

ELECTRO CHEMISTRY

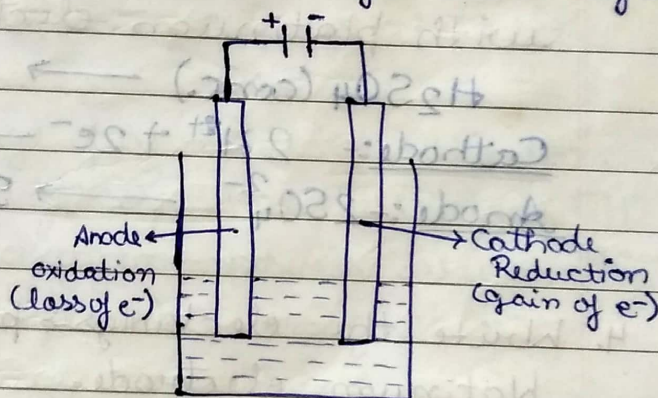
Electrolysis

Electrolysis may be defined as a process of decomposition of electrolyte by passing electricity through its aqueous solution or molten state.

Electrolysis is carried out in electrolytic cell.

Electrolytic cell

A device which convert electrical energy into chemical energy is called electrolytic cell. It consist of two electrode namely anode and cathode. Electrolytic cell may be represented as:



** If more than 1 ion move towards any electrode, that ions convert into product which has lower discharge potential.

The decreasing order of discharge potential are as:

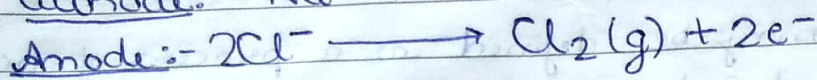
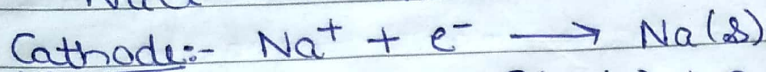
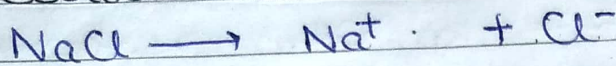
Cations:- $\text{Other} > \boxed{\text{H}^+} > \text{Cu}^{2+} > \text{Ag}^+$

Anions:- $\text{SO}_4^{2-} > \text{NO}_3^- > \text{F}^- > \boxed{\text{OH}^-} > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{Cu or Ag (electrode)}$

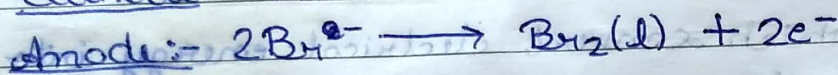
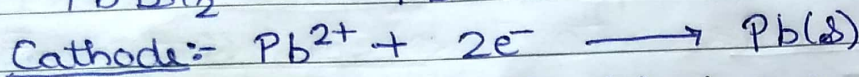
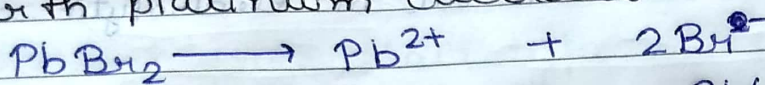
SBG STUDY

Problems:-

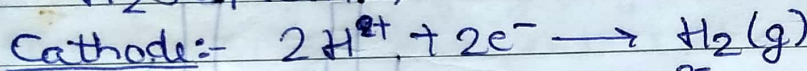
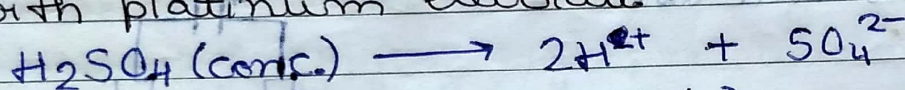
1. Write the electrolysis product of molten NaCl with inert electrode (Pt or Pd).



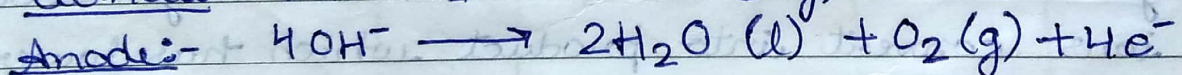
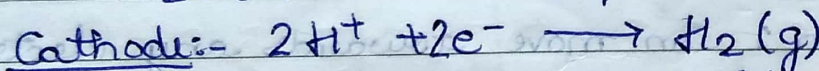
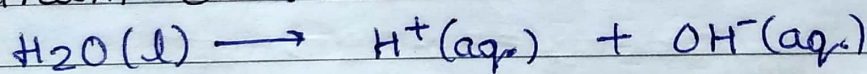
2. Write the electrolysis product of molten PbBr_2 with platinum electrode.



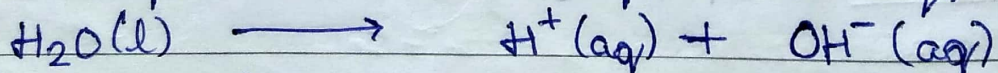
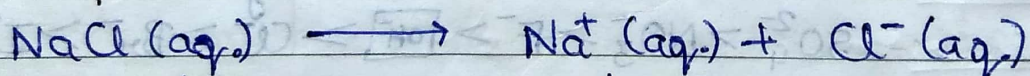
3. Write the electrolysis product of conc. H_2SO_4 with platinum electrode.



4. Write the electrolysis product of pure water with platinum electrode.

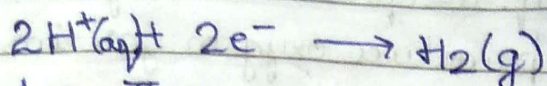


5. Write the electrolysis product of aq. NaCl solution with platinum electrode.

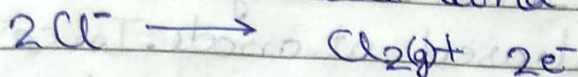


Cathode:- The discharge potential of H^+ ion is smaller than that of Na^+ ions therefore H^+ ions is reduce at cathode and hydrogen gas is

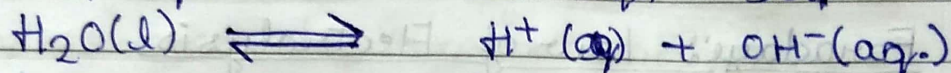
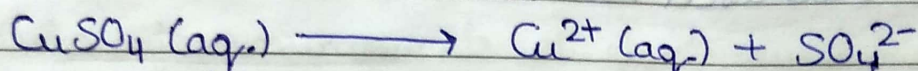
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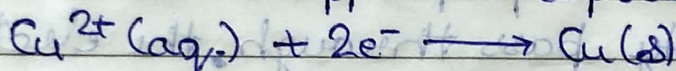
Anode:- The discharge potential of Cl^- ion is lower than that of OH^- ion. Therefore Cl^- ions is oxidised at anode and chlorine gas is released.



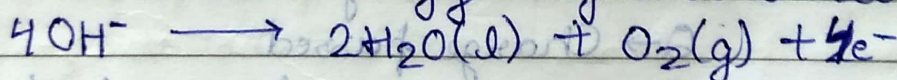
6. Write the electrolysis product of aq. CuSO_4 solution with inert electrode.



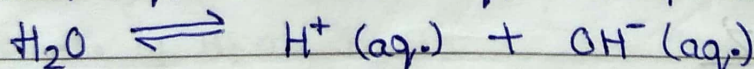
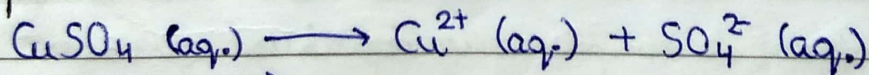
Cathode:- The discharge potential of Cu^{2+} ion is lower than that of H^+ ion. Therefore Cu^{2+} ion is reduced and copper is deposited at cathode.



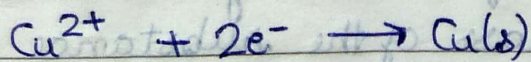
Anode:- The discharge potential of OH^- ion is lower than that of SO_4^{2-} ion. Therefore OH^- ion is oxidised and oxygen gas is released.



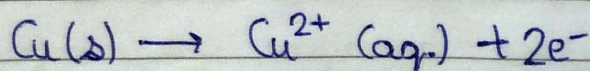
7. Write the electrolysis product of aq. CuSO_4 with copper electrode.



Cathode:- The discharge potential of $\text{Cu}^{2+}(\text{aq.})$ ion is lower than that of H^+ ion. Therefore Cu^{2+} ion is reduced at cathode.



Anode:- Copper electrode is oxidised and produce Cu^{2+} ions.



Q. The electrolysis of aq. KCl produce Cl gas but electrolysis of aq. KF solution produce oxygen gas instead of fluorine gas.

Ans In case of aq. KCl, the discharge potential of Cl^- ion is lower than that of OH^- ion. Therefore Cl_2 gas is released at anode. In case of aq. KF solution, the discharge potential of OH^- ion is lower than that of F^- ion. Therefore oxygen gas is released at anode.

Faraday's Law of Electrolysis

1st Law: The amount of chemical reaction which occurs at any electrode during electrolysis is proportional to the quantity of electricity pass through the electrolyte solution.

$$m \propto Q$$

$$m = ZQ$$

$$m = Z \times I \times t$$

where $m \rightarrow$ mass of substance occurs at any electrode

$Q \rightarrow$ Charge passed

$Z \rightarrow$ Electrochemical equivalent of a substance

and its value is $Z = \frac{E}{F}$ (Equivalent weight)

F (Faraday's constant)

Define 'Z'

If $I = 1 \text{ A}$ and $t = 1 \text{ sec}$.

Then $m = Z$.

Electrochemical equivalent of a substance may be defined as the mass of the substance deposited when a current of 1 A is passed for 1 second.

3rd law :- The amount of different substance liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their equivalent weights.

$$m \propto E$$

For two different electrolytes.

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}$$

Formula for numericals of electrolysis

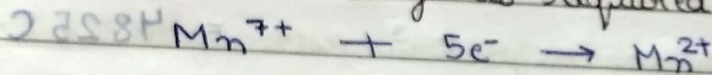
1 mole or gram atomic mass = nF charge.

* (a) Always write electrode reaction then find value of n (no. of electron loss or gain)

(b) $F = 96500 \text{ C}$ or 96487 C

(c) Passing charge = $Q = I \times t$

1. How much charge is required to convert 1 mole of MnO_4^- to Mn^{2+}



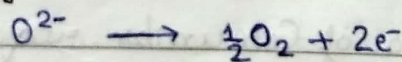
Quantity of charge required for reduction of 1 mole of MnO_4^- to $\text{Mn}^{2+} = 5 \times F$

$$= 5 \times 96500$$

$$= 482500 \text{ C}$$

2. How many Coulomb are required for following oxidation.

(i) 1 mole of H_2O to O_2 .

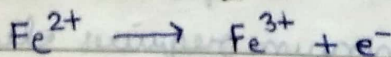


Quantity of charge required for oxidation of 1 mole of $\text{H}_2\text{O} = 2F$

$$= 2 \times 96500$$

$$= 193000 \text{ C}$$

(ii) 1 mole of Fe^{2+} to Fe^{3+}

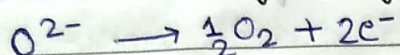


Quantity of charge required = $1 \times F$

$$= 96500 \text{ C}$$

3. How many coulomb of electricity are required for:-

(i) Complete oxidation of 90g of H_2O .



No. of moles in 90g of $\text{H}_2\text{O} = \frac{90}{18} = 5 \text{ moles}$.

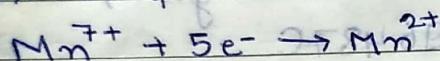
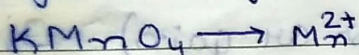
1 mole of H_2O requires electricity = $2 \times F$

5 moles of H_2O requires electricity = $10F$

$$= 965000 \text{ C}$$

(ii) Complete reduction of 100 mL of 0.1M KMnO_4 solution.

No. of moles of $\text{KMnO}_4 = 0.1 \times 0.1 = 0.01$.



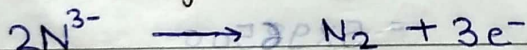
Required charge for 1 mole of $\text{KMnO}_4 = 5F$

Required charge for 0.01 mole of $\text{KMnO}_4 = 0.01 \times 5F$

$$= 0.01 \times 5 \times 96500$$

$$= 4825 \text{ C}$$

4. Find the charge in Coulombs on 1g-ion of N^{3-} .



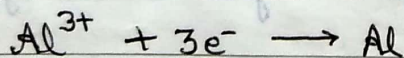
Charge on 1 gram ion (1 mole) = $3F$

$$= 3 \times 96500$$

$$= 289500 \text{ C}$$

5. Calculate the no. of Coulombs required to deposit.

40.5g Aluminium, when the electrode reaction is:-



(Atomic mass = 27g)

27g of Aluminium required = $3F$

1g of Aluminium requires electricity = $\frac{3F}{27}$

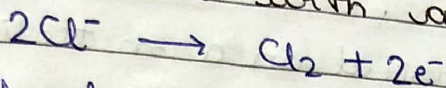
40.5g of Aluminium requires electricity = $\frac{40.5}{27} \times 3F$

$$= 4.5 F$$

$$= 4.5 \times 96500$$

$$= 434250 C$$

5. How many gm of Cl can be produced by the electrolysis of molten NaCl with a current of 1 A for 15 minutes?



2F of electricity produce = 71 gm of chlorine

$$Q = It = 1 \times 15 \times 60 = 900 C$$

1 C of electricity produces chlorine = $\frac{71 \times 2}{2 \times 96500}$ gm

$$900 C \text{ of electricity produces chlorine} = \frac{71 \times 900 \times 2}{2 \times 96500}$$

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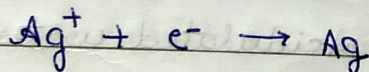
$$= 319.5$$

$$\frac{965 \times 10}{193000}$$

$$= 0.331 g$$

6. Two electrolytic cells containing silver nitrate solution and copper sulphate solution are connected in series. A steady current of 2.5 ampere was passed through them till 1.078 g of silver were deposited. How long did the current flow? What weight of copper will be deposited?

(At mass of Ag = 107.8, Cu = 63.5)



107.8 g of silver requires electricity = 1F

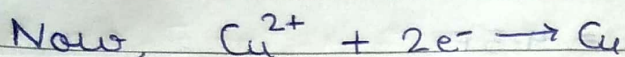
$$1.078 g \text{ of silver requires electricity} = \frac{96500 \times 1.078}{107800}$$

$$= 965 C$$

$$I = \frac{Q}{t} \text{ i.e. } t = \frac{Q}{I}$$

$$t = \frac{9650}{2.5} = 386 \text{ sec.}$$

$$= 6 \text{ min } 26 \text{ sec.}$$



2 F of charge produces copper = 63.5g

9650 C of charge will deposit copper = $\frac{63.5 \times 965}{96500 \times 2}$

$$= \frac{63.5}{200} = 0.3175 \text{ g}$$

7. Silver is electro deposited on a metallic vessel of surface area 900 cm^2 by passing a current of 0.5 A for 2 hours. Calculate the thickness of silver deposited.

(Density of silver = 10.5 g/cm^3 and Atomic mass = 108)

$$Q = It = 0.5 \times 2 \times 60 \times 60$$

$$= 3600 \text{ C} \quad [\text{Ag}^{+} + e^{-} \rightarrow \text{Ag}]$$

9650 C charged deposited = 108 g of silver

3600 C charged deposited = $\frac{108 \times 3600}{96500}$ g of silver

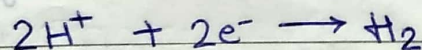
$$= 4.02 \text{ g}$$

$$\text{Volume} = \frac{\text{Mass} \times \text{density}}{(\text{density})^2}$$

$$= \frac{4.02 \times 10.5}{10.5 \times 10.5} = 0.38 \text{ cm}^3$$

$$\text{Thickness} = \frac{\text{Volume}}{\text{area}} = \frac{0.38}{900} = 4.22 \times 10^{-4} \text{ cm}$$

8. In the electrolysis of Acidulated water, it is desired to obtain hydrogen at the rate of 1 cc per sec at NTP condition. What would be the current passed?



22400 cm^3 of hydrogen requires = 2 F

1 cm^3 of hydrogen requires = $\frac{2 \times 96500}{22400} = 8.11$

$$I = Q \times t$$

$$= 8.11 \times 1$$

$$= 8.11 \text{ A}$$

Electrolytic conduction Conductors

Substance which conduct electricity are called conductors. Conductors are divided into two classes:-

Metals or Electronic conductors

Those which conduct electricity without undergoing any decomposition are called electronic conductors. The flow of electricity is due to movements of free electrons.

Factors affecting metallic conduction:-

1. Nature and structure of metal.
2. No. of valence electron per atom.
- * 3. Temperature:- On increasing the temperature, electrical conductivity of metal decrease. This is because metal ions starts vibrating which produce hindrance in the flow of electrons.

Electrolyte or electrolytic conductors

Those which conduct electricity in their molten state or aqueous solution are called electrolyte. The flow of electricity is due to movements of free ions.

There are two types of electrolytes:-

1. Weak electrolyte
2. Strong electrolyte.

1. Strong Electrolyte

Those substance which dissociate completely in aqueous solution or molten state and conduct electricity to a large extent are called strong electrolyte. Example HCl , HNO_3 , H_2SO_4 , NaOH , KOH , KCl , NaCl , CH_3COONa etc.

Weak Electrolyte

Those substance which dissociate partially in aqueous solution or molten state and hence conduct electricity to a small extent are called weak electrolyte.

Example:- CH_3COOH , H_2CO_3 , H_3PO_4 , NH_4OH , $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ etc

Factors affecting electrolytic conduction

1. Nature of electrolyte:- Strong electrolyte conduct electricity to a large extent and weak electrolyte conduct electricity to a small extent.

2. Conc. of electrolyte:- Higher the conc. of solution, less is the conduction (Molar conductivity).

3. Size of ions and their solvation:- Greater the size of ions or greater the solvation of ion, less is the conduction.

4. Nature of solvent and its viscosity:- Greater the polarity of the solvent, greater is the ionization and hence greater is the conductance. Greater is the viscosity of solvent, less is the conductance.

5. Temperature:- On increasing temperature, the dissociation increase and hence conductance increase.

Conductance (G)

The reciprocal of electrical resistance is called conductance. Unit of $G \Rightarrow \text{ohm}^{-1}$ or Sieman (S)

Specific conductance or Conductivity (κ , Kappa)

The reciprocal of electrical resistivity is called conductivity. Unit of $\kappa = \text{ohm}^{-1} \text{m}^{-1}$ or S m^{-1}

* Always used unit of conductivity = S cm^{-1}

Relation between conductivity (κ) and Conductance (G)

We know that,

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

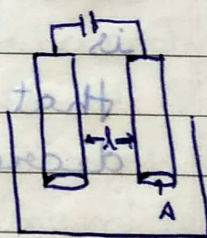
$$\frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$$

$$\boxed{\kappa = G \times G^*}$$

where $\frac{l}{A} = G^*$ (called cell constant)

Cell Constant (G^*)

For a particular cell, the ratio of the distance (l) between the electrode and area of cross section (A) of each electrode is constant. This constant



is called Cell constant. Therefore,

$$\boxed{G^* = \frac{l}{A}}$$

Unit of cell constant = m^{-1}

* Always use unit of $G^* = \text{cm}^{-1}$

Molar Conductivity (Λ_m)

Molar conductivity of a solution at a dilution V is the conductance of all the ions produce

Conductivity = no. of ions per unit volume

$$\Lambda_m = \frac{K \times 1000}{M \text{ or Conc.}}$$

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from 1 mole of the electrolyte dissolved in V ml of the solution when the electrodes are 1 cm apart and the area of electrode is so large so that all the solution is contained between them.

Formula for molar conductivity :-

$$\Lambda_m = \frac{K \times 1000}{M} \left[\frac{L \times l/A \times 1000 \times V}{n} \right]$$

Where M = Molarity of solution.

$$\text{Unit of } \Lambda_m = \frac{\text{Scm}^2}{\text{mol}} = \text{Scm}^2 \text{mol}^{-1}$$

* In case of metre, formula of Λ_m changes,

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

$$\text{Unit of } \Lambda_m = \text{Sm}^2 \text{mol}^{-1}$$

Effect of Concentration on Conductivity

Conductivity decrease with decrease in concentration both for weak and strong electrolyte. This is because no. of ions per unit volume that carry a current in a solution decrease on dilution.

Effect of concentration on Molar Conductivity

Molar conductivity increase with decrease in conc. This is because the total volume of the solution containing 1 mole of electrolyte increase.

The molar conductivity of strong electrolyte is found to depend on Conc. According to the equation (Debye-Huckel-Onsager equation)

$$\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$$

Here Λ_m = Molar conductivity

C = Molar concentration of electrolyte

A is a constant depending upon the type of the electrolyte, nature of the solvent and the temperatures.

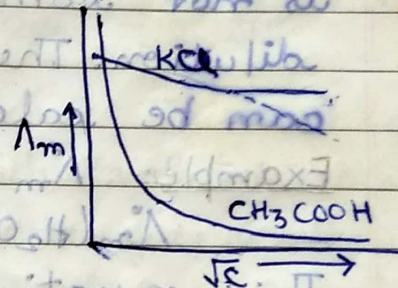
Λ_m° = Limiting Molar Conductivity, OR
Molar conductivity at infinite dilution

Λ_m° \Rightarrow At approx. 0 concentration, molar conductivity is known as limiting molar conductivity.

If molar conductivity is plotted against \sqrt{C} , the following graph is obtained.

Slope = $-A$

Intercept = Λ_m°



The curve obtained for a strong electrolyte shows that there is only a small increase in conductance with dilution. This is because the number of ions remains same but inter-ionic attraction decreases on dilution.

The curve obtained for a weak electrolyte shows that there is a very large increase in conductance with dilution. This is because degree of dissociation decreases.

Kohlrausch's Law

The law states that limiting molar conductivity of an electrolyte can be represented as the sum of individual contribution of anions and cations of the electrolyte.

$$\text{Example:- } \Lambda_m^\circ(\text{NaCl}) = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ$$

$$\Lambda_m^\circ(\text{MgCl}_2) = \lambda_{\text{Mg}^{2+}}^\circ + 2\lambda_{\text{Cl}^-}^\circ$$

Applications of Kohlrausch's Law

1. Calculation of limiting molar conductivity (Λ_m°) for weak electrolyte

Λ_m° of weak electrolyte can not be determined experimentally. This is because weak electrolyte is not completely dissociate at very high dilution. Therefore, Λ_m° of weak electrolyte can be calculated using Kohlrausch's law.

Example:- Λ_m° of water calculated as follows

$$\Lambda_m^\circ(\text{H}_2\text{O}) = \lambda_{\text{H}^+}^\circ + \lambda_{\text{OH}^-}^\circ$$

This equation can be obtain from Kohlrausch law as follows:-

$$\Lambda_m^\circ(\text{HCl}) = \lambda_{\text{H}^+}^\circ + \lambda_{\text{Cl}^-}^\circ$$

$$\Lambda_m^\circ(\text{NaOH}) = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{OH}^-}^\circ$$

$$\Lambda_m^\circ(\text{NaCl}) = \lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ$$

$$\begin{aligned} \therefore \Lambda_m^\circ(\text{HCl}) + \Lambda_m^\circ(\text{NaOH}) - \Lambda_m^\circ(\text{NaCl}) &= \lambda_{\text{H}^+}^\circ + \cancel{\lambda_{\text{Cl}^-}^\circ} + \lambda_{\text{Na}^+}^\circ + \lambda_{\text{OH}^-}^\circ \\ &\quad - \lambda_{\text{Na}^+}^\circ - \cancel{\lambda_{\text{Cl}^-}^\circ} \\ &= \lambda_{\text{H}^+}^\circ + \lambda_{\text{OH}^-}^\circ \\ &= \Lambda_m^\circ(\text{H}_2\text{O}) \end{aligned}$$

2. Calculation of degree of dissociation

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m}{\Lambda_m^\circ}$$

$$\text{Dissociation constant (K)} = \frac{C\alpha^2}{1-\alpha}$$

where C = molar concentration

3. Calculation of solubility of sparingly soluble salt

$$\Lambda_m^{\circ} = \frac{K \times 1000}{S}$$

where S = Solubility of sparingly soluble salt.

Problems

1. The conductivity of 0.2 M KCl solution at 298 K is $0.02485 \text{ S cm}^{-1}$. Calculate its molar conductivity.

$$\Lambda_m = \frac{K \times 1000}{M} = \frac{0.02485 \times 1000}{0.2} = \frac{24.85}{0.2} = 124.25 \text{ S cm}^2 \text{ mol}^{-1}$$

2. Resistance of a conductivity cell filled with 0.1 M per litre KCl solution is 100Ω . If the resistance of same cell when filled with 0.2 M per litre KCl solution is 525Ω . Calculate the conductivity and molar conductivity of 0.2 M KCl solution. The conductivity of 0.1 M per litre KCl solution is 1.29 S cm^{-1} .

For 0.1 mol/L KCl solution,

$$R = 100 \Omega \quad \text{and} \quad K = 1.29 \text{ S cm}^{-1}$$

$$K = \ell_1 \times \ell_1^*$$

$$\ell_1^* = \frac{K}{\ell_1} = K \times R = 1.29 \times 100 = 129 \text{ cm}^{-1}$$

For 0.02 mol/L KCl solution

$$R = 520 \Omega \quad \text{and} \quad K = ? \quad \text{and} \quad \Lambda_m = ?$$

$$K = \ell_1 \times \ell_1^* = \frac{1}{520} \times 129 = 0.248 \text{ S cm}^{-1}$$

$$\Lambda_m = \frac{K}{1000 \times M} = \frac{0.248}{1000 \times 0.2} = 1.24 \times 10^{-3} \text{ S cm}^2 \text{ mol}^{-1}$$

3. Calculate the Λ_m° of CaCl_2 . Given $\lambda_{\text{Ca}^{2+}}^\circ = 119 \text{ Scm}^2 \text{ mol}^{-1}$
 $\lambda_{\text{Cl}^-}^\circ = 76.3 \text{ Scm}^2 \text{ mol}^{-1}$.

$$\lambda_{\text{Ca}^{2+}}^\circ = 119 \text{ Scm}^2 \text{ mol}^{-1}$$

$$2\lambda_{\text{Cl}^-}^\circ = 76.3 \times 2 = 152.6 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ(\text{CaCl}_2) = 119 + 152.6 = 271.6 \text{ Scm}^2 \text{ mol}^{-1}$$

4. Calculate the Λ_m° of CH_3COOH given Λ_m° .

Given $\Lambda_m^\circ(\text{HCl}) = 425 \text{ Scm}^2 \text{ mol}^{-1}$

$$\Lambda_m^\circ(\text{CH}_3\text{COONa}) = 96 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ(\text{NaCl}) = 188 \text{ Scm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = \Lambda_m^\circ(\text{CH}_3\text{COONa}) + \Lambda_m^\circ(\text{HCl}) - \Lambda_m^\circ(\text{NaCl})$$

$$= 96 + 425 - 188$$

$$= 333 \text{ Scm}^2 \text{ mol}^{-1}$$

5. Calculate Λ_m° of Ba(OH)_2 .

Given $\Lambda_m^\circ(\text{NaOH}) = 2.481 \times 10^{-2} \text{ Scm}^2 \text{ mol}^{-1}$

$$\Lambda_m^\circ(\text{BaCl}_2) = 2.800 \times 10^{-2} \text{ Scm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ(\text{NaCl}) = 1.265 \times 10^{-2} \text{ Scm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ(\text{Ba(OH)}_2) = \Lambda_m^\circ(\text{BaCl}_2) + 2\Lambda_m^\circ(\text{NaOH}) - 2\Lambda_m^\circ(\text{NaCl})$$

$$= 2.800 \times 10^{-2} + 2 \times 2.481 \times 10^{-2} - 2 \times 1.265 \times 10^{-2}$$

$$= 2.800 \times 10^{-2} + 4.962 \times 10^{-2} - 2.530 \times 10^{-2}$$

$$= 5.232 \times 10^{-2}$$

6. The conductivity of 0.001024 M acetic acid is $4.95 \times 10^{-5} \text{ Scm}^{-1}$. Calculate its dissociation constant.

If Λ_m° of acetic acid is $390.5 \text{ Scm}^2 \text{ mol}^{-1}$.

$$\Lambda^\circ = \frac{K \times 1000}{M} = \frac{4.95 \times 10^{-5} \times 1000}{0.001024} = 48.155 \text{ cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m^\circ}{\Lambda_m^\circ} = \frac{48.15}{390.5} = 0.1233$$

$$K = \frac{C\alpha^2}{1-\alpha} = \frac{0.001024 \times 0.1233 \times 0.1233}{1-0.1233}$$

$$= 1.78 \times 10^{-5} \text{ mol L}^{-1}$$

Electrochemical cell or Galvanic Cell or Voltaic Cell

A device which convert the chemical energy into produce in a redox reaction into electrical energy is called electro-chemical cell.

- (i) Primary cell.
- (ii) Secondary cell.
- (iii) Fuel cell.

Primary cell

Primary cells are those in which redox reaction occurs only once and the cell become dead after some time and cannot be used again.

For example:- Dry cell, mercury cell.

Secondary Cell

Secondary cell are those which can be recharged by passing electric current through them and can be used over and again.

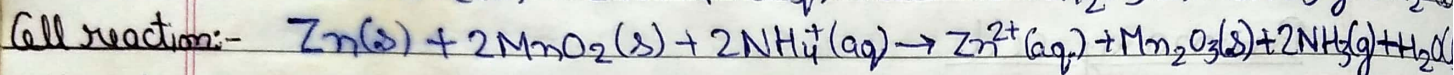
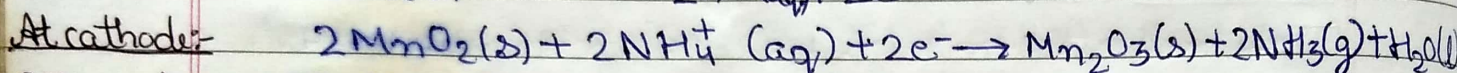
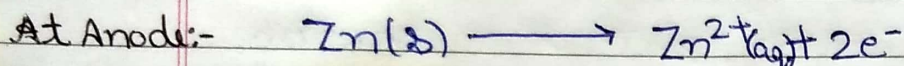
For example:- Lead storage Battery, Nickel-Cadmium cell.

Fuel cell

Fuel cells are those in which energy produce from the combustion of fuels such as hydrogen, Carbon monoxide, Methane etc. is directly converted into electrical energy. For example \rightarrow H_2O_2 fuel cell. It is used to produce electricity in appolo space program.

Dry cell or Leclanche cell

It is used in transistors and clocks. It consists of a cylindrical zinc container which acts as anode. A graphite rod placed in the center acts as the cathode. The space between anode and cathode is so packed that zinc container is in touch with the paste of NH_4Cl and ZnCl_2 and graphite rod is surrounded by powder MnO_2 and Carbon.



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

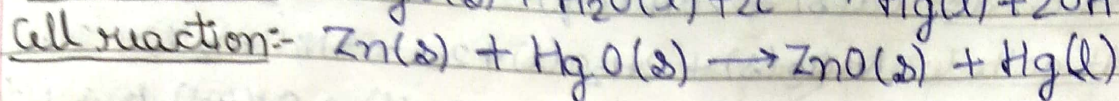
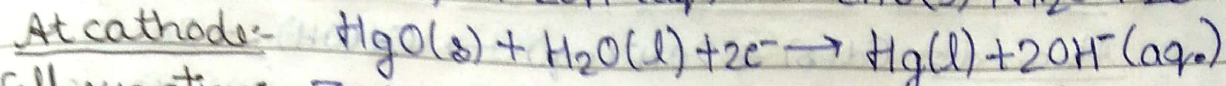
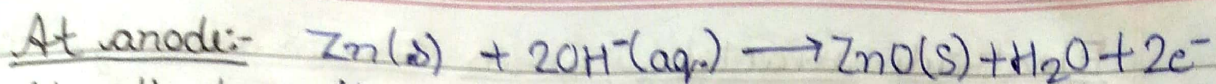
Ans. Zinc chloride combine with ammonium produce to form the complex salt, $(\text{Zn}(\text{NH}_3)_2\text{Cl}_2)$, otherwise the pressure developed due to ammonium would crack the seal of the cell.

Q. Why does a dry cell become dead after a long time even if it has not being used?

Ans. This is because acidic ammonium chloride corrodes the zinc container continuously even when the cell is not in used.

Mercury cell

It is used in low current device such as hearing aids and watch. It consists of zinc container as the anode, a graphite rod as the cathode and a paste of mercuric oxide mixed with KOH as the electrolyte.



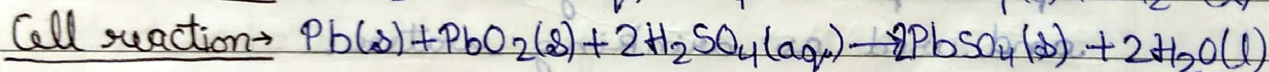
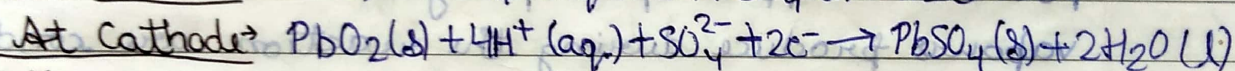
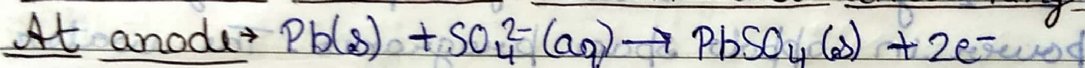
Q. Why a mercury cell gives a constant voltage throughout its life.

This is because the electrolyte KOH is not consumed in the reaction.

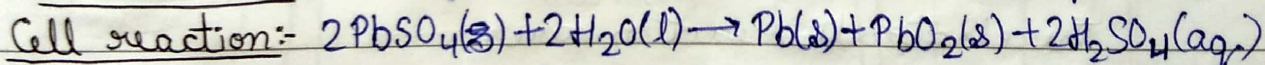
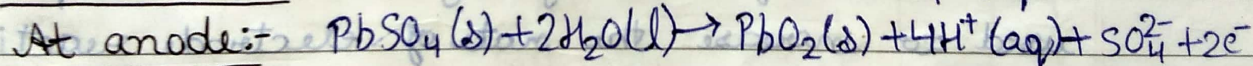
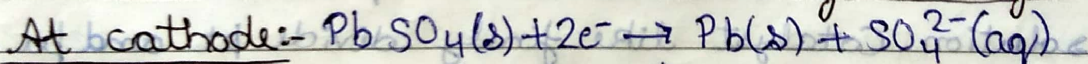
* Lead Storage Battery

It is used in automobiles and inverters. It consists of lead anode and a grid of lead packed with lead dioxide (PbO_2) as the cathode. A dilute solution of sulphuric acid (38% by mass) acts as electrolyte.

Electrode reaction when it is in working or discharged



Electrode reaction when it is being recharged

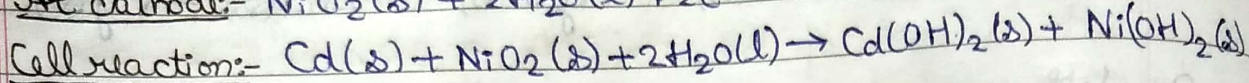
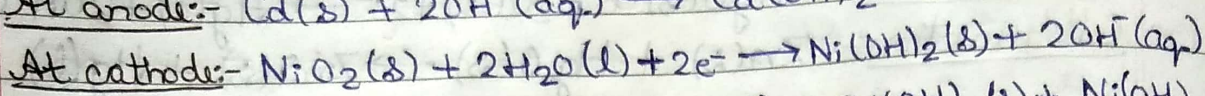
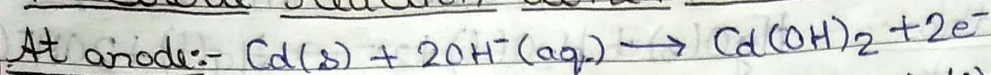


Nickel-Cadmium storage cell (Nickel cell)

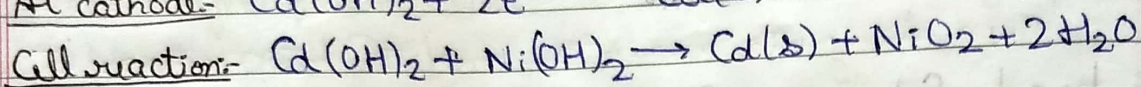
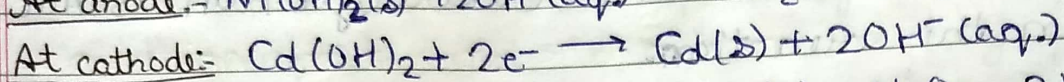
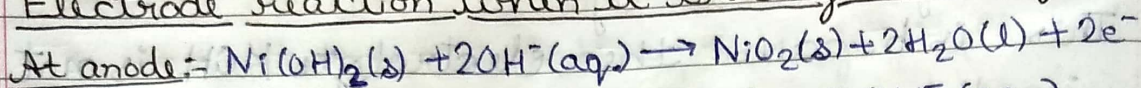
It is used in calculators. It has a longer life than lead storage cell. But it is more expensive.

It consists of a cadmium electrode acting as anode and a metal grid containing Nickel (IV) oxide (NiO_2) (cathode) immersed in KOH solution.

Electrode reaction when it is in working or discharged



Electrode reaction when it is being recharged



Lead storage battery create more pollution problem.
Nickel-cadmium storage cell create less pollution.

Fuel Cell

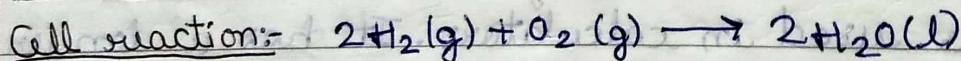
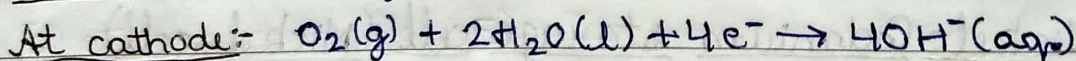
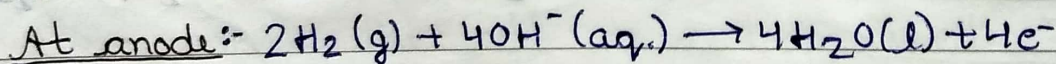
Hydrogen-Oxygen fuel cell

H_2 - O_2 fuel cell is used for providing electrical power in Apollo space programs. The water vapours produce during the reaction are condensed and used as drinking water.

In this cell, H_2 and O_2 are bubbled through porous

Carbon electrode into conc. aq. NaOH solution or KOH solution. Catalyst like finely divide Pt and Pd are used to increase the rate of electrode reaction.

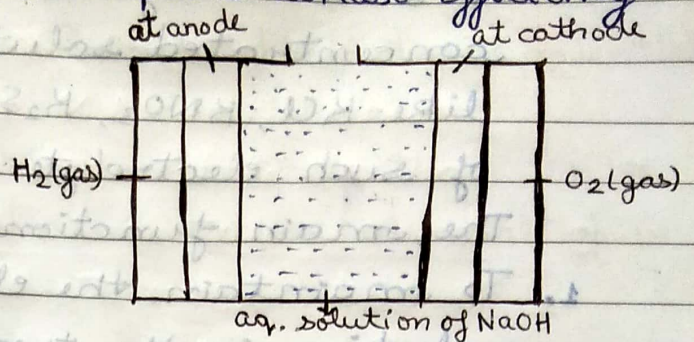
The electrode reaction are:-



Advantages of fuel cell

1. It is pollution free. It doesn't cause any pollution like thermal power plant.

2. Fuel cells produce electricity with an efficiency of 70% compared to thermal power plant whose efficiency is about 40%.



Difficulty and disadvantages of fuel cells

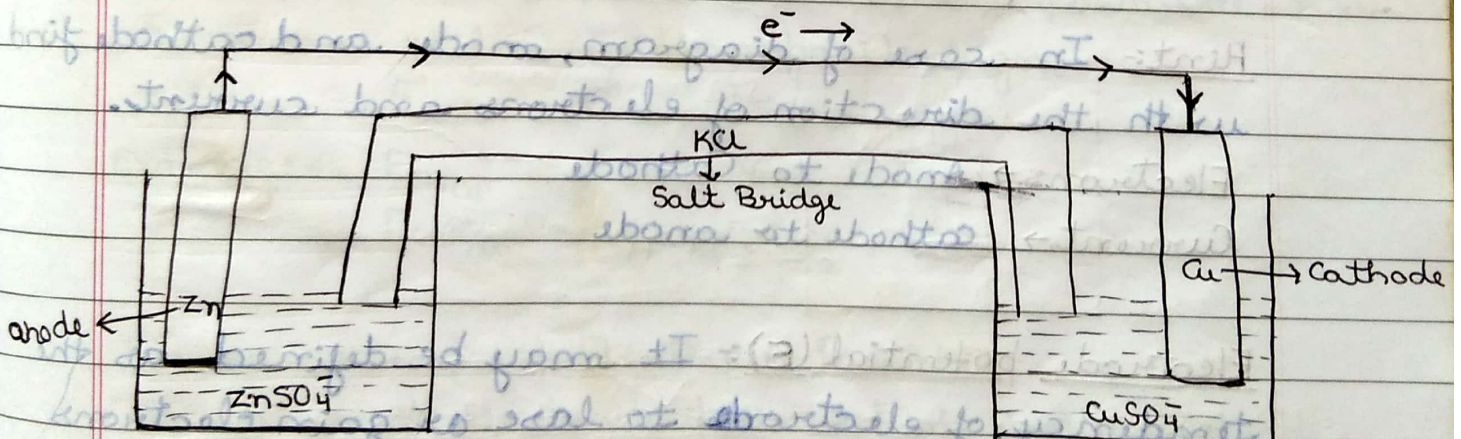
1. The corrosive nature of the electrolyte used.
2. High cost of a catalyst, needed for the electrode reactions.
3. Problem of handling gaseous fuels at low temperature or high pressure.

Electrochemical cell

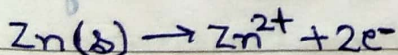
Electrochemical cell consist of two electrodes and also called two half cells.

Anode:- negatively charged (oxidation) ($M \rightarrow M^{n+} + ne^-$)

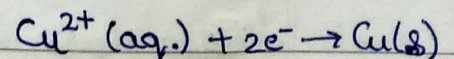
Cathode:- positively charged (reduction) ($M^{n+} + ne^- \rightarrow M$)



Oxidation



Reduction



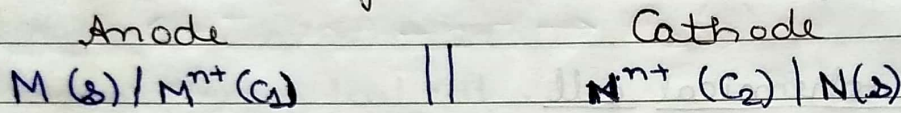
Salt Bridge and its functions

A salt bridge is a 'U' shape tube containing concentrated solution of inert electrolyte like KCl , KNO_3 , K_2SO_4 etc or solidified solution of such electrolyte is agar-agar and gelatin.

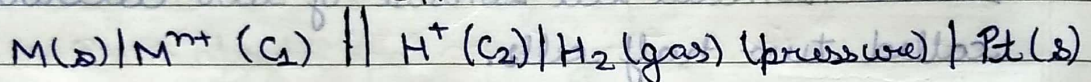
The main functions of salt bridge are:-

1. To maintain the electrical neutrality of the solution in the two half cells.
2. To complete the electrical circuit by allowing the ions to flow from one solution to other, without mixing of two solutions.

Representation of Electrochemical Cell



OR



Hints:- LOAN \rightarrow Left side, oxidation anode negatively charged

Hint:- In case of diagram, anode and cathode find with the direction of electrons and current.

Electrons \rightarrow Anode to Cathode

Current \rightarrow Cathode to anode

Electrode potential (E):- It may be defined as the tendency of electrode to lose or gain electrons when it is in contact with solution of its ions.

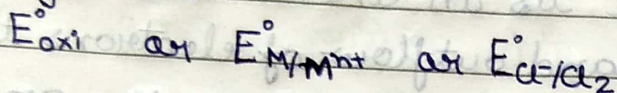
Standard Electrode potential (E°):- If the concentration of solution is '1 molar' and temperature is '298K', Then the electrode potential is called standard

electrode potential.

There are two types of standard electrode potentials:

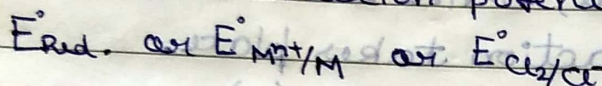
1. Oxidation potential

If oxidation reaction takes place at electrode. It is called oxidation potential. Oxidation potential represents as follows:-



2. Reduction potential

If reduction reaction takes place on electrode, then it is called reduction potential.



According to I.U.P.A.C,

Reduction potential is known as standard electrode potential.

* In case of same elements with same oxidation state, both oxidation and reduction potential have the same value with opposite sign.

$$E^{\circ}_{\text{red}} = -E^{\circ}_{\text{ox}}$$

Example:- $E^{\circ}_{\text{Cu}/\text{Cu}^{2+}} = -0.34\text{V}$

$$E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$$

Measurement of Electrode Potential

The value of electrode potential of single electrode, cannot be determined because oxidation half reaction or reduction half reaction cannot takes place alone.

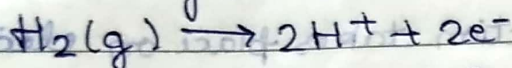
It can be measured by using some electrode as the reference electrode. The reference electrode used is the S.H.E (Standard hydrogen electrode) and N.H.E

(Normal Hydrogen electrode).

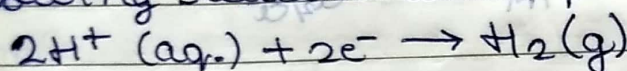
In S.H.E, hydrogen gas at 1 bar pressure is passed into 1M, HCl at 298K in which a foil of platinum coated with platinum black (allotropes) remains emerging.

Platinum act as an inert electrode through which inflow and outflow of electrons takes place.

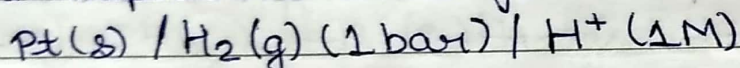
When in a cell, S.H.E act as the anode, the following reaction takes place.



When in a cell, S.H.E act as the cathode the following reaction takes place.

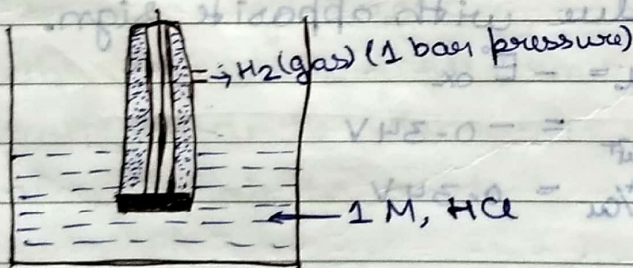


S.H.E represented as follows:-



The standard electrode potential of hydrogen electrode is taken '0' volt at 298 K.

$$E_{\text{H}^+/\text{H}_2}^\circ = 0.0 \text{ volt}$$



Electrochemical series or Activity series
or reactivity series

If elements are arranged in increasing order of value of reduction potential, a series is obtained is called electrochemical series.

| | | | | | | | | |
|-----------------------------------|-------------------|--|--------------|---|-------------|------------------|--------------|------------|
| $E_{\text{red}} = -3.05$ Li ले | K कर | Ba बारह | Sr सरदार | Ca का | Na नाम | Mg माँस | Al अलादिन | Mn महान |
| Zn जान | Cu कर | Fe फैकी | Cd सीदी | | | | | |
| Co कोई | Ni नीचे | Sn सुनो | Pb प्रभात | $\text{H} \rightarrow E_{\text{red}} = 0.0\text{V}$ है | | | | |
| 0.34V Cu कॉप | I आइश | Ag आगे | Hg होगे | Br ब्राह्मण | Pt पड़ित | O ओर | | |
| Cl कलावती | Au ओना लायी | $\text{F} \rightarrow E_{\text{red}} = 2.87\text{V}$ फ्री से। | | | | | | |

Conditions for spontaneous process

$$\Delta G = -ve$$

$$\Delta G = -nFE$$

Therefore, for spontaneous process E must be positive.

Cell potential are Electromotive force (EMF)

The difference between the electrode potential of the two half cells is known as cell potential.

It is called electromotive force of the cell, if no current draw from the cell.

\therefore Cell potential (E_{cell}) = Electromotive force
and Standard cell potential (E_{cell}°) = Standard EMF

Formula for E_{cell}

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad (\text{in case of } E_{\text{red}} \text{ Both})$$

$$\text{or } E_{\text{cell}} = E_{\text{anode}} - E_{\text{cathode}} \quad (\text{in case of } E_{\text{ox}} \text{ both})$$

Conditions for anode

Anode find in the following sequence

- In case of representation of cell, left is anode.
- In case of cell reaction, increase in oxidation state (anode).

3. In case of value of reduction potential, low value of reduction potential act as anode.
4. In case of electrochemical series, first coming element act as anode.

0 Applications of electrochemical series

1. To compare the reducing power of element.
Reducing power of element increase with decrease in the value of standard electrode potential.
Reducing power $\propto 1/E_{red}$.
2. To compare the oxidising power of element.
Oxidising power of element increase with increase in the value of standard electrode potential.
3. To compare the reactivity of metal.
Reactivity of metal increase with decrease in the value of reduction potential.
4. To compare the reactivity of non-metal.
Reactivity of non-metal increase with increase in the value of reduction potential.
5. To calculate the standard emf of the cell.
Standard EMF or $E_{cell} = E_{cathode} - E_{anode}$
(Use E_{red} for both electrode.)
6. To compare the feasibility or spontaneity of a reaction.
If emf comes out to be positive, the reaction is spontaneous, if emf comes out to be negative, the reverse reaction is spontaneous.

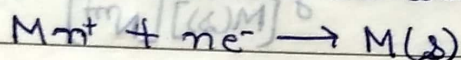
7. To compare the displacement of hydrogen gas from acid. Elements whose reduction potential is negative, displace hydrogen from acid.

Effect of temperature and concentration on electrode potential and cell potential (Nernst equation).

Nernst equation → If the conc. of electrolyte is different from 1 molar and temperature is different from 298 K, the electrode potential and cell potential has a different value. This value is obtained by using Nernst equation.

Nernst equation for single electrode.

Consider a electrode reaction



Applying Nernst equation:-

$$\text{Electrode potential } (E_{M^{n+}/M}) \Rightarrow E_{M^{n+}/M}^{\circ} - \frac{RT}{nF} \ln \frac{[M(s)]}{[M^{n+}]}$$

$$\text{or } E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} - \frac{2.303RT}{nF} \log \frac{[M(s)]}{[M^{n+}]}$$

$$\text{where } R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$F = 96500 \text{ C}$$

T = Temperature in Kelvin

n = no. of electrons gain

* Nernst equation at 298 K,

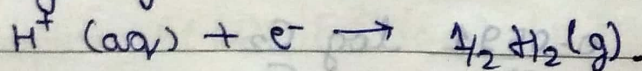
$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} - \frac{0.0591}{n} \log \frac{[M(s)]}{[M^{n+}]}$$

* (i) Always write electrode reaction.

(ii) For solid, $[solid] = 1$

For gas, use pressure in place of concentration.

(iii) For hydrogen electrode-



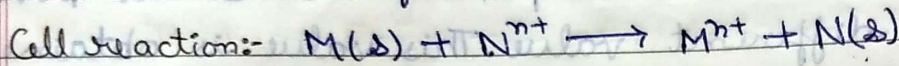
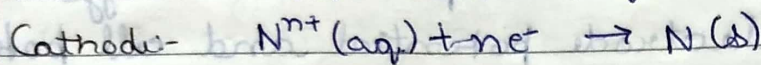
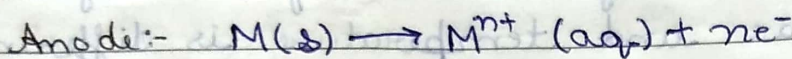
Nernst equation at 298 K, $E_{H^+/H_2} = -0.0591 \log \frac{[pH_2]^{1/2}}{[H^+]}$

At 1 bar or 1 atm

$$E_{H^+/H_2} = 0.0591 \text{ pH}$$

Nernst equation in case of cell

Consider a cell reaction:-



Applying nernst equation,

$$E_{\text{cell or emf}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \log \frac{[M^{n+}][N(s)]}{[M(s)][N^{n+}]}$$

$$\text{or } E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303RT}{nF} \log \frac{[M^{n+}][N(s)]}{[M(s)][N^{n+}]}$$

* Nernst equation at 298 K

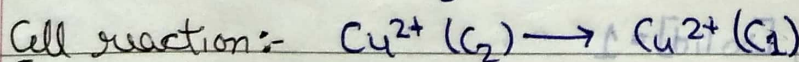
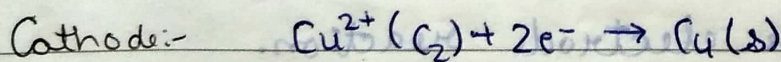
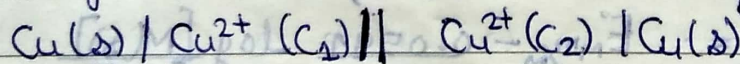
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[M^{n+}][N(s)]}{[M(s)][N^{n+}]}$$

* 1. Always write cell reaction.

2. For solid, $[solid] = 1$

For gas, use pressure in place of concentration.

3. Concentration cell → Conc. cell is the one in which both the electrodes are of the same type but the conc. of the ions in them are different. Example



$$E_{\text{cell}}^{\circ} = 0 \text{ (for conc. cell)}$$

Nernst equation - at 298 K

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Equilibrium ConstantAt equilibrium, $E_{\text{cell}} = 0$

$$E_{\text{cell}} = \frac{2.303 RT}{nF} \log K_c$$

$$\text{At } 298 \text{ K, } E_{\text{cell}} = \frac{0.0591}{n} \log K_c$$

Gibbs free energy (ΔG) and standard Gibbs free energy (ΔG°)

$$\Delta G = -nF E_{\text{cell}}$$

$$\Delta G^\circ = -nF E_{\text{cell}}^\circ$$

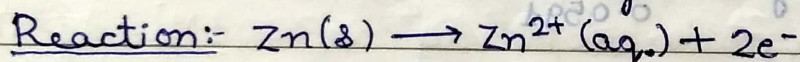
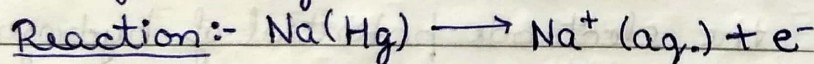
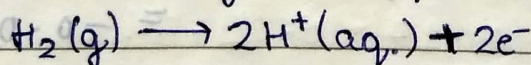
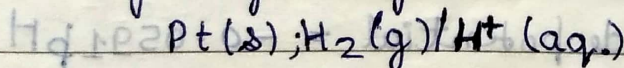
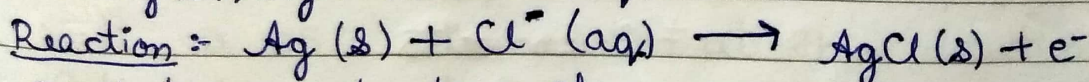
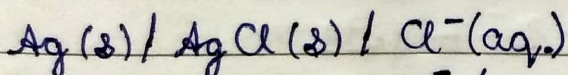
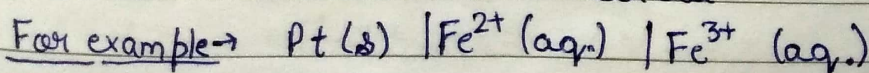
At equilibrium, $\Delta G = 0$

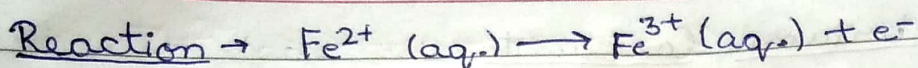
$$\Delta G^\circ = -2.303 RT \log K_c$$

$$* \text{ Efficiency of cell } (\eta) = \frac{\Delta G}{\Delta H} \times 100\%$$

Types of Electrode

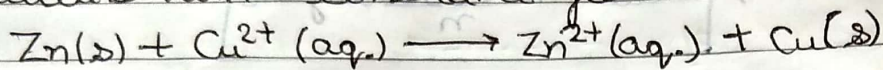
Electrodes are classified into 5 categories:-

1. Metal-metal ion electrode eg. $\text{Zn}(s) / \text{Zn}^{2+}(aq.)$ 2. Amalgam electrode used for active metals like Na, K, etc. eg. $\text{Na}(Hg) / \text{Na}^+(aq.)$ 3. Gas electrode:- Using platinum or gold as inert electrode for flow of electron. For ex \rightarrow 4. Metal-metal insoluble salt-salt anion electrode5. Oxidation-reduction electrode



Problem

1. Calculate the standard Gibbs free energy and equilibrium constant for the reaction.



Given $\Rightarrow E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76\text{V}$ and $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.34\text{V}$

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$= 0.34 - (-0.76)$$

$$= 1.10\text{V}$$

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} = -2 \times 96500 \times 1.10$$

$$= -212700\text{J mol}^{-1}$$

At 298 K,

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c$$

$$1.10 = \frac{0.0591}{2} \log K_c$$

$$\log K_c = \frac{2 \times 20}{0.0591} = 37.2074$$

$$K_c = 1.6 \times 10^{37}$$

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

For hydrogen electrode at 298 K and 1 atm

$$\text{Electrode potential} = -0.0591 \text{ pH}$$

$$= -0.0591 \times 10$$

$$= -0.591 \text{ volts}$$

2. At what pH of HCl solution will hydrogen gas electrode show electrode potential of -0.118 V .
 H_2 gas is bubbled at 298 K and 1 atm pressure.
 Electrode potential $= -0.0591\text{ pH}$

$$= \frac{+0.1180}{-0.0591} = \text{pH}$$

$$\text{pH} = 2$$

3. Calculate the emf of the following conc. cell at 298 K .
 $\text{Zn(s)} / \text{ZnSO}_4(0.05\text{ M}) // \text{ZnSO}_4(0.5\text{ M}) / \text{Zn(s)}$

In case of conc. cell, Nernst equation at 298 K ,

$$\text{emf} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

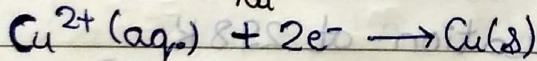
$$\text{emf} = \frac{0.0591}{2} \log \frac{0.50}{0.05}$$

$$\text{emf} = 0.02955 \log 10$$

$$\text{emf} = 0.02955 \text{ volt}$$

4. Calculate the electrode potential of a copper wire dipped in 0.1 M CuSO_4 solution at 25°C .

(given $\Rightarrow E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.34\text{ Volt}$).



$$E_{\text{pot.}} = E_{\text{Cu}^{2+}/\text{Cu}}^\circ - \frac{0.0591}{n} \log \frac{1}{[\text{Cu}^{2+}]}$$

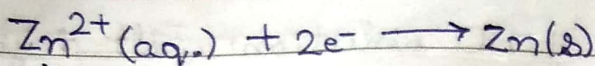
$$\text{Electrode potential} = 0.34 - \frac{0.0591}{2} \log \frac{1}{0.1}$$

$$= 0.34 - 0.02955$$

$$= 0.31045\text{ V.}$$

5. A zinc rod is dipped in 0.1 M ZnSO_4 solution. The salt is 95% dissociated at this dilution at 298 K . Calculate the electrode potential.

$$\text{given } E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76\text{ V}$$



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

Nernst equation at 298 K,

$$\text{Electrode potential} = E_{\text{Zn}^{2+}/\text{Zn}} - \frac{0.0591}{n} \log \frac{1}{[\text{Zn}^{2+}]}$$

$$= -0.76 - \frac{0.0591}{2} \log \left[\frac{1000}{0.95} \right]$$

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

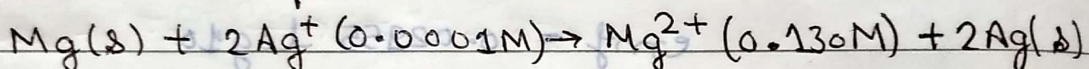
$$= -0.76 - 0.02955 (3 - 1.9777)$$

$$= -0.76 - 0.02955 \times 1.0233$$

$$= -0.76 - 0.0302$$

$$= -0.7902 \text{ V}$$

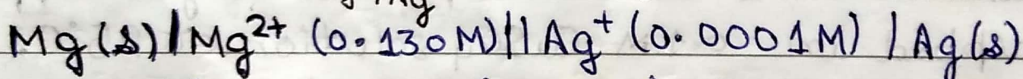
6. Represents the cell in which the following reaction takes place:



Calculate its cell potential.

$$\text{Given} \Rightarrow E_{\text{Mg}^{2+}/\text{Mg}} = -2.37 \text{ V}$$

$$E_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$$



$$E_{\text{cell}} = 0.80 - (-2.37) = 3.17 \text{ V}$$

Nernst equation at 298 K

$$E_{\text{cell}} = E_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 3.17 - \frac{0.0591}{2} \log \frac{0.13}{(0.0001)^2}$$

$$= 3.17 - 0.2955 \log 13 \times 10^4$$

$$= 3.17 - 0.2955 \times 7.9139$$

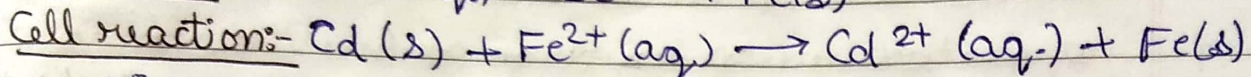
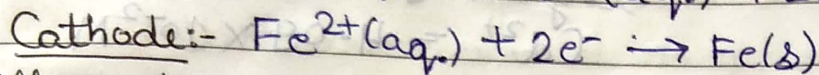
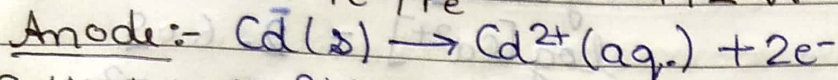
$$= 3.17 - 0.24$$

$$= 2.96 \text{ volts}$$

7. Calculate the emf of the following cell at 298 K
 $\text{Cd}(s) / \text{Cd}^{2+}(0.001\text{M}) // \text{Fe}^{2+}(0.6\text{M}) / \text{Fe}(s)$

Given $E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} = -0.403\text{V}$

$E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.441\text{V}$



$E_{\text{cell}}^{\circ} = -0.441 - (-0.403) = -0.38\text{V}$

Nernst equation at 298 K

$$\text{EMF} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Cd}^{2+}]}{[\text{Fe}^{2+}]}$$

$$= -0.38 + 0.0821 - \frac{0.0591}{2} \log \frac{0.001}{0.6}$$

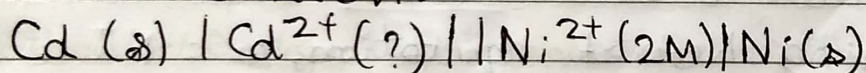
$$= -0.38 - 0.02955 \log 1 - \log 600$$

$$= -0.38 - 0.02955 [0 - 2.7781]$$

$$= -0.38 + 0.0821$$

$$= 0.441$$

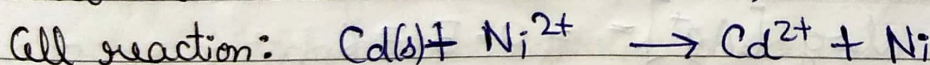
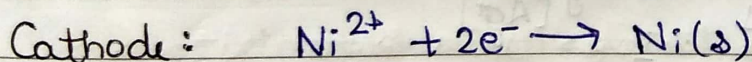
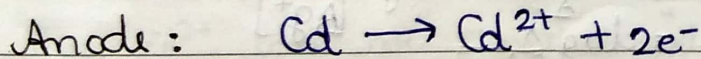
8. The emf of the following cell is found to be 0.2 V at 298 K.



Given $E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} = -0.40\text{V}$

$E_{\text{Ni}^{2+}/\text{Ni}}^{\circ} = -0.25\text{V}$

What is the molar conc. of the solution?



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log$$

$$E_{\text{cell}}^{\circ} = -0.25 - (-0.40)$$

$$E_{\text{cell}}^{\circ} = 0.15\text{Volts}$$

$$= 0.2 = 0.15 - \frac{0.0591}{2} \log \frac{[\text{Cd}^{2+}]}{2}$$

$$0.05 = -0.02955 \log [\text{Cd}^{2+}] - \log 2$$

$$\frac{-0.05}{0.02955} = \log [Cd^{2+}] - 0.3010$$

$$-1.692 = \log [Cd^{2+}] - 0.3010$$

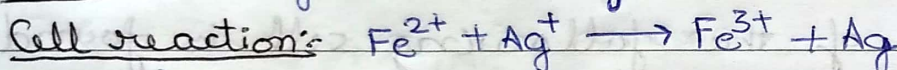
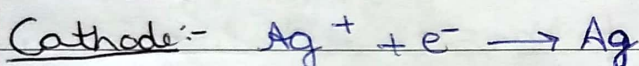
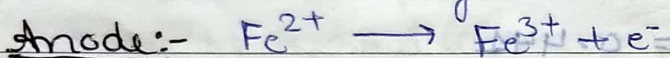
$$\log [Cd^{2+}] = -1.3910$$

$$\log [Cd^{2+}] = -2.609$$

$$[Cd^{2+}] = 4.09 \times 10^{-2} M$$

9. A galvanic cell is constructed with Ag/Ag^+ as one electrode and Fe^{2+}/Fe^{3+} as the second electrode. Calculate the conc. of Ag^+ at which the emf of the cell will be zero. At equimolar conc. of Fe^{2+} and Fe^{3+} ions. Given $E_{Ag^+/Ag} = 0.80V$ and $E_{Fe^{3+}/Fe^{2+}} = 0.77V$

Second electrode act as a anode because it has low value of reduction potential.



$$E_{cell} = 0.80 - 0.77 = 0.03V$$

Applying Nernst equation,

$$EMF = E_{cell} - \frac{0.0591}{n} \log \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^+]}$$

$$0 = 0.03 - \frac{0.0591}{1} \log \frac{1}{[Ag^+]}$$

$$\frac{0.03}{0.0591} = -\log \frac{1}{[Ag^+]}$$

$$\log [Ag^+] = -0.5076$$

$$\log [Ag^+] = -1.4924$$

$$[Ag^+] = 3.1 \times 10^{-1} M$$

$$[Ag^+] = 0.31 M$$

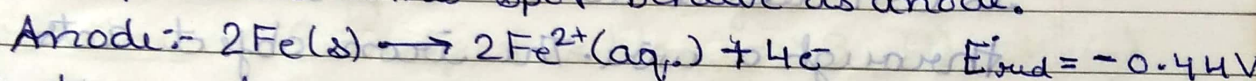
Corrosion

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 compound such as oxide, sulphides, carbonates, sulphates etc is called corrosion.

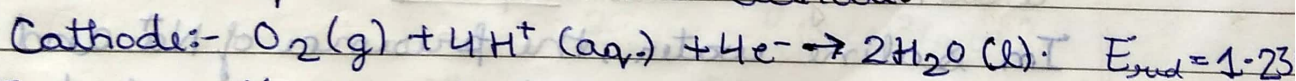
Example → Rusting of iron, green coating on copper, black coating on silver.

Mechanism of rusting of iron

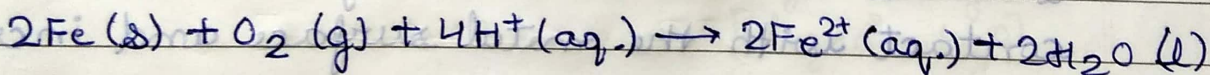
Rusting of iron is an example of electro-chemical phenomenon at a particular spot of iron object, oxidation reaction takes place and this spot behave as anode.



Electron release at anodic spot move through the metal and go to another spot of the metal and reduce oxygen in presence of H^+ ion which is produce from carbonic acid formed reaction between water and CO_2 . This spot behave as a cathode.

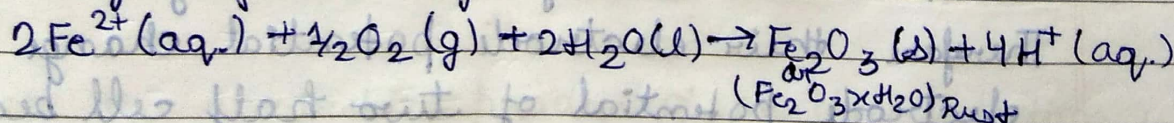


The overall reaction:-



$$E_{\text{cell}} = 1.67 \text{ volt}$$

The Fe^{2+} ion are further oxidised by atmospheric oxygen to ferric ion which come out as rust in the form of hydrated ferric oxide.



Prevention of Corrosion

Temporary method:- Oiling, painting and greasing.

Permanent method:- Use anti-rust solution like alkaline $KMnO_4$. It prevents availability of Hydrogen ions.

Sacrificial protection

It means covering the iron surface with a layer of metal which is more reactive than iron and prevents the iron from losing electrons.

Example:- Galvanisation (coating of zinc on iron object is known as galvanisation).

Cathodic protection

The iron object to be protected from corrosion is connected to a more reactive metal through a wire. The iron object acts as a cathode and protective metal acts as anode.

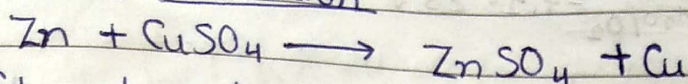
Problems

1. Rusting of iron is quicker in saline water than ordinary water. Explain.

In saline water, the presence of Na^+ and Cl^- ions increases the conductance of the solution in contact with the metal surface and increases the rate of rusting of iron.

2. Why a cell stops working after some time? With time conc. of the electrolytic solution changes. Therefore their electrode potentials change when the electrode potential of two half cells become equal the cell stops working.

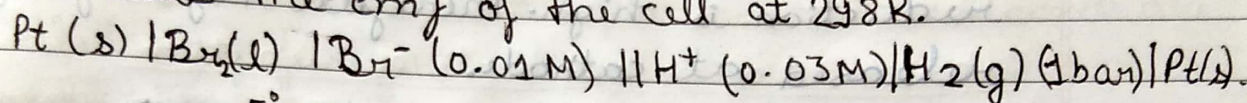
3. Can we store $CuSO_4$ solution in Zinc container (Given:- $E_{Zn^{2+}/Zn} = 0.76V$ and $E_{Cu^{2+}/Cu} = 0.34V$)

Possible reaction

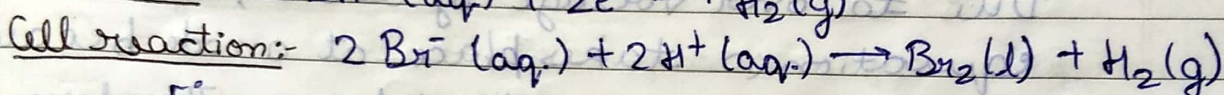
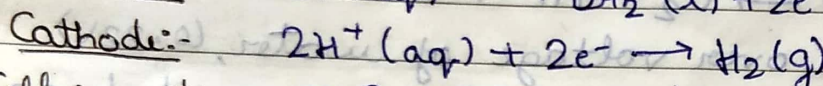
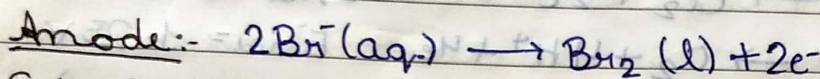
$$\text{Standard emf} = 0.34 - (-0.76) = 1.10 \text{ V}$$

Because standard emf comes out to be +ve, therefore reaction takes place and we cannot store CuSO_4 solution in Zinc container.

4. Calculate the emf of the cell at 298 K.



$$E^\circ_{\text{Br}_2/\text{Br}^-} = 1.08 \text{ V}$$



$$E_{\text{cell}}^\circ = 0 - 1.08 = -1.08 \text{ V}$$

Nernst equation at 298 K,

$$\text{emf} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{1}{[\text{Br}^-]^2 [\text{H}^+]^2}$$

$$= -1.08 - \frac{0.0591}{2} \log \frac{1}{(0.01)^2 (0.03)^2}$$

$$= -1.08 - 0.02955 [\log 10^8 - \log 9]$$

$$= -1.08 - 0.02955 [\log 10^8 - \log 9]$$

$$= -1.08 - 0.02955 (8 - 0.9542)$$

$$= -1.08 - 0.02955 \times 7.0458$$

$$= -1.08 - 0.208$$

$$= -1.288 \text{ V}$$

5. Write the electrolysis product of aq. NaCl solution with platinum electrode. given:-

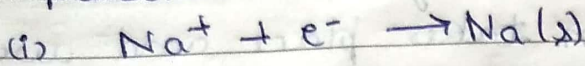
$$E_{\text{Na}^+/\text{Na}}^\circ = -2.71 \text{ V}$$

$$E_{\text{Cl}_2/\text{Cl}^-}^\circ = +1.36 \text{ V}$$

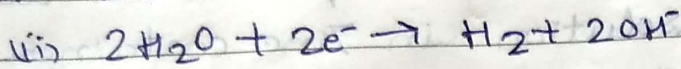
$$E_{\text{H}_2/\text{H}_2\text{O}/\text{OH}^-}^\circ = -0.81 \text{ V}$$

$$E^{\circ}_{H^+/H_2O/O_2} = +1.23V$$

Aq. NaCl contain Na^+ , Cl^- and H_2O . At cathode possible reactions are:-



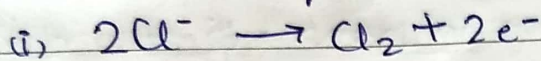
$$E^{\circ}_{red} = -2.71V$$



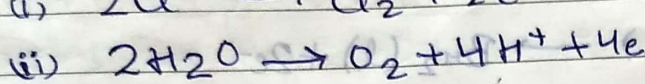
$$E^{\circ}_{red} = -0.81V$$

Equation 2nd takes place at cathode because its reduction is high. Therefore hydrogen gas is released at cathode.

At anode possible reactions are:-



$$E^{\circ}_{red} = +1.36V$$



$$E^{\circ}_{red} = 1.23V$$

Due to over voltage of water, (0.22V)

(p) equation ii takes place at anode because its reduction potential is lower. Therefore chlorine gas is released at anode.

SBG STUDY