



Q. State and explain the Faraday's laws of electrolysis.

SOPM. In 1839 Faraday formulated two laws which are known as Faraday's laws of Electrolysis. These are

First law: The amount of a given product liberated at an electrode during electrolysis is directly proportional to the quantity of the electricity which passes through the electrolyte solution.

Second law: When the same quantity of electricity passes through solutions of different electrolytes, the amount of substances liberated at the electrodes are directly proportional to their chemical equivalence.

Explanation of first law: If w is the mass of the substance (in grams) deposited on electrode by passing Q coulombs of electricity then

$$w \propto Q$$

$$\text{We know that, } Q = I \times t$$

$$\text{therefore } w \propto I \cdot t$$

$$\text{or, } w = ZI t$$

where Z is the constant known as the electrochemical equivalent of the substance (electrolyte).

If $I = 1 \text{ amp}$ and $t = 1 \text{ sec}$ then

$$w = Z$$

Thus the electrochemical equivalent is the amount of substance deposited by 1 ampere current passing for 1 second (i.e. 1 coulomb)

Explanation of Second law:

Let the same quantity of current passes in the same time three electrolyte substance A, B, C then w_A , w_B , w_C amount of element are deposited in the three electrodes respectively.

If z_1 , z_2 and z_3 are the electrochemical equivalence of elements respectively then according to this law,

$$w_A \propto z_1, w_B \propto z_2, w_C \propto z_3$$

$$\text{or, } w_A = k z_1, w_B = k z_2, w_C = k z_3$$

[k = proportionality constant]

$$\therefore \frac{w_A}{z_1} = \frac{w_B}{z_2} = \frac{w_C}{z_3}$$

$$\text{or, } \frac{w_A}{w_B} = \frac{z_1}{z_2} = \frac{z_2}{z_3}$$

Q. 02 Write down the importance of the two laws of Faraday's.

Soln. Importance of the first law of electrolysis:

- (i) With the help of the first law of electrolysis we are able to calculate:
the value of electrochemical equivalents of different substances; and
- (ii) the masses of different substances produced by passing a known quantity of electricity through their solutions

*** Importance of the Second law of Electrolysis ***

The Second law of electrolysis helps to calculate:

- (i) the equivalent weight of metals.
- (ii) the Unit of electric charge
- (iii) the Avogadro's Number.

Q. 03. Write down the Ohm's law and explain this.

Soln. At the definite temperature (T) the amount of electricity passes through a wire is directly proportional to the difference of volt (V).

In mathematically we can write,

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

Here, I = Current of electricity

V = difference of volt.

R = Resistance.

Explanation of Ohm's law: Let, AB is conductor. A and B are the two pole of the conductor and V_A and V_B are the volt of the end of the conductor where $V_A > V_B$ and difference of volt is $V_A - V_B$

$$\equiv V$$



If I is the flow of electricity then from the Ohm's law we can write,

$$I \propto (V_A - V_B) \propto V$$

$$\text{or, } I = Gv \quad \rightarrow ①$$

Here G is the proportional constant and is called the conductance of the conductor.

The opposite value of ' G ' is called the resistance so

$$G = \frac{1}{R}$$



Therefore, from the equation ① we can write

$$I = GV = \frac{1}{R} \cdot V = \frac{V}{R}$$

$$\text{or, } I = \frac{V}{R}$$

$$\text{or, } V = IR$$

This is the mathematical term of ohm's law.

Q. 04. Describe the terms : Conductance, Specific conductance, And equivalence conductance

Soln: Conductance: The electrolyte solutions conduct electrical current through them by movement of the ions to the electrodes. The power of the electrolytes to conduct electrical current is termed as conductivity or conductance.

Specific conductance: We know that the resistance of conductor is directly proportional to its length (l) and inversely proportional to the area (A) of its cross-section. for example,

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

$$\text{or, } R = \rho \frac{l}{A} \longrightarrow ①$$

where ρ is the constant of proportionality called the resistivity or Specific resistance. (ρ)

From ① we can write

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

if $l = 1 \text{ cm}$ and $A = 1 \text{ cm}^2$ then

$$\rho = R$$

Thus the specific resistance of a conductor is the resistance in ohms which one centimetre cube of it offers to the passage of electricity.

The reciprocal of Specific resistance is termed as the specific conductance or specific conductivity.

The specific conductance is denoted by the symbol κ (kappa).

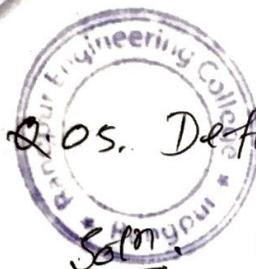
$$\begin{aligned} \text{so, } \kappa &= \frac{1}{\rho} \\ &= \frac{1}{R \cdot A/l} \\ &= \frac{l}{R \cdot A} \end{aligned}$$

Units of Specific Conductance is $\text{ohm}^{-1} \text{cm}^{-1}$

Equivalent conductance: It is defined as the conductance of an electrolyte obtained by dissolving one gram equivalent of it in 1 kg of water. It is denoted by Λ (Lambda)

$$\text{so } \Lambda = \kappa \times V$$

Unit of Λ , $\text{ohm}^{-1} \text{cm}^2 \text{eqvt}^{-1}$


Q.05. Define the molar conductance

Soln. The conductance of all ions produced by one mole (one gram molecular weight) of an electrolyte when dissolved in certain volume V cc

It is denoted by μ . Its value is obtained by multiplying the specific conductance, κ by the volume in cc containing 1 mole of the electrolyte.

$$\therefore \mu = \kappa \times V$$

If c is the concentration of a solution in gm equivalence per litre the volume of the solution containing 1 gm equivalence will be $\frac{1000}{c}$

$$\therefore \mu = \kappa \times \frac{1000}{c}$$

Unit : $\Omega^{-1} \text{cm}^2 \text{ mol}^{-1}$

** Q.06: Define ionic mobility ** **

Soln. In per unit potential gradient the velocity of an ion expressed ($\text{in } \text{cm s}^{-1}$) in unit time is called ionic mobility

$$\text{ionic mobility} = \frac{\text{Actual velocity}}{\text{Potential gradient}}. \quad \rightarrow ①$$

ionic mobility is proportional to the ionic conductance so if the mobility of cations and anions are v_+ and v_- respectively and their conductances are respectively $\gamma_{\text{o+}}$ and $\gamma_{\text{o-}}$ then,

$$\gamma_0^+ \propto V_+$$

$$\text{or, } \gamma_0^+ = f V_+ \longrightarrow \textcircled{\text{II}}$$

$$\text{and } \gamma_0^- \propto V_-$$

$$\text{or, } \gamma_0^- = f V_- \longrightarrow \textcircled{\text{III}}$$

If was measured theoretically that the constant f is equal to farad. From (II) and (III) we can write

$$\gamma_0 = \gamma_0^+ \gamma_0^- = f (V_+ + V_-) = f V_0$$

And generally the ionic movement, $\gamma_0 = f V_0$

$$\text{or, } V_0 = \frac{\gamma_0}{f}$$

So ionic mobility = $\frac{\text{ionic conductance}}{\text{farad}} \longrightarrow \textcircled{\text{IV}}$

from ① and (IV) We can get, actual velocity

$$= \frac{\text{ionic conductance}}{\text{farad}} \times \text{Potential gradient.}$$

Q.07. Write Short Notes on Solubility and Solubility Product.

Soln. Solubility: At constant temperature the amount of solute expressed in gm which dissolved in 100gm (coater) solvent, that is called solubility.

$$\text{Solubility} = \frac{\text{wt. Solute (gm)}}{\text{wt. Solvent (gm)}} \times 100$$



Solubility product : The Solubility product of soluble salt at constant temp. is the maximum possible product of the ions produced on ionization of that salt, each concentration being raised to the power equating to the Number of ions that produced from the concentration of that salt.

for example: for sparingly soluble salt: say AgCl , we can write equilibrium equation



According to the mass action law we can write,

$$K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

The amount of AgCl in contact with Saturated Solution does not change with time and the factor $[\text{AgCl}]$ remain the same. then $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$

K_{sp} = Solubility product.

Q.08. Define Mathematically the Solubility product of the weak electrolyte of the type $M_x A_y$

Soln. Let, $M_x A_y$ is a type of weak electrolyte. At constant temperature (T) we can write the equilibrium equation as. $M_x A_y (s) \rightleftharpoons x M_y^+ + y A_x^-$

According to the law of mass action

$$K_{SP} = \frac{[M^y+]^n [A^{x-}]^y}{[M_x A_y]}$$

$$\text{or, } K_{SP} \times [M_x A_y] = [M^y+]^n \cdot [A^{x-}]^y$$

But the concentration of solid is constant. So that we can write. $[M_x A_y] = 1$

$$\text{then } K_{SP} = [M^y+]^n [A^{x-}]^y$$

where K_{SP} is the solubility product.

Q. 09. Explain common - effect ***

Soln: The reduction of the degree of dissociation of a salt by the addition of common-ion is called the common ion effect.

When a soluble salt (say $A^+ C^-$) is added to a solution of another salt ($A^+ B^-$) containing common ion A^+ , the dissociation of AB is suppressed



By the addition of the salt (AC), the concentration of A^+ increases. Therefore, the equilibrium will shift to the left.

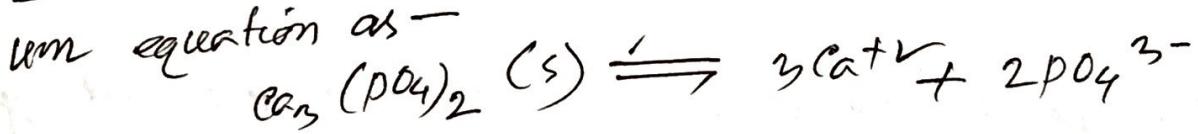
Again by decreasing the concentration of A^+ ions, the degree of dissociation of AB will be reduced. When solid NH_4Cl is added to the NH_4OH solution the equilibrium



shift to the left. Thereby the equilibrium concentration of OH^- decreases.

Q. 10. Deduce the solubility product equation for $C_{s,2} (PO_4)_2$

Soln. At constant temperature, we can write the equilibrium equation as —



According to the law of mass action,

$$K_{SP} = \frac{[Ca^{+2}]^3 [PO_4^{3-}]^2}{[C_{s,2} (PO_4)_2]}$$

$$\text{or, } K_{SP} \times [C_{s,2} (PO_4)_2] = [Ca^{+2}]^3 [PO_4^{3-}]$$

But the concentration of solid is constant. So that we can write $[C_{s,2} (PO_4)_2] = 1$

$$\text{Then } K_{SP} = [Ca^{+2}]^3 [PO_4^{3-}]$$

This is the required equation. Where K_{SP} = Solubility Product.

Q. 11. Define the degree of dissociation ***

Soln. The fraction of the amount electrolyte in solution present as free ions is called degree of dissociation. If the degree of dissociation is represented by α , we can write,

$$\alpha = \frac{\text{amount dissociated (mol/L)}}{\text{initial concentration (mol/L)}}$$

Q. 12. What do you mean by transport number or Hittorf Number. ***

Soln. The fraction of the total current carried by the cation or anion is termed as its transport number or Hittorf's number.

If v_+ represent the speed of migration of the cation and v_- that of anion, then

$$\text{the transport number of cation} = \frac{v_+}{v_+ + v_-}$$

$$\text{the transport number of anion} = \frac{v_-}{v_+ + v_-}$$

The transport number of the cation is represented by t_+ and that of the anion is t_- .

$$\text{Thus, } t_+ = \frac{v_+}{v_+ + v_-}, t_- = \frac{v_-}{v_+ + v_-}$$



then

$$t_+ + t_- = \frac{v_+}{v_+ + v_-} + \frac{v_-}{v_+ + v_-}$$

$$= \frac{v_+ + v_-}{v_+ + v_-} = 1$$

or, $t_+ + t_- = 1 \dots \rightarrow ①$

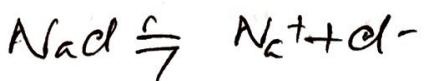
We can calculate that, if the transport number of any of cation or anion is known then the other can be calculated.

** Definition of electrolytes **

Substance which can be ionised either in molten state or in aqueous solution or in solution of any polar solvent are called electrolytes.

or,

Electrolytes are the substances which in either molten state or in aqueous solution, can conduct electrically or electricity or can be electrolysed.



Q.13. How does common ion-effect affect the solubility and solubility product.

Soln: If a solution has a common ion then its solubility decreases. As for example, at 303 K temperature 12 gm PbCl_2 is dissolved in 1 dm^3 of water. If the solvent is a solution of 1 Normal of KCl then in its 1 dm^3 0.5 gm

of PbCl_2 will be dissolved.

A binomial salt BA having less solubility s then

$$[\text{B}^+] = [\text{A}^-] = s$$

And the solubility product, $K_{\text{SP}} = [\text{B}^+][\text{A}^-]$
 $= s^2$

If a salt $\text{B}'\text{A}$ (whose conc is $c \text{ mol L}^{-1}$) is added to the solution of BA then at constant temperature the value of K_{SP} will remain fixed. ~~Because~~ Because when we add $\text{B}'\text{A}$ then the concentration of A^- increases and B^+ decreases, as a result the product $[\text{B}^+][\text{A}^-]$ remains fixed.

Let, after adding $\text{B}'\text{A}$ the solubility of BA is s' then

$$K_{\text{SP}} = s' (s' + c) = s^2$$

Here $s' = [\text{B}^+]$ and $(s' + c) = [\text{A}^-]$

So under the effect of common-ion the solubility decreases and the solubility product remains fixed.

Q. 14. Explain why $\text{Cu}^{+}\checkmark$ behaves as Lewis acid

(i) :NH_3 behave a Lewis base and
(ii) Al(OH)_3 behaves both as acid and base



Soln. (i) According to the Lewis concept we know that an acid is a compound which accept an electron pair.

$\text{Cu}^{+}\checkmark$ is in the ionised state of Cu. In this state it has two electron (one pair) less. When it goes to a base which a donor of a pair of electron then it take this electron pair. So $\text{Cu}^{+}\checkmark$ ion behave as a Lewis acid.

(ii) According to the Lewis concept a base is a compound having an electron pair which donates the pair of electron a compound that have a pair of electron less.

:NH_3 has an electron pair. If donates a pair of electron to a compound that have a pair of electron less. So it acts as a Lewis base.



Explain yourself

Same to the previous concept.

Q. 15. Define Strong and weak electrolytes

Soln. Strong electrolytes: A strong electrolyte is a substance that gives a solution in which almost all the molecules are ionised. The solution itself is called a strong electrolyte. Such solutions are called good conductors of electricity and have a high value of equivalent conductance even at low concentration. They are: HCl, H₂SO₄, HNO₃, NaOH, KOH, KCl, etc.

Weak electrolytes: A weak electrolyte is a substance that give a solution in which only a small portion of the solute molecules are ionised. such as a solution is called weak electrolyte solution low equivalence conductance

for example: NH₄OH, CH₃COOH,  



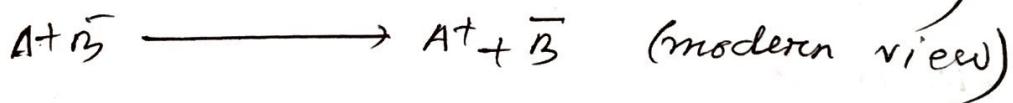
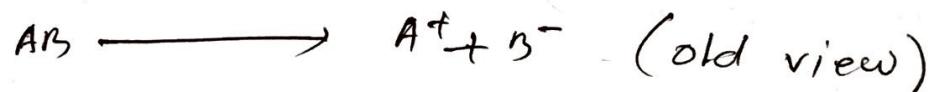
Q 16. Describe about Arrhenius theory of ionisation

Soln Arhenius theory of ionisation may be stated as

(i) When dissolved in water neutral electrolyte molecules are split up into two types of charged particles. These particles are called ions and the process is termed ionization. The positively charged particles are called cations and those having negative charge are called anions.

When the solid electrolyte placed in water, the neutral molecules dissociate to form separate anions and cations.

Thus



for that reason this theory may be referred to as the theory of electrolytic dissociation.

(ii) The ions present in the solution constantly reunite to form neutral molecules. There is a state of equilibrium between the undissociated molecules and the ions.



Applying the law of mass action

$$\frac{[A^+][B^-]}{[AB]} = K$$

where, K is the dissociation constant.

Cell

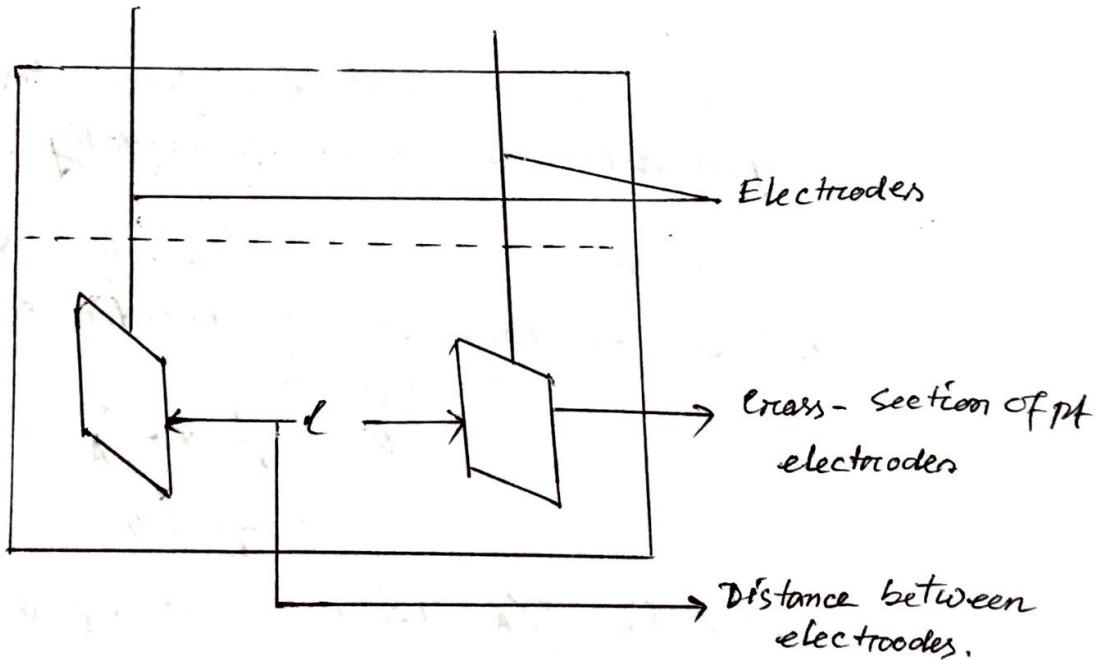
Determination of cell constant: The exact value of the cell constant (ℓ/A) can be determined by measuring the distance between the electrodes and their area of cross-section. Actual measurement of these dimensions is very difficult. Therefore an indirect method is employed to determine the value of the cell constant.

We know,

$$\text{Specific conductance, } K = \frac{1}{R} \times \frac{\ell}{A}$$

or, $K = \text{observed conductance} \times \text{cell constant}$

$$\therefore \text{Cell constant} = \frac{\text{Specific conductance}}{\text{observed conductance}}$$



To determine the cell constant, a standard solution of KCl whose specific conductance at a given temperature is known is used. Then a solution of KCl of the same strength is prepared and its conductance determined experimentally at the same temperature. Substituting the two values in the expression, the

cell constant can be calculated.



Q. 21 How would you determine the Specific conductance experimentally. 04.

Soln. We know that the conduction is the reciprocal of resistance. Therefore it can be determined by measuring the resistance of an electrolytic solution. This can be done in laboratory with the help of a wheatstone bridge

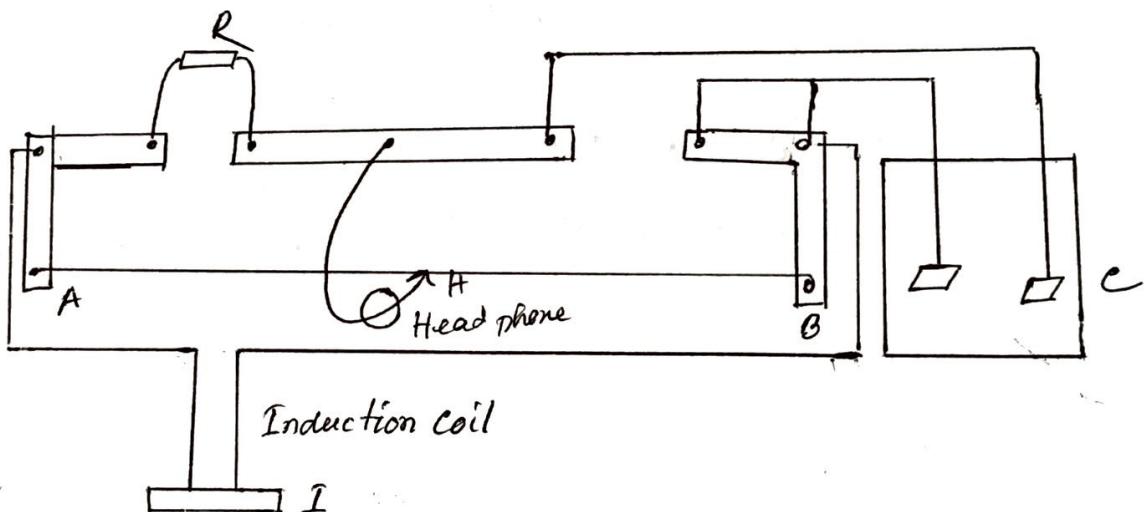


Fig: Apparatus for conduction measurement.

AB is a manganin wire tightly stretched over a meter rule graduated in millimeters. A sliding contact H moves along this wire. R is a resistance box, c is the conductance cell containing electrolytic solution. I is the induction coil from which current is led to the circuit. When current is flowing any resistance is unplugged in the resistance box. The sliding contact H move until the sound the head phone is minimum

from this conductance occur we have

$$\frac{\text{Resistance of } c}{\text{Resistance of } R} = \frac{\text{Resistance of } B_H}{\text{Resistance of } A_H} = \frac{\text{length of } B_H}{\text{length of } A_H}$$

or, Resistance of $c = \frac{\text{length } B_H}{\text{length } A_H} \times \text{Resistance of } R$

$$\text{S.P. Conductance} = \frac{1}{\text{Resistance of } c}$$

$$= \frac{1}{R_c} = \frac{1}{\text{Resistance of } R} \times \frac{\text{length } A_H}{\text{length } B_H}$$

When the cell is 1 cm^3 dimension then

$$\text{S.P. Conductance, } K = \frac{1}{R} \times \frac{L}{A}$$

Q 22. What do you mean by electrode and electrolysis? 09

SIN : Electrode : The process of electrolysis is carried in an apparatus called the electrolytic cell. The cell contains water solution of an electrolyte in which deep two metallic rods, the electrodes. The rods are connected to the two terminals of battery. The electrode connected to the positive terminals of battery attracts the negative ions (anions) and is called the anode. The other electrode connected to the negative end of the battery attracts the positive ions (cations) and is called the cathode.

Electrolysis : The phenomenon of decomposition of an electrolyte by passing electric current through its solution is termed electrolysis.

Example : Let us consider the electrolysis of HCl acid as an example. In solution HCl acid is ionised

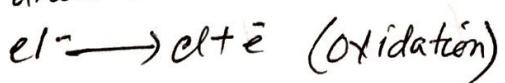


In the electrolytic cell Cl^- ions will move towards the anode H^+ ions will move towards the cathode, the following reaction take place

At cathode,



At anode,



After the chloride ion loses its electron to the anode, pairs of chloride atoms unite to form chlorine gas, Cl_2

The overall reaction is $2\text{HCl} \rightarrow \text{H}_2 + \text{Cl}_2$ (Decomposition)

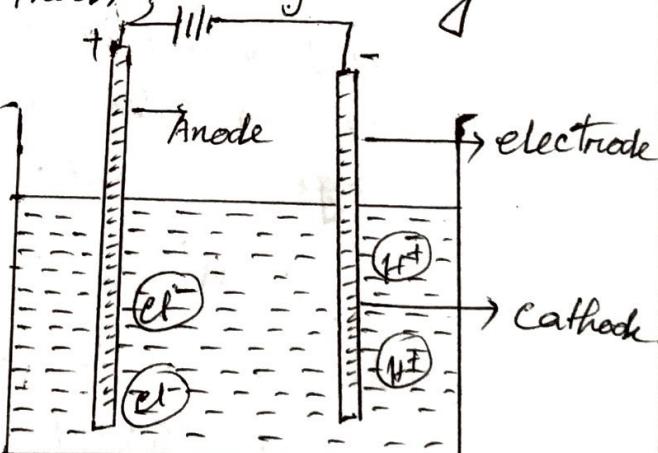


Fig: Electrolysis of HCl

Q.23. What is electrochemical cell, write down the reaction of a daniel cell. 07. 03

Soln. A device for producing electrical current from chemical reaction is called electrochemical cell.

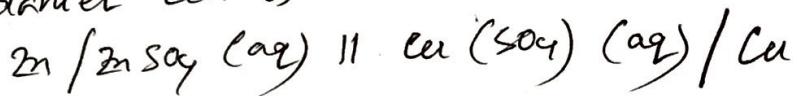
In daniel cell a zinc rod and a copper rod is dipped in solution of ZnSO_4 and CuSO_4 respectively. Now

Oxidation (half cell reaction) $\text{Zn} \longrightarrow \text{Zn}^{+2} + 2\bar{e}$

Reduction (half cell reaction) $\text{Cu}^{+2} + 2\bar{e} \longrightarrow \text{Cu}$

Total reaction, $\text{Zn} + \text{Cu}^{+2} \longrightarrow \text{Zn}^{+2} + \text{Cu}$

The daniel cell is



Q.24. How does electromotive force of a cell and enthalpy of a cell reaction related. 07

Soln: The maximum amount of work obtainable from a cell is the product of the charge flowing per mole and the maximum potential difference, E through which the charge is transferred. i.e

$$W_{\max} = - nFE \longrightarrow ①$$

where n , is the number of moles of the electron
F stands for farad and equal to 96500 coulomb
and E is the em.f of the cell.

According to the thermodynamic the maximum amount of work obtained from a system is equal to the free energy of the reaction.



$$\text{i.e } \Delta G_{\max} = -nFE \longrightarrow (ii)$$

From (i) and (ii) we can write,

$$\Delta G = -nFE \longrightarrow (iii)$$

According to the Gibbs-Helmholtz the decrease in the free energy at constant pressure is

$$-\Delta G = -\Delta H - T \left(\frac{\partial \Delta G}{\partial T} \right)_P \longrightarrow (iv)$$

From (iii) and (iv) we can write,

$$nFE = \Delta H + T \left(\frac{\partial (\Delta G)}{\partial T} \right)_P$$

$$\text{or, } nFE = \Delta H - T \left(\frac{\partial nFE}{\partial T} \right)_P$$

$$\text{or, } nFE = \Delta H - nF \cancel{T} \left(\frac{\partial E}{\partial T} \right)_P$$

$$\text{or, } \boxed{E = \frac{\Delta H}{nF} - T \left(\frac{\partial E}{\partial T} \right)_P}$$

Where ΔH is the heat content or enthalpy of the system.
This is the required relation between emf of the cell and enthalpy of the cell reaction.

Q. 25. Derive the Nernst equation for electrode potential
- 0.5

Soln. For an electrochemical cell, the potential free energy ΔG can be given by a relation

$$\Delta G = -nFE \longrightarrow (i)$$

Where, n is the number of electron, F stands for Farad and is equal to 96,500 coulomb, E is the emf of the cell.

for a chemical reaction, we know

$$\Delta G = \Delta G^\circ + RT \ln Q \longrightarrow \textcircled{I}$$

where α is the quotient of activities and

$$Q = \frac{[\text{Reduced state}]}{[\text{Oxidised state}]}$$

from the equation \textcircled{I} and \textcircled{II} we get,

$$-nFE = -nFE^\circ + RT \ln Q [E^\circ = \text{standard oxidation potential}]$$

$$\text{or, } E = E^\circ - \frac{RT}{nF} \ln Q \longrightarrow \text{(III)}$$

Substituting the value of Q in (III) we get

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Reduced state}]}{[\text{Oxidised state}]}$$

$$\text{or, } E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Oxidised state}]}{[\text{Reduced state}]} \longrightarrow \text{(IV)}$$

Equation (IV) is known as Nernst equation of electrode potential.

Q. 26. Write short notes on (i) Indicators (ii) pH indicator

Soln. Indicator: An indicator is an organic dye that signals the end-point by visual change in colour. Indicators are used to detect the equivalence point in solution of unknown strength with a standard solution. For example solution which strength is exactly known. In acidimetric titration hydrogen ion indicator is used. An indicator is

a substance which in certain limit changes its colour as the pH of the solution changes with titration for an acid with a base. This offers a simple method for determining the pH of a solution by noting the colour of a suitable indicator when placed in that solution.

pH-indicator: Most indicator do not change colour at a particular pH. They do so over a range of pH from two or three unit. This is called the pH range which is different for different indicators. The pH indicators are Methyl orange, Methyl red, Litmas paper, phenolphthalein etc.

The pH range of these indicators are given below:

Indicator	colour change Acid-Base	pH-range
Methyl-orange	Red - orange	3.1 - 4.9
Methyl-red	Red - orange	4.9 - 6.0
Litmas paper	Red - Blue	5.0 - 8.0
Bromoethy mol blue	Yellow - Blue	6.0 - 7.8
phenolphthalein	colourless - pink	8.3 - 10.0