E^0_{Ag^+/Ag} = +0.80V$$

Ans: A metal having lower reduction potential can displace a metal having higher reduction potential from solution of its salt of $Cu^{2+} (E^0_{Cu^{2+}/Cu} = +0.34V)$. Since standard reduction potential of $Zn^{2+} \left(E^0_{Zn^{2+}/Zn} = -0.76V \right)$ is less than the standard reduction potential of $Cu^{2+}(E^0_{Cu^{2+}/Cu} = +0.34V)$, Zn can displace copper from copper sulphate solution. Thus, $CuSo_4$ the solution can be stored in a silver vessel.

5. How many grams of chlorine can be produced by the electrolysis of matters NaCl with a current of 1.02A for 15min?
Ans:

$$2NaCl(1) \rightarrow 2Na^+(1) + 2Cl^-(1)$$

$$\underset{2mole}{2\,Cl^-} \rightarrow \underset{1mole}{Cl_2(g)} + 2e$$
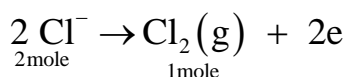
$$Q = nf$$

$$Q = 2 \times 96500 \, C/mol = 1.93 \times 10^5 C$$

Quantity of electricity used $= I \times t = 1.02A \times (15 \times 60)s = 900C$

Molar mass of $Cl_2 = 2 \times 35.5 = 71g$

$\therefore 1.93 \times 10^5 C$ of charge produce chlorine $= 71 gm$

$900C$ of charge produce chlorine $= \dfrac{71 \times 900}{1.93 \times 10^5} = 0.331 gm$

Hence, 0.331 grams of chlorine can be produced by the electrolysis of matters NaCl with a current of 1.02A for 15 min.

6. What is understood by a normal hydrogen electrode? Give its significance.
Ans: Normal hydrogen electrode also known as Standard Hydrogen Electrode which is used for reference on half cell potential reactions.
By using normal hydrogen electrodes, we can calculate cell potentials using different electrodes and this is a standard measurement of an electrode potential for the thermodynamic scale of redox potential.

7. Define electrode potential. Why absolute value of the reduction potential of electrode cannot be determined?
Ans:
The voltage or potential difference of a cell assembled from a standard hydrogen electrode is known as electrode potential for a given electrode.
The potential is determined by using standard hydrogen electrodes as a reference and so absolute potential cannot.

8. Write the equation showing the effect of concentration on the electrode potential.
Ans:
The equation showing the effect of concentration on the electrode potential is known as Nernst Equation.

$$E_{cell} = E_{cell}^0 - \dfrac{RT}{nF} \ln Q$$

Where, E_{cell} = the reduction potential at current conditions

E_{cell}^0 = the standard reduction potential relative to hydrogen's reduction potential at $25^0 C$

R = universal gas constant

T = temperature in K

n = the moles of electrons transferred between the positive and negative terminals of an electrochemical system.

F = faraday's constant

Q = reaction quotient

9. Derive the relationship between Gibbs free energy change and the cell potential.

Ans:

The electrical work of electrical energy produced is equal to the product of e.m.f of a cell. (E_{cell})

$$W_{electrical} = -E_{cell} \times q$$

The negative sign indicates the work done by the system on the surroundings.

Therefore, $W_{electrical} = -nFE_{cell}$

Since, $\Delta G = -W(\text{non-expansion})$

In this case non-expansion work done is electrical work.

Therefore, $\Delta G = -nFE_{cell}$

Considering standard electrode potential, the standard gibbs free energy as follows,

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

10. How can the Nernst equation can be applied in the calculation of equilibrium constant of any cell reaction?

Ans:

Nernst equation, $E_{cell} = E^0_{cell} - \dfrac{RT}{nF} \ln Q$

For any cell reaction in equilibrium, then $Q = K_c$

Where K_c = equilibrium constant

$$E_{cell} = E^0_{cell} - \dfrac{RT}{nF} \ln K_c$$

11. The cell reaction as written is spontaneous if the overall EMF of the cell is positive. Comment on this statement.

Ans: If the e.m.f of a cell is positive, then the Gibbs free energy of the overall reaction is less than zero.

$$\Delta G = -nFE_{cell}$$

Therefore, if E_{cell} is positive, then the cell reaction is spontaneous.

Long Answer Questions   **5 Marks**

1. Explain the term electrolysis. Discuss briefly the electrolysis of
**i.molten NaCl**

Ans: Electrolysis: this is a process of decomposition of a chemical compound in aqueous solutions or in molten state by a chemical change during electric current

The electrolysis of molten NaCl when sodium chloride is melted above 801^0C then two electrodes are inserted into the melt and electric current is passed through the molten salt. The following chemical reactions take place at the electrodes.
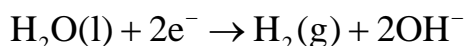
At cathode:

$$Na^+ + e^- \rightarrow Na$$

At anode:

$$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$$
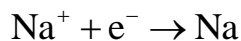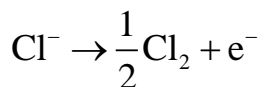
the overall reaction is, $2NaCl \rightarrow 2Na(s) + Cl_2(g)$
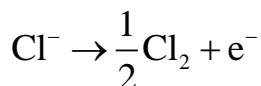
ii. aqueous sodium chloride solution

Ans: Sodium chloride dissolves as Na^+ and Cl^- into water and producing sodium and hydrogen at respective electrodes.
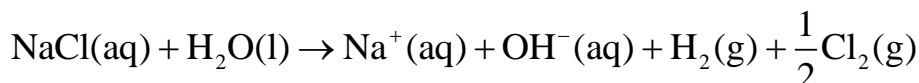
At cathode:

$$H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$$

At anode:

$$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$$

the overall reaction,

$$NaCl(aq) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + H_2(g) + \frac{1}{2}Cl_2(g)$$

iii. molten lead bromide

Ans: Molten lead bromide $PbBr_2$ is an electrolyte.

At cathode: $Pb^{+2} + 2e^- \rightarrow Pb(s)$
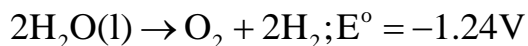
At anode: $2Br^- \rightarrow Br_2 + 2e^-$

iv. water

Ans: The process of water is decomposed into oxygen and hydrogen gas when electric current is passed through is known as electrolysis of water.

At cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-; E^0 = -0.42V$

At anode: $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-; E^o = +0.82V$

The overall reaction of electrolysis of water as follows,

$$2H_2O(l) \rightarrow O_2 + 2H_2; E^o = -1.24V$$

2. State and explain Faraday's laws of electrolysis. What is the electrochemical equivalent?

Ans: First Law of Electrolysis: the deposited mass of an electrode is directly proportional to the quantity of electricity passing through it during electrolysis.

W = zct

Where, W = deposited mass on the electrode

c = current and t = time in sec

If 1 amp current is passed through a solution in one second then the deposited mass of substance on the electrode is equal to its electrochemical equivalent. Here, z is known as the electrochemical equivalent.

Second Law of Electrolysis: the deposited masses on the electrodes are directly proportional to their chemical equivalents when the same quantity of electricity is passed through the different electrolytic cells.

Consider, $W_1, W_2 \& E_1, E_2$ be the amount of mass deposited and their chemical equivalents respectively.

According to faraday's second law of electrolysis,

$W_1 \alpha E_1$, and $W_2 \alpha E_2$

Then, $\dfrac{W_1}{W_2} = \dfrac{E_1}{E_2}$

3. What do you understand by 'electrolytic conduction'? What are the factors on which electrolyte conduction depends? What is the effect of temperature on electrolytic conduction?

Ans:

When electric current passes through the electrolytic solutions then the ability of the solutions to allow the current is known as electrolytic conductance.

Factors affecting on electrolytic conductance,

a. Concentration of ions

b. Nature of electrolyte

c. Temperature

Effect of temperature: when temperature changes the electrolyte gets dissolved in solution. Hence, the temperature increases the solubility of electrolytes and increases the electrolytic conduction.

4. How is electrolytic conductance measured experimentally?

Ans: the resistance between two nodes will give information about the conductance of electrolyte. When electricity passes through electrolyte solution dissociates into positive ions and negative ions. The conductance of electrolyte can be measured by using galvanic cells or the method of electrolysis.

5. Describe normal hydrogen electrodes and its applications.

Ans: An electrode which is used for reference on all half cell potential reactions is known as normal hydrogen electrode or standard hydrogen electrode.

The normal hydrogen electrode potential is zero and this is used to calculate the potentials of different half cells and different concentrations.

VERY IMPORTANT QUESTIONS   **3/5 Marks**

1. What do you mean by
i) negative standard electrode potential
Ans: negative standard electrode potential means the tendency to get reduce is less than hydrogen or greater ease of oxidation compared to that of hydrogen
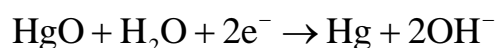
ii) positive standard electrode potential ?
Ans: positive standard electrode potential means the tendency to get reduced more than hydrogen.

2. Which cell is generally used in hearing aids? Name the material of the anode, cathode and the electrolyte. Write the reactions involved.
Ans: Mercury cells are used in hearing aids.
At cathode:
$$HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$$
At anode:
$$Zn + OH^- \rightarrow ZnO + H_2O + 2e^-$$

3. Iron does not rust even if Zinc coating is broken in a galvanised iron pipe but rusting occurs much faster if tin coating over iron is broken. Explain.
Ans: Fe is less electropositive than Zn. So, as long as Zn on the surface of Fe pipe then Zn acts as anode and Fe pipe acts as cathode. As a result of this, rusting of Fe is prevented by Zn.
On the other hand, Zn is more electropositive than Sn, which protects iron until the Sn coating is unbroken. If any pores or breaks are observed, even tin is there the exposed iron gets rusted.

4. 'Corrosion is an electrochemical phenomenon', explain.
Ans: when a metal surface is exposed to a wet environment, due to the presence of moisture or air oxidation takes place.

5. Calculate the pH of following cell: $Pt, H_2(1atm) | H^+(H_2SO_4)$, if its electrode potential is 0.03V.
Ans: Nernst equation for the given cell,
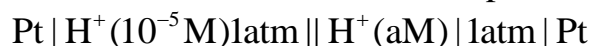$$E_{H_2/H^+} = E^0_{H_2/H^+} - \frac{0.0591}{2} \log \frac{[H^+]^2}{P_{H_2}}$$
$$0.03 = 0.0 - 0.0591 \log \frac{[H^+]}{1}$$

$$0.03 = 0.0591 \text{pH}$$

$$\text{pH} = \frac{0.03}{0.0591} = 0.5076$$

6. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of $10^{-5} H^+$ ions. The emf of the cell is 0.118V at 298K. Calculate the concentration of the H^+ ions at the positive electrode.
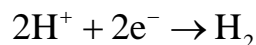
Ans: The cell reaction can be represented as,

$$Pt \,|\, H^+(10^{-5}M)\text{latm} \,||\, H^+(aM)\,|\,\text{latm}\,|\, Pt$$

At anode:

$$H_2 \rightarrow 2H^+ + 2e^-$$

Negative polarity, $[H^+] = 10^{-5}M$

At cathode:

$$2H^+ + 2e^- \rightarrow H_2$$

$$E_{cell} = \frac{0.0591}{2} \log \frac{[H^+]}{[10^{-5}]}$$

$$0.118 = 0.0591 \log \frac{[H^+]}{[10^{-5}]}$$

$$\therefore [H^+] = 10^{-3}M$$

The concentration of the H^+ ions at the positive electrode $= 10^{-3}M$

7. Crude copper containing Fe and Ag as contamination was subjected to electro refining by using a current of 175A for 6.434 min. The mass of anode was found to decrease by 22.260g, while that of cathode was increased by 22.011g . Estimate the % of copper, iron and silver in crude copper.

Ans: $22.260 - 22.011 = 0.249g$ of impurity present.

A current of 175A for 6.434 min(386.04sec) corresponds to
$175 \times 386.04 = 67551.75C$ of electricity.

Equivalent of Cu is 31.77g

The mass of Cu that should be deposited $= \dfrac{67551.75}{96500} \times 31.77 = 22.239g$

Increasing in mass of anode $= 22.011g$

$22.239 - 22.011 = 0.228g$ corresponds to the mass of Cu that is not deposited. This can be equated to the mass of iron that passed into solution.

The equivalent mass of Fe $= 27.75g$

The mass of Fe $= 0.228 \times 27.75 = 0.199g$

The percentage of Fe $= \dfrac{0.199 \times 100}{22.26} = 0.90\%$

8. Zinc electrode is constituted at 298 K by placing Zn rod in 0.1M aqueous solution of zinc sulphate which is 95% dissociated at this concentration. What will be the electrode potential of the electrode given that $E^0_{Zn^{2+}/Zn} = -0.76V$

Ans: $Zn^{+2} + 2e^- \rightarrow Zn(s)$
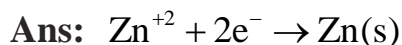
$[Zn^{+2}] = 0.1 \times \dfrac{95}{100} = 0.095M$

According to Nernst equation,

$E_{Zn^{+2}/Zn} = E^0_{Zn^{+2}/Zn} - \dfrac{0.0591}{2} \log \dfrac{1}{[Zn^{+2}]}$

$= -0.76V - \left(\dfrac{0.0591}{2} \log \dfrac{1}{0.095} \right)$

$= -0.76 - \dfrac{0.0591}{2} \times 1.0223 = -0.7902V$

9. At what pH will hydrogen electrode at 298K show an electrode potential of -0.118V , when Hydrogen gas is bubbled at 1atm pressure ?
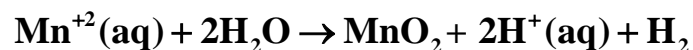**Ans:** From Nernst equation,

$E_{cell} = E^0_{cell} + 0.0591 pH$

for hydrogen electrode, $E^0_{cell} = \pm 0.0V$

Then, $E_{cell} = 0.0591 pH$

Given, $E_{cell} = -0.118V$

pH $= 0.5008$

10. Electrolysis of the solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per the chemical reaction

$Mn^{+2}(aq) + 2H_2O \rightarrow MnO_2 + 2H^+(aq) + H_2$

Passing a current of 27A for 24 Hrs gives 1Kg of MnO_2 . What is the current efficiency? What are the reactions occurring at anode and cathode?
Ans: According to faraday's second law of electrolysis,

weight in grams $= \dfrac{\text{equivalent weight} \times \text{current in amperes} \times \text{time in seconds}}{96500}$

Molecular weight of $MnO_2 = 87g$

The oxidation number of Mn in $Mn^{+2} = +2$
The oxidation number of Mn in $MnO_2 = +4$
Therefore, the change in the oxidation number $= +4-(+2)=+2$

Hence, the equivalent weight of $MnO_2 = \dfrac{87g}{2} = 43g$

Given, weight of $MnO_2 = 1Kg = 1000g$
Current $= 27A$
Time $= 24$ hrs $= (24 \times 60 \times 60)\sec$
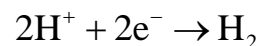Substitute the values in the faraday's second law equation,
$$1000g = \dfrac{43.5 \times i \times (24 \times 60 \times 60)}{96500}$$
i $=25.67A$
The value of current efficiency during the electrolysis of $MnSO_4$ can be calculated as,

Current efficiency $= \dfrac{25.67}{27} \times 100 = 95.074\%$

The reaction takes place at cathode,
$2H^+ + 2e^- \rightarrow H_2$
the reaction takes place at anode,
$Mn^{+2} \rightarrow Mn^{+4} + 2e^-$

Electrochemistry

1. What do you mean by Kohlrauch's law: from the following molar conductivities at infinite dilution
λ_m^∞ **$Ba(OH)_2 = 457.6\ \Omega^{-1}cm^2mol^{-1}$**
λ_m^∞ **$Ba\ Cl_2 = 240.6\ \Omega^{-1}cm^2mol^{-1}$**
λ_m^∞ **$NH_4Cl = 129.8\ \Omega^{-1}cm^2mol^{-1}$**
Calculate λ_m^∞ for NH_4OH
Ans: The Kohlrauch's law states that,
"An infinite dilution each ion migrates independently of it co-ion and makes its own contribution to the total molar conductivity of an electrolyte irrespective of nature."
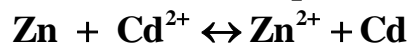$$\lambda_{m(NH_4OH)}^\infty = \lambda_{NH_4^+}^\infty + \lambda_{OH^-}^\infty$$
$$= (\lambda_{NH_4^+}^\infty + \lambda_{Cl^-}^\infty) + \dfrac{1}{2}(\lambda_{Ba^{2+}}^\infty + 2\lambda_{OH^-}^\infty) - \dfrac{1}{2}(\lambda_{Ba^{2+}}^\infty + 2\lambda_{Cl^-}^\infty)$$
$$= \lambda_{m(NH_4Cl)}^\infty + \dfrac{1}{2}\left(\lambda_{m(Ba(OH)_2)}^\infty\right) - \dfrac{1}{2}\left(\lambda_{m(BaCl_2)}^\infty\right)$$

$$\therefore \lambda^{\infty}_{m(NH_4OH)} = 129.8 + \frac{1}{2} \times 457.6 - \frac{1}{2} \times 240.6 = 238.3 \ \Omega^{-1}cm^2mol^{-1}$$

2. Calculate the equilibrium constant for the reaction

$Zn + Cd^{2+} \leftrightarrow Zn^{2+} + Cd$

If $E^0_{Cd^{+2}/Cd} = -0.403V$

$E^0_{Zn^{+2}/Zn} = -0.763V$

Ans: $E^0_{cell} = E^0_{Cd^{+2}/Cd} - E^0_{Zn^{+2}/Zn} = -0.403V - (-0.763V) = 0.360V$

$n = 2$, then the Nernst equation of equilibrium constant and emf of cell

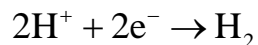$$\log K_c = \left(\frac{nE^0_{cell}}{0.059} \right) = \left(\frac{2 \times 0.360}{0.059} \right) = 12.20$$

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

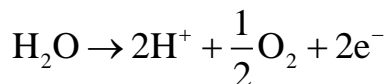## 3. Predict the products of electrolyzing of the following

a. A dil. Solution of H_2SO_4 with Pt electrode

Ans: oxygen gas is liberated at anode and hydrogen gas at cathode.

Reaction at cathode,

$2H^+ + 2e^- \rightarrow H_2$

Reaction at anode,

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$$

b. An aqueous solution of $AgNO_3$ with a silver electrode.

Ans: at cathode: silver ions will deposited in preference to hydrogen ions

At anode : $Ag \rightarrow Ag^+ + e^-$