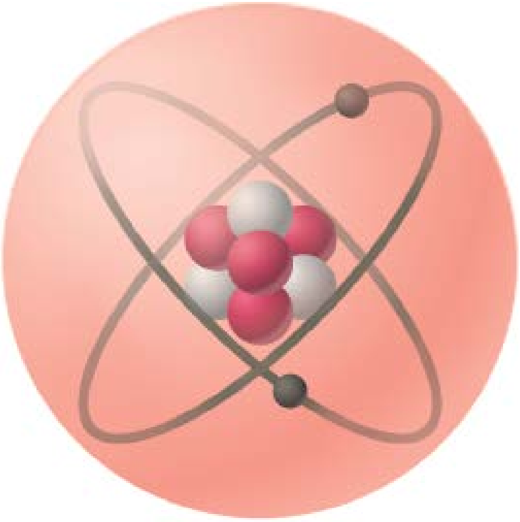
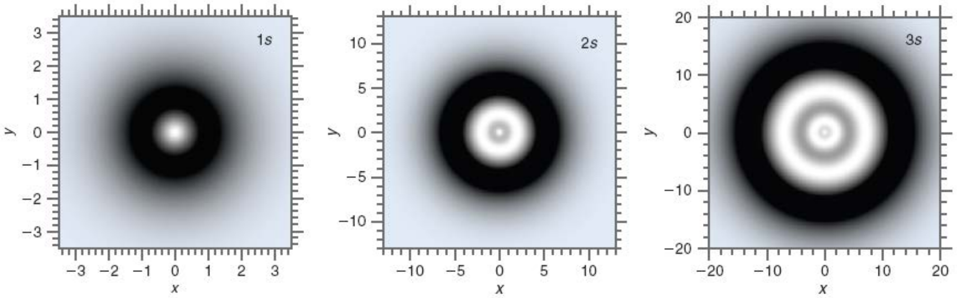
KARNATAKA STATE OPEN UNIVERSITY

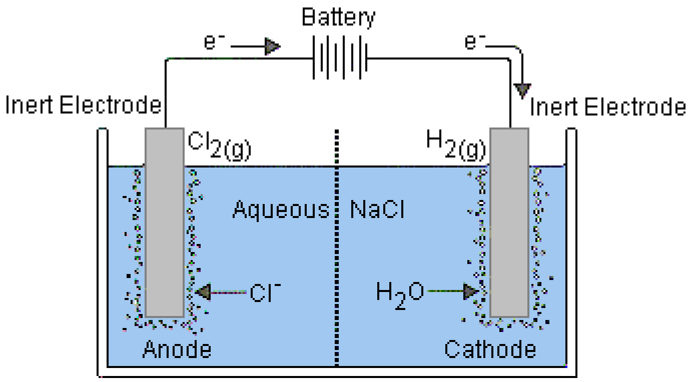
Mukthagangotri, Mysore – 570 006

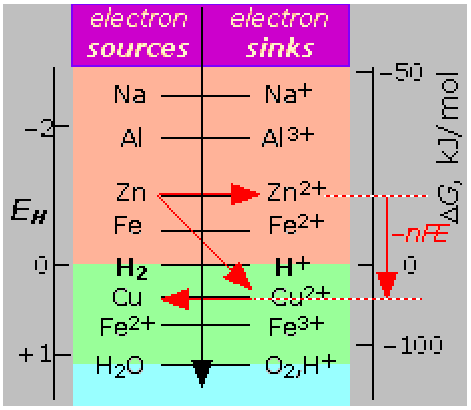
M.Sc. CHEMISTRY

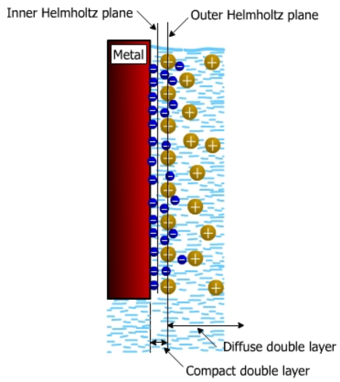
(SECOND SEMESTER)











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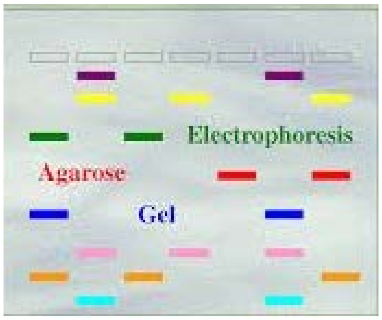

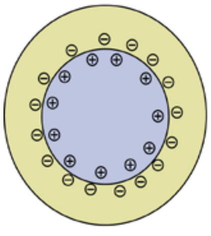

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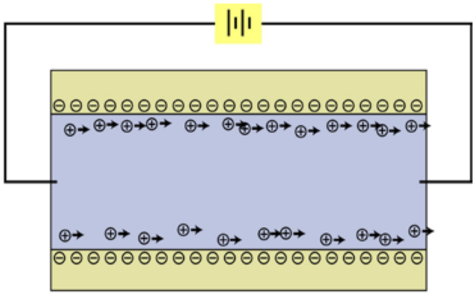

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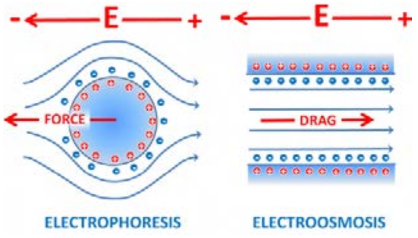

Course: MCH T 2.3 Block 1, 2,3 and 4

PHYSICAL CHEMISTRY- II

M.Sc. CHEMISTRY

SECOND SEMESTER

Course: MCHT 2.3

PHYSICAL CHEMISTRY-II

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TABLE OF CONTENTS

		Page No
Block 2.3.1	**THERMODYNAMICS-II**	
Unit-1	Thermodynamics of non ideal solutions – Activity, activity coefficients, effect of temperature and pressure, determination by vapour pressure and conductivity methods.	01-23
Unit-2	Thermodynamics of ideal solutions – deductions of laws of Raoult, ebullioscopy, cryoscopy and osmotic pressure, quantitative treatment of Lechatelier's principles	24-35
Unit-3	Phase rule – introduction, definition of phase, components and degree of freedom. Derivation of phase rule, one component system	36-46
Unit-4	Two components system, the silver –lead system, the zinc- cadmium system. Three components system- acetic acid, water and carbon tetrachloride.	47-55
Block 2.3.2	**ELECTROCHEMISTRY-I**	
Unit-5	Arrhenius theory of strong and weak electrolytes and its limitations, Debye-Huckel theory of strong electrolytes, Debye-Huckel-Ousager equation.	56-78
Unit-6	Debye-Huckel limiting equation for activity co-efficients, Debye-Huckel equation for appreciable concentrations.	79-88
Unit-7	Brief survey of Helmoltz-Perrin, Gouy-Chapman and Stern electrical double layer (no derivation). Liquid Junction potentials and its determination.	89-102
Unit-8	Transport numbers: Determination of transport number by Hittorf method and emf method. True and apparent transport numbers. Abnormal transport numbers, effect of temperature and concentration on transport number.	103-114
Block 2.3. 3	**QUANTUM CHEMISTRY-II**	

Unit-9	Applications of Schrodinger equation to a free particle and to a particle in a potential field (one dimensional and three dimensional boxes)	115-129
Unit-10	Degeneracy, wave equation for H-atoms. Separation and solution of R, θ and φ equations. Total wave functions for hydrogen like atoms. Application of Schrodinger equation to rigid rotator and harmonic oscillator.	130-162
Unit-11	Approximation methods- Necessity of approximation methods, perturbation methods- first order correction, application to He- atom (first order correction only) calculation of first ionization potential and binding energy.	163-173
Unit-12	Variation theorem- Statement and proof, application variation methods to particle in one dimensional box, linear oscillator, coupling angular momentum- term symbol	174-187

Block 2.3.4	**SURFACE AND COLLOIDAL CHEMISTRY**

Unit-13	Definition-absorption and adsorption, adsorption of gases by solid, factors influencing adsorption- temperature, pressure and pH. Langmuir adsorption for uni molecular and bi molecular reactions.	188-210
Unit-14	Derivation of BET equation, determination of surface area, Gibbs adsorption isotherm.	211-230
Unit-15	Classification of colloids, properties of colloidal solutions, coagulation of colloidal solutions.	231-250
Unit-16	Electrometric properties- electrophoresis, Zeta potential, Zone electrophoresis, gel-electrophoresis. Determination of isoelectric point, separation of proteins. Electrosmosis. Dorn effect.	251-271

COURSE INTRODUCTION

Physical chemistry can be regarded as the study of the physical principles underlying chemistry. We want to know how and why materials behave as they do. The ultimate goal of physical chemistry is to provide a (mathematical) model for all of chemistry

This course consists of four parts. In the first there parts you are going to study theory of solutios, electrocmeistry and quantum chemistry respectively. These are important theoretical tools for understanding the behavior of chemical system.

First part consists of study of dilute solution, A solution in thermodynamics refers to a system with more than one chemical component that is mixed homogeneously at the molecular level. Partial molar quantities tell us how a thermodynamic property of a solution changes when adding or removing an infinitesimal amount of a given chemical component. Often, though, we are also interested in the change of thermodynamic quantities when going from the unmixed state to the mixed state. For example, it may be important to know by how much the volume of a binary solution differs from the combined volumes of the two chemical species before they are mixed. This and other properties will be studied.

The second part contains electrochemistry. As the name suggests, electrochemistry is the study of changes that cause electrons to move. This movement of electrons is called electricity. In electrochemistry, electricity can be generated by movements of electrons from one element to another in a reaction known as a redox reaction or oxidation-reduction reaction. The properties of mater which undergo chnges when electricity is passed will be studied in details in this part

The third part focused on the quatum chemistry. Quantum chemistry is a branch of theoretical chemistry which applies quantum mechanics and quantum field theory to address problems in chemistry. One application of quantum chemistry is the electronic behavior of atoms and molecules relative to their chemical reactivity. Quantum chemistry lies on the border between chemistry and physics. Thus, significant contributions have been made by scientists from both fields. It has a strong and active overlap with the field of atomic physics and molecular physics, as well as physical chemistry. Solutions of the Schrödinger equation for the hydrogen atom gives the form of the wave function for atomic orbitals, and the relative energy of the various orbitals. The orbital approximation can be used to understand the other atoms e.g. helium.

In the fourth part you going to introduce new topic called surface chemistry. Study of chemical reactions in which the reactants are first adsorbed onto a surface medium that then acts as a catalyst for the reaction; after the reaction the products are desorbed and the surface is left unchanged. Since the entire reaction takes place on the surface, the amount of surface area of catalyst per unit weight determines the effectiveness of the surface in the reaction. Some silica surfaces have over 200 square meters of surface area per gram. An example of a surface reaction is the reaction of an unsaturated organic molecule with hydrogen on finely divided platinum or with bromine on finely divided silica. Enzyme reactions can, in principle, also be considered surface reactions, since the reaction takes place on the enzyme surface after the enzyme has bound the reactants; however, usually only heterogeneous (two-phase) reactions are considered true surface reactions, while enzyme reactions are homogeneous (one-phase) systems. Such reactions are studied in this part.

Unit-1

Structure

1.0 Objectives of the unit
1.1 Introduction
1.1 Free energy of mining in the case of ideal solution
1.2 Enthalpy of mixing
1.3 Entropy of mixing
1.4 Volume of mixing
1.5 Raoult’s Law
1.6 Activity of component obeying Raoult’s law
1.7 Characteristics of an ideal solution
1.8 Dilute Solution
1.9 Colligative properties
1.10 Lowering of vapor pressure of a solvent (Derivation of Raoult’s law)*Nature of the*
1.11 Raoult’s law and Molecular weight of the solute
1.12 Boiling point elevation of solutions (Ebullioscopy)
1.13 Determination of the molecular weight of solute
1.14 Freezing point depression (cryoscopy)
1.15 Determination of the molecular weight of solute
1.16 Abnormal Results
1.17 The Van’t Hoff factor (i)
1.18 Osmosis and Osmotic pressure
1.19 Relation between osmotic pressure and vapor pressure
1.20 Van’t Hoff equation and Osmotic Pressure
1.21 Lechatelier Principle
1.22 Quantitative treatment of Lechatelier principle
1.23 Effect of extent of reaction(C_1^1) with temperature and pressure
    (a) Variation of ς_e With temperature at constant pressure
    (b) Variation of ς_e with pressure at constant temperature
1.24 Summary of the unit
1.25 Key words
1.26 References for further study
1.27 Questions for self understanding

1.0 Objectives of the unit

After studying this unit you are able to

- Derive the expression for Enthalpy of mixing
- Derive the expression for Entropy of mixing
- Derive the expression for Volume of mixing
- Explain the Raoult's Law
- Identify the differentiate between Ideal and nonideal solutions
- Explain the significance of different colligative properties
- Calculate the molecular weight of the substance using colligative properties.

1.1 Introduction

A solution is defined as a homogenous mixture of two or more substances. The solution constitutes a single phase.

Various significant types of solutions are:

a) Solid in liquid solutions
b) Liquid in liquid solutions and
c) Gas in liquid solutions

The relative amounts of solute and solvent Present in a solution are expressed in a number of ways. The expressions most often used in chemistry are.

a) *Normality:* It gives the number of gram equivalents of the solute present in one literature of the solution and it is denoted by N.
b) *Molarity:* It gives the number of gram molecular weights of the solute present in one liter of the solution and it is denoted by M.
c) *Morality:* It gives the number of gram molecular weights of the solute present in 1000g of solvent and it is denoted by M.
d) *Mole fraction:* The mole fraction of a solute in a solution is the ratio of number of moles of solute present in the solution to the total number of moles of solute and solvent in the solution. It is denoted by X.

If n_1 and n_2 are the number of moles of solvent and solute present in the solution, then the mole fractions of the solvent (X_1) and solute (X_2) are given by

$X_1 = \frac{n_1}{n_1 + n_2}$ and $X_2 = \frac{n_2}{n_1 + n_2}$

However, the sum of the mole fractions of the solvent and solute are unity

i.e $X_1 + X_2 = 1$

1.1 Free energy of mining in the case of ideal solution

Let us consider an ideal solution containing n_1 moles of solvent and n_2 moles of solute at a given temperature and pressure.

$$n_1A + \ n_2\ B - - \rightarrow ideal\ \ solution$$

The total free energy of the solution (G) is given by

G=$n_1\overline{G_A}\ + n_2\overline{G_B}$

Where $\overline{G_A}$ and $\overline{G_B}$ are the partial molar free energies of pure components A and B.

If ${G_A}^0$and G_B^0 are the particular molar free energies of pure components A and B,

Then the sum of the free energies of the pure components is given by

$$n_1{G_A}^0 + n_2G_B^0$$

Free energy of mixing (ΔG_{mix}) is given by

$$\Delta G_{mix}\ = free\ \ energy\ of\ \ solution\ -\ free\ energy\ of\ pure\ components$$

= G-($n_1G_A^0\ +\ n_2\ G_B^0$)

= $n_1\bar{G}_A + n_2\bar{G}_B - (n_1G_A^0\ + n_2G_B^0)$

ΔG_{mix}=$n_1(\bar{G}_A + G_A^0)$+$n_2(\bar{G}_B\ - G_B^0) - - - - - 1$

The chemical potential or partial molar free energy (μ or $\bar{G}$) of a substances in a given state is given by

$$\mu = \mu^0 + RT\ \ \ln a$$

Where ‘a’ is the activity

For an ideal solution, a = x where x is the molar concentration.

$\therefore\ \mu = \mu^0 + RT\ \ \ln x$

Since the chemical potential is partial molar free energy

$\bar{G}_A\ \ \ = G_A^0 + RT\ln x_A\ and\ \bar{G}_B = G_B^0 + RT\ln x_B$

Substituting the above in eqn (1)

We get $\Delta G_{mix}\ = n_1RTlnx_A + n_2RTlnx_B$

In general, $\Delta G_{mix}\ = RT\sum n_i\ln x_i - - - - - -(2)$

This equation is also applicable for ideal gases

1.2 Enthalpy of mixing

We know that

$$\Delta G_{mix}\ =\ n_1RT\ \ \ln x_A\ + n_2\ RT\ln x_B$$

Or $\frac{\Delta G_{mix}}{T} = n_1Rlnx_A + n_2\ R\ln x_B - - - - - -(3)$

Since the right hand side of equation (3) does not contain the term Differentiating (3) with respect to temperature at constant pressure.

We have $\left[\frac{\delta(\Delta G_{mix})/T}{\delta T}\right]_P = 0$

$$\left[\frac{\partial(\Delta G_{mix})/T}{\delta T}\right]_P = \left[\frac{T\left[\frac{\delta(\Delta G_{mix})}{\delta T}\right]_P - \Delta G_{mix}}{T^2}\right] --- (4)$$

From Gibbs – Helmholtz equation we have$\Delta G = \Delta H + T\left[\frac{\delta(\Delta G)}{\delta T}\right]_P$

Or T$\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = \Delta G - \Delta H --- (5)$

From equations (4) and (5)

$$\left[\frac{\delta(\Delta G_{mix})/_T}{\delta T}\right]_P = \frac{[\Delta G_{mix} - \Delta H_{mix} - \Delta G_{mix}]}{T^2}$$

$= -\frac{\Delta H_{mix}}{T^2} ------(6)$

Since the left hand side of equation (6) is zero,

$$-\frac{\Delta H_{mix}}{T^2} = 0 \quad \text{or } \Delta H_{mix} = 0$$

When two pure liquid or a solute in a liquid are mixed together in any proportion to give an ideal solution, *no change in enthalpy occurs*.

1.3 Entropy of mixing

We know that $\Delta G = \Delta H - T\Delta S$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

For an ideal solution, $\Delta H_{mix} = 0$

$$\therefore\ \Delta G_{mix} = -T\Delta S_{mix} \ --(7)$$

$$\text{But } \Delta G_{mix} = RT\sum n_i \ln x_i$$

$$\therefore\ RT\sum n_i \ln x_i = -T\Delta S_{mix}$$

$$\text{Or } \Delta S_{mix} = -R\sum n_i \ln x_i \ --(8)$$

Equation (8) gives the entropy of mining when a solute is dissolved in a solvent to form an ideal solution.

1.4 Volume of mixing

We know that

$\left(\frac{\Delta G}{\partial P}\right)_T = \Delta V$ Or

$$\left\{\frac{(\Delta G_{mix})}{\partial P}\right\}_T = \Delta V_{mix} \ --(9)$$

The right hand side of equation (9) does not contain pressure term; on differentiation of equation (9) with respect to pressure at constant temperature is equal to zero.

$$\Delta V_{mix} = 0 - - - - - (10)$$

If two pure liquids are mixed together in any proportion to yield an ideal solution, there is no change in volume.

1.5 Raoult's Law

Statement: The partial pressure of any component in a solution at any temperature is equal to the product of vapor pressure of the pure component and the mole fraction of that constituent.

Mathematically for component 1 it can be written as

$$P_1 = x_1 p_1^o - - - - - (11)$$

Where P_1 is the vapour pressure of the component 1, P_1^0 is the vapour pressure of the pure component and X_1 in the mole fraction.

If the component 2 is nonvolatile, P_1becomes the total vapor pressure of the solution .Thus the lowering of vapor pressure is given by

$$p_1^0 - p_1$$

$$= P_1^0 - x_1 p_1^0 = P_1^0(1 - X_1) - - - - - (12)$$

In binary solution, $X_1+X_2 = 1$

i.e., $X_2 = (1-X_1)$

$\therefore P_1^0 - P_1 = X_2 P_1^0$

Or $\frac{P_1^0 - P_1}{P_1^0} = X_2 - - - - - -(13)$

This is an alternative form of Raoult's law which states that the relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute in the solution.

1.6 Activity of component obeying Raoult's law

When components 1 and 2 form an ideal solution,

then $P_1=X_1 P_1^0$

Or $\frac{P_1}{P_1^0} = X_1$

The vapour pressures of components are normally low and therefore their fugacities can be taken to be their partial pressures in the solution

$$\frac{f_1}{f^0{}_1} = X_1$$

But $\frac{f_1}{f^0{}_1} = a_1$, the activity of component 1.

Hence , $a_1 = X_1$ and $a_2 = X_2$

Thus, the activities of components obeying Raoult's law are equal to their mole fractions. Therefore an ideal solution may be defined as one in which the activity of each component is equal to its mole fraction under all conditions of temperature, pressure and concentration.

1.7 Characteristics of an ideal solution

An ideal solution possesses the following characteristics

(a) An ideal solution obeys Raoult's law

(b) On mixing of liquids, $\Delta H_{mix} = 0$

(c) On mixing of liquids, $\Delta V_{mix} = 0$

(d) The activity a = mole fraction X

1.8 Dilute Solution

A dilute solution is one in which the amount of solute present in the solution is negligibly small in comparison with the solvent so that the enthalpy and volume changes accompanying the mixing of solute and solvent are negligible.

Dilute solutions obey Raoult's law and more or less ideal.

1.9 Colligative properties

A colligative property is any property which depends only on the number of particles present in the solution. The colligative properties of a dilute solution are:

(a) Vapor pressure lowering of the solvent
(b) The Boiling Point elevation
(c) The freezing point lowering
(d) Osmotic pressure.

1.10 Lowering of vapor pressure of a solvent (Derivation of Raoult's law)

Addition of a solute to a solvent lowers the vapors pressure of the solvent. The vapor pressure lowering suffered by the solvent can be understood in terms of Raoult's law.

Let P_1^0 is the vapor pressure of the pure solvent and P_1 is that of the solution. Let X_1 be the mole fraction of the solvent and X_2 is that of the solute. According to Raoult's law

$$P_1 = X_1 P_1^0$$

Since $X_1 < 1$ in any solution, P_1 must be less than P_1^0. Consequently, the solute present in a solution leads to a lowering of vapor pressure of the pure solvent.

The extent of vapour pressure lowering (ΔP) *is given by*

$$\Delta P = P_1^0 - P_1 = P_1^0 - X_1 P_1^0$$

$$= P_1^0 (1 - X_1)$$

$$\Delta P = P_1^0 - P_1 = P_1^0 X_2 \quad \text{[since } (1\text{-}X_1) = X_2]$$

The extent of vapor pressure lowering depends both on the mole fractions of the solute and the vapor pressure of the pure solvent.

The relative lowering of vapor pressure is given by

$$\frac{\Delta P}{P_1^0} = \frac{P_1^0 - P_1}{P_1^0} = X_2 ------(14)$$

The relative lowering of vapour pressure depends only on the mole fraction of the solute

1.11 Raoult's law and Molecular weight of the solute

Raoult's derived a relationship between relative lowering of vapor pressure and the composition of a solution.

Raoult's law can be written as

$$\frac{\Delta P}{P_1^0} = \frac{P_1^0 - P_1}{P_1^0} = X_2 ------(14)$$

If n_1 and n_2 are the number of moles of solvent and solute respectively, then

$X_2 = \frac{n_2}{n_1+n_2}$

$$\therefore \frac{P_1^0 - P_1}{P_1^0} = \frac{n_2}{n_1 + n_2} ------(15)$$

If W_2 grm of solute of molecular weight M_2 is dissolved in W_1grm of solvent of molecular weight M_1

Then $n_1 = \frac{W_1}{M_1}$ and $n_2 = \frac{w_2}{M_2}$

Substituting the values of $n_1$and n_2 in eqn (15)

We get

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{\frac{w_2}{M_2}}{\frac{W_1}{M_1} + \frac{W_2}{M_2}} --- (16)$$

The quantity on the left hand side of equation(16) is a measurable quantity and hence the molecular weight of the solute can be determined.

From equation (16)

$$\frac{P_1^0}{P_1^0 - P_1} = \frac{\frac{W_1}{M_1} + \frac{W_2}{M_2}}{\frac{W_2}{M_2}} = \frac{\frac{W_1M_2 + W_2M_1}{M_1M_2}}{\frac{W_2}{M_2}}$$

$$\frac{P_1^0}{P_1^0 - P_1} = \frac{W_1M_2}{M_1W_2} + 1$$

Or $$\frac{W_1M_2}{M_1W_2} = \frac{P_1^0}{P_1^0 - p_1} - 1$$

$$= \frac{P_1^0 - P_1^0 + P_1}{P_1^0 - P_1}$$

$$\frac{w_1 m_2}{m_1 w_2} = \frac{P_1}{P_1^0 - P_1}$$

$$\therefore M_2 = \frac{w_2 m_1}{W_1}\left(\frac{P_1^0}{p_1^0 - P_1}\right) - - - (17)$$

Equation (17) can be used for computing the molecular weights of solutes.

For extremely dilute solution, $n_1 >> n_2$

Then Equation (16) becomes

$$\frac{P_1^0 - P_1}{P_1^0} \approx \frac{n_2}{n_1} = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1}}$$

$$\therefore M_2 = \frac{W_2 M_1}{W_1}\left(\frac{P_1^0}{P_1^0 - P_1}\right) - - - - (18)$$

In the case of sufficiently dilute solutions, equation (18) can be used for the computation of molecular weight of a solute.

1.12 Boiling point elevation of solutions (Ebullioscopy)

Solutions containing nonvolatile substances boil at temperature higher than the boiling points of the pure solvent. The difference between the boiling points of the solution and the pure solvent is known as the boiling point elevation of the solution at constant pressure. The elevation in boiling point depends on the nature of the solvent and the amount of the solute present in the solution.

This phenomenon can be understood in terms of lowering of vapor pressure of the solvent. A relationship between the elevation in boiling point with the mole fraction of the solute can be derived.

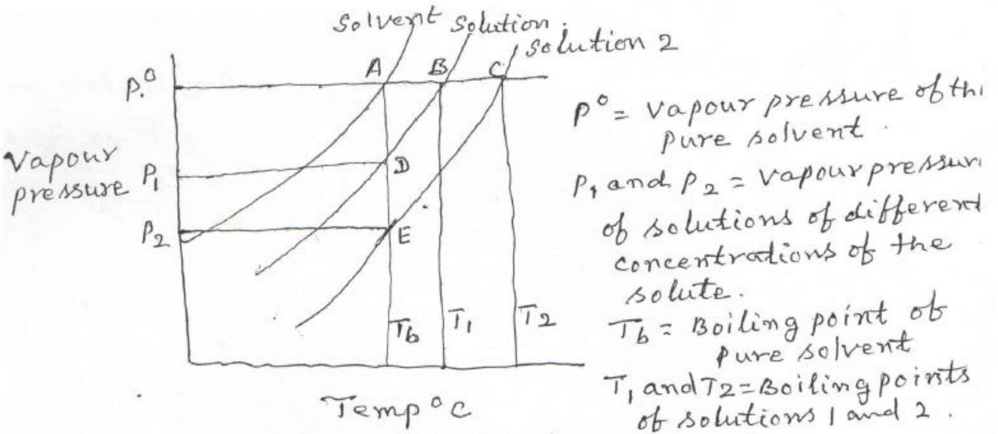


fig (1) Variation of vapour pressure with temperature

Figure1: Variation of vapour pressure with

P^0 = Vapour pressure of the pure solvent

P_1 and P_2 = vapour pressure of solutions of different concentrations of the solute.

T_b= Boiling point of pure solvent

T_1 and T_2 = Boiling points of solutions 1 and 2.

Let us consider the vapour pressure–temperature diagram shown in the fig 1. Since we are dealing with dilute solutions, the curves are approximately parallel Thus, this portion can be considered to consist of two similar triangles ABD and ACE.

$$\frac{AE}{AD} = \frac{AC}{AB}$$

From the graph

$$\frac{P^0 - P_2}{P^0 - P_1} = \frac{T_2 - T_b}{T_1 - T_b}$$

$$\frac{(\Delta P)_2}{(\Delta P)_1} = \frac{(\Delta T)_2}{(\Delta T)_1}$$

Hence

$$\Delta T_b \propto \Delta P ----(19)$$

i.e the elevation in boiling point is directly proportional to the lowering of vapor pressure.

From Raoult’s law, we have

$$\frac{\Delta P}{P^0} = X_2 = \frac{n_2}{n_1 + n_2} --- (20)$$

For sufficiently dilute solutions, the equation (20) can be written as

$$\Delta P = P^0 \frac{n_2}{n_1} = P^0 \frac{n_2}{\frac{w_1}{M_1}}$$

$$= P^0 M_1 \frac{n_2}{w_1} --- (21)$$

For a given solvent, M_1 and P^0 are constants.

$$\therefore \Delta P \propto \frac{n_2}{W_1} --(22)$$

Comparing eqns (19) and (22) ,we get

$$\Delta T_b \propto \frac{n_2}{w_1}$$

$$\Delta T_b = K_b \frac{n_2}{w_1} --(23)$$

When n_2 = 1 mol and W_1=1g equation (23) becomes

$$\Delta T_b = K_b --(24)$$

Where K_b is called the ebullioscopy constant or boiling point constant. K_b is defined as elevation in the boiling point when 1 mol of solute is dissolved in 1 g of solvent, it is a theoretical situation. But in actual practice, the ebullioscopy constant called the molal elevation constant or molal boiling point constant when 1 mol of the solute is dissolved in 1000g of the solvent .Thus,

$$\Delta T_b = K_b \frac{1000 n_2}{w_1} = K_b \frac{1000 w_2}{M_2 w_1} --- (25)$$

Where w_2= weight of solute of molecular weight M_2 dissolved in w_1 g of solvent.

1.13 Determination of the molecular weight of solute

The molecular weight of the given nonvolatile solute (m_2) can be determined by measuring the elevation in boiling point (ΔT_b) for solution of that substance using the relation

$$M_2 = \frac{1000 K_b W_2}{W_1 \Delta T_b}$$

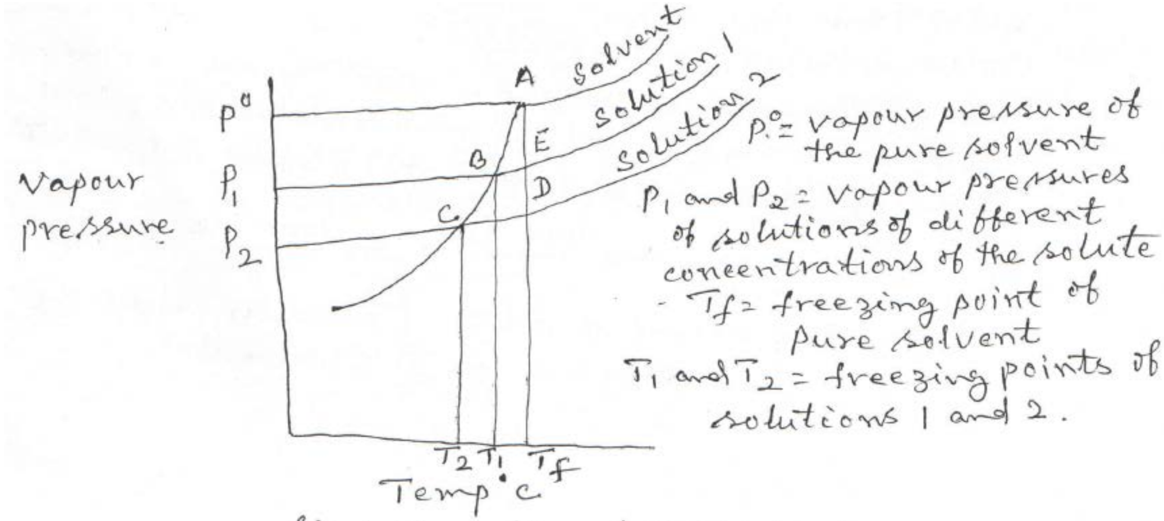
The values of K_b for water is 0.52 and for benzene is 2.53.

Many methods are available for the determination of molecular weight of nonvolatile solute which you have studied in your undergraduate course.

(Ex:- (1) Beckmann's method (2) cottrell's method)

1.14 Freezing point depression (cryoscopy)

Freezing point of a substance is defined as the temperature at which the vapor pressure of the liquid is equal to that of the solid. The presence of a nonvolatile solute always lowers the vapor pressure of the solvent. Hence, the freezing point of a solution will be less than that of solvent. The difference in the freezing points of solutions and solvent is called freezing point of depression. The variation of vapors pressures with temperature of pure solvent and solutions are given in fig. 2



p_0^0 = vapour pressure of the pure solvent

p_1 and p_2 = vapour pressures of solutions of different concentrations of the solute

T_f = freezing point of pure solvent

T_1 and T_2 = freezing points of solutions 1 and 2.

fig.2. Variation of vapour pressure with temperature

P^0 = Vapour pressure of the pure solvent

$P_1$and P_2 = vapour pressure of solutions of different concentrations of the solute.

T_1 and T_2 = freezing points of solutions 1 and 2.

T_f= Freezing point of pure solutions 1 and 2

In the above figure A, B and C refer to the freezing points of pure solvent and two solutions of different concentrations of the same solute.

For dilute solutions, AC, BE and CD would be almost linear hence the triangles ACD and ABE are similar.

$$\frac{AE}{AD} = \frac{BE}{CD}$$

From the graph,

$$\frac{P^0 - P_1}{P^0 - P_2} = \frac{T_f - T_1}{T_f - T_2}$$

$$\frac{(\Delta P)_1}{(\Delta P)_2} = \frac{(\Delta T_f)_1}{(\Delta T_f)_2}$$

In general, $\Delta p \propto \Delta T_f --- (26)$

From Raoult's law ,we have

$$\frac{\Delta P}{P^0} = X_2 = \frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1}$$

$$\Delta P = P^0 \frac{M_1 n_2}{w_1}$$

$$\boxed{Since\ n_1 = \frac{W_1}{M_1}}$$

$$\therefore \Delta P \propto \frac{n_2}{w_1}$$

Hence, $\Delta T_f \propto \frac{n_2}{w_2}$

$$\Delta T_f = K_f \frac{n_2}{w_1} \text{ ---- } (27)$$

Where K_f is called the cryoscopic constant or freezing point constant and ΔT_f is the depression in freezing point

When n_2=1 mol and w_1=1 g equation (27) becomes

$$\Delta T_f = K_f \text{----}(28)$$

The cryoscopy constant is defined as depression in the freezing point when 1 mol of solute is dissolved in 1g of solvent but it is a theoretical situation. But in practice, the cryoscopy constant called the molar depression constant or molar freezing point constant when 1 mol of the solute is dissolved 1000g of the solvent. Thus,

$$\Delta T_f = K_f \frac{1000 n_2}{w_1} = K_f \frac{1000 w_2}{M_2 W_1} --- (29)$$

Where W_2 is the weight of solute of molecular weight M_2 dissolved in W_1grm of solvent

1.15 Determination of the molecular weight of solute

The molecular weight of the given nonvolatile solute (M_2) can be determined by measuring the depression in freezing point (ΔT_f) for solution of that substance using the expression.

$$M_2 = \frac{1000 K_f w_2}{\Delta T_f w_1}$$

The vales of K_f for water is 1.86 and for benzene it is 5.12

The methods used for the determination of molecular weights of nonvolatile solutes are

(1) Beckmann's method and

(2) Rast's method which you have studied in your undergraduate degree course.

1.16 Abnormal Results

Since the colligative properties depend upon the number of particles of the solute, abnormal results are obtained in the case of solutes undergoing either dissolution or association in solution.

(a) Dissociation of solutes

Inorganic substances when dissolved in a solvent dissociate into two or more ions. In such cases the effective particles increase and colligative properties are much higher than those calculated on the basis of undissociated molecule. Example, Sodium chloride in water

Experimentally determined molecular weight will be around 29 and calculated value is 58 since sodium chloride dissociates in solution giving rise to two ions namely Na^+ ions and cl^-.

(b) *Association of solutes*

Many organic solutes when dissolved in organic solvent undergo association i.e two or more molecules of the solute associate to form a bigger molecule. Thus, the effective molecules or particles decrease and hence the colligative properties also decrease. In such cases, the experimentally determined molecular weight of the solute is found to be higher than the actual molecular weight.

Ex:- benzoic acid in benzene

The molecular weight of benzoic acid in benzene solvent found by cryoscopic method is around 242 whereas the actual molecular weight is 122 since two molecules of benzoic acid associate to form $(C_6H_5COOH)_2$.

1.17 The Van't Hoff factor (i)

Van't Hoff introduced this factor to account for all abnormal cases .The van't Hoff factor (i) is defined as the ratio of the colligative effect produced by a concentration(c) of electrolyte divided by the effects observed for the same concentration of non-electrolyte or it is defined as the ratio of actual molar mass to the experimentally observed molar mass.

$$\text{i} = \frac{Actual\ \ molar\ \ mass}{Observed\ \ molar\ \ mass}$$

Osmotic coefficient (g)

It is defined as the ratio of Van’t Hoff factor (i) to the number of ions given out by one molecule of the electrolyte.

$$\text{g} = \frac{i}{n} = \frac{van't\ \ Hoff\ \ factor}{number\ \ of\ ions\ out\ by\ one\ molecule\ \ of\ the\ electrolyte}$$

1.18 Osmosis and Osmotic pressure

When a solution is separated from a pure solvent by a semipermeable membrane (semipermeable membrane permits only the passage of solvent) it is observed that solvent tends to pass through the membrane into the solution. This phenomenon is known as osmosis.

The best semipermeable membrane for the low molecular weight solutes in water is a film of copper Ferro cyanide which is prepared by treating a solution of $CUSO_4$ with potassium Ferro cyanide. For high molecular weight solutes in organic solvents, the membranes used are thin films of either cellulose or cellulose nitrate.

It is necessary to define another quality called the osmotic pressure. Consider the diagram shown in fig 3

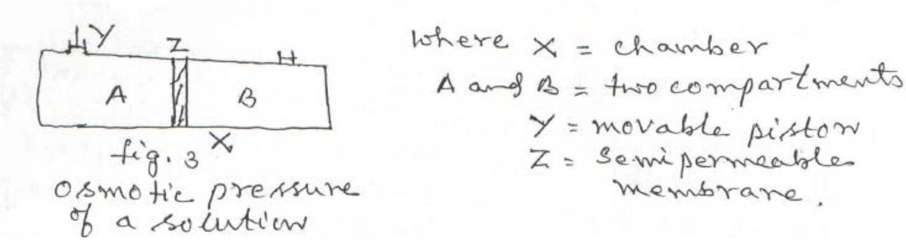


Figure 3: Osmotic Pressure of a solution

X is a chamber open at one end and the other end is fitted with a movable piston Y. The chamber is divided into two compartments (A and B) by means of a semipermeable membrane Z.

Compartment A is filled with the solution of the solute and compartment B is filled with the pure solvent which is used for preparing the solution. The solvent will tend to pass through the membrane into the solution and displace the position upward due to osmosis of the solvent can be prevented by the application of pressure to the pistol in order to keep it its original position. The pressure which must be applied on a solution to prevent osmosis of the solvent is called the osmotic pressure of the solution which is denoted by $\boldsymbol{\pi}$. The osmotic pressure is expressed in units of pressure. The osmotic pressure of a solution depends on the concentration of the solution as well as temperature.

The experimental determination of osmotic pressure of aqueous solutions was made by Berkelley and Hartley which you have studied in your undergraduate degree course.

1.19 Relation between osmotic pressure and vapor pressure

A relation between osmotic pressure and the vapour pressure lowering of a solution can be derived from pressure lowering of a solution can be derived from thermodynamic considerations. At constant tempreture and an external pressure of 1 atm, the transfer of solvent into solution occurs because the molar free energy of the pure solvent G_1^0 is grater than the partial molar free energy of the solvent in solution $\overline{G_1}$ In order to bring about equilibrium between the two and thus to stop osmosis it is necessary to increase the value of $\overline{G_1}$ I to $\overline{G_1^1}$ by increasing the extrernal pressure on the solution from 1 atm to a pressure of p. If this increase in free energy is ΔG. Then the condition for osmotic equilibrium must be

$$G_1^0 = \overline{G_1} + \Delta G$$

Or

$$\overline{G_1} - G_1^0 = -\Delta G$$

We know that

$$\overline{G_1} - G_1^0 = RT \ln \frac{P_1}{P_1^0}$$

When the vapour pressure of the solvent behaves ideally, we have

RT $\ln \frac{P_1}{P_1^0} = -\Delta G$ or

$$\Delta G = RT \ln \frac{P_1^0}{P_1}$$

We also know that

$$d\overline{G}_1 = \overline{V}_1\, dp - - - - - - - - (30)$$

Where $\overline{V1}$ is the partial molar volume of the solvent in solution.

Integrating eqn(29) between the limits

$\overline{G}_1 = \overline{G}_1$ at P=1 And $\overline{G}_1 = \overline{G}_1^{\,1}$ at a pressure p

$$\int_{\overline{G}_1}^{\overline{G}_1^1} d\overline{G}_1 = \int_1^P \overline{V}_1\, dp$$

$$\overline{G}_1^1 - \overline{G}_1 = \int_1^p \overline{V}_1\, dp ----------(31)$$

But $\overline{G_1^1} - \overline{G_1} = \Delta G$, if $\overline{V}_1$is to be independent of pressure eqn (31) becomes

$$\Delta G = \overline{V}_1(P-1)$$
$$= \overline{V}_1\pi ------(31)$$

Where π=(P-1) is the pressure which must be applied to stop the osmosis i.e the osmotic pressure.

Substituting the value of $\Delta G = RT \ln \frac{P_1^0}{P_1}$---

Gives $\pi = \frac{RT}{\overline{V_1}} \ln \frac{P_1^0}{P_1}$----(32)

If the solutions involved are very dilute , $\overline{V}_1$may be taken to be identical with V_1^0, the molar volume of the solvent and the eqn(32) can be written as

$$\pi = \frac{RT}{\vec{V}_1^0} \ln \frac{P_1^0}{P_1} ------(33)$$

Eqn(33) can be used for the calculation of osmotic pressure of a solution from its vapor pressure and that of the pure solvent at constant temperature.

1.20 Van’t Hoff equation and Osmotic Pressure

We have

$$\pi = \frac{RT}{V_1^0} \ln \frac{P_1^0}{P_1} --(33)$$

For dilute solutions obeying Raoult’s law we have

$$\frac{P_1}{P_1^0} = X_1 = (1 - X_2)$$

Where X_1 and X_2 are the fractions of the solvent and solute respectively

Substituting the above in eqn(33)

$$\pi = -\frac{RT}{V_1^0} \ln(1 - X_2)$$

Or $\pi\ V_1^0 = -RT \ln(1 - X_2)$

Expanding $\ln(1-X_2)$ and taking only the first term neglecting other terms for dilute solutions

$$\ln(1-X_2) \approx -X_2$$

$$\therefore \pi V_1^0 = -RTX_2$$

But $X_2 = \frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1}$

$$\therefore \pi V_1^0 = -RT\frac{n_2}{n_1}$$

Or

$$\therefore \pi V_1^0 n_1 = RTn_2$$

Where $V_1^0 n_1$=V= total volume of the solvent containing n_2 moles of solute. For dilute solutions V is the volume of the solution then the above equation can be written as

$\pi V = n_2 RT$ ------(34)

Or

$\prod = \frac{n_2}{V}$RT=CRT-----(35)

Where c is the molar concentration of the solution Equn(34) is known as van’t Hoff law for ideal solutions.

Van’t Hoff’s equation can be used to find the molecular weights of solutes

$\prod V = n_2 RT$-----(34)

Or $\pi = \frac{w_2}{M_{2v}}RT$ where $n_2 = \frac{W_3}{M_2}$

Or

$$M_2 = \frac{w_2 RT}{\pi V} \text{------}(36)$$

Knowing the weight of the solute present in the solution, osmotic pressure and the volume of the solution, the molecular weight of the solute can be calculated at any temperature T using eqn(36).

1.21 Lechatelier Principle

The equilibrium of a system depends on number of variable such as pressure ,temperature, concentration, addition of foreign substances etc. A change in any one of the variables may affect the position of equilibrium .The principle that governs the displacement of equilibrium was formulated by lechatelier and Braun and is called Lechatelier principle or the principle of mobile equilibrium.

It states that if a system at equilibrium is subjected to a stress such as change in variables, the system such as change in variables, the system adjusts itself in such a manner as to undo the effect of the applied stress.

To understand the statement of Lechatelier principle let is consider an example of synthesis of ammonia from nitrogen and hydrogen

$$N_{2(g)} + 3H_{2(g)} \gtreqless 2NH_{3(g)} \triangle H = -93.4RJ$$

This is an exothermic reaction and the number of moles of product formed are less than the sum of the number of moles of reactants .Thus ,according to Lechatelier principle.

(a)Increase of temperature will shift the reaction in reverse direction which is endothermic i.e heat is absorbed .The amount of NH_3 will decrease and the Amounts of the reactants increase.

(b)Decrease of temperature will shift reaction in the forward direction so that the amount of NH_3 will increase and concentration of the reactants decrease.

(c) Increase of pressure shift the reaction in the forward direction.

(d) Increase of concentration of reactants will make the reaction to take place in the forward direction.

1.22 Quantitative treatment of Lechatelier principle

The effect of temperature and pressure on the position of equilibrium and the extent of reaction changes with the change in temperature and pressure in a reaction which has attained the state of equilibrium has been studied.

(I) The effect of temperature on the equilibrium constant (Van'thoff reaction isochore)

This has been discussed in first semester M.Sc degree course under thermodynamics-I

(II)Variation of equilibrium constant with pressure:-

The equilibrium constants K_p and K_c are independent of pressure for ideal gases whereas the constant K_x is pressure dependent.

(a) K_p is independent of pressure:

We have the relation

$$-\Delta G^0 = RT \ln kp$$

$$Or \; -\frac{\Delta G^0}{RT} = \ln Kp ----------(37)$$

Differentiating equation (37) with respect to pressure at Constantan temperature

We get

$$\left(\frac{d/nK_p}{dp}\right)_T = -\left[\frac{\partial}{\partial P}\left(\frac{\Delta G^0}{RT}\right)\right]_T --- (38)$$

Eqn(38) is equated to zero because the standard free energy change of the reaction when the reaction and products of a chemical reaction when the reactants and products of a chemical reaction are at 1 atm pressure and is function of temperature only.

Hence,

$$\left(\frac{d/nK_p}{dp}\right)_T = -\left[\frac{\partial}{\partial P}\left(\frac{\Delta G^0}{RT}\right)\right]_T = 0\text{-------}(39)$$

The equilibrium constant K_p is independent of pressure through there is a change in the amounts of reactants and products with the change in pressure ,K_p remains the same.

(iii) K_c is independent of pressure:

We know that

$K_p = K_c(RT)^{\Delta n}$

$$\ln K_p = \ln K_c + \Delta n \ln RT \;--(40)$$

Differentiating eqn(40) with respect to pressure at constant temperature

We get

$$\left(\frac{d/n\ K_p}{dp}\right)_T = \left(\frac{d/n\ K_c}{dp}\right)_T + \left[\frac{\partial(\Delta n \ln RT)}{\partial p}\right] = 0$$

Since K_p and $\Delta n \ln RT$ are independent of pressure at constant temperature

$\left(\frac{d/nK_p}{dp}\right) = 0$ and $\left[\frac{\partial(\Delta n\ \ln RT)}{\partial p}\right]_T = 0$

$$\therefore \left(\frac{d/nK_c}{dp}\right)_T = 0 --- (41)$$

(iv) K_x is depending on pressure:

We have the relation

$$K_p = K_x(P)^{\Delta n}$$

$\ln K_p = \ln K_x + \Delta n \ln p$------(42)

Differentiating eqn(42) with respect to pressure at constant temperature.

$\left(\frac{d/nK_p}{dp}\right) = \left(\frac{d/nK_x}{dp}\right)_T + \left[\frac{\partial(\Delta \ln p)}{\partial P}\right]_T + \left[\frac{\partial}{\partial p}(\Delta n \ln p)\right]$

$= \left(\frac{d/nK_x}{dp}\right)_T + \frac{\Delta n}{P}$

$\therefore \left(\frac{d/nK_x}{dp}\right)_T = \left(\frac{d/n\ K_p}{dp}\right)_T - \frac{\Delta n}{P}$

Since $\left(\frac{{}^{d}\!/_{nkp}}{dp}\right)_T = 0$

$$\left(\frac{d/nK_x}{dp}\right)_T = -\frac{\Delta n}{P} ---------(43)$$

Where is the change in the number of moles .If Δn=0, K_x is the same as K_p or K_c.

1.23 Effect of extent of reaction(C_1^1) with temperature and pressure

The change in free energy is a function of temperature ,pressure and the extent of reaction.

$$\Delta G = f(T, P, \varsigma)$$

For an infinitesimal change

$$\partial(\Delta G) = \left[\frac{\partial(\Delta G)}{\partial T}\right]_{P,\varsigma} \mathrm{dT} + \left[\frac{\partial(\Delta G)}{\partial \varsigma}\right]_{T,P} d\varsigma + \left[\frac{\partial(\Delta G)}{\partial \varsigma}\right]_{T,P} d\varsigma$$

But $\Delta G = f(T, P, \varsigma)$

For an infinitesimal change

$$\therefore \partial(\Delta G) = \left[\frac{\delta(\Delta G)}{\delta T}\right]_{P,\varsigma} dt + \left[\frac{\delta(\Delta G)}{\partial p}\right]_{T,\varsigma} dp + \left[\frac{\partial(\Delta G)}{\Delta \varsigma}\right]_{T,P} d\varsigma$$

But $\Delta G = \left(\frac{\delta G}{\delta \varsigma}\right)_{T,P}$

$$\therefore \partial(\Delta G) = \frac{\partial}{\partial T}\left\{\left(\frac{\partial G}{\partial \varsigma}\right)_{T,P}\right\}_{P,G} dt + \frac{\partial}{\partial P}\left\{\left(\frac{\partial G}{\partial \varsigma}\right)_{T,P}\right\}_{T,\varsigma} dP + \left(\frac{\partial^2 G}{\partial \varsigma^2}\right)_{T,P} d\varsigma -----(44)$$

Since G is a state function and

$$\frac{\delta}{\delta T}\left[\left(\frac{\delta G}{\delta \varsigma}\right)_{T,P}\right]_{P,\varsigma} = \frac{\delta}{\delta \varsigma}\left\{\left(\frac{\delta G}{\delta T}\right)_{P,\varsigma}\right\}_{T,P} =-\left(\frac{\delta S}{\delta \varsigma}\right)_{T,P}$$

$$\frac{\delta}{\delta P}\left\{\left(\frac{\delta G}{\delta \varsigma}\right)_{T,P}\right\}_{T\varsigma} = \frac{\delta}{\delta \varsigma}\left\{\left(\frac{\delta G}{\delta \varsigma}\right)_{T,\varsigma}\right\}_{T,P} = \left(\frac{\delta V}{\delta \varsigma}\right)_{T,P}$$

Where $\left(\frac{\partial G}{\partial T}\right)_{P,G}$=-S and $\left(\frac{\partial G}{\partial P}\right)_{T\varsigma} = V$

Substituting the above in equn(44)

$$\partial(\Delta G) = -\left(\frac{\partial S}{\partial \varsigma}\right)_{T,P} dT + \left(\frac{\delta V}{\delta \varsigma}\right)_{T,P} \mathrm{dp} + \left(\frac{\partial^2 G}{\partial \varsigma^2}\right)_{T,P} d\varsigma - - - - - (45)$$

In equn (45) ,$(\frac{\delta S}{\delta \varsigma})$ is the rate of change of entropy with the extent of reaction =ΔS

$(\frac{\delta V}{\delta \varsigma})$ is the rate of change of volume with the extending of reaction=ΔV

$$\partial(\Delta G) = -\Delta S\, dT + \Delta V\, dp + \left(\frac{\partial^2 G}{\partial \varsigma^2}\right)_{T,P} d\varsigma - - - -(46)$$

Let us consider a case wherein T,P and ζ are changed in such a way that the reaction is still maintained at equilibrium .Then, $\Delta G = 0$and $\delta(\Delta G) = 0$

$$\therefore -\Delta S\, dT + \Delta V dp + G^1 d\varsigma = 0$$

Where ,$G^1 = \frac{\delta^2 G}{\delta \varsigma^2}$ a positive quantity as G is minimum at equilibrium.

We know that $\Delta S = \frac{\Delta H}{T}$

$\therefore -\frac{\Delta H}{T} dT + \Delta V\, dP + G^1 d\varsigma_e$=0----(47)

Equn (47) can be used to discuss the variation of $\varsigma_e$with temperature and pressure.

(c) Variation of ς_e With temperature at constant pressure

At constant pressure ,dp =0 ,equn(47) reduces to

$$-\frac{\Delta H}{T} dT + G^1 d\varsigma_e = 0$$

$$G^1 d\varsigma_e = \frac{\Delta H}{T} dT$$

$$\left(\frac{d\xi_e}{dT}\right)_p = \frac{\Delta H}{TG^1} - - - - - (48)$$

(i) ΔHIs negative for exothermic reactions eqn(48) will be negative.

If dT is positive i.e the temperature is increased then $d\varsigma_e$must be negative ,hence the extent of reaction should decrease with the Increase in temperature . If dT is negative i.e the tempreture is decreased $d\varsigma_e$must be positive .The extent of reaction will increase .

(ii) ΔHIs positive for endothermic reactions . equn(48) will be positive. If the tempreture is decreased,then $d\varsigma_e$ should also be negative.

(iii) If $\Delta H = 0$ then equn(48) is equal to zero and hence ,the extent of reaction should be independent of tempreture at constant pressure.

(d) Variation of ς_e with pressure at constant temperature

At constant temperature, equation (47) reduces to

$$\Delta V dp + G^1 d\varsigma_e = 0$$

$\left(\frac{d\varsigma_e}{dP}\right)_T = -\frac{\Delta V}{G^1}$----(49)

Since G^1 is positive,the sign of $\left(\frac{d\varsigma_e}{dp}\right)$ will depend on the nature of ΔV

(i) If $V_p = V_r$, $\Delta V=0$

ς_e Will be independent of pressure.

(ii) If $V_p > V_r$, $\Delta V=+ve$ The subscript ‘P’ stands for products and ‘r’ for reactants.

(iii) If $V_p < V_r$, $\Delta V=-ve$

Increase of pressure (dp>0) increase ς_e and decrease of pressure (dp<0) decrease ς_e

To summarizing, an increase in pressure shifts the equilibrium to then low volume side of the reaction while decrease in pressure shifts the equilibrium to the high volume side.

1.24 Summary of the unit

Properties of solutions that depend on the number of molecules present and not on the kind of molecules are called colligative properties. These properties include boiling point elevation, freezing point depression, and osmotic pressure. Historically, colligative properties have been one means for determining the molecular weight of unknown compounds. In this chapter we discuss using colligative properties to measure the molecular weight of polymers. Because colligative properties depend on the number of molecules, we expect, and will show, that colligative property experiments give a number average molecular weight.

Another colligative property is osmotic pressure. Osmotic pressure measurements appear to be a suitable method for measuring number average molecular weights in polymers. It is therefore worthwhile considering practical aspects of polymer characterization by osmotic pressure. The first practical consideration is that we expect polymer solutions to deviate from ideal behavior and thus the osmotic pressure expression will need to be corrected. In the limit of zero concentration, the solution will eventually become ideal. We can therefore take a series of measurements and extrapolate back to zero concentration to get the ideal result.

1. 25 Key words

Enthalpy of mixing; Entropy of mixing; Volume of mixing; Ideal solution; Raoult’s law; Colligative properties; Lowering of vapor pressure; Boiling point elevation; Freezing point depression; Osmosis; Osmotic pressure; Vapor pressure; Van’t Hoff factor; Lechatelier Principle.

1.26 References for further study

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1.27 Questions for self understanding

1) Derive the expression for enthalpy of mixing

2) Derive the expression for entropy of mixing

3) Derive the expression for volume of mixing

4) Write the Statement of the Raoult’s Law

5) Write a note on activity of component obeying Raoult’s law

6) What are the characteristics of an ideal solution?

7) What is meant by dilute solution?

8) What is Colligative propertie? What are the different colligative properties exists?

9) Derive the expression for lowering of vapor pressure of a solvent

10) Write a note on Raoult’s law and Molecular weight of the solute

11) Derive the expression for boiling point elevation of solutions (Ebullioscopy)

12) How the molecular weight of solute can be determined using of boiling point elevation?

13) What is meant by freezing point depression (cryoscopy)?

14) How the molecular weight of solute can be determined freezing point depression

15) Write a note on Abnormal Results of colligativve properties

16) Derive the expression for the Van’t Hoff factor (i)

17) Explain Osmosis and Osmotic pressure

18) Derive the expression for relation between osmotic pressure and vapor pressure

19) Write a note on Van’t Hoff equation and Osmotic Pressure

20) Explain Lechatelier Principle

21) Write a note on Quantitative treatment of Lechatelier principle

22) Write a note on

a) Effect of extent of reaction(C_1^1) with temperature and pressure

b) Variation of ς_e With temperature at constant pressure

c) Variation of ς_e with pressure at constant temperature

Unit-2

Structure

2.0 Objectives of the Unit
2.1 Introduction
2.2 Thermodynamics of non ideal solutions
(a) Positive deviation from ideal behavior
(b) Negative deviation from ideal behavior
2.3 Activity and activity coefficients
2.4 Variation of activity with temperature
2.5 Variation of activity with pressure
2.6 Determination of activity and activity coefficient
    (a) Activity of solvent by vapor pressure method
    (b) Activity and activity coefficient of a solute by vapour pressure method
    (c) Activity and activity coefficient by conductivity method(solubility method)
2.7 Summary of the unit
2.8 Key words
2.9 references for further study
2.10 questions for self understanding

2.0 Objectives of the Unit

After studying this unit you are able to

- Explain the thermodynamics of non ideal solutions
- Explain the nositive deviation from ideal behavior
- Explain the negative deviation from ideal behavior
- Determine the Activity and activity coefficients for a given solution mixture
- Identify the variation of activity with temperature
- Identify the variation of activity with pressure
- Calculate the Activity and activity coefficient of a solute by vapour pressure method
- Calculate the Activity and activity coefficient by conductivity method(solubility method

2.1 Introduction

The ideal solution assumes equal strength of self- and cross-interactions between components. When this is not the case, the solution deviates from ideal behavior. Deviations are simple to detect: upon mixing, nonideal solutions exhibit volume changes (expansion or contraction) and exhibit heat effects that can be measured. Such deviations are quantified via the excess properties. An important new property that we encounter in this chapter is the activity coefficient. It is related to the excess Gibbs free energy and is central to the calculation of the phase diagram

2.2 Thermodynamics of non ideal solutions

A solution is said to be ideal if it obeys Roult’s law .when an ideal solution is formed between two components A and B. The behavior of each in that mixture remains unaffected. The attractive forces between A-A, A-B and B-B are the same. When attraction between adjacent molecules of different types becomes greater than A-A and B-B attraction then the solution become non ideal. This effect lowers the partial vapour pressure of A and B and solution fails to obey Raoult’slaw. In these solutions the chemical potential of the components A and B are given by

$$\mu_A = \mu_A^0 + RT\ln a_A \; and \; \mu_B = \mu_B^0 + RT\ln a_B$$

$$\mu_A = \mu_A^0 + RT\ln \wp_A X_A \; and \; \mu_B = \mu_B^0 + RT\ln \wp_B X_B$$

At low pressures

$$\frac{f_A}{f_A^0} = \frac{p_A}{P_A^0} = a_A = \wp_A X_A$$

$$\therefore P_A = P_A^0 \wp_A X_A$$

Depending upon the values of $\wp_A$ the partial pressure of the component may be greater or lesser than the Raoult's pressure. If $\wp_A > 1$,then the system shows the positive deviation from Raoul'ts law while $\wp_A < 1$ it shows the negative deviation from Raoult's law.

(c) Positive deviation from ideal behavior

If $\wp_A > 1$, A-B interaction is weaker than A-A and B-B interactions ,then the tendency of each of the components to pass into vapor phase is increased

And these are positive deviations from Raoult'slaw. The observed vapor pressure is greater than that predicted by Raoult'slaw. This is shown in fig .4 for dioxane –water system .Dotted lines represent.

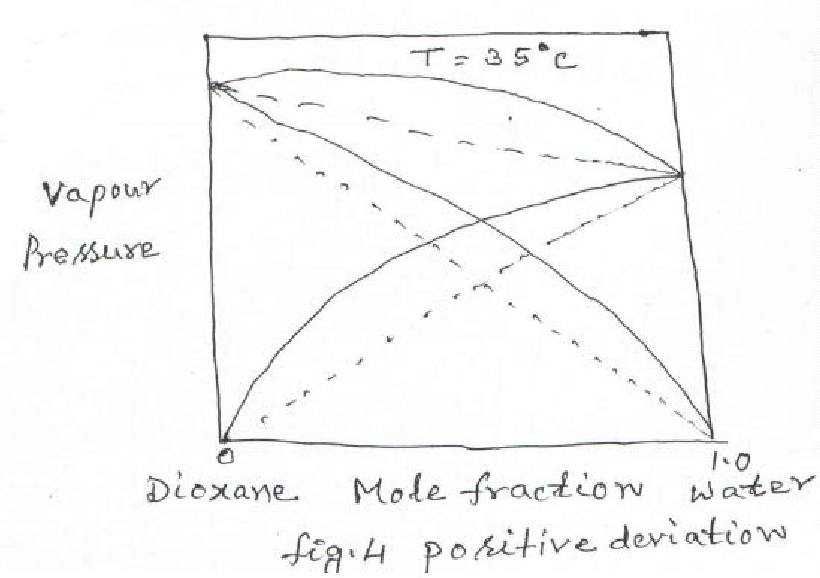

Figure 4: Positive deviation

Ideal behavior CCL_4-benzene, heptane –ethyl alchoholetc are the other examples.

(d) Negative deviation from ideal behavior

These occur when interaction between A-B is stronger than that between A-A and B-B. A plot for the system acetone –chloroform showing negative deviation is given the fig5.Other examples are

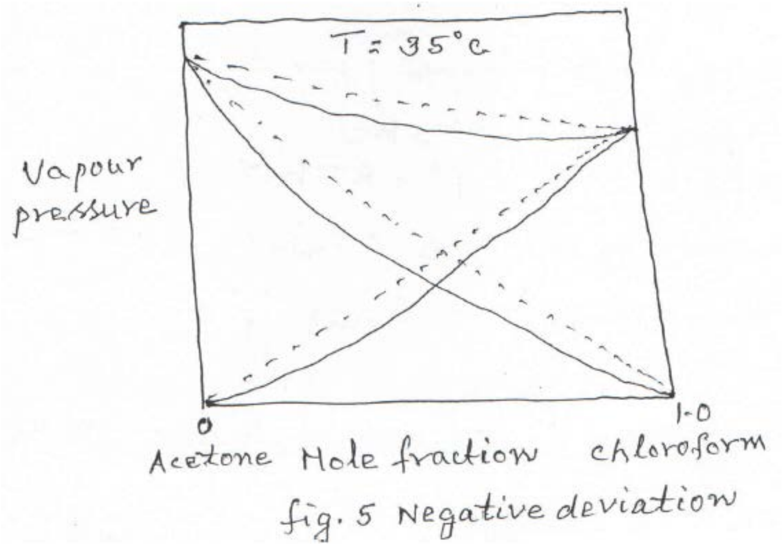

Figure 5: Negative deviation

Water –H_2SO_4, water – HNO_3, water-$HClO_4$,chloroform-ethyl ether…...etc. In the case of acetone and chloroform mixture, a hydrogen bond is formed between the hydrogen in chloroform and carbonyl oxygen of acetone and shows the negative deviation

Criteria of ideal and non ideal solutions are summarized in the following table:

Criteria	**Ideal solution**	**Non ideal solution**	
		Positive Deviation	Negative deviation
Interactions	A-A ,A-B and B-B are identical	A-B interaction Is weaker	A-B interaction is stronger
Vapor pressure	P(observed)= P(calculated)	P(observed)> P(calculated)	P(observed)< P(calculated)
ΔH_{mix}	~0	>0 endothermic	< 0 Exothermic
ΔV_{mix}	~0	$\neq 0$	$\neq 0$

2.3 Thermodynamic functions of mixing of non ideal solutions

Let us consider two pure liquids 1 and 2 .Let n_1 moles of liquid 1 and n_2 moles of liquid 2 are mixed carefully .

The free energy before mixing

$G_{initial} = n_1\mu_1^0 + n_2\mu_2^0$

The free energy after mixing

G$_{\text{final}}$ $= n_1\mu_1 + n_2\mu_2$

$$But\, \mu_1 = \mu_1^0 + RT\ln a_1 = \mu_0^1 + RT\ln \bar{\gamma}_1 X_1$$

(a) The free energy of mixing ΔG_{mix} is given by

$\Delta G_{mix} = G_{final} - G_{initial}$

$= \sum n_i\, \mu_i - \sum n_i\, \mu_i^0$

$$= \sum n_i\, \mu_i^0 + RT \sum n_i \ln a_i - \sum n_i\, \mu_i^0$$

$= RT \sum n_i \ln a_i$

$$\Delta G_{mix} = RT \sum n_i\, \bar{\gamma}_1 + RT \sum n_i \ln X_i$$

(b) Entropy of mixing ΔS_{mix} is given by

$$\Delta S_{mix} = -\left[\frac{\partial(\Delta G_{mix})}{\partial T}\right]_P$$

$= -RT \sum n_i \left(\frac{\partial \ln a_i}{\partial T}\right)_P - R \sum n_i \ln a_i$

$$\Delta S_{mix} = -RT \sum n_i \left(\frac{\partial \ln \bar{\gamma}_i}{\partial T}\right)_P - R \sum n_i \ln a_i$$

Since $\left(\frac{\partial \ln x_i}{\partial T}\right) = 0$

(c) Enthalpy of mixing is given by

$\Delta H_{mix} = \Delta G_{mix} + T\Delta S_{mix}$

Substituting the values of ΔG_{mix} and ΔS_{mix} on simplification

We get $\Delta H_{mix} = -RT^2 \sum n_i (\frac{\partial \ln \bar{\gamma}_i}{\partial T})_p$

Since $\left(\frac{\partial (\ln X_i)}{\partial T}\right) = 0$

(d) Volume of mixing ΔV_{mix} is given

$$\Delta V_{mix} = \left[\frac{\partial(\Delta G_{mix})}{\partial P}\right]_T$$

$= \text{RT} \sum n_i \left(\frac{\partial \ln \bar{\gamma}_i}{\partial p}\right)_T$

Since $\left(\frac{\partial \ln x_i}{\partial P}\right) = 0$

2.4 Activity and activity coefficients

The partial pressure or fugacity is proportional to the mole fraction in the case of ideal solutions. In the case of non-ideal solutions, the term activity was introduced. The ratio of fugacity of a component in any given state to the fugacity in the standard state is said to be activity which is denoted by

$$a_i=\frac{f_i}{f_i^0}$$

a_i *is the activity of i th component*

F_i the fugacity of ith component in any state

F_i^0 the fugacity ith component in the standard state.

The chemical potential or partial molar free energy is related to the activity by the relation

$$\mu_i = \mu_i^0 + RT \ln a_i$$

The activity a_i of the ith component approaches the concentration when the solution becomes ideal or in the case of infinitely dilute solutions. In such cases

$$\mu = \mu_x^0 + RT \ln X$$

$$\mu = \mu_c^0 + RT \ln c$$

$$\mu = \mu_m^0 + RT \ln m$$

Where X is the mole fraction c is the molar concentration m in the molal concentration.

In the case of non ideal solutions, the activity is related to the activity co-efficient which was introduced by G.N.Lewis by the relation

$a = \bar{\gamma}_X$ x=$\bar{\gamma}_C$ c=$\bar{\gamma}_m m$

$\gamma_X = \frac{a}{x}$; *molar activity coefficiant*

$\gamma_c = \frac{a}{c}$; molar activity coefficient

$$\gamma_m = \frac{a}{m}; molal\ activity\ coefficient$$

The activity coefficient is a measure of the deviation from behavior .If the solution is ideal ,then

$\gamma_X = \gamma_C = \gamma_m = 1$

$$\therefore a = X = c = m$$

The activity coefficient in the case of ideal solutions is unity $(\bar{\gamma} = 1)$ and for non ideal solutions $\bar{\gamma}$ may be less than one. However, in some cases it is notified that "$\bar{\gamma}$ "is greater than one.

2.4 Variation of activity with temperature

We know that

$\mu_i = \mu_i^0 + RT \ln a_i$

RTln $a_i = \mu_i - \mu_i^0$

R ln $a_i = \frac{\mu_i}{T} - \frac{\mu_i^0}{T}$---------(50)

Differentiating eqn(50) with respect to temperature at constant pressure and composition, we get

$$\left(\frac{\frac{\partial}{n}a_i}{\partial T}\right)_{P.X} = \frac{H_i^0 - \overline{H_i}}{RT^2} --- (51)$$

Where H_i^0 is the molar enthalpy of the component in the pure state at 1 atm. Pressure and $\overline{H_i}$ is the partial molar enthalpy of the component eqn(51) gives the variation of activity with temperature. The same expression gives the effect of temperature on the activity coefficient since $Va_i = \bar{\gamma}_{x} X$

2.5 Variation of activity with pressure

We know that

$$\mu_i = \mu_i^0 + RT \ln a_i$$

$$RT \ln a_i = \mu_i - \mu_i^o --- (52)$$

Differentiating eqn(52) with respect to pressure at constant temperature and composition, we get

RT$\left(\frac{d/n\, a_i}{dp}\right)_{T,X} = \left(\frac{d\mu_i}{dp}\right)_{T,X,} - \left(\frac{d\mu_i^0}{dP}\right)_{T,X}$

$\left(\frac{d/n\ a_i}{dP}\right)_{T,X} = \frac{1}{RT}\left(\frac{d\mu_i}{dp}\right)_{T,X} - 0$

$\left(\frac{d/n\, a_i}{dp}\right)_{T,X} = \frac{1}{RT}\overline{V_i} = \frac{\overline{V_i}}{RT} -------- (53)$

Where $\overline{V_i}$ is the partial molar volume of the component i in the solution .Eqn(53) gives the effect of pressure on activity and the same equation gives the variation of activity coefficient with pressure.

2.6 Determination of activity and activity coefficient

Number of methods are available for the determination of activity and activity coefficient only two methods are discussed because the syllabus contains only two methods namely vapour pressure method and conductivity method.

(d)Activity of solvent by vapor pressure method

The activity of methods of any constituent of a solution is given by the ratio of fugacities.

$$a_i = \frac{f_i}{f_i^0}$$

If the vapour pressure of the solvent is not too high ,the fungacities are placed by respective vapour pressures

$a_i = \frac{P_i}{P_i^0}$--------(54)

Where P_i is the partial vapour pressure of the solvent in equilibrium with the solution and P_i^0 is the vapour pressure of the pure solvent at the same temperature.

The equation (54) thus provides a simple method for determining the activity of solvent in a solution. The same equation has been applied to aqueous solutions and to the solutions of organic liquids .The activity coefficient at any composition may be obtained by dividing the activity of the solvent by its mole fraction.

(b) Activity and activity coefficient of a solute by vapour pressure method

If the solute and solvent are completely miscible , the activity of the solute(a_2) may then be determined using the equation $a_2 = \frac{p_2}{p_2^0}$,However ,for dilute solutions , it is more convenient to use infinitely dilute solution as the reference state

Hence, $a_2 = \frac{f_2}{\Re}$

Where f_2 the fugacity of the solute in the given solution and $\Re$ is a constant quantity.

Replacing the fugacity f_2 by the partial vapor pressure of the solute P_2 in the above equation.

We get $a_2 = \frac{P_2}{\Re}$

$\Re$ Value may be obtained by making use of the fact that at infinite dilution, the activity of the solute $\left(a_2^*\right)$ is equal to its mole fraction $\left(X_2^*\right)$ If $\left(P_2^*\right)$ is the corresponding vapour pressure, then

$$\left(X_2^*\right) = \frac{P_2^*}{\Re} ----------- (56)$$

Combining equation (55) and (56),we get

$$\left(a_2\right) = P_2 \frac{X_2^*}{P_2^*} ----------- (57)$$

Dividing equation (57) by the mole fraction of the solute, we get

$$\wp_X = \frac{a_2}{X_2} = \frac{p_2}{X_2} \cdot \frac{X_2^*}{p_2^*} ----------- (58)$$

A number of solutions of different mole fractions are prepared and P_2/X_2 are determined , A graph of P_2/X_2 is plotted against X_2 and the resulting graph is extra plated to X_2=0 the value of the intercept is equal to X_2^*/p_2^* which is required to evaluate activity and activity coefficient using equations (57) and (58) .The mole fraction term in the above equations may be replaced by either molarity(c) or molality(m) to get molar activity coefficient $(\bar{\gamma}_c)$ or molar activity coefficient $(\bar{\gamma}_m)$

(e) Activity and activity coefficient by conductivity method(solubility method)

The activity or activity coefficient of a sparingly soluble salt in the presence of other electrolytes can be determined by this method.

The solid salt $M_{\gamma_+}A_{\gamma_-}$ will be in equilibrium with $\gamma_+ M^{Z+}$ and $\gamma_- A^{z-}$ in solution. Thus The equilibrium constant is given by

$$k_{sp} = a_+^{\gamma+} . a_-^{\gamma-} \quad \text{since } aM_\gamma = A\gamma_- = 1$$

Where K_{sp} is the activity solubility product. The activity of each ion may be replaced by the product of molality and activity coefficients, so that

$$K_{sp} = m_+^{\gamma+}\,\bar{\gamma}_+^{\gamma+} \times m_-^{\gamma-}\,\bar{\gamma}_-^{\gamma-}$$

$$K_{sp} = (m_\pm \bar{\gamma}_\pm)^\gamma$$

Since $\gamma = \gamma_+ + \gamma_-$

Where $m_\pm$ is the mean ionic molality and $\gamma_\pm$ is the mean ionic activity coefficient

$$\therefore \bar{\gamma}_\pm = \frac{(K_{sp})^{1/\gamma}}{m_\pm} ------------- (59)$$

In the case of solid salt containing one action and one anion(Ex: AgCl,AgBr,TiCl etc) the above equation can be written as

$$\therefore \bar{\gamma}_\pm = \frac{(K_{sp})^{1/2}}{m_\pm} ------------- (60)$$

This method is described for the solid salts containing one and one anion.

The following solutions are prepared by making use of conductivity water.

(i) 0.1 N solution of potassium chloride to determine the cell constant.

(ii) Saturated solutions of sparingly soluble sat in different concentrations of electrolyte.

Measure the conductance of 0.1N solution of potassium chloride

Cell constant=$\frac{specific\ \ conductance}{Observed\ \ conductance}$

$=\frac{0.01286}{Observed\ \ conductance}$

Measure the conductance of saturated solutions of sparingly soluble salt in different concentrations of electrolyte. Determine the specific and equivalent conductance's.

Specific conductance (K)=Cell constant × observed conductance

Equivalent conductance = $\frac{1000K}{Normality\ \ or\ molarity}$

Equivalent conductance (Λ) and) and molar Conductance(Λ) are taken as Λ^0 *and* Λ^0_m respectively since the solubility of sparingly soluble salt is to a very small extent

The above equation may be written as

$$\Lambda^0_m = \frac{1000K}{molarity} = \frac{1000K}{solubility}$$

$solubility = \frac{1000\ k}{\Lambda^0_m}$--------(61)

Λ^0_mCan be obtained from Kohlrausch law which is given by

$$\Lambda^0_m = \Lambda^0_c + \Lambda^0_a$$

Where Λ^0_c and $\Lambda^0_a$are the ionic Conductance's at infinite dilution of the cation and anion respectively.

Determine the solubility's of sparingly soluble salt in the presence of concentrations of other electrolytes using equation (61) from

Which m± can be calculated. A plot of m± again ($\sqrt{\underline{T}}$ (where I is the iconic strength of the solution whose value can be calculated using the equation

$\underline{T}$=1/2($C_1Z_1^2$,+$C_2\ \ Z_2^2$+----)=1/2 $\sum C_i\ Z_i^2$ where C_i is the concentration in normality or molarity or ith kind is drawn and entrapolated to zero ionic strength(infinite dilution). The intercept value$(k_{sp})^{1/2}$ using the equation(60) the activity coefficient can be calculated for any molarity of the solution knowing the value of activity coefficient ,activity can be evaluated. In this way both activity coefficient can be determined.

2.7 Summary of the unit

Deviation from ideal solution behaviour can be classified as positive or negative, depending on whether the total pressure exerted by the solution is greater or less than, that predicted by

Raoult's Law. Recall that for an ideal solution, the total pressure varies linearly with liquid mole fraction, i.e. a straight-line relationship. The greater the departure from a straight line, the greater is the deviation from ideal behaviour, The Non-ideal behaviour is best demonstrated using constant temperature phase diagrams.

When the total pressure of a system at equilibrium is less than the ideal value, the system is said to deviate negatively from Raoult's Law. In this case, the activity coefficients for both A and B are less than 1.0, and the p vs. x lines are located below the straight lines provided by Raoult's Law. The partial pressures of each component are large than ideal, and the total pressure curve PT vs. x is located below the straight line for ideal solution.

A mixture whose total pressure is greater than that computed for ideality is said to show positive deviations from Raoult's Law. Most mixtures fall into this category.

In this case, the activity coefficients are greater than 1.0, and the p vs. x lines are located above the straight lines provided by Raoult's Law. The partial pressures of each component are larger than ideal, and the total pressure curve PT vs. x is located above the straight line for ideal solution.

Molecules that are dissimilar enough from each other will exert repulsive forces. For example, polar water molecules are strongly repulsed by organic hydrocarbon molecules. The repulsive forces result in activity coefficients greater than unity, since the molecules tend to leave the liquid phase. A greater partial pressure will be exerted, leading to a positive deviation from ideality.

On the other hand, if the molecules of the components attract each other strongly, the activity coefficients will be less than unity (but still greater than zero), and less molecules will leave the liquid phase. The mixture will exert lower partial pressure, and producing a negative deviation from ideality.

2.8 Key words

Non ideal solutions; Positive deviation; Negative deviation; Activity coefficients

2.9 references for further study

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2.10 questions for self understanding

1) Discuss the thermodynamics of non ideal solutions

2) Explain the Positive deviation from ideal behavior

3) Explain the negative deviation from ideal behavior

4) What is activity and activity coefficients?

5) Explain variation of activity with temperature

6) Explain variation of activity with pressure

7) How the Activity and activity coefficient of a solute is determined by vapour pressure method

8) Explain the determination of activity and activity coefficient by conductivity method (solubility method)

Unit-3

Structure

3.0 Objectives of the unit
3.1 Introduction
3.2 The Phase Rule
3.3 Definition of terms involved in the equation
  a) Phase
  b) Components
  d) Degrees of freedom or variance
3.4 Derivation of phases rule from the concept of chemical potential
3.5 Applications of phase rule
3.6 One component System
  (a) The water system
3.7 Polymorphism
  (b)The sulphur system
3.8 Summary of the unit
3.9 Key words
3.10 Reference for further study
3.11 Questions for self understanding

3.0 Objectives of the unit

- After studying this unit you are able to
- Explain the phase rule
- Identify the components present in a given system
- Explain the degree of variables in phase system
- Calculate the number of variables for a given system
- Derive the phase rule for one component system

3.1 Introduction

The physical and chemical state of a system may be defined by the values of its properties. The properties that are usually used to define the state are pressure, volume, temperature and composition, although there are other properties such as density, viscosity and enthalpy that could equally well be used.

Not all properties are, however, necessarily independent. For example, we know that for an ideal gas, the pressure, volume and temperature are related by the ideal gas equation PV = n RT so that if we know the values of any two variables, we can determine the value of the third. Thus we need not specify the values of every property in order to define the state of a system.

In practice, we usually need to state the composition and the values of only two other independent variables in order to define the state of a system. We could select from a large number of combinations of variables, but we usually choose composition, as well as pressure, p and temperature, T as the independent variables. Other parameters such as volume, density and refractive index are then dependent variables. If we wish to define the total amount of substance present, then one of the variables must be an extensive property. We must therefore define our composition in terms of the amounts of substance of the independent components ni, nj etc. In many cases, however, we are not interested in the total amount of substance present and we can define the intensive state of the system using only intensive variables. We then choose the mole fractions xi, xj, etc. to define the composition.

3.2 The Phase Rule

The phase rule was put forward by Willard Gibbs. He derived the phase rule from thermodynamics considerations and it is the most useful generalization concerning the equilibrium in heterogeneous systems. Roozeboom, ostward and van’t Hoff showed the wide possibility of its applications and pointed out its unique importance. The phase rule predicts the effect of temperature, pressure and composition on a heterogeneous system.

The mathematical form of Gibbs phase rule is

F+P=C+2

Where

F=number of degrees of freedom or variance

P=number of phases

C= number of components

Z= number of variables

Statement of Phase rule

The number of degree of freedom plus the number of phases is equal to the number of components plus two in a heterogeneous system in equilibrium.

3.3 Definition of terms involved in the equation

(a)Phase: A Phase is defined as a physically distinct, mechanically separable but homogenous part of an heterogeneous system.

Example,

(i) Water has three phases namely ice, liquid water and water vapour.

(ii) A gaseous mixture always single phase.

(iii) If the liquids are completely miscible with each other, then it is single phase.

(iv) If the liquids are completely miscible with each other, then it is single phase.

(v) If two liquids are immiscible with each other, then the number of phases will be two

(b) Components The minimum number of independent chemical constituents by which the composition every phase of system can be expressed determines the number of components.

Example,

(i) The system ice-liquid water vapour contains only one component,water.

(ii) Sulphur system consists of four phases namely, monoclinic sulphur, rhombic sulphur, liquid sulphur and sulphurvapour.It is a one component system is sulphur.

(c) Degrees of freedom or variance

It is defined as the smallest number of independent variables such as temperature, pressure or composition which must be specified in order to define the system completely.

Suppose the system consists of one component and two phases at equilibrium, then

F=C-P+2 =1-2+2=1

It is necessary to specify only one variable to describe the system.

Suppose the system consists of one component and three phases at equilibrium ,then

F=C-P+2=1-3+2=0

In this case ,one need not have to specify by any variable to describe the system.

Thus,

F=0,Invariant system

F=1 ,Univariant system

F=2 ,bivariate system

3.4 Derivation of phases rule from the concept of chemical potential

Consider a system of several phases a,b,c,d…P Let each phase consists of a total of c components such as 1,2,3,…etc. Each phase may contain two or more components in different proportions. In order to deduce the conditions of equilibrium, chemical potential or partial molar free energy concept is used.

Consider a closed system of four phases a,b,c,d i e P=4 and C=3 (1,2,3) are in equilibrium at constant temperature and pressure.

The chemical potentials of various components may be represented as :

$\mu_1(\mathrm{a})\mu_2(a)\mu_3(a) \longrightarrow$ Phase a

$\mu_1(b)\mu_2(b)\mu_3(b) \longrightarrow$ Phase b

$\mu_1(c)\mu_2\,(c)\mu_3(c) \longrightarrow$ Phase c

$\mu_1(d)\;\mu_2(d)\;\mu_3(d) \longrightarrow$ Phase d

At constant temperature and pressure, if a small amount of each component in mole (dn) is transferred from one phase to another, then according to Gibbs-Duhem equation

$\mu_1 dx_1 + \mu_2 dx + \;\ldots.\;. = 0$

Or $\sum \mu_i \mathrm{d}n_i = 0$

We could set up the following equations for the system,

$$\left.\begin{array}{r} \mu_1^{(a)}dn_1^{(a)} + \mu_1^{(b)}dn_1^{(b)} + \mu_1^{(c)}dn_1^{(c)} + \mu_1^{(d)}dn_1^{(d)} \\ + \mu_2^{(a)}dn_2^{(a)} + \mu_2^{(b)}dn_2^{(b)} - - - - \\ + \mu_3^{(a)}dn_3^{(a)} + \mu_3^{(b)}dn_3^{(b)} + \text{--------------} \end{array}\right\} = 0\text{-----}(1)$$

Since the system is closed system, total mass of the system should be constant

$$\left.\begin{array}{r} dn_1^{(a)} + dn_1^{(b)} + dn_1^{(c)} + dn_1^{(d)} = 0 \\ dn_2^{(a)} + dn_2^{(b)} + dn_2^{(c)} + dn_2^{(d)} = 0 \\ dn_3^{(a)} + dn_3^{(b)} + dn_3^{(c)} + dn_3^{(d)} = 0 \end{array}\right\}\text{-----------}\ (2$$

Multiplying equations (2) by $\lambda_1, \lambda_2, \lambda_3 \ldots$(Legrange method of undetermined multipliers) ,we get

$$\left.\begin{array}{l} \lambda_1 dn_1^{(a)} + \lambda_1 dn_1^{(b)} + \lambda_1 dn_1^{(c)} + \lambda_1 dn_1^{(d)} = 0 \\ \lambda_2 dn_2^{(a)} + \lambda_2 dn_1^{(b)} + \lambda_2 dn_2^{(c)} + \lambda_2 dn_2^{(d)} = 0 \\ \lambda_3 dn_3^{(a)} + \lambda_3 dn_3^{(b)} + \lambda_3 dn_3^{(c)} + \lambda_3 dn_3^{(d)} = 0 \end{array}\right\} \text{--------} \quad (3)$$

Adding equations (1) and (3) and equating coefficients to zero

$$\left.\begin{array}{l} dn_1^{(a)}[\lambda_1 + \mu_1^{(a)}] + dn_1^{(b)}[\lambda_1 + \mu_1^{(b)}] \pm --= 0 \\ dn_2^{(a)}\left[\lambda_2 + \mu_2^{(a)}\right] + dn_2^{(b)}\left[\lambda_2 + \mu_2^{(b)}\right] + --= 0 \\ dn_3^{(a)}[\lambda_3 + \mu_3^{(a)}] + dn_3^{(b)}[\lambda_3 + \mu_3^{(b)}] + --= 0 \end{array}\right] \quad (4)$$

From equation (4)

$$\lambda_1 + \mu_1^{(a)} = 0 \text{ or } \mu_1^{(a)} = -\lambda_1$$

$$\lambda_1 + \mu_1^{(b)} = 0\, r \;\; \mu_1^{(b)} = -\lambda_1$$

$\therefore\ \mu_1^{(a)} = \mu_1^{(b)} = \mu_1^{(c)} = \mu_1^{(d)} = -\lambda_1$------(5)

$\mu_2^{(a)} = \mu_2^{(b)} = \mu_2^{(c)} = \mu_2^{(d)} = -\lambda_2$----(6)

$\mu_3^{(a)} = \mu_3^{(b)} = \mu_3^{(c)} = \mu_3^{(d)} = \lambda_3$----(7)

At constant temperature and pressure for a system of P number of phases containing several components in equilibrium ,the chemical potential of each component is same in all the phases according to equations (5),(6) and (7).

In a closed system of different phases at equilibrium, the composition of the phase is more important. Instead of specifying the amount of material in moles or grams ,the mole fraction of the phase .Suppose a phase contains two components it is enough if the mole fraction of one component is known, that of the other can be calculated by difference .In general ,if a phase contains C components it can defined completely by (c-1) composition variables.

For a system of P phases ,P(c-1) composition variables exit. Besides composition variables,
The other variables are temperature and pressure.

$\therefore$ the number of variables= P(c-1)+2

For a system of 3 components and 4 phases, the requirement is that the chemical potential of any component is the same in all phases at equilibrium according to equations(5),(6) and (7) .Therefore , three independent equations are available to describe the equilibrium of 4 phases between a,b,c and d for each of the components.In general ,for a system of P phases ,(P-1) equations are known for each components, Hence for a system of P phases and C components the number of equations known will be C(P-1).

$\therefore$ Number of variables defined by the system =C(P-1)

The degrees of freedom (F) of the system is given by

F=[P(C-1)+2] –[C(P-1)

F=C-P+2 --------(8)

Thus in order to define a system completely, (C-P+2) variables must be fixed arbitrarily which is equal to the number of degrees of freedom (F).

3.5 Applications of phase rule

The number of phases which exist in equilibrium depends on temperature and pressure or temperature and composition or pressure and composition .These conditions are determined experimentally and interdependence of values of the variables can be shown graphically using appropriate co-ordinates. These diagrams are termed as phase diagram. The diagram with the help of which the coexistence of different phases in a multiphase system can be studied is called a phase diagram.

3.6 One component System

In a one component system,the value of F can be calculated by taking the minimum value of P=1 As c=1 for one component system, the phase rule

F=1-1+2=2

Thus, it is sufficient to know two variables namely temperature and pressure for studying the equilibrium between phases.

(b) The water system

The system consists of three phases namely ice, liquid water and water vapour. These three single phases may form four possible equilibrium as

(i) Soild ↔ liquid
(ii) Solid ↔ vapour and
(iii) Liquid ↔ vapour
(iv) Solid ↔ liquid ↔ vapour

The phase diagram for water system is obtained by plotting pressure against tempreture(fig.1)

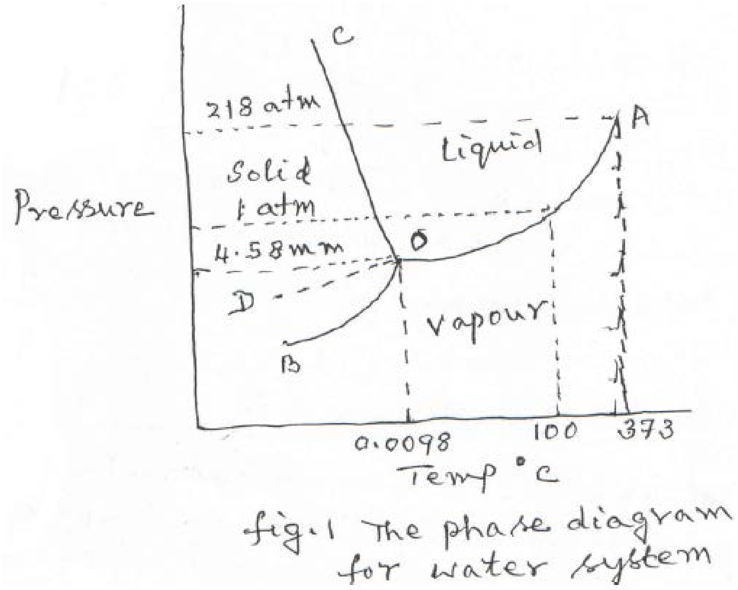

Figure 1: The phase diagram for water

The phase diagram consists of the following:

- Three stable curves OA,OB and OC and one meta stable curves OD.
- Three areas BOA,AOC and BOC and
- A definite point O

The above are discussed separately.

1.curves: (i) OA represents the vapour pressure curve of water. The vapour pressure of water increases with increase of temperature. The rate of increase of vapour pressure with temperature is higher at higher temperature and therefore the curve OA stands upward. The curve starts at the point o i.e the the freezing point 0.0098^0C at 4.58 mm pressure and terminates at A, The critical temperature (373^0C at 218 atm). Above the critical temperature only vapour phase exists .The phase rule.

$F=C-P+2=1-2+2=1$

Such equilibrium is characterized by only one degree of freedom i.e univariant.

(ii) OB is the sublimation curve.OB starts at the temperature 0.0098^0 above which ice cannot exist. Freezing point of water is 0^o C at 1 atm but is lowered by 0.0075 ^{0}C by 1 atm increase in pressure. when the pressure of water is lowered by 0.006 atm ,the freezing point is increased by 0.0075 ^{0}C. The water therefore freezes under its own vapour pressure at 0.0098^0C due to combined influence. The curve OB extends at B as the temperature decreases and the vapour pressure of ice becomes insignificant .The degree of freedom of ice becomes insignificant .The degree of freedom is one. Thus for each temperature, there may be one pressure and for each pressure there may be one tempreture.

(iii) OC represents the melting point or fusion curve ice. Along this curve two phases namely ice and water are in equilibrium. The line OC is inclined towards the pressure axis because the melting point of ice is slightly lowered by increase of pressure. As the melting point is accompanied by decrease in volume it should be lowered by the increase of pressure. The curve starts from 0 and extends upto a point corresponding to 2000 and -20^{0}C .The degree of freedom is one.

(iv)OD represents the meta stable curve. when water is cooled below its freezing point, the water is said to be super cooled.

2.Areas:- BOA,BOC and COA give the conditions of temperature and pressure under which single phase ie ice or liquid water or water vapour can exist. It is necessary to specify the both temperature and pressure to define a system within this area. These areas are bivariate.

3. Triple point: It is a point where all the three curves OA, OB and OC meet. At this point all the three phases are in equilibrium $\therefore$F=0 which shows that there is only one set of variables pressure, Temperature at which the three phases exist together. If any of the variables are changed then the number of phase decrease. The system is invariant at the triple point .The triple point o is a self defined point corresponding to a definite temperature and definite pressure.

3.7 Polymorphism

Existence of substances in more than one crystalline form possessing different physical properties is known as a polymorphic Substance and the phenomenon is called polymorphism .This phenomenon is observed in both elements and compounds .when it occurs in elements, it is known as allotropy.

The temperature at which one polymorphic form changes into other is called the transition temperature

Ex:- $\text{Sulphur}_{(\text{monoclinic})} \xleftrightarrow{95.60C} \text{Sulphur}_{(\text{rhombic})}$

The polymorphic form which undergo reversible transformation into one another at the transition temperature are called enantiotropic and the phenomenon is known as enantiotropy when polymorphic forms do not undergo reversible transformations into one another are said to be monotropic and the phenomenon is known as monotropy.

Ex:- white phosphorous can be transformed into red phosphorous under suitable conditions but reverse cannot takes place.

(b)The sulphur system

Sulphur exists in two solid modifications namely rhombic and monoclinic. These two solid phases along with the liquid sulphur and sulphur vapour gives a possibility of existence of four single phases. The four phases can never coexist together because according to Phase rule F in that case will be -1 which is impossible .Hence ,F=0 for a triple point representing three phases in equilibrium. The schematics representation of the phase diagram is given in the fig 2 .The diagram consists of six stable cureves BO,OA,AE ,OC,AC and CF and four metastable curves OD,OG,AD and CD .The curves divide the diagram into four areas BOCF ,BOAE,FCAE and the one enclosed by OCA.

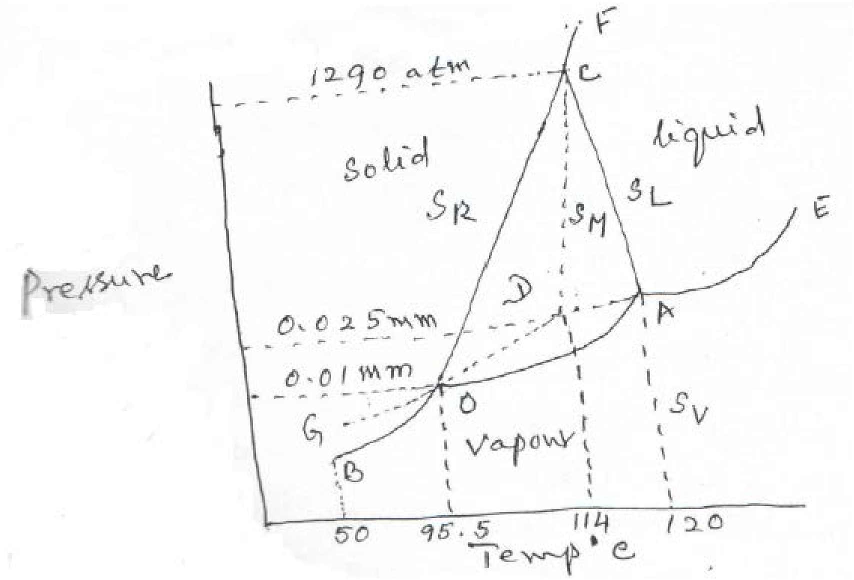

Figure 2: Sulphur system

1.Areas: They are bivariant because both the temperature and pressure are to be specified to locate any point in the areas .Each are represents the conditions for the stable existence of a single phase(P=1)

F=C-P+2

=1-1+2=2

In the are to the left of BOCF only rhombic sulphur (S_r) exists while in the area below BOBE only sulphur vapour(S_v) exists. Liquid sulphur(SL) is present to the right of FCAE and in the region OCA, Monoclinic sulphur(S_M)exists.

2.curves:(i) OB is the sublimation curve of S_R .The two phases present in equilibrium along this curve are S_R and S_V .The curve starts from O, the transmission temperature of S_R to S_M.

(ii) OA is the sublimation curve of S_M. The two phases present in equilibrium along this curve are S_M and S_V .The curve starts from the point A, melting point of S_M (120^0C) and ends at

0,the transition temperature of S_R(95.5^{0}C) only two phases S_V and S_M are in equilibrium at any point where three phases S_R ,S_M and S_V are in equilibrium F=1.

(iii) AE is the vapour pressure curve of liquid sulphur. Liquid sulphur(S_L) and sulphur vapour are in equilibrium along this curve F=1.

(iv) OC is a transition curve and represents the equilibrium between S_R and S_M and is obtained from the effect of pressure on the transition temperature of S_R. The curve ends at C after which S_M phase disappears.

(v) AC is the melting point curve of S_M .It represents equilibrium between S_M and S_L .If is obtained from the effect of pressure on the melting point of S_M. The curve is inclined Away from the pressure axis showing that the melting point is raised by the increase of pressure.The curve at C beyond which Sm ceases to exist. F =1

(vi) CD is the metastable melting point curve of S_R. This curve represents the equilibrium between S_R and S_L. Since the curve OC and AC meet at C it follows that if S_L is cooled at a pressure higher than 1290 atm, then S_R would crystalline at once .The curve passes through the point C and beyond this it becomes a stable melting point curve CF of S_R.

3. Triple point: O, A and C are the three stable triple points. At the point O, S_R, S_M and S_V are in equilibrium. If one of the variables is changed one of the phase disappears. A is triple point between SM,SV and S_L .Further, OC and AC interest at c to yield a three phase equilibrium between S_R ,S_M and S_L .At the triple points, the phase rule

$$F=C-P+2=1-3+2=0$$

Hence,the system is invariant

D is a meta stable triple point. At this point S_R, S_L and S_v are in equilibrium.

3.8 Summary of the unit

In general we normally need to state the values of only three variables, usually taken as composition and two of pressure, volume and temperature in order to define the state of a system. The variance, or number of degrees of freedom of a system, F is the number of such variables that may be varied independently without changing the number of phases present at equilibrium.

Systems for which F = 0 have no degrees of freedom and are said to be invariant. Changing the value of any of the properties that define the state of an invariant system will result in a change in the number of phases present.

Systems with one degree of freedom, F = 1, are univariant. For a univariant system, the value of one property may be adjusted without changing the number of phases. However, the values of all other properties then become fixed. For example, if the temperature of a univariant system is adjusted, then the values of the pressure, volume and composition must change in a particular way if the number of phases present is to remain the same. Systems with two degrees of freedom, F = 2, are bivariant. For these systems, the values of two properties may be adjusted independently without a change in the number of phases present. A bivariant system of different phases may therefore remain at equilibrium over a range of values of temperature and of pressure.

3.9 Key words

Phase Rule; Phase; Components; Degrees of freedom or variance; One component System; water system; sulphur system.

3.10 Reference for further study

1) Solid State Chemistry and its Applications; Anthony R. West; *John Wiley & Sons*, **2014**.

2) Engineering Chemistry; Dr. B.S. Chauhan; *Laxmi Publications, Ltd.,* **2008**.

3) Phase Rule; Gurdeep Raj; *Krishna Prakashan Media*.

4) A Textbook of Physical Chemistry, 4th ed. K K Sharma; *Vikas Publishing House Pvt Ltd*, **2009**.

5) The Phase Rule and Its Applications; Alexander Findlay; *Longmans, Green, and Company*, **1904**.

3.11 Questions for self understanding

1) Define the following terms
    i) Phase
    ii) Component
    iii) Degree of freedom

2) State the phase rule and discuss its application to the system of Water vapor and ice

3) Define the following terms
    i) Degree of freedom
    ii) Transition temperature
    iii) Heterogeneous system

4) Derive the diagram of the water system and explain the term triple point

5) Discuss the application of the phase rule for sulphur system

6) Explain the phase diagram of one component system defining terms involved

7) Explain how phase rule is helpful in studying heterogeneous equilibrium system

8) explain the term eutectic temperature

Unit-4

Structure

4.0 Objectives of the unit
4.1 Introduction
4.2 Two component system
    (a)The silver –Lead system
    (b)The Zine –Cadmium system
4.3 The three component system
4.4 Summary of the unit
4.5 Key words
4.6 Reference for further study
4.7 Questions for self understanding

4.0 Objectives of the unit

After studying this unit you are able to

- Apply the phase rule for two component system
- Apply the phase rule for three component system
- Explain the phase diagram of the silver –Lead system
- Explain the phase diagram of the Zine –Cadmium system

4.1 Introduction

The phase rule allows one to determine the number of degrees of freedom (F) or variance of a chemical system. This is useful for interpreting phase diagrams. $F = 2 + C – P$. Where F is the number of degrees of freedom, C is the number of chemical components and P is the number of phases in the system. The number two is specified because this formulation assumes that both T and P can be varied.

Phase diagrams are constructed by carrying out experiments under specified conditions of P, T and X. Minerals or compounds representing the system are mixed with each other in a capsule made of non-reacting material (e.g. Au or Pt), sealed, then placed in a furnace/ hydrothermal bomb/ piston cylinder, where they are allowed to reach a specific P and T. After a sufficient time period, the experiment is stopped, and the capsule is quenched to prevent the minerals/ liquids from back-reacting or re-equilibrating at lower P and T. The capsule is opened, and the phases are identified and analyzed chemically. Glass in the capsule would represent the melt that was in equilibrium with whatever minerals coexisting with it. Each experiment would therefore yield one point on a phase diagram. By plotting the results of many experiments, we are finally able to draw the various phase boundaries (often with some interpolation).

4.2 Two component system

A two component system can be defined as one in which it is possible to express the composition of all the phases in terms of two substances. A two component system may have F=3 when P=1 .Thus the system will have temperature, pressure and composition variable. Naturally a three dimensional model is required .But in actual practice, a simple diagram with two variables only is considered, the third variable is considered as constant. In most of the cases, it is convenient to keep the pressure constant at the atmospheric value and thus ,a temperature-composition diagram is used.

In case of systems consisting of only solids or liquids, there is a very little effect of charge of pressure on the systems. Such system is called condensed system. The phase rule,equation for a condensed system is $F^1=C-P+1$-----(9)

Equation (9) is the reduced phase rule equation.

(a)The silver –Lead system

The number of phases are (i) solid lead (ii) solid silver (iii) solution of lead and silver in the molten state and (iv)Vapour

According to reduced phases rule equation

F^1=C-P+1= 2-3+1=0 when p=3 , thus ,the maximum number of phase that can coexist would be there (other than vapour)

A number of compositions of silver and lead are prepared covering 0 to 100%. Each mixture is melted to form a liquid and then allowed to cool. A cooling curve is drawn between the temperature and time for each one of the mixture the temperature at which the mixture freezes is noted for all the compositions. The freezing points obtained from the cooling curves are plotted against the composition. The phase diagram obtained is shown in the fig3

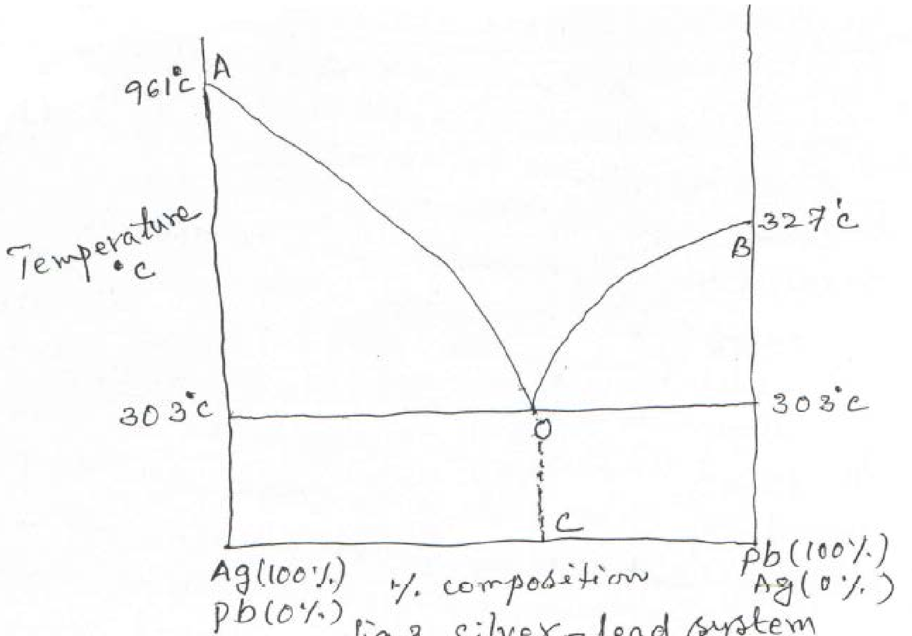

fig.3 silver–lead system

The equilibrium diagram consists of two curves OA and OB interesting at point O. Curves (i) OA represents the freezing point curve of silver to which successive small amounts of lead are added. Point A denotes the melting point of pure silver (961^o C) The melting point of silver is gradually decreased by the addition of lead into it. The added lead goes into the solution all along this curve and the separation of silver occurs when the point O is reached. At this point no more lead goes into the solution and hence the melting point of silver does into the solution and hence the melting point of silver does not fall any longer. Thus the point O represents the lowest possible temperature (303^0C) in the system that corresponds to a fixed composition

(C). The point O is called the Eutectic point .The system is univarient because two phase are present in equilibrium.

(ii) OB denotes the freezing point curve of lead to which successive small quantities of silver are added B represents the melting point of lead (327^0 C) addition of silver to lead decreases the melting point of lead. Along this curve the silver which is added goes into the solution while the separation lead takes place which continues till the point O is reached the system is univarient because two phases are present in equilibrium.

2.Eutectic point: O is the point at which OA and OB meet. At this point three phases are present namely solid silver and solid lead are in equilibrium with the fused mass – According to reduced phase rule equation

F^1 =C-P+1 = 2-3+1=0

The system is invariant .The point O denotes the lowest possible temperature (303^0 C) . Such a composition of two components- Ag and Pb which has the lowest freezing point compared to all other compositions is called Eutectic composition (Point C).The temperature corresponding to the Eutectic point Is called Eutectic points of pure components.

(b)The Zine –Cadmium system

A number of compositions of zinc and cadmium covering 0 to 100% are prepared. Each mixture is melted to form a liquid and then allowed to cool .A cooling curve is drawn between the temperature and time for each one of the mixture. The temperature at which the mixture freezes is noted for all the compositions. The freezing points obtained from the cooling curves are plotted against the composition. The phase diagram obtained is given in the fig.4

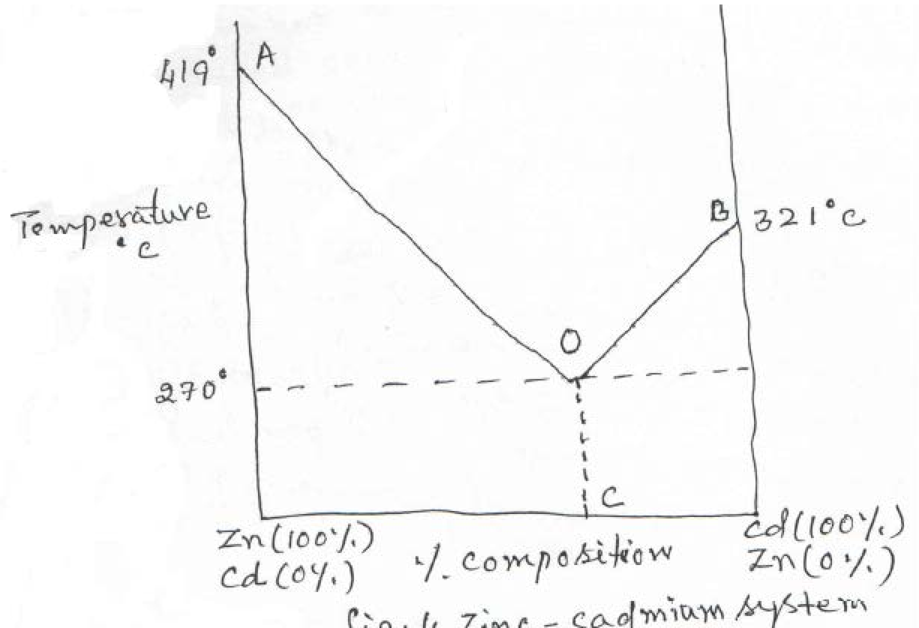

fig. 4 Zinc - cadmium system

Curves(i) AO represents the freezing point curve of zinc .A denoted the freezing point (melting point) of zinc(419^0 C).The melting point of zinc is lowerd by the addition of cadmium. Along AO solid is in equilibrium with the liquid solution of Cadmium and zinc $F^1 = C-P+1=2-2+1=1$

The system is univariant.

(ii) Bo denotes the freezing point curve of cadmium. The point B represents the melting point of pure cadmium (321^0 C). Melting point of cadmium is lowered on addition of zinc. Solid cadmium is in equilibrium with the liquid solution of zinc and cadmium along this curve.

So $F^1= C- P+ 1=2-2 +1 =1$

The system is uninvariant.

The Eutectic point; O is the point at which both OA OB meet. O is called the Eutectic point. At o the three phases namely solid zine, solid cadmium and solution are in equilibrium.

$F^1 = C- P+1=2- 3+1 = O$

The system is invariant The Eutectic composition is denoted by C and the Eutectic temperature is 270^0 C

Areas: areas above AO and BO, both the components are present as liquid solutions of different compositions. The solution being homogeneous,

P=1

So $F^1= C-P+1 +2 –1+1=2$

The system is bivariant.

If the solution in the areas above AO and BO is cooled, zinc and cadmium separates out respectively form the area above AO and form the area above BO

4.3 The three component system

In a ternary system, if all the three components form a homogeneous single phase, the degrees of freedom will be

$F=C-P+2 =3-1+2 = 4$

The four variables to be specified are temperature, pressure and the concentration of any two of the components. The procedure adopted is to consider a condensed system i.e at constant temperature and pressure. By fixing two variables, the remaining two independent variables are the concentration terms. A planar diagram can be used to indicate this condition. Triangular diagrams are most commonly employed. An equilateral triangle is taken, each side of which represents the concentration of one component in the mixture. In order to facilitate the plotting of composition in the triangular diagram, the sides of the triangle are divided into

10 or more equal parts and a series of lines are drawn parallel to the sides Thus, the number of properties are connected with the triangle makes it useful with respect to phase rule studies of ternary composition A representation of three component system C Gibbs- Roozeboom triangle) is shown in the fig .5

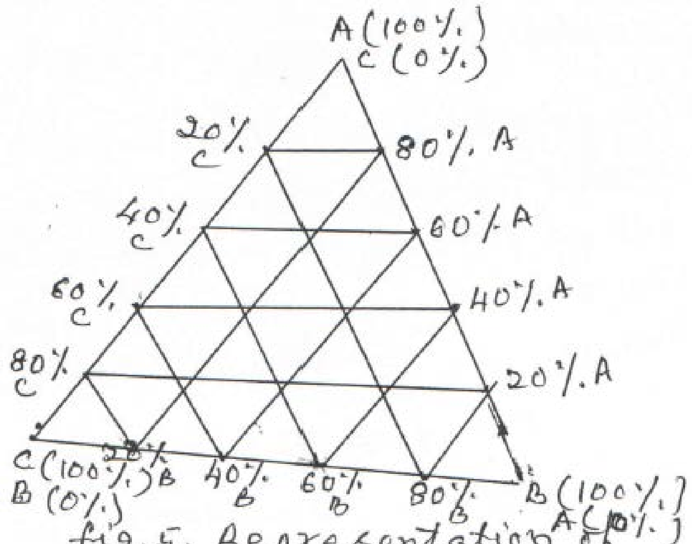

fig. 5. Representation of three component system

The corners of the triangle represent the pure components A.B and C respectively. The sides of the triangle opposite the corner labeled a for instance implies the absent the of A Thus, the horizontal lines across the triangle show increasing percentage of A from zero at the base to 100%. At the apex. Similarly the percentages of B and C are given by the distances from the other two sides to the remaining two apices. It is possible to read off the composition corresponding to any point from the three composition scales of the diagram. The total composition is always 100% because of sum of the three perpendicular distances from any point to the three sides of the triangle is always equal to the height of the triangle.

In a system of three liquids, there can be three possibilities depending on the nature of the substance

The three possibilities are:

(a) 1 pair of partially miscible liquids

(b) 2 pairs of partially miscible liquids

(c) 3 pairs of partially miscible liquids

The system, acetic acid-carbon tetra chloride water belongs to 1 pair of partially miscible liquid. The fig 6 gives the phase diagram for a system of acetic acid – carbontets chloride – water.

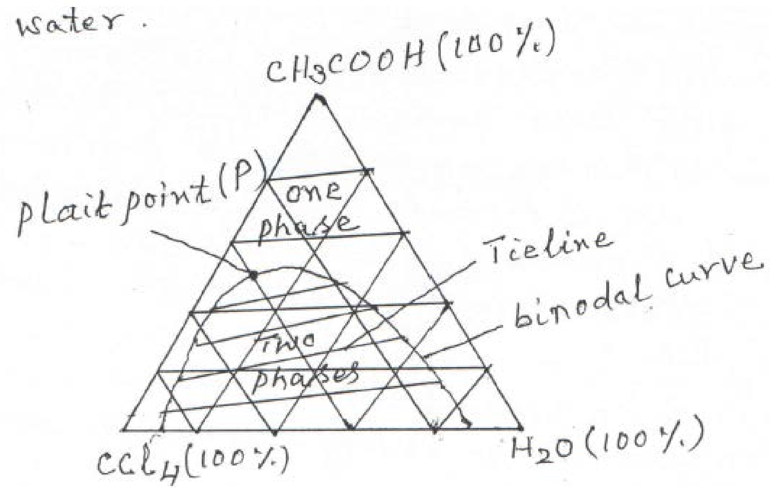

Figure 6: Phase diagram for CH_3COOH-CCl_4-H_2O

The natural solubility of a pair of partial miscible liquids may be markedly altered by the addition of a third component. In general, when the third component is soluble in only one of the two components, the mutual miscibility of the two liquids is diminished but when the third component dissolves readily in each of the other two components the mutual miscibility of the latter is increased. When water is added to a homogeneous mixture of acetic acid and carbon tetrachloride, a heterogeneous mixture of two liquid solution is formed.

Mixtures of acetic acid and carbon tetrachloride of varying compositions are prepared. These mixtures are maintained at a constant temperature. Water is taken in the burette. Rundown water in small quantities to a mixture of acetic acid carbon tetrachloride and shake well. Addition of waters is continued until the turbidity appears on shaking from the volume of water added and initial amount of acetic acid and carbon tetrachloride, the percentage composition of the mixture is calculated and the results are plotted on a triangular graph sheet (fig.6). the tie, lines through the two phase regions joining the composition of two phases which are in equilibrium. The tie lines are no longer horizontal because the miscibility of component in the other two components will be different. A unique point on the two phase boundary is shown by p. This point is called the plait point or isothermal critical point when various points representing the composition of the conjugated layers are joined, a bimodal curve is formed. Inside the bimodal curve there are two phases

F=C-P-3-2=1 at any point outside the bimodal curve, there is only one phase F=C-P-3-1=2. The shape of the bimodal curve varies with temperature since the mutual solubility also varies with temperature,

4.4 Summary of the unit

The simplest phase diagram is the water which is a one component system. It is also known as pressure-temperature or P-T diagram. Two phases exist along each of the three phase boundaries. At low pressure (0.006 atm) and temperature (0.01^0C) all the three phases coexist at a point called triple point. A binary phase is a two component system. Binary phase diagrams are most commonly used in alloy designing. The simplest binary system is the Cu-Ni which exhibits complete solubility in liquid and solid state. The line above which the alloy is liquid is called the liquidus line. At temperature just below this line crystals of solid solution start forming. The line below which solidification completes is called solidus line. Hence, only solid solution exists at any temperature below the solidus line. The intermediate region between liquidus and solidus lines is the two-phase region where liquid and solid coexist. It can be noted that the two metals are soluble in each other in the entire range of compositions in both liquid and solid state. This kind of system is known as 'Isomorphous' system.

4.5 Key words

Two component system; The silver –Lead system; The Zine –Cadmium system; three component system

4.6 Reference for further study

1) Solid State Chemistry and its Applications; Anthony R. West; *John Wiley & Sons*, **2014**.

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4.7 Questions for self understanding

1) Discuss the phase diagram of two component system for below systems
    (a)The silver –Lead system
    (b)The Zine –Cadmium system
2) Discuss the phase diagram for the three component system

Question Bnak

(a) What is ideal and non ideal solution?

(b) Show that enthalpy of mixing and volume of mixing are zero in the case of ideal solutions

(c) State Raoult’s law and show that the mole fraction of the solute is equal to relative lowering of pressure.

(d) What are colligative properties? Name them

(e) Derive ther relation between the Raolt’s law and molecular weight of solute.

(f) Define the terms (i) elevation in boiling point and (ii) depression in freezing point

(g) Define the relation between the fairing point elevation and molecular weight of solute.

(h) Derive the expression between the freezing point depression and molecular weight solute

(i) Define the terms (i) osmosis and (ii) osmotic pressure

(j) Derive the relation between osmotic pressure and vapour pressure

(k) State lechatecher principle

(l) Discuss briefly the quantitative treatment of lechatecher principle

(m) Define the terms activity and activity coefficient.

(n) Describe conductivity method of determining activity and activity coefficient

(o) Define the terms i) phase ii) component and iii) degrees of freedom

(p) Deduce phase rule from the concept of chemical potential.

(q) Discuss the phase rule for water system

(r) Discuss the phase rule for three component system.

Unit-5

Structure

5.0 Objectives of the unit
5.1 Introduction
5.2 Electrochemistry
5.3 Basic aspects
5.4 Conductivity
5.5 Faradays laws of electrolysis
5.6 Electrolytes
5.7 Arrhenius theory of electrolytic dissociation
5.8 Postulates of Arrhenius theory
5.9 Limitations of Arrhenious theory
5.10 Debye – Huckel theory of strong electrolytes
5.11 Mathematical Analysis of Debye – Huckel concept
5.12 Debye – Huckel- Onsager conductance equation
(a) Relaxation effect or asymmetric effect
(b) Electrophoretic effect
5.13 Validity of the Deby – Huckel – Onsager equation
5.14 Summary of the unit
5.15 Key words
5.16 References for further study
5.17 Questions for self understanding

5.0 Objectives of the unit

After studying this unit you are able to

- Define the electrochemistry
- Explain the Basic aspects of electrochemistry
- Define the conductivity
- Derive the Faradays laws of electrolysis
- Identify the difference between weak and strong electrolytes
- Derive the expression of Arrhenius theory of electrolytic dissociation
- Point out the limitations of Arrhenious theory
- Derive the mathematical Analysis of Debye – Huckel concept

5.1 Introduction

Electrochemistry is the study of changes that cause electrons to move. This movement of electrons is called electricity. In electrochemistry, electricity can be generated by movements of electrons from one element to another in a reaction known as a redox reaction or oxidation-reduction reaction. A redox reaction is a reaction which involves a change in oxidation state of one or more elements. When a substance loses its electron, its oxidation state increases, thus it is oxidized. When a substance gains an electron, its oxidation state decreases thus being reduced. The oxidation of Zn(s) into Zn^{2+} and the reduction of Cu^{2+} to Cu(s) occur spontaneously. In other words, the redox reaction between Zn and Cu^{2+} is spontaneous. This is caused by the difference in potential energy between the two substances. The difference in potential energy between the anode and cathode dictates the direction of electrons movement. Electrons move from area of higher potential energy to area of lower potential energy. In this case, the anode has a higher potential energy so electrons move from anode to cathode. The potential difference between the two electrodes is measured in units of volts. One volt (V) is the potential difference necessary to generate a charge of 1 coulomb (C) from 1 Joule (J) of energy.For a voltaic cell, this potential difference is called the cell potential, and is denoted E_{cell}.

5.2 Electrochemistry

Electrochemistry is the subject of physical chemistry which deals with the interrelation of chemical phenomena and electricity. It also deals with the study of electrical properties of solutions of electrolytes and with the elucidation of the relation between electricity in such system and chemical action. The phenomena encountered in electrochemistry are of such theoretical and practical importance. Electrochemical methods of chemical analysis example; electro analysis, condnctometry, potentiometry, Polarography and other methods have been developed.

5.3 Basic aspects

There are two types of substances namely conductors and non conductors. Conductors are those through which electric current can easily pass.

Eg: Metals such as copper, silver etc, solutions of salts, acids, bases etc.

Non conductors are those which do not allow the current to flow through

Eg: Mica, wax, glass etc.

There are two types of conductors namely electronic and electrolytic conductors.

Electronic conductors are those where the electricity is carried exclusively by the transport of electrons. Electron flow from a higher negative Potential to a lower negative potential and there is no transport of matter.

Eg: Metals etc

In electrolytic conductors, the flow of current is accompanied by actual transfer of matter. Such transfer of matter leads to the decomposition of matter at the points where electricity enters or leaves the electrolyte and in the process helps in the transfer of electrons. The electrolytes may be pure substances in fused states such as fused salts, acids, bases etc.

The flow of electric current in both types of conductors is governed by ohm’s law. In electronic conductors, there is no chemical change and in electrolytic conductors there occurs decomposition when the current is passed.

If the temperature is increased, the conductivity of electronic conductors decreases best that of the electrolytic conductors increases.

The decomposition of the electrolyte due to the passage of electrolyte is called electrolysis the current usually enters or leaves the electrolyte through some strips of metals, these are called electrodes, *The one through which the current enters is called the anode and the one through which current leaves is called the cathode*. Electrolysis takes place only on the electrodes and not throughout bulk of the electrolyte.

5.4 Conductivity

The resistance of an electrolytic conductor can be determined by the application of ohm's law According to ohm's law

$$I = \frac{E}{R} \text{ -------- } (1)$$

Where 'I' is the strength of electric current flowing through a resistance 'R' under an applied potential 'E'. *The reciprocal of the resistance of a solution is called the conductance and the reciprocal of specific resistance is called the specific conductance (K)*; where k is the conductance of ions in l cc of the solution

$$\text{Thus conductance} = \frac{1}{R} \text{ - ----- } (2)$$

$$K = \frac{X}{R} = \frac{l}{a}\,\frac{1}{R} \text{ - ----- } (3)$$

Where X is the cell constant which is equal to $\frac{l}{a}$; where ι is the distance between the two electrodes in cm and a is the area of each in sq. cm. The cell constant of a conductivity cell is determined experimentally by measuring the conductance of aqueous solution of KCl of Knows specific conductance. The unit of cell constant is $cm^{-1,}$

Equivalent conductance is the conductance of all the ions in a solution containing one gm equivalent of the electrolyte. So, if the volume of this solution is V liters

$$\wedge = KV \text{ -------- } (4)$$

If C is the concentration in equivalents per litre, then the concentration per cc is $\frac{C}{1000}$ and the volume containing one gm equivalent of the electrolyte is there fore

$$V = \frac{1000}{C} \text{ ------- } (5)$$

Molar conductance is the conductance of all ions in a solution containing one gm mole of the electrolyte.

Hence, Equation (4) can be written as

$$\wedge = \frac{1000K}{C} \text{ -------- } (6)$$

Unites

The unit of resistance is ohm (Ω)

Conductance in ohm^{-1} or mho (Ω^{-1})

The S I unit of conductance is siemens (S)

(I S = 1 Ω^{-1})

Equivalent conductance increases with dilution and reaches a constant value infinite dilution (^ $_\infty$ or ^$_o$)

According to kohlrausech law

$$\Lambda_0 = \Lambda_+^0 + \Lambda_-^0 ----------(7)$$

Where Λ_+^0 and Λ_-^0 are called ionic conductance of cations and anions. For each ion, it is constant in a given solvent at a given temperature.

The ability of an electrolyte to transport current and hence its conductance depends on

(i) The number of ions

(ii) The charge on the ions and

(iii) The speed of ions.

The speed with which an ion moves depends on applied potential gradient. If the applied potential gradient is unity (volt/cm), the speeds of ions are known as the mobilities of ions

Let u_+^0 *and* u_-^0 are the actual velocities of ions at infinite dilution under unit potential gradient.

$$\Lambda_+^0 = Fu_+^0 \text{ and } \Lambda_-^0 = F\,u_-^0$$

$$\therefore \Lambda_0 = F(u_+^0 + u_-^0) ----- (8)$$

For a solution of finite concentration it is possible to write

$$\wedge = \wedge_+ + \wedge_-$$

$$\wedge_0 = \alpha F(u_+ + u_-) --------(9)$$

Where α is the true degree of dissociation of the electrolyte ot that concentration

$$\Lambda_0 = F(u_+^0 + u_-^0)$$

$$\Lambda = \alpha F(u_+ + u_-)$$

$$\therefore \frac{\Lambda}{\Lambda_0} = \frac{\alpha F(u_+ + u_-)}{F(u_+^0 + u_-^0)} ----(10)$$

For a weak electrolyte, $(u_+^0 + u_-^0) \approx (u_+ + u_-)$

$$\therefore \quad \alpha = \frac{\wedge}{\wedge o} \text{ ------- } (11)$$

$$Again, \Lambda = \Lambda_+ + \Lambda_- = \alpha F(u_+ + u_-)$$

$$\therefore \Lambda_i = \alpha F u_i$$

$$\Lambda_i^0 = F u_i^0$$

$$\frac{\Lambda_i}{\Lambda_i^0} = \frac{\alpha u_i}{u_i^0}$$

$$\alpha = \frac{\Lambda_i}{\Lambda_i^0}, \frac{u_i^0}{u_i} ------(12)$$

Conductivity water

Conductivity water should be used in preparing the solutions for conductivity experiments. The purest water has a specific conductance of about 5.0×10^{-8} ohm^{-1} at 18^0 C

5.5 Faradays laws of electrolysis

The two laws put forward by Faraday are stated as follows:

(i) **I law-** The amount of chemical change which occurs at any electrode is proportional to the quantity of the electricity passed through the electrolyte.

Suppose Q coulombs of electricity is passed through an electrolyte, W gm of substance is deposited. Then

$$W \ \alpha \ Q$$

$$W = Z\,Q$$

$$= Z\,I\,t \text{ ------ } (13) \qquad [\text{since } Q = It]$$

Where Z is the propersonality constant known as the electrochemical equivalent, I is the current in amp and t is the time in sec. Thus every substance has a definite electrochemical equivalent.

(ii) **II law-** If the same quantity of electricity is passed through different electrolytes, the different amounts of chemical changes produced are all chemically equivalent.

The quantity of electricity required to liberate 1.008 g of hydrogen or deposit 107.88 g of silver has been found to be 96500 coulombs. This quantity has been named as Faraday.

Thus one Faraday = 96500 coulombs.

5.6 Electrolytes

Electrolytes were classified into two groups namely

(i) strong electrolytes and

(ii) weak electrolytes.

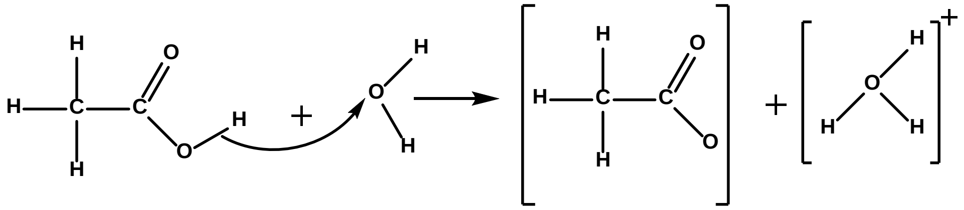
This division was made purely on the basis of conductivities of the solutions of these substances in water. Thus, NaCl, KCl etc were regarded as strong electrolytes because their aqueous solutions were highly conducting and acetic acid, formic acid etc, were considered as weak electrolytes due to the poorly conducting nature of their aqueous solutions. But it was soon discovered that acetic acid behaves like NaCl when it was dissolved in liquid ammonia so this type of classification of electrolytes is considered to be obsolete.

The most recent classification of electrolytes is again into two categories,

i) True electrolytes or ionospheres (ionophoric = bearer of ions) and

ii) Potential electrolytes or ionogens (ionongens = ion producers).

All ionic crystals are true electrolytes. When they are heated, the ionic lattice is dismantled and the pure molten true electrolyte shows considerable ionic conductance. X–ray diffraction studies of gaseous acetic acid have revealed that it contains separate neutral molecules and the bonding of the atoms inside these molecules is essentially nonionic. These neutral molecules retain their identity and separate existence when the gas condenses to give liquid acetic acid. Here, there are hardly any ions in liquid acetic acid and there fore little conductivity. But when acetic acid is dissolved in water an interesting phenomenon occurs; ions are produced and so the solution conducts electricity. When acetic acid molecule collides with a water molecule, the H of the acetic acid OH group is transferred form the oxygen atom of the OH to the oxygen atom of H_2O. A proton will be transferred from CH_3 COOH to H_2O.



The result of the proton transfer is that two ions have been produced, (i) an acceptation and (ii) a hydrated portion . Thus potential electrolytes dissociate into ions by inorganic or ion forming chemical reactions with solvent molecules; in contrast the true electrolytes which given rise to ionic solutions by physical interactions between ions present in the ionic crystal and solvent molecules

5.7 Arrhenius theory of electrolytic dissociation

Arrhenius (1887) put forward the theory of electrolytic dissociation which forms the basis of modern treatment of electrolytes

5.8 Postulates of Arrhenius theory

(i) When an acid, base or salt is dissolved in water a considerable portion becomes spontaneously dissociated into positive and negative ions.

Suppose MA is an acid or a base or a salt

$$MA \leftrightarrow M^+ + A^-$$

(ii) On passing electricity the ions migrate towards the electrodes of apposite sign.

(iii) The electrolyte solution as whole in electrically neutral

(iv) The fraction of the total number of molecules of the electrolyte that dissociates into ions is called the degree of dissociation or ionization.

(v) The fraction of molecules which dissociate into ions vary with the concentration and the fraction of the total electrolyte split up into ions was considered to approach unity at infinite dilution, in other words, in extremely dilute solutions almost the whole of the acid, base or salt is dissociated into ions.

Suppose a solution of electrolyte contains n molecules in a given volume and each molecule splits up into γ number of ions. It α is the degree of ionization, there will be $n(1-\alpha)$ un-dissociated molecules and $\gamma\ \alpha n$ ions in solution ie a total of $n(1-\alpha + \gamma\alpha)$ particles.

Suppose there is no dissociation, the osmotic pressure of the solution will be proportional to n. But there are actually $n(1-\alpha + \gamma\alpha)$ particles in the given volume,

The van't Hoff factor (i) is the ratio of the observed to the calculated osmotic pressure which is given by

$$ί = \frac{n(-\alpha+\gamma\alpha)}{n} = 1-\alpha + \gamma\,\alpha$$

$$ί = \alpha(\gamma-1)$$

$$\therefore\ \alpha = \frac{(i-1)}{(\gamma-1)} \quad \text{----(14)}$$

The value of ί for any solution can be calculated from any of the colligative properties. Arrhenius used this ratio of observed to calculated freezing point depressions and using equation (14), he calculated the degree of dissociation of various electrolytes at different concentrations He found the values of α by conductance measurement. The agreement between the two sets of values was regarded as the strong evidence for the theory of electrolytic dissociation

5.9 Limitations of Arrhenious theory

(a) Arrhenius theory is satisfactory for weak electrolytes. However, when applied to strong electrolytes many anomalies and inconsistencies arise. Some of the important discrepancies are,

(i) The degree of dissociation obtained from conductance measurement and form colligative properties are in poor agreement for strong electrolytes.

(i) Oswald's dilution law which is derived on the basis of Arrhenius theory is not obeyed by strong electrolytes

(ii) This theory assumes the existence of ions but does not take into account the electrostatic attractions between ions

(b) Arrhenius suggested that ionization of the electrolyte takes place when dissolved in water. However, X ray studies have shown that many electrolytes are already in the ionized state.

5.10 Debye – Huckel theory of strong electrolytes

The equivalent conductance of an electrolyte depends on

(í) The number of ions

(ii) The charge on the ions and

(ííí) The speed of the ions,

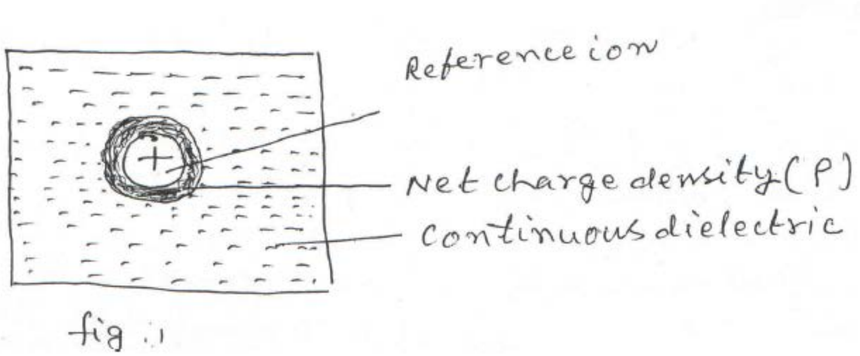
For a given electrolyte, the charge on the ions is constant so, the variation of equivalent conductance of an electrolyte with concentration is either due to the number of ions or the change in the velocity of ions or both. Arrhenius made an assumption that the speed of the ions is independent of the concentration of the solution, the change in the equivalent conductance would then be due to the change in the number of ions produced from one equivalent of electrolyte as a result of change in concentration This view fits well in the case of potential electrolytes but as true electrolytes are ionic crystals, they dissociate completely even at moderate dilutions Hence, the variation of equivalent conductance with dilution will then be only due to the change in the speed of ions in true electrolytes the mutual interaction of the oppositely charged ions result in a considerable decrease in the velocities of ions as the concentration of the solution is increased. In solutions of potential electrolytes the number of ions per unit volume is relatively small and so, the effect of ion-ion interaction will also be small.

Though many leading electrochemists Noyes (1904), Sutherland (1906), Bjerrum (1909) and Milner (1912) tried to explain the possibility of the attractive forces between ions might have some influence on electrolytic conduction, the quantitative treatment of this concept is mainly due to the work of Debye and Huckel (1923) and its extension chiefly by Onsager and Falkenhagen (1926)

The essential postulate of Debye – Huckel theory is that every ion may be considered as being surrounded by an ionic atmosphere of opposite sign. This ionic atmosphere can be considered to be arising in the following way:

Let us consider an aqueous solution of sodium chloride containing 10^{-3} moles/litre Thus the solution contains $6.023\times10^{23}\times10^{-6}$ Na^+ per cc and an equal number of cl^- per cc together with the corresponding number of water molecules Nature takes these $2\times6.023\times10^{17}$ ions per cc and arrange them so that there is a particular time average spatial distribution of the ions. The genius of Debye and Hukel lay in their formulation of a very simple but a powerful model for the time average distribution of the ions in very dilute solution of electrolytes. The electrolytic solution consists of solvated ions and water molecules. The first step in the Debye- Huckel’s approach is to select arbitrarily any one in out of the assembly and call it the reference or central ion. only the reference ion is given the individuality of a discrete charge. The water molecules are looked upon as a continuous dielectric medium the remaining ions except the central ion is lapsed into ananimity, their chargers being smeared out into a continuous spatial distribution of charge whenever the concentration of ion of a particular sign exceeds that of opposite sign there will arise a net or excess charge in the particular region under consideration obviously the total charge in the atmosphere must be of apposite sign and exactly equal to the charge on the reference ion.

Thus, the electrolytic solution is considered to consist of a central ion standing alone in the continuum of water molecules (fig.1)



This continuum acquires a deictic constant. The charges of the discrete ions which populate the environment of the central ion are thought of as smoothed out and contribute to the continuum dielectric a net charge density (excess charge Per unit volume). Thus, water enters the analysis in the guise of a dielectric constant (D) and the ions except the central ion in the form of an excess charge density (P). So the complicated problem of the time average distribution of ions inside an electrolytic solution reduces in the Debye-Huckel model to mathematically simpler problem of finding how the excess charge density (P) varies with distance v from the central ion. It should however be noted that the electrolytic solution as a whole is electrically neutral ie P = O, but P ≠ O everywhere. This is because a positive reference ion will exert an attraction for negative ions, hence there should be a greater aggregation of negative ions than of positive ion in the neighborhood and so P ≠ O. At the same time thermal forces will be knocking the ions about in all directions and bringing to establish electroneutrality i.e to make P = O. Thus, the time charge of the electrostatic forces of ordering and the thermal forces of disordering is a local excess of negative charges near the positive ion and an excess of positive charges near the negative ion. Of course the excess positive charge near a negative ion will compensate the excess negative charge near at a positive ion and over all effect is electroneutrality ie P = O for the whole solution.

5.11 Mathematical Analysis of Debye – Huckel concept

Let us consider a small volume element dv situated at a distance r form the arbitrarily selected central ion and let the charge density inside the volume element be P. (fig.2) Let the average electrostatic potential in the volume element be ψ These two quantities, p and ψ are related by poisson's equation

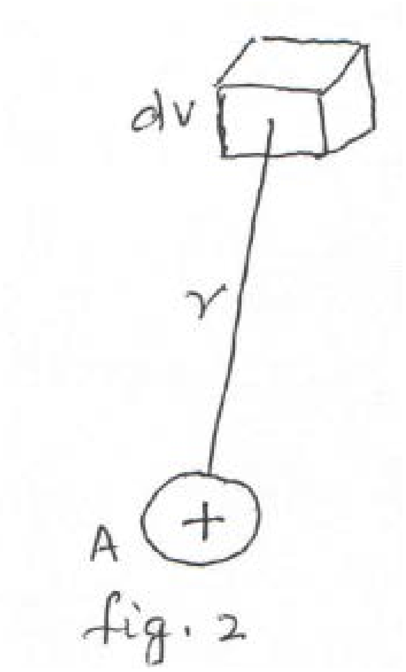


fig. 2

$$\frac{1}{r^2}\quad\frac{d}{dr}\ (r^2\ \frac{d\psi}{dr})\ = -\ \frac{4\Pi p}{D}\qquad \text{---- (15)}$$

Where D is the dielectric constant of the medium. The work required to bring a positive ion from infinity upto the volume element is $Z_+ \varepsilon\ \psi$ and to bring a negative ion is $-Z_-\ \varepsilon\ \psi$ where Z_+ and Z_- are the valence of positive and negative ions respectively and t is the electronic charge

If the Boltzmann law of distribution of particles in a field of varying potential energy is applicable to ions, the time average number of positive ions (dn_+) and of negative ions (dn_-) present in the volume element dv are given by

$$d_{n_+} = n_+ e^{-\left(Z_+\varepsilon\psi / RT\right)} dv$$

$$d_{n_-} = n_- e^{-\left(Z_-\varepsilon\psi / RT\right)} dv$$

Where n_+ and n_- are the total numbers of positive and negative ions present in unit volume of the solution

The charge density in the volume element is

$$p = \frac{\varepsilon\left(z_+ dn_+ - z_- dn_-\right)}{dv}$$

Substituting the values of dn_+ and dn_-

$$p = \varepsilon\left(n_{+}z_{+}e^{-z_{+}\varepsilon\psi/RT} - n\_z\_e^{z\_\varepsilon\psi/RT}\right) ------(16)$$

For a uni – uni valent electrolyte, $Z_+ = Z_- = 1$ and

$n_+ = n_- = n$

Equation (16) can be written as

$$p = \varepsilon n\left(e^{-\varepsilon\psi/RT} - e^{\varepsilon\psi/RT}\right)$$

Put $x = \frac{\varepsilon\psi}{RT}$; and expend the two exponential series, we get

$$P = -\ \varepsilon x\ 2n\ (1+\frac{x^2}{3!}+\frac{x^4}{5!}+\ldots\ldots\ldots)$$

$$P = \frac{\varepsilon^2\psi}{RT}\ 2n\ (1+\frac{x^2}{3!}+\frac{x^4}{5!}+\ldots\ldots\ldots\ (17)$$

Neglecting the terms involving χ^2, χ^4 etc in egn (17)

We get $P= -\ \frac{\varepsilon^2\psi}{RT}\ 2n$ ------- (18)

In a general case where Z_+ and Z_- are not equal to unity, if the assumption is made that $Z\varepsilon\psi/RT$ is very much smaller than unity, the expression for the charge density becomes

$$P= -\ \frac{\varepsilon^2\psi}{RT}\ \Sigma\, n_i\, Z^2_i \text{ -------} \qquad (19)$$

Where n_i and Z_i represent the number and valence of ions of the ith kind. This is a general equation applicable to different types of ions

Substituting the value of P in eqn (15)

$$we\, get \frac{1}{r^2}.\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \frac{4\pi\varepsilon^2}{DRT}\psi\sum n_i z_i^2$$

$$= k^2\psi ------(20)$$

$$where\, k^2 = \frac{4\pi\varepsilon^2}{DRT}\sum n_i z_i^2$$

The eqn (20) is known as the linerized poission Boltzmann equation. This differential equation .

$$\psi = -\frac{Ae^{-kr}}{r} + \frac{A^1e^{kr}}{r} ------(21)$$

Where A and A^1 are constants. To evaluate the values of the constants A and A^1, the boundary conditions can be applied ie when r= ∞, 'ψ =0, but this can happen only when $A^1 = 0$

$$\therefore \psi = \frac{Ae^{-kr}}{r} ----- (22)$$

To evaluate the constant A, a hypothetical condition will be considered in which the solution is so dilute and on an average the ions so far apart that there is a average the ions are so far apart that there is a negligible interionic field. Further, the central ion is assumed to be a point charge1, Hence, the potential near the central ion is simply due to an isolated point charge of value z;t

$$\therefore \ \psi = \frac{z_i\varepsilon}{Dr} \text{ ------- } (23)$$

For a dilute solution, Σ ní $Z^2{}_{\text{í}}$ is almost zero

$\therefore$ k=0 Hence eqn (22) becomes

$$\psi = \frac{A}{r} -------- (24)$$

Comparing equations (23) and (24), we get

$$\frac{A}{r} = \frac{Zit}{Dr} \text{ or } A = \frac{Zi\varepsilon}{D}$$

Substituting for a in eqn (22), we get

$$\psi \ = \frac{Zi\varepsilon}{Dr} \ .e^{-kr} \text{ ------ } (25)$$

The eqn (25) can be written as

$$\psi \ = \frac{Zi\varepsilon}{Dr} - \frac{Zi\varepsilon}{Dr}\left(1-e^{-kr}\right) \text{--------- } (26)$$

If the solution is very dilute,

$$\therefore \left(1-e^{-kr}\right) \approx kr$$

$$\therefore \ \psi = \frac{Zi\varepsilon}{Dr} - \frac{Zi\varepsilon}{Dr} \ . \ kr$$

$$\psi = \frac{Zi\varepsilon}{Dr} - \frac{Zi\varepsilon k}{D} \ - (27)$$

The first term on the right hand side of eqn (27) is the potential at a distance r due to a given point ion when there are no surrounding ions. The second term must therefore represent the potential arising form the ionic atmosphere.

So, the potential due to the ionic atmosphere is

$$\psi_i = - \frac{z_i \varepsilon k}{D} \text{ -------- 28) for a dilute solution.}$$

It should be noted that this expression is independent of r and so, it may be assumed to hold good when r=0 so that the potential on the ion itself due to the surrounding atmosphere is = - $\psi_i = -\frac{z_i \varepsilon k}{D}$. The charge of the ionic atmosphere is $-Z_i\varepsilon$ since it equal in magnitude and opposite in sign to that of the central ion itself is placed at a distance 1/k form the ion, the potential produced at it would be $-\frac{z_i \varepsilon k}{D}$ which is identical with eqn (28) Therefore, it is seen that the effect of the ionic atmosphere is equivalent to that of a single charge of the same magnitude placed at a distance 1/k form the ion. The quantity, 1/k is thus regarded as a measure of the thickness of the ionic atmosphere in a given solution (1/k is also known as radius of the ionic cloud or Debye – Huckel reciprocal length)

According to the definition of --------

$$k = \left(\frac{4\pi\varepsilon^2}{DRT} \quad \sum n_i x_i^2 \right)^{1/2}$$

or $$\frac{1}{k} = \left(\frac{DRT}{4\pi\varepsilon^2} \quad \frac{1}{\sum n_i z_i^2} \right)^{1/2} - - - - - (29)$$

The thickness of the ionic atmosphere will depend on the number of ions of each kind and on their valence.

If C_i is the concentration of the ion of the $ί^{th}$ kind in moles/litre

$n_i = \frac{C_i N}{1000}$, where N is the Avogadro number

substituting the value of n_i in eqn (29)

we get $$\frac{1}{k} = \left(\frac{DRT}{4\pi\varepsilon^2} \frac{1}{\sum \frac{c_i N}{1000} Z_i^2} \right)^{1/2}$$

$$= = \left(\frac{DRT}{4\pi\varepsilon^2} \frac{1000}{\sum c_i Z_i^2} \right)^{1/2}$$

We know that $\Re = 1.38 \times 10^{-16}$ erg/deg, N= 6.023×10^{23} and $\varepsilon = 4.802 \times 10^{-10}$ esu substituting the above values in egn(30) and on simplification, we get

$$\frac{1}{k} = 2.81 \times 10^{-10} \left(\frac{DT}{\Sigma c_i Z_i^2} \right)^{1/2} \text{ cm}$$

For water at 25· c, D = 78.6 and T = 298 K

$$\frac{1}{k} = \frac{4.31 \times 10 - 8}{\left(\sum c_i z_i^2 \right)^{1/2}} \text{ cm ---(31)}$$

So, the ionic atmosphere will be 10^{-8}cm thick and it decreases with increase in concentration and increase in valence of ions. However, $\frac{1}{k}$ increases as dielectric constant and temperature are increased.

5.12 Debye – Huckel- Onsager conductance equation

If the ion is stationary with respect to the solvent, the ionic atmosphere will also remain stationary and it will be spherically symmetrical However, when the ion is under the influence of an applied electric field i.e when the ion moves say to the right, it will constantly have to build up its ionic atmosphere to the right, while the charge density to the left gradually decays. The rate at which the atmosphere to the right forms and that to the left dies ways is expressed in terms of a quantity called the time of relaxation of the ionic atmosphere.

Debye – Huckel theory explains the increase in conductance of strong electrolytes with dilution based on the following:

(a) Relaxation effect or asymmetric effect

In a dilute solution of a true electrolyte, every ion is surrounded by a symmetrical ionic atmosphere. But when this solution is subjected to an electric field, the ions will move towards the electrodes. The ionic atmosphere surrounding a moving ion is not symmetrical. The charge density behind the ion will be greater than in front. This asymmetry of the ionic atmosphere will result in a retardation of the ions moving under the influence an applied field. This influence on the speed of an ion is called the relaxation effect or asymmetry effect onsager modified the equation deduced by Debye and Huckel for the relaxation force by taking the Brownian movement of the ions into consideration as

$$\text{Relaxation force} = \frac{\varepsilon^3 Z_i k}{6D\Re T} wV \quad \text{---------(32)}$$

$$\text{Where } w = Z_+ Z_- \frac{2q}{1+\sqrt{q}}$$

$$\text{and the value of } q = \frac{Z_+ Z_-}{Z_+ Z_-} \quad \frac{\lambda_+ + \lambda_-}{Z_-\lambda_+ + Z_+\lambda_-}$$

(b) Electrophoretic effect

There is yet another factor which tends to retard the motion of an ion in solution. This is the tendency of the ionic atmosphere with its associated solvent molecules to move in a direction opposite to that in which the reference ion is moving. An additional retarding influence equivalent to an increase in the viscous resistance of the solvent is thus exerted on the moving ion. This is known as electrophoretic effect. Since it is analogous to the resistance acting against the movement of a colloidal particle in an electric field by considering the applicability of stokes low to the movement of an ion in solution, Debye and Huckes calculated the electrophoretic force as

$$\text{Electrophoretic force} = \frac{\varepsilon Z_i k}{6\pi\eta} k_i V \quad \text{------- (33)}$$

Where K_i is the coefficient of frictional resistance of the solvent opposing the motion of the ion of i^{th} kind. Onsager derived the same result in an alternate way without applying the stokes law in the immediate vicinity of the ion.

Now, let us equate the forces acting on an ion of i^{th} kind when it is moving through a solution with a steady velocity u_i

The driving force on the ion is $\varepsilon z_i V$ this is opposed by the frictional force of the solvent $k_i u_i$ together with the electrophoretic and relaxation forces.

$$\varepsilon z_i v = k_i u_i + \frac{\varepsilon z_i k}{6\pi\eta} k_i v + \frac{\varepsilon^3 z_i k}{6D\Re T} wV$$

Dividing the above equation by K_i V_i we get

$$\frac{\varepsilon z_i}{k_i} = \frac{u_i}{v} + \frac{\varepsilon z_i k}{6\pi\eta} + \frac{\varepsilon^3 z_i k}{6D\Re T}\frac{w}{k_i}$$

$$\frac{u_i}{v} = \frac{\varepsilon z_i}{k_i} - \frac{\varepsilon z_i k}{6\pi\eta} - \frac{\varepsilon^3 z_i k}{6D\Re T}\frac{w}{k_i} ------(34)$$

Taking V = $\frac{1}{300}$ esu = 1 volt/cm

Equation (34) becomes

$$u_i = \frac{\varepsilon z_i}{300k_i} - \frac{\varepsilon\ k}{300}\left[\frac{z_i}{6\pi\eta} + \frac{\varepsilon^2 z_i}{6D\Re T}, \frac{w}{k_i}\right] ----(35)$$

At finite dilution k=0

$$\therefore u_i^0 = \frac{\varepsilon z_i}{300k_i} ---------(36)$$

$$\Lambda_i^0 = Fu_i^0\ ;\ u_i^0 = \frac{\Lambda_i^0}{F} -------- (37)$$

Comparing equation (36) and (37)

$$\frac{\Lambda_i^0}{F} = \frac{\varepsilon z_i}{300k_i} -------- (38)$$

$$u_i = \frac{\Lambda_i}{\alpha F} -----------(39)$$

Inserting equations (38) and (39) in egn (35)

We get

$$\frac{\Lambda_i}{\alpha_F} = \frac{\Lambda_i^0}{F} - \frac{\varepsilon k}{300}\left[\frac{z_i}{6\pi\eta} + \frac{\varepsilon^2 z_i}{6D\Re T}\frac{w}{K_i}\right]$$

If the assumption is made that the electrolyte is completely dissociated ie α =1

$$\Lambda_i = \Lambda_i^0 - \frac{\varepsilon k}{300}\left[\frac{z_i F}{6\pi\eta} + \frac{\varepsilon^2 F z_i}{6D\Re T}\frac{w}{K_i}\right] ------(40)$$

According to egn (38)

$$\Lambda_i^0 = \frac{\varepsilon z_i F}{300 K_i} \ or \ \frac{\varepsilon z_i F}{K_i} = 300\Lambda_i^0$$

Inserting in egn (40), we get

$$\Lambda_i = \Lambda_i^0 - \frac{\varepsilon k}{300}\left[\frac{z_i F}{6\pi\eta} + \frac{300\varepsilon\Lambda_i^0 w}{6D\Re T}\right] ----(41)$$

$$As\, k = \left(\frac{4\pi\varepsilon^2 N}{D\Re T}\frac{\sum c_i z_i^2}{1000}\right)^{1/2}$$

Substituting the value of K in egn (41) and inserting the values for $\Re$ ε and N and on simplification

We get

$$\Lambda_i = \Lambda_i^0 - \left[\frac{29.15 z_i}{(DT)^{1/2}\eta} + \frac{9.9\times10^5}{(DT)^{3/2}}\Lambda_i^0 w\right]\sqrt{C_+Z_+^2 + C_-Z_-^2} ------(42)$$

By replacing C_+ and C_-, the concentrations of ions in modes/llitre by C, the concentration in gm equivalents per litre which is the same for both the ions. Then

$$\Lambda_i = \Lambda_i^0 - \left[\frac{29.15 z_i}{(DT)^{1/2}\eta} + \frac{9.9\times10^5}{(DT)^{3/2}}\Lambda_i^0 w\right]\sqrt{C(Z_+ + Z_-)} ------(42)$$

or

$$\Lambda = \Lambda^0 - \left[\frac{29.15(Z_+ + Z_-)}{(DT)^{1/2}\eta} + \frac{9.9\times10^5}{(DT)^{3/2}}\Lambda^0 w\right]\sqrt{C(Z_+ + Z_-)} -----(43)$$

For a simple case of uni- univalent electrolyte

Z $_+$=Z$_-$=1 $\therefore w = 2 - \sqrt{2}$

$$\therefore \Lambda = \Lambda^0 - \left[\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.2 \times 10^5}{(DT)^{3/2}} \Lambda^0 \right] \sqrt{C} - - - - - (44)$$

Equations (42), (43) and (44) represent various forms of Debye – Huckel – Onsager equation.

This equation is based on the assumption that dissociation of the electrolyte is complete. Attempt to account for the falling off of the equivalent conductance at appreciable concentrations in terms of a decrease in the ionic velocity resulting form inter ionic forces. The decrease of conductance due to these forces is represented by the quantities in the square brackets. The first term in the bracket give the effect due to the electrophortic effect and the second represents the influence of relaxation force. It is apparent form eqn (43) that for the given solvent at a definite temperature the magnitude of the inter ionic force increases with increase in valences of ions and with the increase in concentration of the electrolyte.

5.13 Validity of the Deby – Huckel – Onsager equation

For a uni- univalent electrolyte, the onsager egn (44) can be written as

$$\Lambda = \Lambda^0 - \left(A + B\Lambda^0\right)\sqrt{C} - - - - - - (45)$$

Where A and B are constants which are dependent only on the nature of solvent and temperature.

$$A = \frac{82.4}{(DT)^{1/2}\eta} \text{ and } B = \frac{8.2 \times 10^5}{(DT)^{3/2}}$$

The values of A and B for different solvents can be calculated at a given temperature.

It has been found that a plot of ^ against $\sqrt{c}$ is linear in the case of many uni-univalent electrolytes and the slope of a live is found to be equal to (A + B Λ^0) (fig.3) . However, it has been observed that the points lie on the line upto concentration of 2×10^{-3} equivalents/lit for uni-univalent electrolytes in water. In the case of aqueous solutions of uni- bivalence or bi-univalent electrolytes, the agreement with onsager equation seems to be quite good. However in the case of bi-bivalent electrolytes (ex: CuSO$_4$), the plots are found to be concave and further the slopes at appreciable concentrations are much larger than the theoretical values. (Fig 4). This may be probably due to incomplete dissociation of the electrolyte at these concentrations But at sufficiently dilute solutions the slopes would probably be very close to the theoretical values.

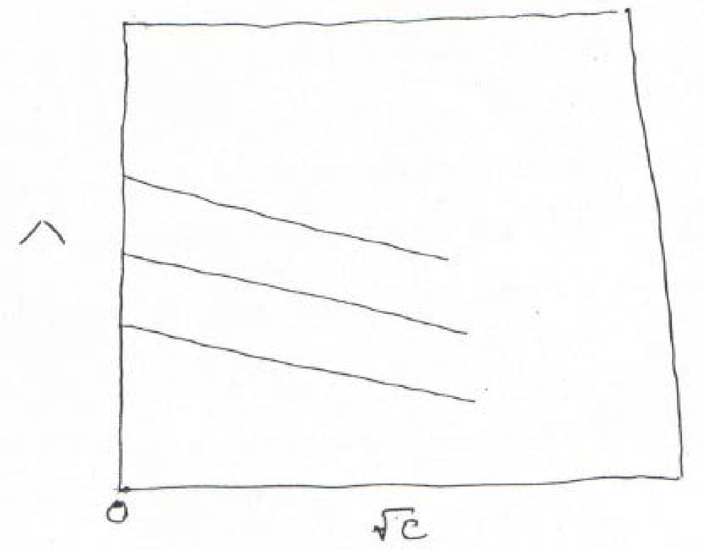


Fig.3 validity of Onsager equation

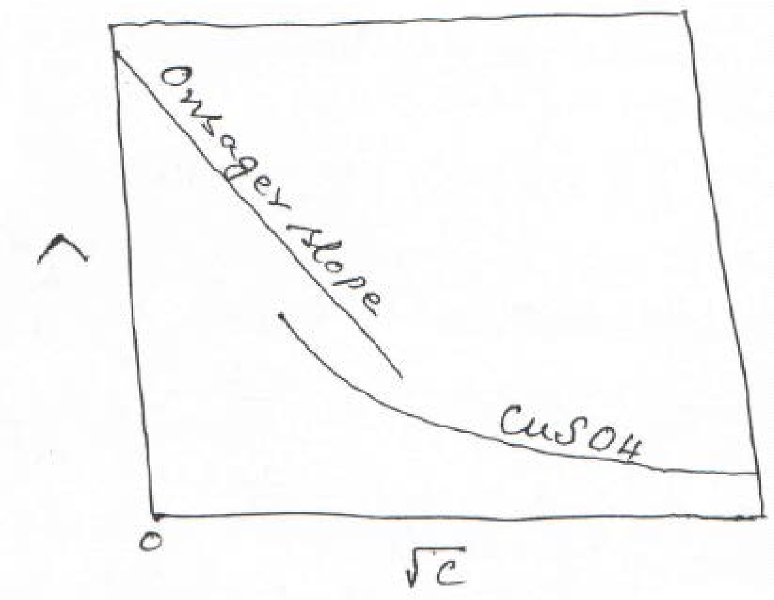


Fig. 4 Deviation form Onsager equation

Hence Debye- Huckel-Onsager equation should regarded as a limiting equation which holds good only for very dilute solutions.

5.14 Summary of the unit

Electrochemistry is a science concerned with the properties of solutions of electrolytes and with processes occurring when electrodes are immersed in these solutions. Nonelectrolyte solution cannot dissociate, e.g. sucrose and electrolyte solution can be dissociated into ions, e.g. NaCl, CH_3COOH. There are two types of electrolytes they are, strong electrolyte which have greater extent of dissociation, e.g. NaCl and weak electrolyte which have weak extent of dissociation, e.g. CH_3COOH.

From Ohm's law, the resistance *R* is defined to be $R = V/I$. The reciprocal of the resistance is the electrical conductance, *G*, which is defined by $G = 1/R$. The electrical conductance of material of length *l* and cross-sectional area *A* is given by $G = \kappa \frac{A}{l}$. For a solution of an electrolyte, κ is called the *electrolytic conductivity*. Its unit is $\Omega^{-1} cm^{-1}$. However, the electrolytic conductivity is not a suitable quantity for comparing the conductivities of different solutions, since the electrolytic conductivity *depends* on the *concentration* of solution. It is defined the molar conductivity as. $\Lambda\left(\Omega^{-1} cm^{2} mol^{-1}\right) = \kappa/C$

Arrhenius theory fails in strong electrolyte because the conductivity of strong electrolyte does not vary largely compared with that of weak electrolyte.

The assumptions of Debye-Huckel theory are i) Ions in electrolyte solutions are completely random. ii) More negative ions tend to be attracted into the neighborhood of positive ions. iii) The decrease in the molar conductivity of a strong electrolyte was attributing to the interaction between opposite ions. iv) The concentration is higher, the interaction is larger. v) Two effects are pronounced in the strong electrolytes.

5.15 Key words

Electrochemistry; Conductivity; Faradays laws of electrolysis; Strong electrolytes; Weak electrolytes; Arrhenius theory of electrolytic dissociation; Debye – Huckel theory; Relaxation effect; Asymmetric effect; Electrophoretic effect.

5.16 References for further study

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6) Fundamentals of Electrochemistry; Vladimir S. Bagotsky; *John Wiley & Sons*, **2005**.

5.17 Questions for self understanding

1) What is electrochemistry?
2) Explain the Basic aspects of electrochemistry
3) What is conductivity? What is the unit of conductivity?
4) Explain the Faradays laws of electrolysis
5) What are electrolytes? How they are classified? Identify the difference between weak and strong electrolytes
6) Derive the expression of Arrhenius theory of electrolytic dissociation
7) Point out the limitations of Arrhenious theory
8) Derive the mathematical Analysis of Debye – Huckel concept
9) Derive he expression for Debye – Huckel- Onsager conductance equation
10) Write a note on a) Relaxation effect or asymmetric effect
    b) Electrophoretic effect
11) Verify the validity of the Deby – Huckel – Onsager equation.

Unit-6

Structure

6.0 Objectives of the unit
6.1 Introduction
6.2 Debye – Huckel theory of activity coefficient (Debye – Huckel limiting equation)
6.3 Limitations
6.4 Debye-Huckel equation for appreciable Concentration
6.5 Calculating ionic strength
6.6 Summary of the unit
6.7 Key words
6.8 References for further study
6.9 Question for self understanding

6.0 Objectives of the unit

After studying this unit you are able to

- Derive the expression for Debye – Huckel theory of activity coefficient
- Point out the limitations of Debye – Huckel theory
- Derive the equation for Debye-Huckel equation for appreciable Concentration

6.1 Introduction

Coulombic interactions between ions in solution are relatively strong, long-range forces compared to the other types of intermolecular force in solution. They are thus an important contributor to the non-ideality of ionic solutions, and in the Debye-Hückel theory of such solutions, they are taken to dominate the non-ideality to such an extent that all other contributions may be neglected. The theory is based around the simple fact that oppositely charged ions attract one another, whilst like-charged ions repel each other. As a result, the motion of ions in solution is not entirely random, there is a slight tendency for ions of opposite charge to encounter each other more frequently than ions of the same charge. A time-averaged picture of the solution shows that near any given ion, there is an excess of counter-ions.

This time-averaged spherical distribution (in which ions of the same charge as the central ion and counter-ions are both present, though counter-ions predominate) has a net charge equal in magnitude but opposite in sign to the central ion, and is known as its ionic atmosphere. There is a stabilising Coulombic interaction between the central ion and its ionic atmosphere, which has the effect of lowering the energy (and thus the chemical potential) of the central ion.

This model leads to the Debye-Hückel Limiting Law, which applies only at very low concentrations of solute. This law enables calculation of the mean activity coefficient from basic properties of the solution.

6.2 Debye – Huckel theory of activity coefficient (Debye – Huckel limiting equation)

Let us now make a quantitative measure of the extent of ion-ion interaction in an electrolyte solution. Let us consider an initial state in which ion-ion interactions do not exist and in which ion-ion interaction do not exist and a final state in which the interactions are in play. Then the free energy change in going form the initial state to the final state is considered as the free energy change of ion – ion interaction($\Delta\ G_{I-I}$)

Thus, the process of going form an initial state of non interacting ions to a final state of ion –ion interactions is equivalent to taking an assembly of discharged ions, charging them up and setting the electrostatic charging work equal to the free energy change of ion–ion interaction. However, it should be noted that this is the free energy change involving all the ions in the solution but generally the desire is to isolate the contributions to the free energy of ion–ion interaction arising from one ionic species ί only. This partial free energy change is by definition the chemical potential change $\Delta \mu_{ί-I}$ arising from interactions of one ionic species with the ionic assembly. To get the value of this, we have to compute the work of charging a reference ion of radius r form a state of zero charge to its final charge $Z_{i\varepsilon}$ and multiply it by the Avogadro number.

$$\Delta \mu_{ί-I} = N W$$

But the work done in charging a sphere of radius r form charge zero to $Z_{i\varepsilon}$

$$W = \frac{(z_i\varepsilon)^2}{2Dr}$$

$$\therefore \mu_{i-I} = \frac{N(z_{i\varepsilon})^2}{2Dr} ---------(46)$$

But it has been shown that the potential ψ at the surface of an ion is

$$\frac{z_i\varepsilon}{Dr} ------$$

$$\therefore \Delta\mu_{i-I} = NW = \frac{Nz_i\varepsilon}{2}\frac{z_i\varepsilon}{Dr}$$

$$\Delta\mu_{i-I} = \frac{Nz_i\varepsilon}{2}\psi -----(47)$$

If we consider a hypothetical system of ideal (non interacting) particles the chemical potential is given by the relation

$$\mu_i(ideal) = \mu_i^0 + RT \ln X_i$$

and for a real system (of interacting particles), the chemical potential is given by

$$\mu_i(real) = \mu_i^0 + RT \ln X_i + RT \ln f_i$$

The difference $\left[u_i(real) - \mu_i(ideal)\right]$ is the change in chemical potential $\Delta\mu_{i-I}$ arising from interactions between the solute particles

$$\Delta\mu_{i-I} = RT \ln f_i -----(48)$$

So the activity co efficient is a measure of the chemical potential change arising from ion -ion interactions

The potential at the ion due to the ionic atmosphere has been given by Debye-Huckel theory to be

$$\psi = -\frac{z_i \varepsilon K}{D} --------(28)$$

$$Inserting\, equ(28)\, in\,(47)$$

$$\Delta\mu_{i-I} = -\frac{N(z_i\varepsilon)^2}{2D} k ------(49)$$

$$Comparing\, equation\,(48)\, and\,(49)$$

$$RT \ln f_i = -\frac{N(z_i\varepsilon)^2 k}{2D} --------(50)$$

Now, let us consider an electrolyte which dissociates giving γ_+ cations and γ_- anions and let $\gamma = \gamma_+ + \gamma_-$, if f_+ and f_- are the activity coefficient, the mean ionic activity coefficient is given by

$$f_\pm = \left(f_+^{\gamma+}\ f_-^{\gamma-} \right)^{1/\gamma}$$

$$\ln f_\pm = \frac{1}{\gamma}\left[\gamma_+ \ln f_+ + \gamma_- \ln f_-\right] ------(51)$$

$$from\, equation\,(50)$$

$$\ln f_i = -\frac{N(z_i\varepsilon)^2 k}{2DRT}$$

$$Substituting\, in\, equation\,(51)\, we\, get$$

$$\ln f_\pm = \frac{1}{\gamma}\left[\frac{N(z_i\varepsilon)^2 k}{2DRT}\left(\gamma + z_+^2 + \gamma_- z_-\right)\right] ---(52)$$

Since the solution as a whole is electrically neutral

$$\gamma_+ z_+ = \gamma_- z_-$$

$$\begin{aligned}\gamma_+ z_+^2 + \gamma_- z_-^2 &= \gamma_+ z_+ z_- + \gamma_- z_- z_+ \\ &= z_+ z_- (\gamma_- + \gamma_-) \\ &= z_+ z_- \gamma\end{aligned}$$

Inserting this in equation (52) *we get*

$$\ln f_{\pm} = -\frac{1}{\gamma}\left[\frac{N\varepsilon^2 k}{2DRT}\gamma z_+ z_-\right]$$

$$= -\frac{N\varepsilon^2 k}{2DRT}(z_+ z_-) ---------(53)$$

$$But\; k = \left(\frac{4\pi\varepsilon^2}{DRT}\sum n_i z_i^2\right)^{1/2}$$

if c_i *is the concentration in mol / lit*

$$n_i = \frac{c_i N}{1000}$$

$$\therefore \sum n_i z_i^2 = \sum \frac{c_i N}{1000} z_i^2 = \frac{N}{1000}\sum c_i z_i^2 ------(54)$$

$$But\; \mu = \frac{1}{2}\sum c_i z_i^2 \qquad \therefore \sum c_i z_i^2 = 2\mu ---------(55)$$

comparing equation (54) *and* (55)

$$\sum n_i z_i^2 = \frac{2N\mu}{1000}$$

$$\therefore k = \left(\frac{4\pi\varepsilon^2}{DRT}\frac{2N}{1000}\right)^{1/2}\sqrt{\mu}$$

$$= B\sqrt{\mu} --------(56)\; where\; B = \left(\frac{8\pi\varepsilon^2 N}{1000DRT}\right)^{1/2}$$

Inserting equation (56) in *to equation* (53)

$$\ln f_{\pm} = -\frac{N\varepsilon^2 (z_+ z_-)}{2DRT}B\sqrt{\mu}$$

$$\log f_{\pm} = -\frac{1}{2.303}\frac{N\varepsilon^2}{2DRT}B(z_+ z_-)\sqrt{\mu} ------(57)$$

$$put\; A = \frac{1}{2.303}\frac{N\varepsilon^2}{2DRT}B$$

$$\therefore \log f_{\pm} = -A z_+ z_- \sqrt{\mu} ----(59)$$

for uni − univalent electrolyte $z_+ = z_- = 1$

$$\therefore \sqrt{\mu} = \sqrt{C}$$

$$\log f_{\pm} = -A\sqrt{C} ------------(60)$$

Equation (58) is known as Debye – Huckel limiting equation which represents the variation of activity coefficient with the ionic strength of the solution.

The equation (58) indicates that the logarithm of the mean ionic activity coefficient must decrease linearly with the square root of the ionic strength or in the case of 1:1 electrolyte with $\sqrt{c}$. Further, the slope of the line can be evaluated form fundamental physical constants and z_+ z_- finally, the slope does not depend upon the particular electrolyte but depends only on its valence type (fig .5). It is also noticed that at infinite dilution $\sqrt{\mu}$ =0 $\therefore$ log $f_{\pm} = 0$ i.e $f_{\pm} = 1$ which should be the value for a solution at infinite dilution.

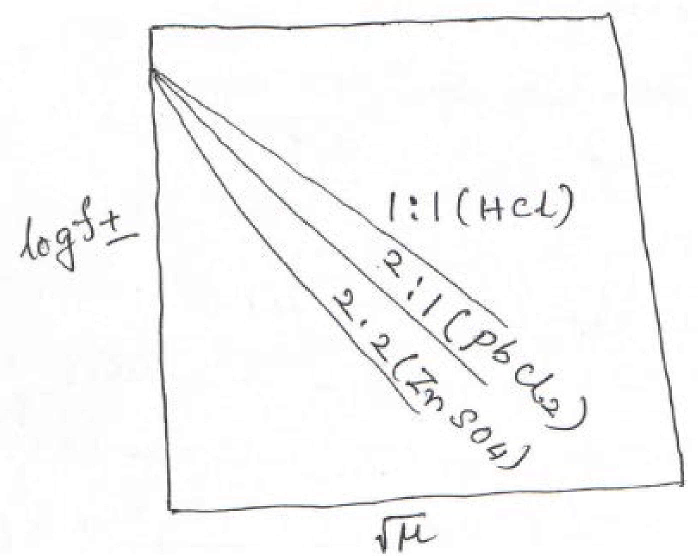

Figure 5: verification of limiting equation

Further, if one takes the experimental values of the activity coefficient at extremely low concentrations of electrolyte and a plot of log f_+ against $\sqrt{\mu}$, it is seen that

(i) They are linear and
(ii) They are grouped according to the valence type of the electrolyte. (fig.5).

Finally, on comparing the experimental and theoretical slopes they agree to within ± 0.5%

6.3 Limitations

Debye – Huckel limiting law has its own inadequacies if we plot log $f_{\pm}$ against $\sqrt{\mu}$ at higher concentrations it turns out to be a curve. Further the curves depend not only on the valence type but also on the particular electrolyte. [fig 6 (a) and 6(b)]

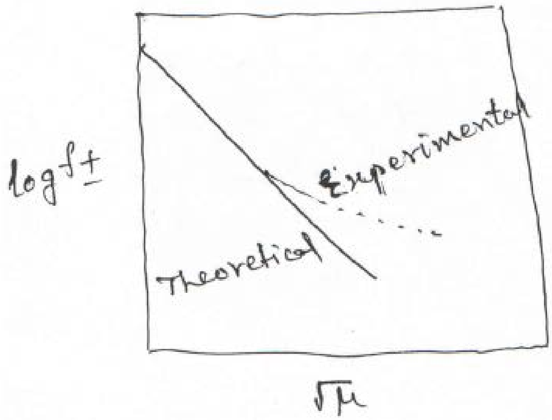

fig. 6(a)

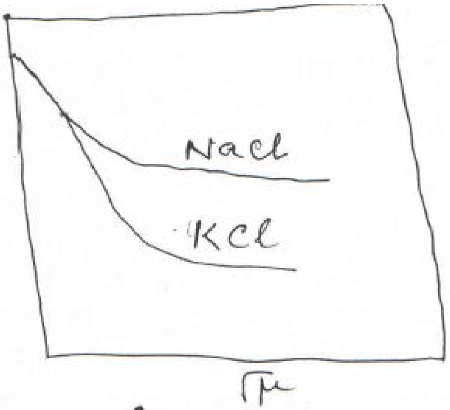

fig. 6(b)

So, the Debye – Huckel limiting law is applicable only upto concentrations of 0.01 N for 1:1 type electrolyte. The equation (58) is applicable only for dilute solution. That is why this equation is known as limiting equation.

6.4 Debye-Huckel equation for appreciable Concentration

In the derivation of $k = \left(\frac{4\pi\varepsilon^2}{DRT} \sum n_i z_i^2 \right)^{1/2}$ the approximation was made with regard to the ion as being equivalent to point charge. This approximation is valid provided the radius of the ionic atmosphere is large in comparison with that of the ion. This condition is satisfactory only in dilute solutions, when the concentration approaches 0.1 M, the radius of the ionic atmosphere is almost the same as that of an ion. In such cases the approximation leads to a serious error. Necessary correction has been proposed by Debye – Huckel

If ‘a’ is the average distance of approach of other ions Eg. B to the central ion (fig7)

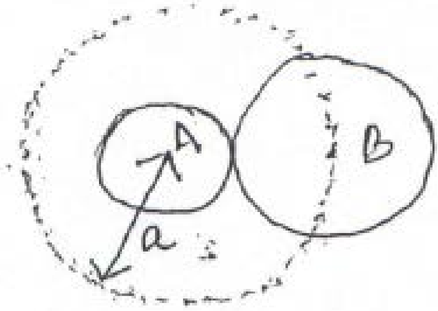

fig. 7.

The potential due to ions of ί th kind is given by

$$\psi = \frac{z_i \varepsilon}{Dr} - \frac{z_i \varepsilon k}{B} \frac{1}{1+ka}$$ instead of equation (27)

The average distance of approach ‘a’ is known as average effective diameter of the ions. The correction term, $\frac{1}{1+ka}$ approaches unity in dilute solution since k=0

The activity coefficient of ί th kind of ion will be given by

$$\ln f_i = -\frac{N z_i^2 \varepsilon^2 k}{2DRT} \frac{1}{1+ka} -----(61)$$

where N is the Avogadro number

instead of in $\ln f_i = -\frac{N z_i^2 \varepsilon^2 k}{2DRT}$

For a given solvent at a definite temperature

k = B $\sqrt{\mu}$ where B is a constant

Hence, 1 + ka may be replaced by 1+ aB $\sqrt{\mu}$

Substituting in eqn (61), we get

In f$_{ί}$ = - $\ln f_i = -\frac{N z_i^2 \varepsilon^2 k}{2DRT} \frac{1}{1+aB\sqrt{\mu}}$

Hence, the Debye – Huckel limiting law corresponding to equation,

$$\log f_i = -A z_i^2 \sqrt{\mu} \quad now\, becomes$$

$$\log f_i = -\frac{A z_i^2 \sqrt{\mu}}{1+aB\sqrt{\mu}}$$

The expression for mean ionic activity coefficient of an electrolyte is

$$\log f_{\pm} = -\frac{A Z_+ Z_- \sqrt{\mu}}{1+aB\sqrt{\mu}} ------(62)$$

Both A and B depend on the nature of the solvent and the temperature.

The value of B for water is approximately 0.33 × 10 ^{8} and for most of the electrolytes, the mean effective ionic diameter a is about 3 to 4 $\times 10^{-8}$ cm and hence, the product, $aB \approx 1$

$\therefore$ Eqn (62) reduces to

$$\log f_{\pm} = -\frac{AZ_{+}Z_{-}\sqrt{\mu}}{1+\sqrt{\mu}} \quad \text{------------- (63)}$$

Equation (63) can be used to evaluate $f_{\pm}$ at appreciable concentrations.

6.5 Calculating ionic strength

Calculate *I* for a solution that is 0.3 molal in KCl and 0.5 molal in $K_2Cr_2O_7$.

$$I = \frac{1}{2} \cdot \left(m_{K^+} \cdot 1^2 + m_{Cl-} \cdot (-1)^2 + m_{Cr_2O_7} \cdot (-2)^2 \right)$$

$$m_{K^+} = m_{KCl} + 2 \cdot m_{K_2Cr_2O_7} \qquad \text{mol/kg}$$

$$I = 0.5 \cdot (1.3 + 0.3 + 2) = 1.8$$

$\gamma_{\pm}$(KCl)

$$\lg \gamma_{\pm} = \frac{-0.511 \cdot 1 \cdot 1.8^{1/2}}{1 + 1.8^{1/2}} = -0.2928$$

$$\gamma_{\pm} = 0.5096,$$

$\gamma_{\pm}$($K_2Cr_2O_7$)

$$\lg \gamma_{\pm} = \frac{-0.511 \cdot 2 \cdot 1.8^{1/2}}{1 + 1.8^{1/2}} = -0.5855$$

$$\gamma_{\pm} = 0.26$$

Therefore ionic activities are clearly dependent on the overall composition of the solution.

6.6 Summary of the unit

Solutions of electrolytes are non-ideal at relatively low concentrations. The activities of ions in solution are relatively large compared to neutral compounds. Ions interact through a Coulombic potential that varies as 1/r (r is the distance between ions). Neutral solutes interact through London dispersion forces that vary as $1/r^6$. The greater the charge on the ions, the larger the deviations from ideality. For example, per mole of $CaCl_2$ dissolved the deviation from ideal behavior is larger than for NaCl due to the 2+ charge of calcium ion. These considerations lead to the concept of an ionic atmosphere. We cannot define the activity coefficients of individual ions, but we can determine the mean activity coefficients by the same means used to determine the activity coefficients of other substances. The mean activity coefficients are defined based on single-ion activity coefficients. Debye-Hückel theory is valid only in the limit of low concentrations. The theory breaks down when the concentration of the electrolyte is greater than about 100 mM.

6.7 Key words

Debye – Huckel theory; Activity coefficient; Debye – Huckel limiting equation; Debye-Huckel equation for appreciable Concentration; Ionic strength.

6.8 References for further study

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6.9 Question for self understanding

1) Derive the expression for Debye – Huckel theory of activity coefficient
2) What are the limitations of Debye – Huckel theory?
3) Derive the equation for Debye-Huckel equation for appreciable Concentration

Unit-7

Structure

7.0 Objectives of the unit
7.1 Introduction
7.2 Brief survey of Helmholtz–Perrin, Gouy – chapmanw and stern electrical double layer
7.3 Types of interfaces
7.4 Helm Holtz – Perrin model
7.5 Gouy – Chapmann model
7.6 The Stern model
7.7 Concentration cells
7.8 Liquid Junction Potential (Diffusion Potential)
7.9 Elimination of liquid junction potential
7.10 Determination of liquid Junction potential
7.11 Effect of concentration of solution of KCl on liquid junction potential
7.12 Migration of ions
7.13 Summary of the unit
7.14 Key words
7.15 References for further study
7.16 Question for self understanding

7.0 Objectives of the unit

After studying this unit you are able to

- Explain the Helm Holtz – Perrin model of electrical double layer
- Explain the Gouy – Chapmann model of electrical double layer
- Explain the Stern model of electrical double layer
- Give the methods for elimination of liquid junction potential
- Derive the expression for determination of liquid Junction potential
- Explain the Migration of ions

7.1 Introduction

When a surface is immersed or created in an aqueous solution, a discontinuity is formed at the interface where such physicochemical variables as electrical potential and electrolyte concentration change significantly from the aqueous phase to another phase. Because of the different chemical potentials between the two phases, charge separation often occurs at the interfacial region. This interfacial region, together with the charged surface, is usually known as the electrical double layer (EDL). This layer, which can extend as far as 100 nm in a very dilute solution to only a few angstroms in a concentrated solution, plays an important role in electrochemistry, colloid science, and surface chemistry. Applications of the electrical double layer can be found in energystoring devices in the form of capacitors, electrosorption of metal ions, purification of drinking water, nanomaterial processing, and sensor assembly. The importance of the EDL has led to numerous studies, and many models were proposed in the past. The best known is the Gouy–Chapman model in which ions are considered as point charges and water is considered as a continuum. The electrical potential distribution and the concentration profiles can be predicted simply by using the Poisson–Boltzmann (P–B) equation. This theory, which has been proven very successful at low electrolyte concentrations and low surface charge densities has been applied to many EDL problems, such as heavy metal adsorption and ion transport through membrane channels.

7.2 Brief survey of Helmholtz–Perrin, Gou –chapmanw and stern electrical double layer

The knowledge of the structure of the double layer is of fundamental importance in the study of electrode kinetics mainly because the nature of the charge distribution at a metal-electrolyte interface is of interest in connection with the mechanism of electrode reactions.

7.3 Types of interfaces

An electrical double layer exists whenever two phases are in contact except in the case of gas-gas, non polar - non polar liquid and gas – non polar liquid interface. The interface between metal –electrolyte and semiconductor–electrolyte are of interest in electrochemical reactions. Metal – electrolyte interfaces play a dominant role in electrochemical kinetics and electro chemical energy conversions. In order to understand the structure of electrified interfaces, three models are considered.

7.4 Helm Holtz – Perrin model

The simplest concept of the electrical conditions at a charged interface is that due to Helmholtz and perrin who proposed that the site of potential difference between two phases lay across two layers of charges of opposite sign Thus, an electrified interface consists of two layers of charges one on the electrode and other in the solution (fig.8(a)).

The structure of the charge distribution is clearly analogous to a parallel plate condenser with a distance between the plates replaced by the thickness of the double layer. The electrostatic theory of capacitors for the double layers can be used since the charge distribution is equivalent to an electrical interface.

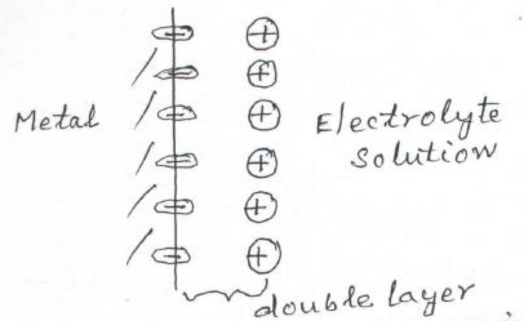


fig. 8(a) Helmholtz - perrin model.

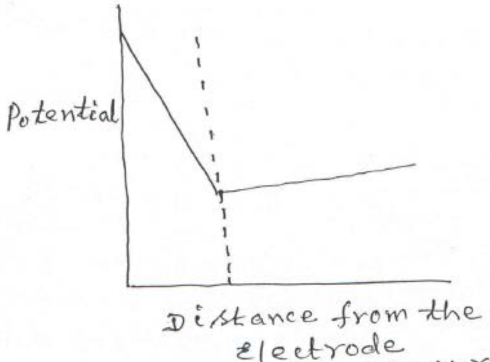


fig. 8 (b) The variation of potential with distance.

The capacitance C per unit area of the double layer (dl) should therefore be given by

$$C = \frac{\varepsilon}{4\Pi d} \text{ -------------- (64)}$$

Where d is the thickness of the dl and ε the dielectric constant of the medium.

In order to given this expression a numerical basis, let it be assumed that the dl at a metal-solution interface consists of a layer of positive ions immediately adjacent of a negatively charged metal surface. Many common ions have an effective radius of 2×10^{-8} cm and accordingly this thickness may be taken as a minimum of the dl

The dielectric constant ε within the dl presumably lies between unity (as in vacuum) and the bulk dielectric constant of the electrolyte (about 80 for an aqueous solution at 25 ^{0}c)

If for numerical simplicity, the value of ε in eqn (64) is taken as 80, then the capacitance of the dl is

$$C = \frac{80}{4\pi\times2\times10^{-8}} = \frac{10^7}{\pi} \text{ esu/cm}^2$$

$$C = \frac{10^7}{3.14\times96500} \text{ farads/cm}^2$$

$$= \frac{10^7}{3.14\times96500\times10^6} = \text{microfarads/cm} \quad (1F = 10^6\ \mu F)$$

$$\mathbf{C \approx 35\ \mu F/cm^2}$$

The capacitance of dl is found to vary according to the nature and concentration of the electrolyte and the potential difference across the metal electrolyte interface.

7.5 Gouy – Chapmann model

A different model which predicts a dependence of the measure capacitance on the both potential and electrolyte concentration was proposed by Gouy and chapmann independently. This model comes to be known later as the diffused double layer model.

Gouy and chapmann showed that the like charges in the solution side of the Helmholtz Perrin double layer would attract unlike charges causing a more extensive disturbance of the bulk charge distribution near the phase boundary than Helmholz has proposed. Both Gouy and chapmann therefore suggested that the solution side of the dl has a diffused structure in which, there would be a nonlinear fall in potential away form the interface [fig. 9 (a)]. This fall in potential and the corresponding distribution of charged are predicted [fig.9(b)]

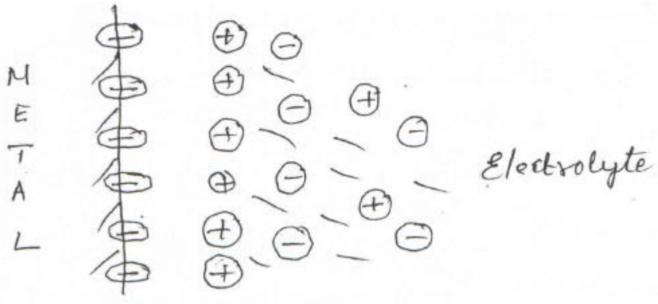


fig. 9(a) Gouy–chapmann diffuse double layer

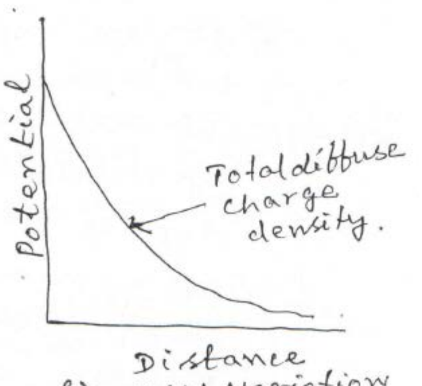


fig. 9(b) variation of potential with distance.

Gouy and chamann were able to calculate the total charge density q_D of the diffuse double layer in terms of the concentration C of the electrolyte and the interfacial difference V the expression being

$$q_D = \frac{(\varepsilon RTc)^{1/2}}{2\pi}\left(e^{\frac{FV}{2RT}} - e^{\frac{-FV}{2RT}}\right) ----(65)$$

By definition, the capacitance per unit area of the diffuse dl is $\frac{dq_D}{dv}$ and may be obtained by differentiating equation (65). It is found that the calculated variation of the capacitance of the double layer with concentration is much greater than the observed.

7.6 The Stern model

A combination of the two precious models developed by Stern who recognized the role that the ionic adsorption could play at the interface. The ions adhering to the electrode as suggested by Helmhotz and some forming Gouy –chapmann type of diffuse layer was suggested by Stern as a more realistic way of describing the physical situation at the interface. Therefore, the Stern dl consists of the combination of the Helmhottz –perrin and diffuse layers as shown bleow [fig.10(a) and fug.10 (b)]

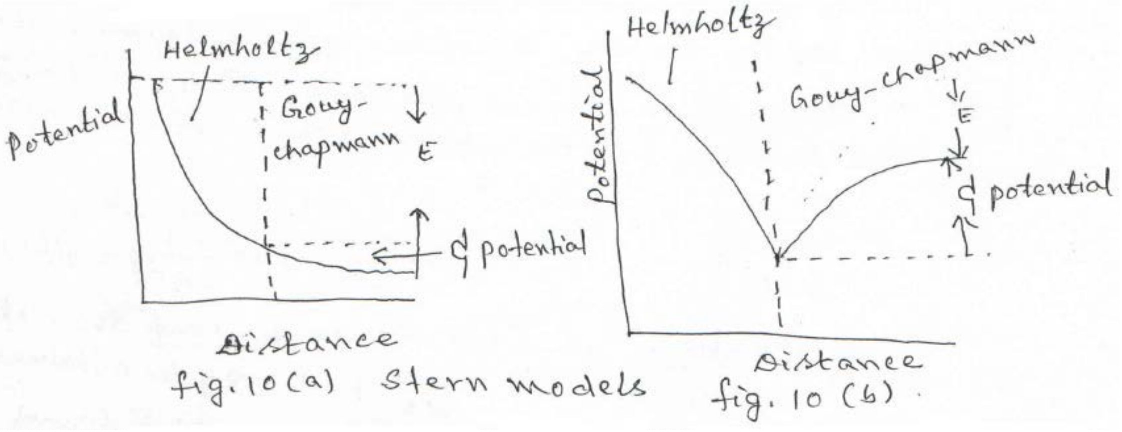


fig. 10 (a) Stern models fig. 10 (b).

It is seen that the interfacial potential difference contains two components corresponding to separate potentials across Helmholtz and diffuse layers since the two components may be of opposite sign, since the two types of stern model for dl are shown.

The total charge density, q_S of the Stern dl is equal to sum of the charge densities of Hdmhottz and diffused components. q_H and q_D

The value of q_D in given by equation (65)

$$q_{D} = \frac{(\varepsilon RTC)^{1/2}}{2\Pi} \quad (\text{emp}\ \frac{FV}{2RT} \ - \ \text{Enp}\frac{-FV}{2RT} \quad - (65)$$

with the interfacial potential V, replaced by the potential fall in the diffuse component of the stern double layer.

This potential will be identified with the electro kinetic potential or zeta potentials (ς)

The Value of q_H is calculated and is given by

$$q_H = FN\left(\frac{1}{2+\frac{1}{c}\exp\left[\frac{\phi^1 - F\varsigma}{RT}\right]} - \frac{i}{2+\frac{1}{c}\exp\left[\frac{\phi^{11} - F\varsigma}{RT}\right]}\right) ----(66)$$

Where ϕ^I and ϕ^{II} are the adsorption energies of negative and positive ion

The capacitance C_S of the Stern dl is derived by treating it as the condensers in series using the expression,

$$\frac{1}{C_S} = \frac{1}{C_H} + \frac{1}{C_D} \text{ ------------ } (67)$$

Where C_H and C_D are the capacitances of the Helmholtz – Perrin and diffused components of the Stern dl respectively. A value for C_D many be obtained from the modified from of eqn (65).

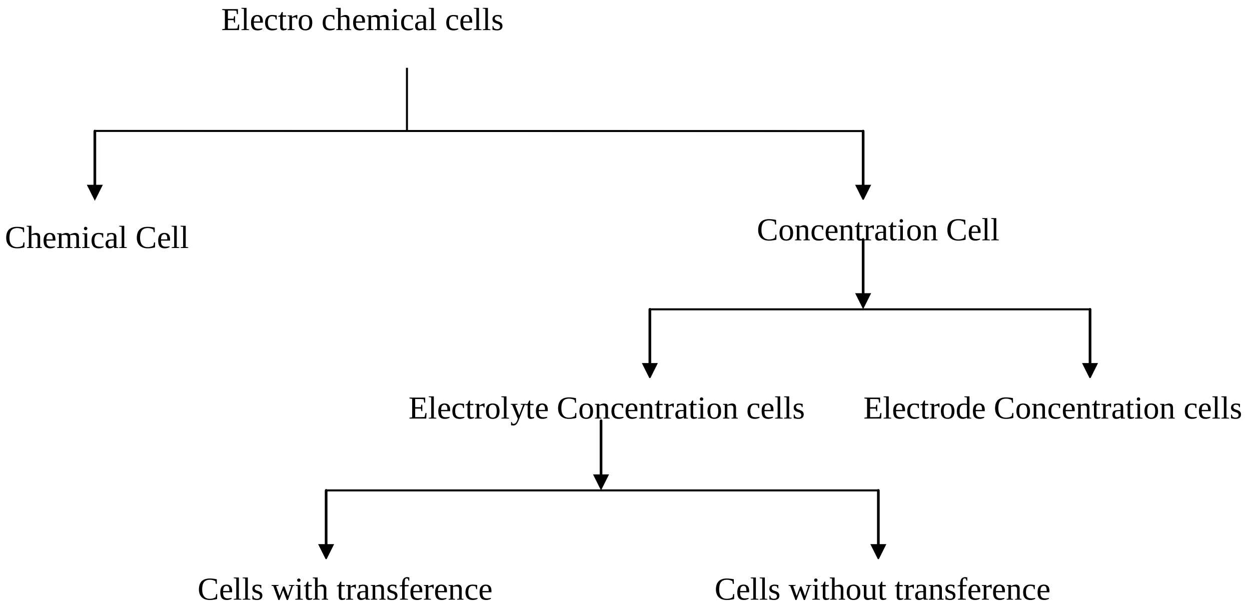
Graham has however used the calculated values of C_D in conjunction with observed values of C_S to estimate C_H for the interface between H_g and aqueous. NaF. The result of this work demonstrate that in spite of large variation of C_D with concentration, the major contribution to the dl capacity is due to Helmholtz component throughout a considerable range of concentration and zeta potentials.

Example; if the observed dl capacity $C_S = 25\ \mu F/cm^2$ and the calculated capacity of the diffused component, C_D is $250\ \mu F/\ cm^2$. Application of eqn (67) givens the value for C_H $27.8\ \mu F/\ cm^2$, a value which is not radically different from C_S.

The usefulness of the Stern concept as a working hypothesis for the structure of electrical dl has been much enhanced by the works of Graham who has elaborated the theory in terms of the finite size of the ions and has considered the question of their salvation in the dl.

7.7 Concentration cells

Electro chemical cells may be classified as follows:



Concentration cells depend for their emf on a transfer of material form one electrode to the other due to a difference in concentration between the two. This difference in concentration may arise from the fact that two like electrodes dipping in the same solution may be at different concentrations as;

$H_{2(g)}$ (P_{H2} = P_1 m m) / $HCl_{(aq)}$ / $H_{2(g)}$ (P_{H2} = P_2 mm)

Cd (Hg) (cd =c_1)/ Cd^{++} (aq) /Cd (Hg) (C_{Cd} = C_2)

The first cell is the gas concentration in which H_2 at different pressures is bubbled over platinum foils dipping in a solution of same [H^+]. The second cell is an amalgam cell in which cadmium amalgams of different concentrations are in contact with a solution having the same [cd^{++}]. In both the cases there is no liquid Junction present and so there will not be any transfer, such cells are called concentration calls without transference.

In some cases the difference in concentration may not be in the electrodes but in the solution with which they are in contact as in cells

H_2 (1 atm)/ $H^+_{(a1)}$ // $H^+_{(a2)}$/ $H_{2\,(1atm)}$

$Ag_{(s)}$/$Ag^+_{(a1)}$ /(a_2)/$Ag_{(s)}$

The above cells involve a liquid junction between two solutions of different activities and such cells are called concentration cells with transference.

7.8 Liquid Junction Potential (Diffusion Potential)

When two solutions of different concentrations are brought together, a potential difference develops at the junction. This potential difference is called the liquid junction potential or Diffusion potential. The potential difference arises mainly due to the unequal rates of diffusion of the ions across the junction.

Let us consider a cell

H_2 (1 atm) / Hcl(a_2) // Hcl (a_1) / H_2 (1atm)

For the passage of one faraday of electricity through the cell, then t_+ gm ions of H^+ migrate form left to right (from a_2 to a_1) and t_- gm ions of chloride will migrate from a_1 to a_2.

The total free energy change for this transfer is

$$\Delta G = t_+ RT \ln \frac{(a_{H^+})_1}{(a_{H^+})_2} + t_- RT \ln \frac{(a_{Cl^-})_2}{(a_{cl^-})_1}$$

But $\Delta G = -n FE_L$

For this process, n =1

$\therefore \Delta G = -FE_L$; where E_L is the liquid junction potential.

Substituting for ΔG in the above equation

We get - $FE_{L} =$ t_{+} RT $\ell n \frac{(a_{H^+})_1}{(a_{H^+})_2}$ + t- RT $\ell n \frac{(a_{Cl^-})_2}{(a_{cl^-})_1}$

$$= EL = t_{+} \frac{RT}{F} \ell n \frac{(a_{H^+})_1}{(a_{H^+})_2} + t_{-} \frac{RT}{F} \ell n \frac{(a_{Cl^-})_2}{(a_{cl^-})_1} \quad \text{------ (68)}$$

we know that, $t_{+} + t_{-} = 1$

or $t_{+} = (1 - t_{-})$

substituting the above in eqn (68), we get

$$E_L = (1 - t_{-}) \frac{RT}{F} \ell n \frac{(a_{H^{++}})_2}{(a_{H+})_1} + t_{-} \frac{RT}{F} \ell n \frac{(a_{Cl^-})_1}{(a_{cl^-})_2}$$

$$E_{L} = \frac{RT}{F} \ell n \frac{(a_{H^+})_2}{(a_{H+})_1} - t_{-} \frac{RT}{F} \ell n \frac{(a_{H^+})_2}{(a_{H+})_1} + t_{-} \frac{RT}{F} \ell n \frac{(a_{Cl^-})_1}{(a_{cl^-})_2}$$

$$= \frac{RT}{F} \ell n \frac{(a_{H^+})_2}{(a_{H+})_1} + t_{-} \frac{RT}{F} \ell n \frac{(a_{H^+})_1}{(a_{H}+)_2} + t_{-} \frac{RT}{F} \ell n \frac{(a_{Cl^-})_1}{(a_{cl^-})_2}$$

$$= t_{-} \frac{RT}{F} \ell n \frac{(a_{H^+}.a_{u^-})_2}{(a_{H^+}.acl^-)_2} + \frac{RT}{F} \ell n \frac{(a_{H^+})_2}{(a_{H^+})_1}$$

$$E_{L} = 2\, t_{-} = 2t_{-} \frac{RT}{F} \ell n \frac{a_1}{a_2} - \frac{RT}{F} \ell n \frac{(a_{H^+})_1}{(a_{H^+})_2} \quad \text{----------- (69)}$$

Where a_1 and a_2 are the activities of HCl solution. Equation (69) is the correct form of the expression for liquid Junction potential.

If $\frac{(a_{H^+})_1}{(a_{H^+})_2} \approx \frac{a_1}{a_2}$

Then equation (69) can be written as

$$EL = (2t_{-} - 1) \frac{RT}{F} \ell n \frac{a_1}{a_2} \quad \text{-------------- (70)}$$

Equation (70) can be put in alternate forms as:

$$E_L = (1-2t_-)\ \frac{RT}{F}\ \ell n\ \frac{a_2}{a_1}$$

$$E_L = (t_+ - t_-)\ \frac{RT}{F}\ \ell n\ \frac{a_2}{a_1}$$

If $t_+ > t_-$, E_L is Positive

$t_+ = t_-$, E_L is zero

$t_+ < t_-$, E_L is negative

From the above equations, it is evident that the sign of E_L depends on the relative values to the transference numbers of two ions.

7.9 Elimination of liquid junction potential

In order to eliminate or minimize the liquid junction potential, a salt bridge consisting usually of a saturated solution of KCl or KNO_3 or NH_4 NO_3 is placed between the two solutions.

The liquid junctions potential depends upon the concentration of KCl or KNO_3 or NH_4NO_3 which is present in the salt bridge.

7.10 Determination of liquid Junction potential

Set up a concentration cell with transference

H_2 (atm)/HCL(a_2) // HCL(a_1)/H_2(1atm)

For the above cell, we have derived an expression for liquid Junction potential as

$$E_L = (2\ t_- -1)\ \frac{RT}{F}\ \ell n\ \frac{a_1}{a_2} \quad ---------- (70)$$

The above equation can also be written as

$$E_L = (t_+ - t_-)\ \frac{RT}{F}\ \ell n\ \frac{a_2}{a_1} \quad ------------ (71)$$

Knowing the activities of aqueous solutions of HCl (a_1 and a_2) and the transference number of either a cation or an anion at any temperature T, the liquid Junction Potential can be determined using the above equations. In the present case, n =1. The transference number of a cation and anion can be determined by Hittorf's method or an emf method. Conductivity method can also be used for the determination of liquid Junction potential. Suppose two 1:1 electrolytes having an ion in common are at the sane concentration say c Example, Nacl and KCl, the liquid Junction potential is given by

$$E_{L} = \frac{RT}{F} \ln \frac{\wedge 1}{\wedge 2} \quad \text{--} \quad (72)$$

Where $\wedge_1$ and $\wedge_2$ are the equivalent conductance of the two solutions, NaCl and KCl forming the Junction, Equation (72) is known as Lewis and Sargent relation

7.11 Effect of concentration of solution of KCl on liquid junction potential

As the concentration of the solution is the salt bridge is increased, the emf falls to a very small value which cannot be very different form that of the cell freeform liquid junction potential (Table)

Table

Con. of KCl (N)	emf (mv)	conc. of KCl (N)	emf (mv)
0.2	19.95	1.75	5.15
0.5	12.55	2.50	3.40
1.0	8.40	3.50	1.10

The theoretical basis of using a bridge containing a concentrated salt solution to eliminate liquid junction potential is that the ions of this salt are present in large excess at this junction and they consequently carry almost the whole of the current across the boundary. When the two ions have approximately equal equivalent conductance, the liquid junction potential will be almost equal to zero (eqn 72). If the transference number of ions are almost the same, then also $E_L \approx 0$ (egn. 71).

7.12 Migration of ions

When the electrolyte solution is subjected to electrolysis, the ions present in the solution are moving towards the electrodes. The movement of ions towards the oppositely charged electrodes is called migration of ions. To know the information regarding the contribution of each individual ion to the transport of current, it is necessary to establish a quantitative relation between the fraction of the current carried by an ion and its velocity.

Let us consider the flow of current through the electrolyte solution held between two ectrodes, d cm apart. Let ϑ_+ and ϑ_- are the mean velocities of cations and anions having charges z_+ and z_- respectively.

Then the current carried by the cations is given by

$$I_+ = \left(\frac{n_+\vartheta_+ Z_+ e}{d}\right)$$

Similarly, the current carried by the anions is given by

$$I_- = \left(\frac{n_+\vartheta_+ Z_+ e}{d}\right)$$

When n_+ and n_- are the number of cations and anions present in the electrolyte held between the electrodes and e is the electronic charge. The total current carried by both the ions (I) is given by.

$$I = I_+ + I_- + = \frac{(n_+\vartheta_+ Z_+ e + n_-\vartheta_- Z_- e)}{d}$$

For the condition of electronentrality

We have $n_+ z_+ = n_- z_-$

Hence, $I = \left(\frac{n_+ Z_+ e}{d}\right)\ (\vartheta_+ + \vartheta_-)$

Therefore, the fraction of current carried by the cations is given by

$$t_+ = \frac{I_+}{I} = \frac{\vartheta_+}{\vartheta_+ + \vartheta_-} \text{ ---------------- (73)}$$

and the fraction of current carried by the anions is given by

$$t_- = \frac{I_-}{I} = \frac{\vartheta}{\vartheta_+ + \vartheta_-} \text{ -------------- (74)}$$

where t_+ and t_- are termed as transference number or transport number of the cation and anion respectively.

Thus, the fraction of the total current carried by anion is called the transference number or transport number of that ion.

Adding equations (73) and (74), we get

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

$$t_+ + t_- = \ = \frac{\vartheta_+ + \vartheta_-}{\vartheta_+ + \vartheta_-} = 1 \text{ ----------------- (75)}$$

that means the sum of the transference numbers of cations and anions is equal to unity

The ratio of transport numbers in given by

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

Or $t_+ \propto \vartheta_+$ and $t_- \propto \vartheta_-$

Thus, the transport number of any ion is directly proportional to its velocity in the solution. The transport number of an ion is related to the ionic conductance of that ion and is given by

$$t_+ = \frac{\lambda_+}{\wedge_o} \text{ and } t_- \frac{\lambda_-}{\wedge_o}$$

where $\wedge_0$ is the equivalent conductance at infinite dilution.

7.13 Sumarry of the unit

Because not all of interfaces are of the same kind, the characteristic behavior of the EDL depends on the properties of the particular interface. Ideally, such interfaces can be characterized either as polarizable or nonpolarizable, depending on the interfacial resistance. The adsorption of ions at an electrode is usefully classified as specific or non-specific. This is an operationa1 classification which in, practice depends on the simple model of non-specific adsorption introduced by Gouy and Chapman. This model is analogous to the Debye-Huckel theory of electrolytes. In this model adsorption arises as a result of the electrostatic interaction between point charge ions and the charge on the electrode. The size of the ions is introduced only as a distance of closest approach to the electrode (x_2). This results in an ionic atmosphere or diffuse layer extending from x_2 and decaying out into the bulk of the solution. The net charge on this diffuse layer being equal and opposite to that on the metal surface. Specific adsorption is then all adsorption which cannot be accounted for by the Gouy-Chapman theory. Most obviously it will occur when ions can approach the electrode more closely than x, and specific 'chemical' interaction occurs between ion and electrode, but other effects, such as the 'squeezing out' of a structure-breaking ion from the bulk of the solution may also contribute to the specific interaction. Because such specific forces are short-range, specifically adsorbed ions are usually located in a monolayer with their centers in a plane at X, from the electrode.

7. 14 Key Words

Helm Holtz – Perrin model; Gouy – Chapmann model; The Stern model; Concentration cells; Liquid Junction Potential; Migration of ions.

7.15 References for further study

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7.16 Questions for self understanding

1) What are different types of interferences occurs
2) Explain the Helm Holtz – Perrin model of electrical double layer
3) Explain the Gouy – Chapmann model of electrical double layer
4) Explain the Stern model of electrical double layer
5) Discuss the methods for elimination of liquid junction potential
6) Derive the expression for determination of liquid Junction potential
7) What are concentration cells? give two examples
8) What is Liquid Junction Potential or Diffusion Potential?
9) Discuss briefly effect of concentration of solution of KCl on liquid junction potential
10) What is Migration of ions?

Unit-8

Structure

8.0 Objectives of the unit
8.1 Introduction
8.2 Determination of transport number
8.3 Hittorf's method
8.4 Experimental procedure
8.5 Calculation
8.6 Emf method
8.7 True and apparent transport numbers
8.8 Abnormal transport number
8.9 Effect of concentration on transport number
8.10 Effect of temperature on transport number
8.11Summary of the unit
8.12 Key words
8.13 References for further study
8.14 Question for self understanding

8.0 Objectives of the unit

After studying this unit you are able to

- Explain the significance of transport number
- Explain the Hittorf's method of determination of transport number
- Explain the Emf method of determination of transport number
- Differentiate between true and apparent transport numbers
- Explain the characteristics of abnormal transport number
- Explain the effect of concentration and temperature on transport number

8.1 Introduction

Electric force field directs migrating ions parallel to the force field lines and accelerates them toward the electrodes. A counter force prevents their speed to exceed a limit. This is the friction force resisting the relative motion of fluid layers. The condition for mechanical equilibrium of transporting ion is $F_{friction} = F_{field}$,

Cations and anions contribute to charge transport in electrolytic processes in accordance with their different mobilities in an electric field. Hittorf transport numbers characterise the fraction of the total charge transported by a particular ion during electrolysis. They enable the calculation of ionic conductivities, the values of which are important in electrochemical practice. Transport numbers are to be experimentally determined from the characteristic concentration changes which take place at the cathode and the anode during electrolysis.

8.2 Determination of transport number

There methods are available for the determination of transference number. They are

1. Hittorf's method
2. Moving boundary method and
3. emf method.

We discuss Hittorf's method and end method because these two methods are there in the syllabus

8.3 Hittorf's method

This method is based on the principle that the decrease in concentration around an electrode is directly proportional to the velocity of the ion that moves away from the electrode.

Velocity of cation $\propto$ decrease in concentration around anode

Similarly, velocity of anion ∝ decrease in concentration around cathode.

$$\therefore \frac{\vartheta\text{elocity of cation}}{\vartheta\text{elocity of anion}} = \frac{\text{decrease in concentration around anode}}{\text{decrease in concentration arounnd cathode}}$$

$$\frac{\vartheta_+}{\vartheta_-} = \frac{t_+}{t_-} = \frac{\text{Loss incation equivalents at anode due to migration}}{\text{Loss in anion equivalents at cathode due to migration}}$$

Since, the total current passed through the cell, expressed in equivalents, in proportional to $t_+ + t_- = 1$

$$\frac{\text{Loss in cation equivalents at anode due to migration}}{\text{Equivalents of current passed}} = \frac{t_+}{1} = = t_+$$

and
$$\frac{\text{Loss in cation equivalents at cathode due to migration}}{\text{Equivalents of current passed}} = \frac{t_-}{1} = t_-$$

8.4 Experimental procedure

A typical setup for determination of transference number is shown in the fig. 11

where

A = transport cell
B= battery
P = plug key
R = Variable re sistance
C = copper coulometer
M = milli ammeter

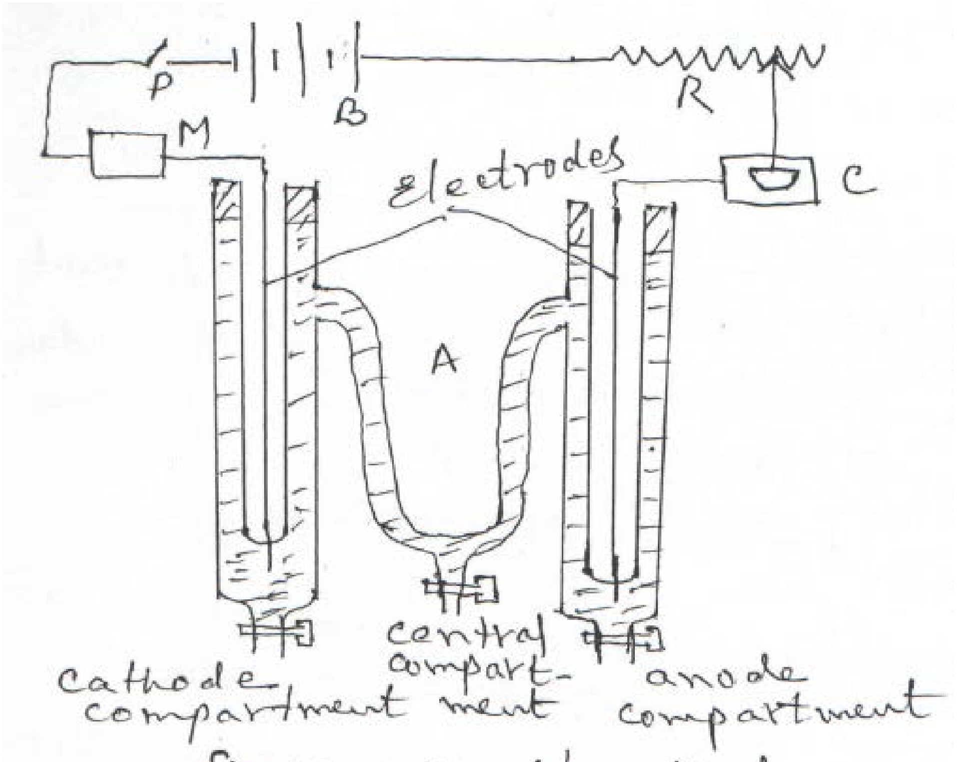

Fig. 11 Hittorf's method.

Let us take an example of determining the transference number of silver ion (t Ag^+) present in silver nitrate solution. The apparatus consists of a transport cell in series with a copper coulometer, both connected to a battery through the variable resistance. The milliammeter is included in the circuit which permits adjustment of the current at any desired value. The cell is filled with electrolyte solution to be investigated. In the present case, silver nitrate solution of known concentration is taken in the cell. The electrodes are pure silver electrodes. A steady current of 10 to 20 mA is then passed through the solution for about 2 to 3 hours. Larger currents and a larger time interval will have an adverse impact on results due to diffusion. After electrolysis an appropriate amount of solution from each compartment is withdrawn and analyzed. The total amount of electricity passed is found experimentally by means of a coulometer.

8.5 Calculation

Let χ g of the solution collected form the anode compartment contains y g of the electrolyte, $AgNO_3$

$\therefore$ The amount of water containing y g of $AgNO_3 = (\chi - y)$ g

Let = Z g of $AgNO_3$ be preset in (χ –y)g of water before the electrolysis (initially)

If w g is the weight of silver deposited on the cathode,

the increase in the weight of $AgNO_3$ in the anode compartment due to the dissolution of silver from the anode is

$= \frac{w \times 170}{108} =$ A g Eg. Wt. of $AgNO_3$: 170

Atomic mass of silver = 108

If no migration occurs, then the total weight of $AgN0_3$ which should have been present is (χ –y)g of water in the anode compartment is

= (A + Z) g

But the actual weight of $AgNO_3$ present is y g

Therefore Loss due to migration = (A+Z) –y

= A-(y-Z) g

Thus, the transport number of silver ion is given by

$$t_{Ag^+} = \frac{\begin{array}{c}Number\ of\ equivalent\ of\ AgNO_3\ lost\ from\ anode \\ compartment\ due\ to\ migration\end{array}}{number\ of\ equivalents\ of\ metal\ deposited\ in\ the\ coulometer}$$

$$t_{Ag+} = \frac{A-(y-Z)}{170} \times \frac{108}{W} \text{ ---------- (76)}$$

$$and\ t_{NO_3^-} = 1 - t_{Ag^+}$$

8.6 Emf method

This method is based on the measurements of emf of cells containing the same electrolyte with and without transference.

Consider a cell without transference

H_2 (g.1atm)/$Hcl_{(ai)}$ $Agcl_{(S)}$/Ag/Agcl($_S$) $Hcl_{(a2)}$/H2(g,atm)

The emf of this cell is given by

$$E = \pm\ E = \pm \frac{\gamma}{\gamma_\pm} \frac{RT}{z_\pm F} \ln \frac{a_2}{a_1} \text{ --------(77)}$$

Where γ is the total number of ions and γ_+ or γ_- is the number of positive or negative ions produced by the ionization of one molecule of electrolyte; z_+ or z_- is the valence of the ion with respect to which the extreme electrodes are reversible. If this ion is positive, the positive signs apply through out but it is negative, the negative signs are applicable.

In the above cell, by removing the intermediate electrodes, the cell becomes with transference and is represented by

$H_{2(g\ 1atm)//}HCl_{(a1)\ /}$ / HCl $_{(a2)}$ / H_2 (g,1atm)

The emf of the cell (E_t) is given by

$$E_t = \pm t_{\pm}\frac{\gamma}{\gamma_{\pm}}\frac{RT}{z_{\pm}F}\ln\frac{a_2}{a_1} \quad ----------- \quad (78)$$

From equation (77) and (78), we get

$$\frac{E_t}{E} = t_{\pm} \quad ----------- \quad (79)$$

The transference number of either a cation or an anion can be determined using eqn (79).

8.7 True and apparent transport numbers

The fundamental assumption of the Hittot's method for determining the transport numbers from concentration changes is that the water remains stationary. But there are evidences that ions are solvated in solution and hence they carry water molecules with them in their migration. This will result in concentration changes which affect the measured or apparent transport number.

Suppose each cation and anion has associated with it W_+ and W_- molecules of water respectively. Let T_+ and T_- are the true transport numbers. For the passage of 1 faraday of current, the cations will carry W_+T_+ moles of water in one direction and anion will carry W_-T_- moles of water in the opposite direction. The resultant transfer of W_+T_+ - W- T_- = x moles of water from the anode to the cathode compartment.

If the original solution contains N_5 equivalents of salt associated with N_w moles of water, then the removal of χ moles of water will increase the amount of salt by $(\frac{Ns}{Nw})\chi$ equivalents. The apparent transport number of the cation will this be smaller. Then the true transport number is given by.

$$T_+ = t_+ + (\frac{Ns}{Nw}) \quad \chi - \quad ------------- \quad (80)$$

Similarly, it can be shown that the water transported by the ions will course a decrease of concentration in the cathode compartment and hence the apparent transport number will be larger than the true value by an amount.

$$T_- = t_- \left(\frac{Ns}{Nw}\right)\ (\chi \text{ ------- } (81)$$

If the value of x is known, it is possible to

Evaluate the true and apparent transference number from the results obtained by Hittor's method.

8.8 Abnormal transport number

In certain cases, the transport number of cations Eg: aqueous solutions of CdI_2, iron in potassium ferroeyanide Etc. vary significantly with concentration of solution. At relatively higher concentration, the transport number becomes zero or even negative. This can be explained by taking an example of aqueous solution of CdI_2.

N dilute solutions,

$CdI_2 \leftrightarrow Cd^{2+} + 2I^-$

Cd^{2+} possesses a normal transport number upto 0.02 N concentration. With the increase in concentration of the salt, the iodide ion combines with the un dissociated molecule of CdI_2 forming the complex species CdI_4^{2-}

$$CdI_2 + 2I^- \leftrightarrow CdI_4^{2-}$$

and thus cadmium would be transported to anode thereby decree sing the effective transport number of Cd^{2+} when Cd^{2+} and CdI_4^{2-} carry equal current, then $t_{cd}^{2}+ =0$

At still higher concentration, virtually all the iodide ion would be present as CdI_4^{2-} and the current would be carried by both Cd^{2+} and CdI_4^{2-} if CdI_4^{2-} moves faster than Cd^{2+}, t_{Cd}^{2+} becomes negative.

Factors affecting the transport number:

The following factors affect the transport number of an ion.

a) Nature of the ion

b) Nature of other ions present

c) Hydration of ions

d) Concentration

e) Temperature.

8.9 Effect of concentration n transport number

The transference number of an ion varies with the concentration of the electrolyte in solution due to inter ionic attraction, hydration, ion association and complex formation. The following relationship was proposed to represent this variation.

$$t = t^0 - A\sqrt{c} \text{ ---------- } (82)$$

Where t and t^0 are the transference number of a given ion in a solution of definite concentration C and that extrapolated to infinite dilution respectively and A is a constant Egn (82) is applicable only for dilute solutions. For higher concentrations, the expression is

$$t = \frac{t^o + 1}{1 + B\sqrt{c}} - 1$$

where B is a constant for a given electrolyte .The above equation may be written in the form

$$t = \frac{t^0 + 1}{t + 1} = 1 + B\sqrt{c} = (83)$$

A plot of $\frac{1}{t+1}$ against $\sqrt{c}$ should be a straight line. From the intercept, t^0 can be calculated.

For a 1:1 electrolyte, the following generalization can be made,

(i) For cases where $t_+^0 \approx 0.5$ the transference number vary very little with concentration.

(ii) If $t_+^0 < 0.5$, the transference number of action decreases with increase in concentration. And

(iii) Of $t_+^0 > 0.5$, the transference number of a cation increases with increase in concentration

8.10 Effect of temperature on transport number

The extent of variation of transport number with temperature is slight as is seen form the table given here under.

Table. Influence of temperature on t_+ in 0.01 N solution

Temp	HCl	Nacl	Kcl	Bacl2
0	0.846	0.387	0.493	0.437

18	0.833	0.397	0.496	-----
30	0.822	0.404	0.498	0.444

The transport number of K^+ very little with temperature but that of Na^+ and H^+, the change is appreciable. It has been observed that at least for uni-univalent electrolytes if the transport number of an ion is greater than 0.5. Eg- the H^+ there is a decrease as the temperature is raised. Therefore, it appears that transference number measured at appreciable concentration to approach a value of 0.5 as the temperature is raised. This may be due to the fact that at higher temperature, the ions tend towards equal speeds (ionic conductance).

8.11 Summary of the unit

Transport number in electrochemistry, or just transference number, is described as a fraction of the total current carried by an ion. It is denoted by sets symbols such as t_+ and t_- or t_c and t_a or n_c and n_a.

According to the definition, we have

$$t_a = \frac{\text{current carried by an anion}}{\text{total current passed through the solution}}$$

$$t_e = \frac{\text{current carried by a cation}}{\text{total current passed through the solution}}$$

Hence, $t_a + t_e = 1$

Transport number, in fact, is an amount or a quantity, which is effectively used during a transport number calculation, also known as electrochemical calculations. As shown in the transport number equation above, transport number is always equivalent to the ratio between the velocity or mobility of an ion and the sum of the velocities of cation and anion. This is described as a characteristic, which is dependent on the mobilities of ions, concentrations and the temperature of the ions in an electrolytic solution.

Generally, transport number is calculated or determined through the famous Hittorf method, which introduces changes in the concentrations of the ions near electrodes. In fact, during the process of electrolysis, ions transport solvent in their solvation sheaths. The process is not just limited to transporting electric charge. This is why they are also called “apparent transport numbers”.

Transport number calculation is done through various integral methods. However, two of the most contemporary methods include Hittorf's method and the emf method.

Hittorf's method is the most common method for calculating transport or transference number. It is a process to determine transport number wherein one determines changes in the composition of an electrolytic solution around its cathode and anode. However, a new version of this method has been introduced to find out transport numbers in polyelectrolyte solutions. A key transformation or change in the new method is that the current-induced concentration change can now be calculated in a compartment wherein current is supplied through an ion-exchange membrane. In this Hittorf's method, the current in a membrane is supplied through counterions. As solutions stays free from foreign ions, the change in concentration can be monitored accurately through conductivity measurements.

When multiple experiments were performed on sodium and potassium salts of polyacrylic acid and carboxymethylated hydroxyethyl, the measurements showed that there was an apparent suggestion of the existence of a significant change or variance in the ion binding of Na+ and K+. More importantly, it was discovered that polyion equivalent conductivity was dependent on counterion species.

The EMF technique for transport number determination is based on open cell voltage measurements on a sample equipped with two reversible electrodes and subjected to a gradient in chemical potential.

The emf method is an equally important method for calculating transport number, which, like Hittorf's method, has undergone a transformation of late. A newer version of this method has been introduced to obtain the transference number of two ions in ion exchange membranes. The new and modified emf method processes emf measurements in a cell with membrane stack by clearly avoiding difficulties in concentration-polarization, diffusion and water transport.

The new emf method is precise and takes less time than the popular Hittorf's method. This new method has been created for a cation exchange membrane with cation sites Me in equilibrium with aqueous solutions of two electrolytes, HCl and KCl and then HCl and NaCl. There is a precision of +1% in transport numbers for both the systems. Upon a careful study of the results, we realize that the ratios of the ionic mobilities, u, /++, for z = K+ and Na+ in the membrane are unending while the mole fractions vary. Rise in temperature is the main factor that affects a transport number. With a rise in temperature, the transport number or transference number of cation and anion comes closer to 0.5.

Ionic Mobility, also known as Ionic Conductance, is defined as the conductivity of a solution containing 1 g ion at infinite dilution when two sufficiently large electrodes are placed 1cm apart. Ionic mobilities (λ_a or λ_e) $\propto$ speeds of ions (u_a or u_e) and unit of ionic mobility is Ohm $^{-1}$ cm^2 or $V^{-1}S^{-1}$ cm^2. The following equation shows how Ionic Mobility and transport number are related to each other.

λ_a or $\lambda_e = t_a$ or $t_e \times \lambda m$

Absolute ionic mobility is the mobility with which an ion moves under unit potential gradient. Its unit is *cm sec* $^{-1}$.

$$\text{absolute ionic mobility} = \frac{\text{ionic mobility}}{96{,}500}$$

8.12 Key words

Transport number; Hittorf's method; Emf method; True transport numbers; Apparent transport numbers; Abnormal transport number.

8.13 References for further study

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2) Advanced Physical Chemistry; Gurdeep Raj; *Krishna Prakashan Media*, **1978**.
3) A Textbook of Physical Chemistry, Volume 1; K L Kapoor; *Macmillan*, **2000**.
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8.14 Questions for self study

1) What are transport numbers? Explain their significance

2) How Transport numbers are determined by Hittorf's method

3) Explain the Emf method of determination of transport number

4) What is True and Apparent transport numbers?

5) Differentiate between true and apparent transport numbers

6) What re abnormal transport number?

7) Explain the effect of concentration on transport number

8) Discuss effect of temperature on transport number

Question Bank

a) What are electrolytes?

b) Mention the assumptions of Arrhenius theory of electrolytic dissociation

c) List the limitations of Arrhenious theory of electrolytic dissociation

d) Give the mathematical analysis of Debye – Huckel concept.

e) Explain (i) Relaxation effect and

(ii) Electrophoretic effect

f) Deduce Deby – Huckel – Onsager conductance equation

g) How do you test the validity of Debye – Huckel onsafer equation

h) Derive Debye – Huckel limiting equation

i) Deduce Debye – Huckel equation for appreciable concentration

j) Discuss brirfly

  (i) Helmholt$_3$ – perrin model
  (ii) Goug – Chapmann model
  (iii) Stern model

k) What are concentration cells?

l) Define the term liquid Junction potential?

m) How do you determine liquid Junction potential?

n) How do you minimize liquid Junction potential?

o) What are transport number of ion? Method of determining transport number

p) Describe (i) Hittorf's methhod and (ii) Emf

q) Explain (i) true and apparent transport number and (ii) abnormal transport number

r) Discuss the effect of concentration and temperature on the transport number.

Unit-9

Structure

9.1 Objectives of the unit
9.1 Introduction
9.2 Application of Schrodinger equation to a free particle
9.3 Application of Schrödinger equation to a particle trapped in a one dimensional box (infinite potential walls)
    a) Boundary Conditions
    b) Value of n
    c) *Width of box*
    d) *The value of D (Normalization)*
9.4 To prove orthogonality of Wave function
9.5 Selection Rules for transition
9.6 Wave functions
9.7 Factors influencing color
9.8 Particle in a three dimensional Box (Rectangle)
9.10 Particle trapped in a three dimensional potential box with finite walls (Tunnel effect)
9.11 Summary of the unit
9.12 Key words
9.13 References for further study
9.14 questions for self understanding

9.0 Objectives of the unit

After studying this unit you are able to

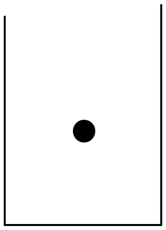
- Derive the Schrodinger equation to a free particle
- Derive the Schrödinger equation to a particle trapped in a one dimensional box
- Prove orthogonality of Wave function
- Explain the factors influencing color
- Derive the Schrodinger equation to a particle in a three dimensional Box
- Derive the Schrodinger equation particle trapped in a three dimensional potential box

9.1 Introduction

In classical mechanics the state of motion of a particle is specified by giving the particle's position and velocity. In quantum mechanics the state of motion of a particle is specified by giving the wave function. In either case the fundamental question is to predict how the state of motion will evolve as time goes by, and in each case the answer is given by an equation of motion. The classical equation of motion is Newton's second law F = ma, if we know the particle's, position and velocity at time t = 0 Newton's second law determines the position and velocity at any other time. In quantum mechanics the equation of motion is the time-dependent Schrödinger equation. If we know a particle's wave function at time t = 0, the time-dependent Schrödinger equation determines the wave function at any other time

The particle in a box problem is a common application of a quantum mechanical model to a simplified system consisting of a particle moving horizontally within an infinitely deep well from which it cannot escape. The solutions to the problem give possible values of E that the particle can possess. E represents allowed energy values, is a wave function, which when squared gives us the probability of locating the particle at a certain position within the box at a given energy level.

9.2 Application of Schrodinger equation to a free particle



Particle trapped in potential field equivalent to a box. Suppose walls of the box are removed particle is free to move without any constraint in a field where potential energy acting on it is zero (V=0). Then Schrodinger equation is one dimension is (x-direction only)

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E_x\psi = 0 -------(1)$$

$$Put \frac{8\pi^2 mE_x}{h^2} = k^2 or k = \frac{2\pi}{h}\sqrt{2mE_x}$$

$$i.e \frac{d^2\psi}{dx^2} + k^2\psi = 0 ---------(2)$$

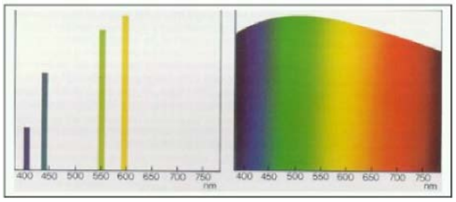
Solution of the above equation is $\psi = A\sin k_x$

Or $\psi = A\sin\left(\frac{2\pi}{h}\right)\sqrt{2mE_x}\,x -----(3)$

Solution is allowed as long as E_x is +ve, since Sine of a real quantity is everywhere single valued, finite, continuous. All positive values of E_x are allowed and the free particle will have a continuous spectrum of energy states i.e $E_x = \frac{k^2h^2}{8\pi^2 m}$ is not quantized in this case.

Note:-Electron bound in an atomic system gives rise to quantized energy levels and leads to discrete spectrum. But a free electron moving without any restriction has a continuous energy spectrum. Qualitatively explains the occurrence of continuous in atomic or molecular spectra on ionization, because an electron lost by an atom or molecule is free to move without any restriction.

Line spectra Continuous



Note $\frac{d^2y}{dX^2} + k^2 y = 0 -------(1)$

$\Re^2$ =is constant

Solution is $y = e^{mx} ---------(2)$

Substituting for y in (1)

$$\frac{dy}{dx} = me^{mx}$$

$$m^2e^{mx} + k^2e^{mx} = 0$$

We have $m^2 + k^2 = 0$, Roots are $m = \pm lk$

So the particular solutions of (1) are e^{ikx} and e^{-ikx}. Adding these particular solutions, there results a solution with two independent orbitrary constants.

$$y = A_1 e^{ikx} + A_2 e^{-ikx} ------(3)$$

Expansion gives

$$\begin{aligned} y &= A_1(\cos kx + i\sin kx) + A_2(\cos kx - i\sin kx) \\ &= (A_1 + A_2)\cos kx + (A_1 - A_2)i\sin kx \\ y &= c\cos kx + D\sin kx ------------(4) \end{aligned}$$

Where $A_{1,}$ A_2, C and D are arbitrary constant.

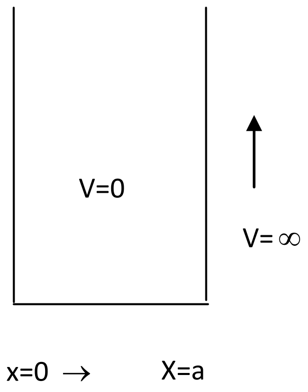
Schrödinger equation for a system (electron) in a box where V=0 or constant and is ∞ everywhere outside the box illustrate some important properties of quantum mechanics.

9.3 Application of Schrödinger equation to a particle trapped in a one dimensional box (infinite potential walls)

Consider one dimensional closed box of width L. A particle of mass 'm' is moving in a one-dimensional region along X-axis specified by the limits x = 0 and x = L as shown in fig. The potential energy of particle inside the box is zero and infinity elsewhere. I.e Potential energy V(x) is of the form

V(x) = {o; if o < x < L

∞: elsewhere



The one-dimensional time independent Schrodinger wave equation is i.e., Schrödinger equation outside the box is

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - \infty)\psi = 0$$

Above equation satisfied only if ψ = 0 at all points outside the box i.e the electron cannot be found outside the box.

Here we have changed partial derivatives in to exact because equation now contains only one variable i.e x-Co-ordinate. Inside the box V(x) = 0 therefore Inside the box, V=0

$$\therefore \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2} E_x \psi = 0 ----(1)$$

Mean value of E_x observable and independent of the co-ordinate of the electron.

$$k^2 = \frac{8\pi^2 m}{h^2} E_x \therefore \frac{d^2\psi}{dx^2} + k^2\psi = 0 ------(2)$$

'k' is called the Propagation constant of the wave associated with particle and it has dimensions reciprocal of length.

The general solution of equation 2 is $\psi = c\cos kx + D\sin kx$

Where C and D are arbitrary conditions and these will be determined by the boundary conditions

a) Boundary Conditions

The particle will always remain inside the box because of infinite potential barrier at the walls. So the probability of finding the particle outside the box is zero i.e.$\psi_x = 0$ outside the box.

We know that the wave function must be continuous at the boundaries of potential well at x = 0 and x = L, i.e. ψ must be a continuous function of x

$\Psi(x) = 0$ at $x = 0$

$\Psi(x) = 0$ at $x = L$

The ψ = 0 when X = 0 , satisfied only by the since term so C = 0, hence $\psi = D\sin kx$

ψ = 0 when x = a possible only if $D\sin ka =$ 0 or $\sin ka =$ 0, or $ka = n\pi$, where n = 0,1,2…………..n is a quantum number and is +ve so $\frac{n\pi}{a} = k$

$\therefore \psi_n = D\sin\frac{n\pi}{a}x$, so $E_x = \frac{k^2h^2}{8\pi^2 m} = \frac{n^2h^2}{8ma^2}$

b) Value of n

Although n can be zero it is not acceptable since it makes $\psi_n = 0$ inside the box which is not true because the particle is assigned to be always present inside the box. So the minimum value of n is 1

Lowest KE is called the ZPE of the particle in the box

$$E_{ZPE} = \frac{h^2}{8ma^2}$$

Particle is not at rest even at 0^0 K. So its position cannot be precisely known. Since only mean KE is known, momentum of the particle is not precisely known, so occurrence of ZPE is a direct consequence of uncertainty principle.

e) Width of box

Increase 'a' provides more room for movement of electrons. It decreases the KE E_x of the particle so delocalization occurs. Hence more localized its motion higher will be its K.E observed.

f) The value of D (Normalization)

$$\psi_n = D\sin\frac{n\pi}{a}x \text{ or } \psi_n^2 = D^2\sin^2\left(\frac{n\pi}{a}x\right)$$

$$\int_0^a \psi_n^2 dx = \int_0^a D^2\sin^2\left(\frac{n\pi}{a}x\right)dx = 1; \sin^2\theta = ½$$

$$= D^2\left[½\int_0^a dx - ½\int_0^a \cos\frac{2\pi n}{a}xdx\right]$$

$$= D^2\left[\tfrac{a}{2} - 0\right] = 1 or D = \sqrt{\frac{2}{a}}$$

Thus the normalized wave function or Eigen function of an electron in a one dimensional box is

$$\psi_n = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$$

9.4 To prove orthogonality of Wave function

To show that $\int_0^a \psi_n\psi_n^1 dx = 0$ where $\psi_n \neq \psi_n^1$

i.e., the wave or eigen functions for different states of this system are thus orthogonal

$$\int_0^a \psi_n \psi_n^1 dx = {}^2\!/_a \int_0^a \sin\left(\frac{n\pi}{a}x\right)\sin\left(\frac{n^1\pi x}{a}\right)dx$$

$$\sin n\theta . \sin n^1\theta = {}^1\!/_2\left[\cos(n-n^1)\theta - \cos(n+n^1)\theta\right]$$

$$=\frac{1}{a}\left[\int_0^a\left\{\cos(n-n^1)\frac{\pi x}{a} - \cos(n+n^1)\frac{\pi x}{a}\right\}dx\right]$$

$$=\frac{1}{a\pi}\left[\frac{a}{n-n^1}\sin\left(\frac{n-n^1}{a}\right)\pi x - \left(\frac{a}{n+n^1}\right)\sin\left(\frac{n+n^1}{a}\right)\pi x\right]_0^a = 0$$

This property illustrates that the various states are truly independent of one another

Eigen Function	Eigen Values
$\psi_1 = \sqrt{\frac{2}{a}\sin\frac{\pi}{a}x}$	$E_1 = \frac{h^2}{8ma^2}$
$\psi_2 = \sqrt{\frac{2}{a}\sin\frac{2\pi}{a}x}$	$E_2 = \frac{4h^2}{8ma^2}$
$\psi_3 = \sqrt{\frac{2}{a}\sin\frac{3\pi}{a}x}$	$E_3 = \frac{9h^2}{8ma^2}$
$\psi_4 = \sqrt{\frac{2}{a}\sin\frac{4\pi}{a}x}$	$E_4 = \frac{16h^2}{8ma^2}$

The energy spectrum is given by $E = \frac{n^2h^2}{8ma^2} + V$ this is the Constant potential V acting on the particle

9.5 Selection Rules for transition

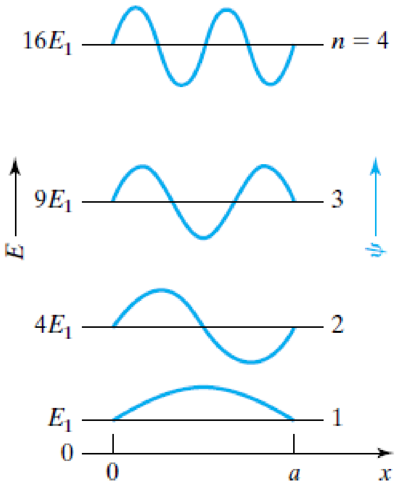
Transition between a pair of states permitted if sum or difference in equation is an odd number if both are even transition is strictly forbidden.

$n_1 \neq n_2$ is odd Allowed transition TDI does not Vanish

$n_1 \neq n$ is even forbidden transition TDI =0.

9.6 Wave functions

At walls $\psi = 0$, also at nodes $\psi = 0$ number of nodes increases as n increases as ψ_n has (n-1) nodes increase nodes decrease λ increasing K.E



9.7 Factors influencing color

The wave mechanical treatment of an electron in a box gives rise to large number of discrete energy levels on suitable excitation the electron may undergo transition from one level to another.

Transition from n_1 to n_2 $E_{n_1} = \frac{n_1^2 h^2}{8ma^2}, E_{n_2} = \frac{n_2^2 h^2}{8ma^2}$

Transition ψ_{n_2} to ψ_{n_1} Transition energy ΔE is

$$\Delta E = E_{n_2} - E_{n_1} = \frac{(n_2^2 - n_1^2)h^2}{8ma^2} \text{ or } h\vartheta = \left(\frac{n_2^2 - n_1^2}{8ma^2}\right)h^2$$

$$\vartheta = \frac{n_2^3 - n_1^2}{8ma^2}h \qquad \lambda = c/\nu = \frac{8ma^2c}{(n_2^2 - n_1^2)h}$$

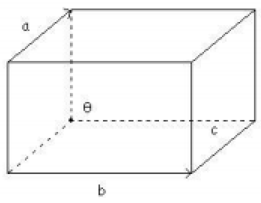
Longer the box (a), longer the λ at which optical transition of system occurs. By suitably adjusting the length of the box the wave length of an electronic transition can be made to appear in the visible region. Then the system becomes colored. If the transition between two levels is not permissible then transition dipole moment integrals are to be considered

9.8 Particle in a three dimensional Box (Rectangle)

Infinite Potential walls

Edges a,b,c Volume V = abc

Potential V=0 inside the box



Consider rectangular box of length a, b, c

At the boundaries and in the remainder of space v $=\infty$ (x,y,z) axes along the edges and origin at one corner of the box.

We have $H\psi = E\psi$ i.e $\left(-\frac{h^2}{8\pi^2 m}\nabla^2 + v\right)\psi = E\psi$

Since V=0, inside for the particle

$$-\frac{h^2}{8\pi^2 m}\nabla^2\psi = E\psi$$

$$-\frac{h^2}{8\pi^2 m}\left[\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right] = E\psi$$

There are three variable so solution is $\psi_{(x,y,z)} = X_{(x)}Y_{(y)}Z_{(z)}$ or

$$\psi = XYZ$$

$$-\frac{h^2}{8\pi^2 m}\nabla^2(XYZ) = E(XYZ)$$

$$i.e -\frac{h^2}{8\pi^2 m}\left[\frac{\partial^2(XYZ)}{\partial x^2}+\frac{\partial^2(XYZ)}{\partial y^2}+\frac{\partial^2(XYZ)}{\partial z^2}\right] = E(XYZ)$$

$$\therefore -\frac{h^2}{8\pi^2 m}\left[yz\frac{\partial^2 x}{\partial x^2}+XZ\frac{\partial^2 y}{\partial y^2}+XY\frac{\partial^2 z}{\partial z^2}\right] = E(XYZ)$$

$$\div XYZ$$

$$-\frac{h^2}{8\pi^2 m}\left[\frac{1}{X}\frac{\partial^2 x}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 z}{\partial z^2}\right] = E$$

$$Since E = E_x + E_y + E_z$$

$$-\frac{h^2}{8\pi^2 m}\frac{1}{y}\frac{\partial^2 y}{\partial y^2}-\frac{h^2}{8\pi^2 m}\frac{1}{z}\frac{\partial^2 z}{\partial z^2}-E = \frac{h^2}{8\pi^2 m}\frac{1}{X}\frac{\partial^2 x}{\partial x^2} = -E_x$$

Since RHS is the Hamiltonian on X and V=0, we have

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2 X}{\partial x^2} = E_x X \text{---------------}(1)$$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2 X}{\partial y^2} = E_y y \text{---------------}(2)$$

$$-\frac{h^2}{8\pi^2 m}\frac{\partial^2 Z}{\partial z^2} = E_z Z \text{---------------}(3)$$

These are three differential equations involving one variable each. Therefore these equations can easily solvable

Considering the equation (1) and rearranging

$$\frac{\partial^2 X}{\partial x^2}+\frac{8\pi^2 m}{h^2}E_x X=0, i.e \frac{\partial^2 X}{\partial x^2}+k^2 X=0$$

Where $k^2=\frac{8\pi^2 m}{h^2}E_x$ or $k=\frac{2\pi}{h}\sqrt{2mE_x}$

Solution of (1) is of the form $X_{(X)}=A_1\cos kx+A_2\sin kx$

$$\therefore X_{(x)}=A_1\cos\left(\frac{2\pi}{h}\sqrt{2mE_x}x\right)+A_2\sin\left(\frac{2\pi}{h}\sqrt{2mE_x}x\right)\text{----------------} (4)$$

Boundary conditions are

$\psi=0$ At x=0 and x=a i.e. particle is not found beyond 0 or a

X=0 and x=0 this is satisfied only by the sine term so $A_1=0$

So $X_x=A_2\sin\left[\frac{2\pi}{h}\sqrt{2mE_x}x\right]$

X=0 and x=0 possible if $\frac{2\pi}{h}\sqrt{2mE_x}a=n_x\pi$

Where n_x is an integer i.e $n_x=0,1,2,3\ldots\ldots$but n_x= 0has no meaning since $X_{(x)}$ become zero everywhere

i.e $\frac{4\pi^2}{h^2}2mE_x a^2=n_x^2\pi^2$

or $E_x=\frac{n_x^2h^2}{8ma^2}$ so $X_{(x)}=A_2\sin\left(\frac{n_x\pi}{a}x\right)$

A_2 is an arbitrary constant. Here normalization condition is used that is normalization factor.

$\int_0^a X^2dx=\int_0^a A_2^2\sin^2\left(\frac{n_x\pi}{a}x\right)dx=1$ i.e total probability is unity between 0 & a

$$\sin^2\theta = \tfrac{1}{2}(1-\cos 2\theta)$$

$$i.e\, \frac{A_2^2}{2}\int_0^a\left(1-\cos\frac{2n_x\pi}{a}x\right)dx = 1$$

$$i.e\, \frac{A_2^2}{2}(a) = 1$$

$$i.eA_2 = \sqrt{\frac{2}{a}}$$

Similarly for y and Z directions

$$X_{(x)} = \sqrt{\frac{2}{a}}\sin\frac{n_x\pi}{a}x \qquad E_x = \frac{h^2 n_x^2}{8ma^2}$$

$$Y_{(y)} = \sqrt{\frac{2}{b}}\sin\frac{n_x\pi}{b}y \qquad E_y = \frac{h^2 n_y^2}{8mb^2}$$

$$Z_{(z)} = \sqrt{\frac{2}{c}}\sin\frac{n_x\pi}{c}z \qquad E_z = \frac{h^2 n_z^2}{8mc^2}$$

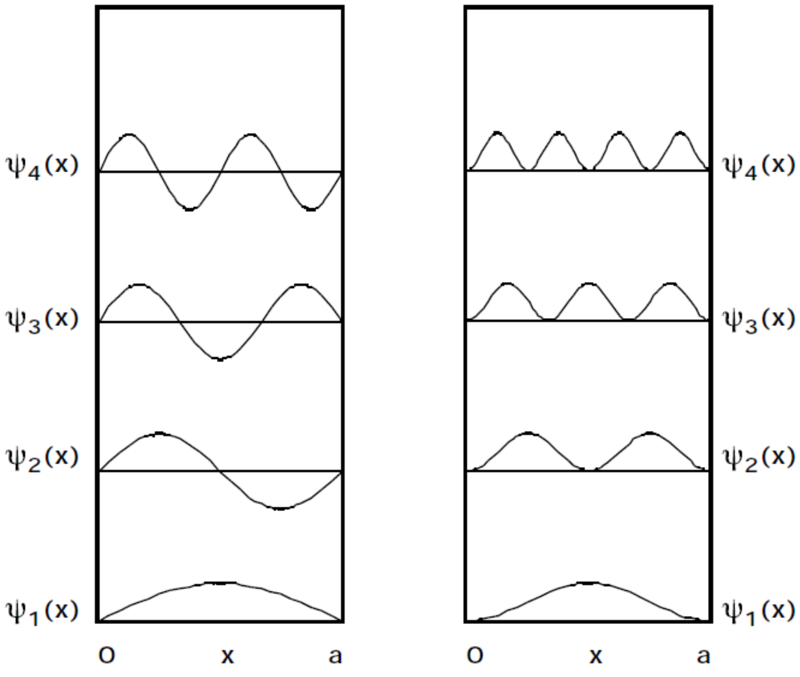
$$\psi_{(xyz)} = \sqrt{\frac{8}{abc}}\sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{b}\right)\sin\left(\frac{n_z\pi}{c}z\right)$$

So

$$i.e\psi = \sqrt{\frac{8}{\vartheta}}\sin\left(\frac{n_x\pi}{a}x\right)\sin\left(\frac{n_y\pi}{b}\right)\sin\left(\frac{n_z\pi}{c}z\right)$$

$$E = E_x + E_y + E_z = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2}+\frac{n_y^2}{b^2}+\frac{n_z^2}{c^2}\right)$$

Suitable standing waves with in 0 and a



Ψ_0 does not exist since it is zero energy wave, Ψ_1 represent the ZPE of the particle since V= 0, it is only the KE of the particle.

9.9 Important Generalization

(1) As ‘a’ increases, E_x decreases, E_x is only K. E. so if these is more room for the movement of the electrons, lower is its K E. So lower the energy greater is the stability. i.e., more localized its motion higher will be the K.E.

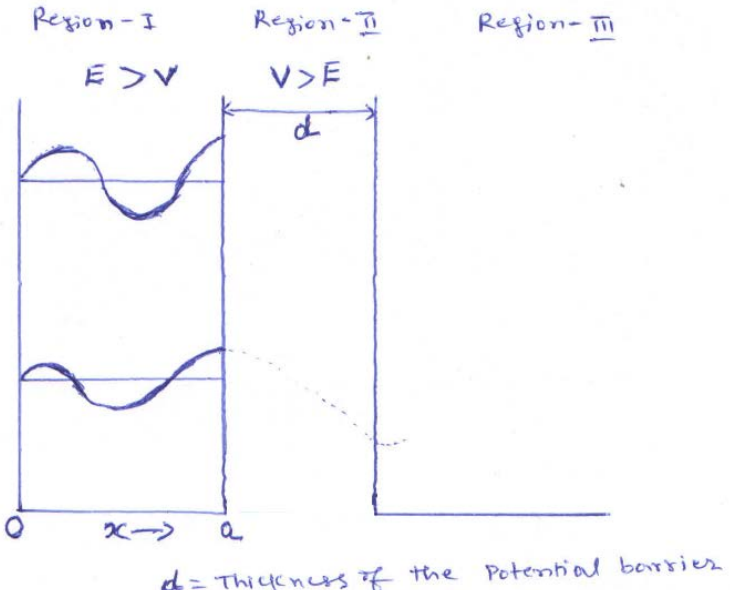
(2) ‘n’ appears naturally and indicates the number of nodes in the particle wave for equation. For equation ‘n’ there are (n-1) nodes.

(3) Value of E depends on n^2 and so rises rapidly as the nodes increases.

(4) From the last equation it is clear that even translational energy of the particle in the box is quantized. Since h^2 is extremely small, levels are very closely spaced, except where the dimensions of the box are vanishingly small. For a normal molecule $\frac{h^2}{m}$ is very small of the order of 10^{-30}, so separation of successive translation levels is so small that the distribution of energy may be regarded as continuous. For this reason under ordinary conditions translational motion of the molecules is adequately treated by the methods of classical mechanics.

9.10 Particle trapped in a three dimensional potential box with finite walls (Tunnel effect)

The so-called tunnel effect of quantum mechanics can be derived from a special case of the potential well, by changing $-V_0$ in to $+V_0$ thus creating a potential barrier



Particle confined in a potential energy well V is finite E is the K.E and E > V inside. But outside the box, V > E i.e. the barrier height is greater than the energy available for the particle. (The particle cannot escape from the box. Classical probability of escape is Nil.

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0----------(1)$$

$$\psi = Ae^{ikx}$$

$$k = \frac{2\pi}{h}\sqrt{2m(E-v)}$$

General Solution is $\psi = Ae^{2\pi x/h\sqrt{2m(E-V)}}$ ---------(2)

In the region within the box E > V and the particle is bound with in the space i.e 0<x<a

So the solution inside the box is simply

$$\psi = A\sin\left(\frac{8\pi^2 mE}{h^2}\right)^{1/2}x-----------(3)$$

But in the region within the barrier V > E so that $\sqrt{2m(E-V)}$ is negative (Region of –Ve energy)

Multiplying by $\sqrt{-1}$ and make the term +ve

$$\frac{2\pi ix}{h}\sqrt{2m\left(E-V\right)}=-\frac{2\pi x}{h}\sqrt{2m(V-E)}$$

$$\left[\frac{2\pi ix}{h}\sqrt{-1X\,2M\left(V-E\right)}=\frac{2\pi ix}{h}\sqrt{-1}\sqrt{2m(V-E)}\right]\left(i=\frac{1}{\sqrt{-1}}\therefore\left(\frac{\sqrt{-1}}{\sqrt{-1}}\right)=-1\right)$$

$$\therefore\psi = Ae^{\frac{-2\pi x}{h}\sqrt{2m(V-E)}}--------(4)$$

This describes the behavior of ψ within the barrier so probability of finding particle in the region of –ve energy is exactly not zero but a certain positive number which falls off exponentially with the distance of penetration in the barrier. So long as the barrier is not infinitely high nor infinitely wide, always a certain probability exits that electrons or particles in general will leak through this is common in the word of atoms. This phenomenon is called Tunnel effect.

Wide barrier---- x is High

High barrier -----V is high

When x or V increases -------- ψ decreases

A good example is emission of α - particle from radioactive nuclei

9.11 Summary of the unit

The time-dependent Schrödinger equation is a partial differential equation, a complete understanding of which requires more mathematical preparation than what we assuming here. Fortunately, the majority of interesting problems in quantum mechanics do not require use of the equation in its full generality. By far the most interesting states of any quantum system are those states in which the system has a definite total energy, and it turns out that for these states the wave function is a standing wave, analogous to the familiar standing waves on a string. When the time-dependent Schrödinger equation is applied to these standing waves, it reduces to a simpler equation called the time-independent Schrödinger equation. We will need only this time-independent equation, which will let us find the wave functions of the standing waves and the corresponding allowed energies. Because we will be using only the time-independent Schrödinger equation we will often refer to it as just “the Schrödinger equation.” Nevertheless, you should know that there are really two Schrödinger equations (the time-dependent and the time-independent). Unfortunately, it is almost universal to refer to either as “the Schrödinger equation” and to let the context decide which is being discussed. A significant feature of the particle-in-a-box quantum states is the occurrence of nodes. These are points, other than the two end points (which are fixed by the boundary conditions), at which the wavefunction vanishes. At a node there is exactly zero probability of ¯nding the particle. The nth quantum state has, in fact, n-1 nodes. It is generally true that the number of nodes increases with the energy of a quantum state.

9.12 Key words

Schrodinger equation; Free particle; Particle trapped in a one dimensional box; Boundary Conditions; Normalization; Orthogonality; Wave functions; Three dimensional Box; Tunnel effect

9.13 References for further study

1) Quantum Mechanics in Physics and Chemistry with Applications to Biology; Rabi Majumdar; *PHI Learning Pvt. Ltd*; **2011**.

2) Quantum Chemistry; Donald Allan McQuarrie; *University Science Books*; **2008**.

3) Quantum Mechanics:Theory and Applications; Ajoy K. Ghatak, S. Lokanathan; *Macmillan*, **2004**.

4) Introduction to Quantum Mechanics with Applications to Chemistry; Linus Pauling, E. Bright Wilson; *Courier Dover Publications*; **2012**.

5) Quantum Mechanics and Spectroscopy; Gupta Tandon; *Galgotia Publications*.

9.14 questions for self understanding

1) Derive the mathematical expression for Application of Schrodinger equation to a free particle

2) Derive the mathematical expression for application of Schrödinger equation to a particle trapped in a one dimensional box (infinite potential walls)

3) Write a note on

a) Boundary Conditions

b) Value of n

c) Width of box

d) The value of D (Normalization)

4) Prove the orthogonality of Wave function

5) Explain selection Rules for transition

6) What are wave functions?

7) Explain factors influencing color

8) Derive the mathematical expression for Particle in a three dimensional Box (Rectangle)

9) Derive the mathematical expression for Particle trapped in a three dimensional potential box with finite walls (Tunnel effect)

Unit 10

Structure

10.1 Objectives of the unit
10.1 Introduction
10.2 Degeneracy
10.3 Application of Schrödinger wave equation for hydrogen atom
10.4 Separation & solution of r, Φ, φ equation & orbital diagram
10.5 Eigen Function and probability distribution
10.6 Section of Spherical s and p eigin functions
10.7 Physical significance of S orbital
10.8 Application of Schrodinger wave Rigid Rotator
10.9 Application of Schrodinger wave equation for Harmonic Oscillator
10.10 Summary of the unit
10.11 Key words
10.12 References for further studies
10.13 Questions for self understanding

10.0 Objectives of the Unit

After studying this unit you are able to

- Explain the Degeneracy according to quantum theory
- Solve the Schrödinger wave equation for hydrogen atom
- Separate the terms r, Φ, φ and find the solution for them
- Derive the expression for Eigen function and probability distribution
- Explain the physical significance of S orbital
- Solve the Schrodinger wave equation for rigid rotator
- Solve the Schrodinger wave equation for harmonic oscillator

10.1 Introduction

Quantum systems with symmetry generally exhibit degeneracy in their energy levels. This means that there can exist distinct eigen functions which share the same eigenvalue. An eigenvalue which corresponds to a unique eigenfunction is termed nondegenerate while one which belongs to n different eigenfunctions is termed n-fold degenerate. As an example, we enumerate the first few levels for a cubic box, with E_{n1}, E_{n2}, E_{n3} expressed in units of $h^2/8ma^2$.

$E_{1,1,1} = 3$ (nondegenerate)

$E_{1,1,2} = E_{1,2,1} = E_{2,1,1} = 6$ (3-fold degenerate)

$E_{1,2,2} = E_{2,1,2} = E_{2,2,1} = 9$ (3-fold degenerate)

$E_{1,1,3} = E_{1,3,1} = E_{3,1,1} = 11$ (3-fold degenerate)

$E_{2,2,2} = 12$ (non-degenerate)

$E_{1,2,3} = E_{1,3,2} = E_{2,1,3} = E_{2,3,1} = E_{3,1,2} = E_{3,2,1} = 14$ (6-fold degenerate)

10.2 Degeneracy

Analysis of the Schrödinger wave equation in three dimensions introduces three quantum numbers that quantize the energy. A quantum state is degenerate when there is more than one wave function for a given energy. Degeneracy results from particular properties of the potential energy function that describes the system. A perturbation of the potential energy can remove the degeneracy.

Consider a cubic box ----- a = b = c, the magnitudes of particle momentum in all three directions in a cubic box are similarly and is given by

$$\psi_{211} = \sqrt{\frac{8}{a^3}} \sin\frac{2\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{\pi y}{a}$$

$$\psi_{121} = \sqrt{\frac{8}{a^3}} \sin\frac{\pi x}{a} \sin\frac{2\pi y}{a} \sin\frac{\pi y}{a}$$

$$\psi_{112} = \sqrt{\frac{8}{a^3}} \sin\frac{\pi x}{a} \sin\frac{\pi y}{a} \sin\frac{2\pi y}{a}$$

Above equations have different special distribution but same characteristic energy

$$E = \frac{h^2}{8ma^2}\left(n_1^2 + n_2^2 + n_3^2\right)$$

Such an energy heavy made than are wave function for the same value of energy is called ‘degenerate state and the phenomenon is called degeneracy.

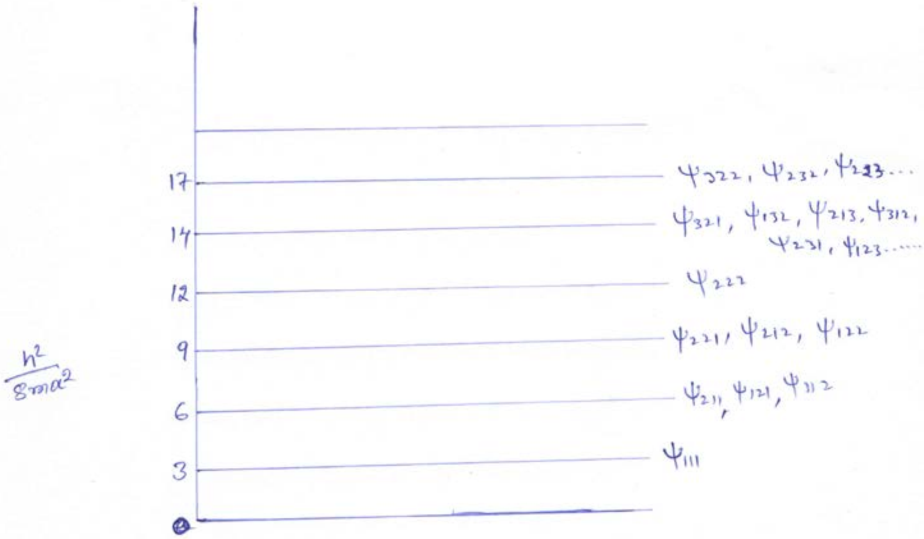
So The ground state, for which $n_1 = n_2 = n_3 = 1$, has energy

$$E = \frac{3h^2}{8ma^2}$$

There are three first excited states, corresponding to the three different combinations of n1, n2, n3, whose squares sum to 6 that is we obtain the same energy for the three combinations n1 = 1, n2 = 2, n3 = 1, or n1= 1, n2 = 1, n3 = 2. The excited state has energy

$$E_{211} = E_{121} = E_{112} = \frac{h^2}{8ma^2}\left(1^2 + 1^2 + 2^2\right) = \frac{6h^2}{8ma^2}$$

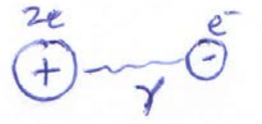
So E_{211} is degenerate (three fold) since there are 3 eigin functions that belong to it. If a, b, c have no internal relationship each eigin value will have a single unique eigin functionf(i.e, non degenerate levels)



10.3 Application of Schrödinger wave equation for hydrogen atom

The motion of a single electron represent by the wave equation is

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}(E - V)\psi = 0 \quad \text{where } \mu = \frac{mM}{m + M}$$



$$f = \frac{-e.Z_e}{r^2} = -\frac{Ze^2}{r^2}$$

$$V_{PE} = -\int fdr = -\frac{Ze^2}{r}$$

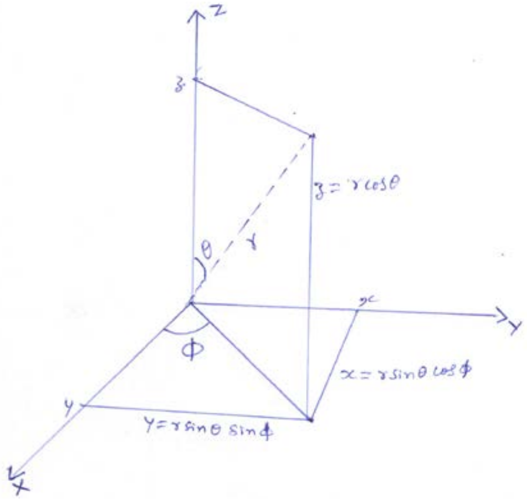
For H atom V = $-\frac{e^2}{r}$

Therefore the modified Schrödinger equation is

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}(E + \frac{e^2}{r})\psi = 0 - - - - - (1)$$

This equation is in Cartesian co- ordinates. It is difficult to solve this equation in Cartesian co-ordinate and it can be made simpler if it is converted into an equation in polar (spherical) co-ordinates therefore converted into spherical polar co-ordinates (r, θ, ϕ)

It is note that for a sphere $x^2 + y^2 + z^2$ = constant and also r = constant in spherical co-ordinates.



$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

On Substituting in (1) we get

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\theta^2} + \frac{8\pi^2\mu}{h^2}\left(E + \frac{e^2}{r}\right)\psi = 0 ----(2)$$

Solution in the form

$$\psi_{(r,\theta,\phi)} = R_{(r)}\phi_{(\theta)}\varphi_{(\phi)}$$

Where $R_{(r)}$ is a function of r only similarly

$\varphi_{(\theta)}$ is a function of θ only and

$\phi_{(\varphi)}$ is a function of ϕ only

Substitute $\psi = R\Phi\Theta$ and multiply by $\frac{r^2\sin^2\theta}{R\Phi\varphi}$ in ------2 we get

$$\frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{\sin\theta}{\varphi}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\varphi}{\partial\theta}\right) + \frac{1}{\Phi}\partial^2\Phi\Big/\partial\Phi^2 + r^2\sin^2\theta\frac{8\pi^2\mu}{h^2}(E + \frac{e^2}{r}) = 0 --- (3)$$

Fo rhte above equation, it is possible to separate out in to 3 differential equations one containing ϕ terms, second θ terms and third r terms only.

10.4 Separation & solution of r, Φ, φ equation & orbital diagram

1) Solution of ϕ equation

$$\frac{1}{\phi}.\frac{d^2\varphi}{d\varphi^2} = -m^2 \text{ -------------- } (3a)$$

or

$$\frac{d^2\varphi}{d\varphi^2} + m^2\varphi = 0$$

Solution can be written in both real and complex forms

a) <u>Complex form</u>

$\Phi = ce^{im\phi}$ or $\Phi = ce^{-im\phi}$ i.e $\Phi = ce^{\pm im\phi}$

Where C is normalization Constant

If Φ is to be an acceptable solution (single valued) Then the function has to repeat itself after every 2π. i.e, the same value for $\phi = 0$, and $\phi = 2\pi$

Therefore, when $\phi = 0$; $\Phi = C$ when $\phi = 2\pi$; $\Phi = Ce^{\pm 2\pi mi}$

Since the two solution are identical, $e^{\pm 2\pi mi} = 1$, i.e

$$e^{\pm 2\pi mi} = \cos 2\pi m \pm i \sin 2\pi m = 1$$

This is time only if m is zero or an integer .

So 'm' has to be single valued m can be $0, \pm 1, \pm 2, \pm 3$ ……………….

To find the value of C-(Normalization procedure)

$$\int_0^{2\pi} \Phi\Phi^* d\phi = 1 \quad \text{i.e} \quad C^2 \int_0^{2\pi} e^{\pm im\phi} e^{\pm im\phi} d\phi = 1$$

i.e $C^2 \int_0^{2\pi} d\phi = 1$ or $2\pi c^2 = 1$ or $C = \frac{1}{\sqrt{2\pi}}$

So the normalized wave function is $\Phi = \frac{1}{\sqrt{2\pi}} e^{\pm im\phi}$

b) Real form

Let $\Phi = c^1 \sin m\phi$ or $\Phi = c^1 \cos m\phi$, which are obtained from the linear combination of $Ce^{im\varphi}$ and $Ce^{-im\varphi}$

To find C^1

$$\int_0^{2\pi} \Phi\Phi^* d\phi = 1 \quad \text{i.e} \quad \left(c^1\right)^2 \int_0^{2\pi} \sin^2 m\phi d\phi = 1$$

i.e $\frac{\left(c^1\right)^2}{2}\int_0^{2\pi}\left(1-\cos 2m\phi\right)d\phi = \frac{\left(c^1\right)^2}{2}\left[\phi - \frac{1}{2m\phi}\sin 2m\phi\right]_0^1 = 1$

$i.e\frac{\left(c^1\right)^2}{2}X\,2\pi = 1$ or $C^1 = \frac{1}{\sqrt{\pi}}$

So the normalized wave function is $\Phi = \frac{1}{\sqrt{\pi}}\sin m\phi$ or $\frac{1}{\sqrt{\pi}}\cos m\phi$ m is called the magnetic quantum number and appears as a direct consequence of the association of a wave function appropriate to a standing wave system with the motion of electron in the atom.

$$\therefore \frac{\sin^2\theta}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{\sin\theta}{\varphi}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\varphi}{\partial\theta}\right) + \frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\Phi^2} + r^2\sin^2\theta\frac{8\pi^2\mu}{h^2}\left(E+\frac{e^2}{r}\right) = 0$$

Substitute (-m^2) for ϕ in equation (3) and divide by $\sin^2\theta$ we get

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{1}{\varphi\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\theta}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta} + \frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{e^2}{r}\right) = 0 - - - - - - - (4)$$

$$PUT\frac{1}{\varphi\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\theta}{\partial\theta}\right) - \frac{m^2}{\sin^2\theta} = -\beta - (5)$$

$$\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{e^2}{r}\right) = \beta - (6)$$

Or dividing by r^2 and multiplying by R we get

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{8\pi^2\mu}{h^2}\left(E + {}^{e^2}\!/_{r}\right)R - \frac{\beta R}{r^2} = 0 - - - - - - - - - - - - - - (7)$$

Equation (7) defines the distance between the nucleus and the electron. Each of these functions must be single valued continuous and finite.

Equations (3a) and (5) define the angular motion of the electron and equation (1) define the translation motion of the atom.

The wavefunction for H atom has thus been separated into four above functions.

c)Solution of θ equation

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{m^2\varphi}{\sin^2\theta}=-\beta\varphi-------------(7a)$$

$$or\,\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\varphi}{d\theta}\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)\Theta=0-----------(8)$$

Define a new variable $x=\cos\theta$ i.e $\sin\theta=\sqrt{1-x^2}$

$$\frac{d\varphi}{d\theta}=\frac{dx}{d\theta}\frac{d\varphi}{dx}=-\sin\theta\frac{d\varphi}{dx}$$

In general $\frac{d}{d\theta}=-\sin\theta\frac{d}{dx}\,or\,\frac{1}{\sin\theta}\frac{d}{d\theta}=-\frac{d}{dx}$

Also $\sin\theta\frac{d\varphi}{d\theta}=-\sin^2\theta\frac{d\varphi}{dx}=-(1-x^2)\frac{d\varphi}{dx}$

$$\frac{d}{dx}\left[\left(1-x^2\right)\frac{d\varphi}{dx}\right]+\left[\beta-\frac{m^2}{(1-x^2)}\right]\varphi=0--------(9)$$

Equation 9 is the familiar from of legendre equation solution is given by the associated legendre polynomial of degree l and order m i.e $p_l^m(x)$

$$p_l^m(x)=(1-x^2)^{m/2}\,d^m p_l(x)\big/dx^m \text{ --------------------------}(10)$$

Where $p_l(x)$ is the legendry polynomial= $\frac{1}{2^l\,|\,l\,|}\frac{d^l\left(x^2-1\right)^l}{dx^l}$

Complete solution of θ equation is

$$\Theta_{(\theta)}=c^{11}p_l^m\left(x\right)=c^{11}p_l^m\left(\cos\theta\right)------------------(11)$$

To find c^{11}

Since $x=\cos\theta$ it can have physical significance only for values between +1 and -1

So, $(c^{11})^2\int_{-1}^{+1}\left[p_l^m(x)\right]^2dx=1, c^{11}=\sqrt{\frac{2l+1}{2}\frac{\underline{|l-|m|}}{\underline{|l+|m|}}}$

So $\Theta_{(\theta)} = \sqrt{\frac{2l+1}{4\pi}\frac{\underline{\lfloor l-|m|}}{\underline{\lfloor l+|m|}}}\, p_l^{|m|}(\cos\theta) ------(12)$

Equation(7a) has acceptable solution only if (l-m) is an integer. Since m is an integer, l must have integral values and l cannot be –ve. Also, if m > l, $p_l^m(x) = 0$ So $m \geq l$ So l has values |m|, |m|+1, |m|+2---------- So m has values from –l to +l i.e (2l+1) values

Spherical harmonics

So $\Theta_{(\theta)}\Phi_{(\theta)} = \sqrt{\frac{2l+1}{4\pi}\frac{\underline{\lfloor l-|m|}}{\underline{\lfloor l+|m|}}}\, p_l^m(\cos\theta)e^{\pm im\varphi}$

$$\sqrt{\frac{2l+1}{2\pi}\frac{\underline{\lfloor l-|m|}}{\underline{\lfloor l+|m|}}}\, p_l^m(\cos\theta)\sin m\varphi$$

I Normalization spherical function for H-like atoms

l	m	$\Theta_{(l,m)}$	$\Phi_{(m)}$
0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
1	0	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$
1	+1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{\pi}}\cos\phi$
1	-1	$\sqrt{\frac{3}{4}}\sin\theta$	$\frac{1}{\sqrt{\pi}}\sin\phi$

II Normalized associated legendry polynomial $\Theta_{l,m(\theta)}$

l=0	m=0	$\Theta_{00} = \frac{1}{\sqrt{2}}$
l=1	m=0	$\Theta_{1,0} = \sqrt{\frac{3}{2}}\cos\theta$
l=1	$m = \pm 1$	$\Theta_{1,\pm 1} = \sqrt{\frac{3}{4}}\sin\theta$
l=2	m=0	$\Theta_{2,0} = \sqrt{\frac{5}{8}}(3\cos^2\theta - 1)$

l=2	$m=\pm1$	$\Theta_{2,\pm1}=\sqrt{\frac{15}{4}}\sin\theta\cos\theta$
l=2	$m=\pm2$	$\Theta_{2,\pm2}=\sqrt{\frac{15}{16}}\sin^2\theta$

Solution of r equation

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{e^2}{r}\right)=l(l+1)$$

$l(l+1)=\beta$ [see earlier equation -------------------------(6)]

Multiplying by R

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2\mu r^2}{h^2}\left(E+\frac{e^2}{r}\right)R-l(l+1)R=0$$

$$2r\frac{dR}{dr}+r^2\frac{d^2R}{dr^2}+\left[\frac{8\pi^2\mu r^2}{h^2}(E+{}^{e^2}\!/_{r})-l(l+1)\right]R=0$$

$\div by r^2$

$$\frac{d^2R}{dr^2}+\frac{2}{r}\frac{dR}{dr}+\left[\frac{8\pi^2\mu}{h^2}\left(E+\frac{e^2}{r}\right)-\frac{l(l+1)}{r^2}\right]R=0---------(13)$$

Necessary to distinguish between +ve and –ve values of E.

In the classical atomic theory, the –ve values of E corresponds to non-ionized atom with closed electronic shell. Assume E to be –ve and introduce a new parameter ‘n’ such that $n^2=\frac{-2\pi^2Z^2\mu e^4}{h^2E}$ and a new variable x in place of r such that $x=\frac{2Z}{na_0}r,$ where a_0 is identical with the radius of the first Bohr orbit $i.e a_0=\frac{h^2}{4\pi^2\mu e^2}$ (Z=effective nuclear charge, Z=1, for H atom).

Introducing n and x, replace $R_{(x)}$ with $X_{(x)}$ in ---(13) we get

$$\frac{d^2X}{dx^2}+\frac{2}{x}\frac{dX}{dx}+\left[-\frac{1}{4}+\frac{n}{x}-\frac{l(l+1)}{x^2}\right]X=0---------------(14)$$

Possible solution is $X_{(x)} = e^{-\frac{x}{2}} F(x)$ where $F_{(x)} = x^l G_{(x)}$ where $G_{(x)}$ and $F_{(x)}$ are function of X

So $X_{(x)} = e^{-\frac{x}{2}} x^l G(x)$

Calculate $\frac{d^2 X}{dx^2}$ and $\frac{dX}{dx}$ in terms of $G_{(x)}$

$$x\frac{d^2G}{dx^2} + [(2l+1) + (1-x)]\frac{dG}{dx} + (n-l-1)G = 0 - - - - - - - - 15$$

Solution given by associated lauguerre polynomial $L_R^P(x)$ of degree (k-P) and order p Here P=(2l+l) and R=(n+l)

$$L_R^p(x) = \frac{d^p L_R(x)}{dx^p} - - - - - - - - - - (16)$$

Where $L_R(x)$ is the Laguerre polynomial in X of degree R

$$L_k(x) = e^x \frac{d^k (x^k e^{-x})}{dx^k}$$

So the solution of r equation is

$$R_{(r)} = c^{111} e^{-\frac{x}{2}} x^l \lfloor_{n+1}^{2l+1}(x)$$

(i) P & k must be zero or integral i.e (k- P) should be an integer for meaningful solutions. i.e $[(n+l) - (2l+1)] = (n-l-1)$ is an integer.
Since l is an integer n becomes an integer, so n=1,2,3…………

(ii) $p \le k$ if the associated polynomial is to be different from zero . so $k \ge P$ i.e $n + l \ge 2l + 1$ or $l \le (n-1)$. So l could be 0,1,2--------------(n-1) Although n can be zero, This has no physical significance since $E_n = \infty$

To find C^{111}

$$\int_0^\infty R_{(r)}R^*_{(r)}r^2dr = 1$$

$$C^{111} = \sqrt{\left(\frac{x}{r}\right)^3 \frac{\underline{|n-l-1}}{2n(\underline{|(n+1)}^3)}}$$

$$R_{(r)} = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{\underline{|n-l-1}}{2n\underline{|(n+l)}^3}}e^{-\frac{Zr}{na_0}}\left(\frac{2Zr}{na_0}\right)^l \lfloor^{2l+1}_{n+l}\left(\frac{2Zr}{na_0}\right)$$

Therefore complex solution is

$$\psi = k_{(r)}\Theta_{(\theta)}\Phi_{(\varphi)}$$

$$\psi_{(r,\theta,\varphi)} == \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{\underline{|n-l-1}}{2n\underline{|(n+l)}^3}}e^{-\frac{Zr}{na_0}}\left(\frac{2Zr}{na_0}\right)^l \lfloor^{2l+1}_{n+l}\left(\frac{2Zr}{na_0}\right)\sqrt{\frac{2l+1}{2}\frac{\underline{|l-|m|}}{\underline{|l+|m|}}}P_l^m(\cos\theta)\frac{1}{\sqrt{2\pi}}e^{\pm im\varphi}$$

III Normalized Radial Function for H like atoms

n	l	$R_{nl(r)}$
1	0	$R_{10} = 2\left(\frac{Z}{a_0}\right)^{3/2}\left(e^{-Zr/a_0}\right)$
2	0	$R_{20} = \frac{1}{\sqrt[2]{2}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)\left(e^{-\frac{Zr}{2a_0}}\right)$
2	1	$R_{21} = \frac{1}{\sqrt[2]{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)\left(e^{-Zr/2a_0}\right)$
3	0	$R_{30} = \frac{2}{\sqrt[81]{3}}\left(\frac{Z}{a_0}\right)^{3/2}\left[27-18\left(\frac{Zr}{a_0}\right)+2\left(\frac{Zr}{a_0}\right)^3\right]\left(e^{-Zr/3a_0}\right)$
3	1	$R_{31} = \frac{4}{\sqrt[81]{6}}\left(\frac{Z}{a_0}\right)^{3/2}\left[6\left(\frac{Zr}{a_0}\right)-\left(\frac{Zr}{a_o}\right)^2\right]\left(e^{-\frac{Zr}{3a_0}}\right)$
3	2	$R_{32} = \frac{4}{\sqrt[81]{30}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right)^2\left(e^{-\frac{Zr}{3a_0}}\right)$

IV Complete eigen function for H like atoms

n	l	m	State	Eif
1	0	0	1s	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{z}{a_0}\right)^{\frac{3}{2}} e^{\frac{-Zr}{a_0}}$
2	0	0	2s	$\psi_{200} = \frac{1}{\sqrt[4]{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(2-\frac{Zr}{a_0}\right)e^{-\frac{Zr}{2a_0}}$
2	1	0	$2p_z$	$\psi_{210} = \frac{1}{\sqrt[4]{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} e^{-\frac{Zr}{2a_0}} r\cos\theta$
2	1	+1	$2p_x$	$\psi_{211} = \frac{1}{\sqrt[4]{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} e^{\frac{-Zr}{2a_0}} r\sin\theta\cos\theta$
2	1	-1	$2p_y$	$\psi_{21-1} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{\frac{5}{2}} e^{\frac{-Zr}{2a_0}} r\sin\theta\sin\phi$

ψ_{100} =G.s of H atom when Z=1

$\psi_{100} = \left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} e^{\frac{-r}{a_0}}$ one electron wavefunction

V Normalized complete spherical eif's Θ_θ and Φ_ϕ

l	m	Symbol	Eif	Normalized to 4π
0	0	&	$\frac{1}{\sqrt{4\pi}}$	1
1	0	P_z	$\sqrt{\frac{3}{4\pi}}\cos\theta$	$\sqrt{3}\cos\theta$
1	-1	P_y	$\sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi$	$\sqrt{3}\sin\theta\sin\phi$
1	+1	P_x	$\sqrt{\frac{3}{4\pi}}\sin\theta\cos\phi$	$\sqrt{3}\sin\theta\cos\phi$

10.5 Eigen Function and probability distribution

(1)The values of the square of the radical function R(r) is a measure of the probability of finding electron in an element of unit length at a distance r from the nucleus.

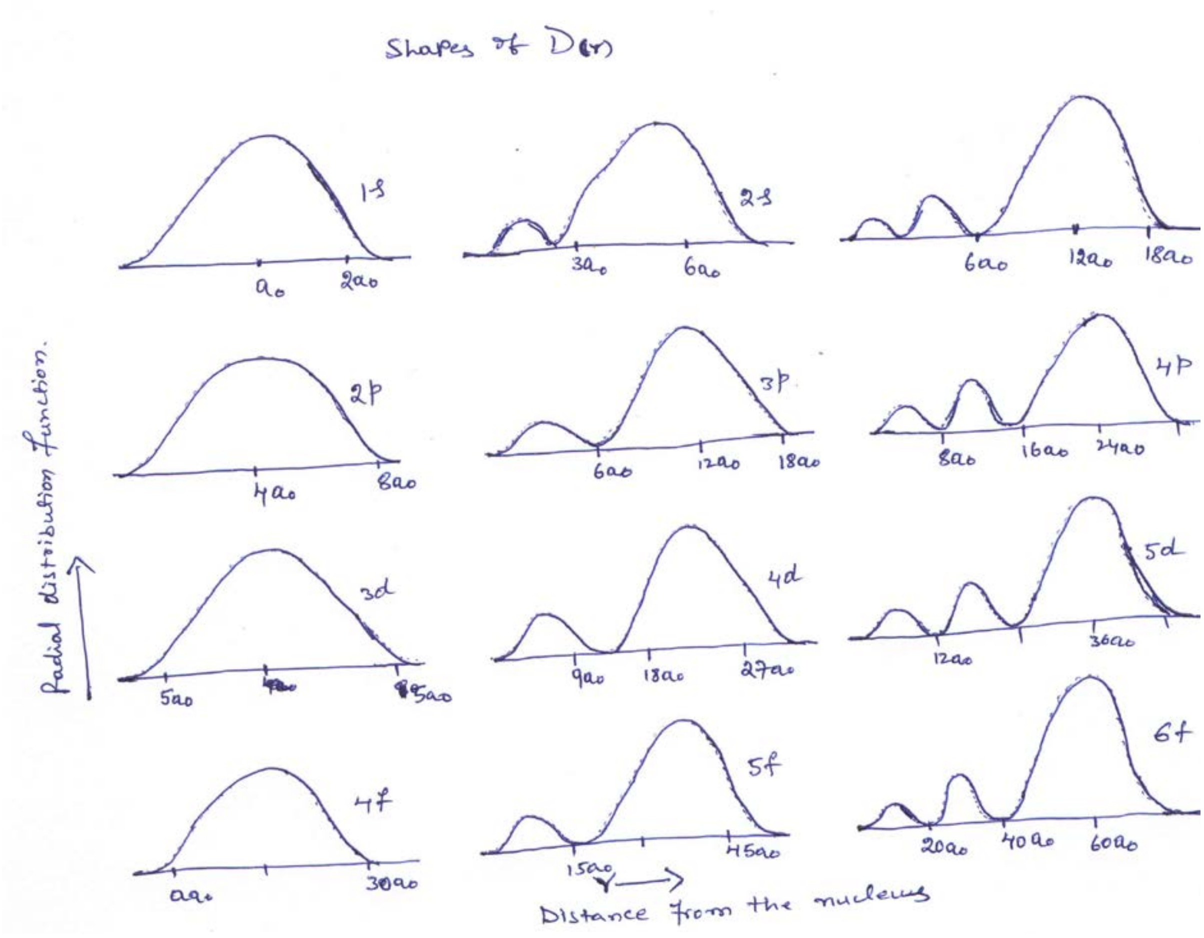
(2)Instead of studying R(r) a more useful property known as the distribution function (radical) which is $4\pi r^2 R^2_{(r)}$ a measure of the probability D(r) that the electron will be found in a spherical shell at a distance r from the nucleus.

Curve for ls, 2p, 3d, 4f etc (electron) show one maximum only and in each the maxima occur at distances from the nucleus equal to the corresponding Bohr orbital.

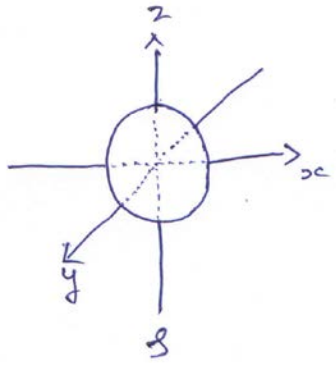
General rule

The s and p eigin functions (l=0& 1) for the same value of n e.g $\psi_{200,}\psi_{210}$ & ψ_{211} show approximately the same dependence on r but difference essentially in θ and ψ i.e the radial parts of the eif's are approximately the same but the speherical parts differ appreciably.

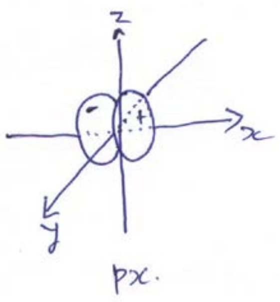
Table V brings to light a no of significant points

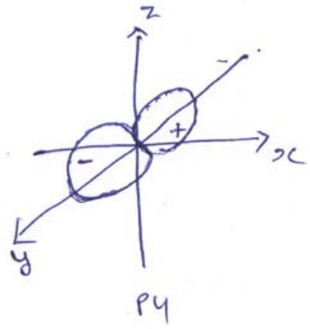


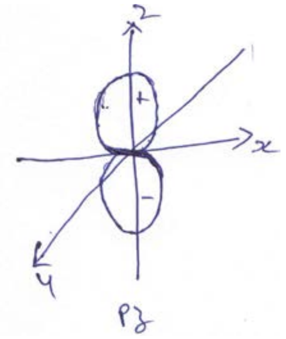
i) s function is independent of θ and ϕ hence spherically symmetrical as shown below



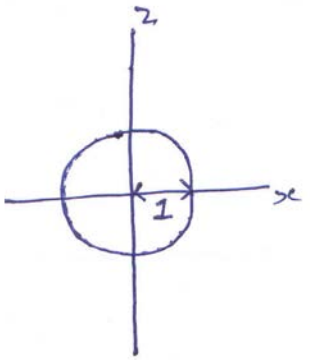
ii) p functions exhibit angular distribution as shown below

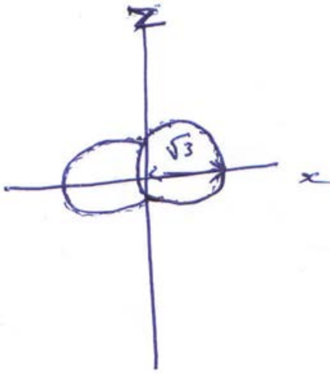






10.6 Section of Spherical s and p eigin functions





The relative magnitude of s eigin function is unity in evry direction (Table V) p function will $\sqrt{3}$ if $\sin\theta$, $\cos\theta$, $\sin\phi$ & $\cos\phi$ =1. Maximum value of spherical p eigifunction is thus $\sqrt{3}$ times as great as that of the s function.

(1) The probability of finding an s electron is the same in all directions around the nucleus of the hydrogen like atom but a p electron will tend to concentrate in certain preferred direction(Right angle to each other)

(2) Maximum probability of the P electron being in one of these preferred direction is $\sqrt{3}$ times as greater as that of an electron being in any direction.

Thus Orbital can be considered as mathematical function given by Schrödinger equation and Orbit can be considered as Physical function given by Bohr for the path of the electron

10.7 Physical significance of S orbital

n=1, l=0, m=0 ls orbital

$$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}} e^{\frac{-r}{a_0}}$$

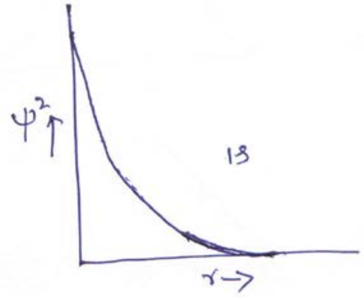
n=2, l=0, m=0 2s orbital

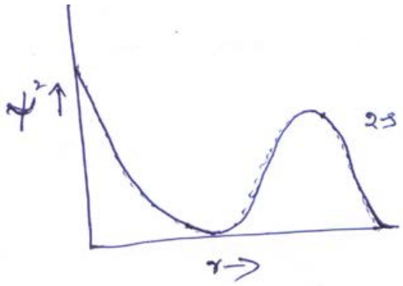
$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}}\left(2-\frac{r}{a_0}\right) e^{\frac{-r}{2a_0}}$$

$$a_0 = \frac{h^2}{4\pi^2\mu^2e^2} = 0.53A^0$$

No angular dependence means spherically symmetrical wave function

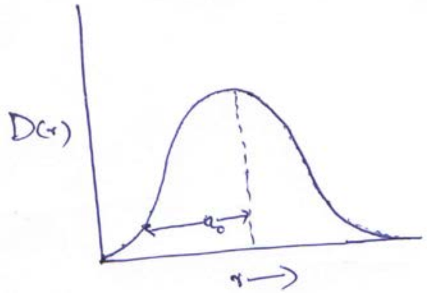
$\psi^2 dv$ gives the probability of finding the electron in an element of volume element dv

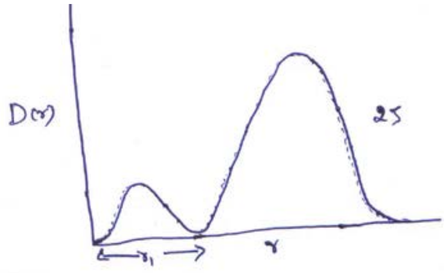




Plot of radial distribution function D(r) Vs r.

D(r) = $4\pi r^2\psi^2$ this gives the probability of finding the electron in a spherical shell of radius r and thickness dr.



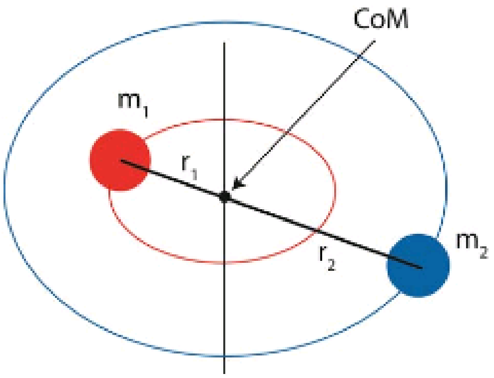


10.8 Application of Schrodinger wave Rigid Rotator

Energy states and wave functions for a rotating system consisting of two masses held apart by a rigid bond (Rotation of diatomic molecules in space) makes as point particles and rigid bond holding them at a fixed distance apart in space. In this system interest is only in the rotational energy. The center of mass is fixed at the co-ordinate system

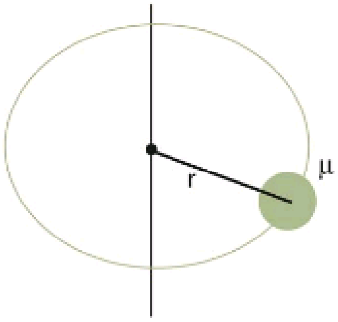
Classical Model of Rotation

Consider the rotation of a diatomic molecule.



The radius is fixed, and the centre of mass $m_1 r_1 = m_2 r_2$. The bond distance or bond length is $r_1 + r_2 = R$ where $r_1 = \frac{m_2 R}{m_1 + m_2}$ and $r_2 = \frac{m_1 R}{m_1 + m_2}$

We can transform this problem to that of a single mass rotating around the origin using the reduced mass as follows



Reduced Mass: $\mu = \frac{m_1 m_2}{m_1 + m_2}$

Velocity: $\mathrm{v} = \nu_{rot}\left(2\pi r\right)$

$= \omega r$

Kinetic Energy: $K = \frac{1}{2}\mu \mathrm{v}^2 = \frac{1}{2}\mu\omega^2 r^2$

$= \frac{1}{2} I\omega^2$

Moment of Inertia: $I = \mu r^2$

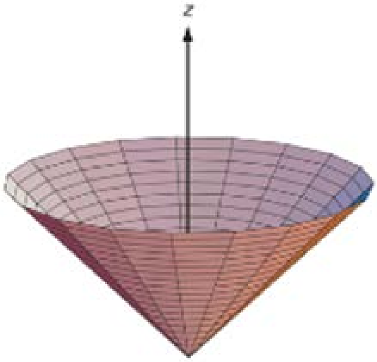
Angular Momentum: $\ell = I\omega$

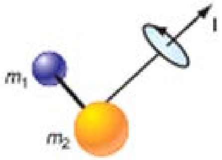
K.E of rotation of masses is $E = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$

$$= \frac{1}{2} m_1 \omega^2 r_1^2 + \frac{1}{2} m_2 \omega^2 r_2^2 = \frac{1}{2} \omega^2 I = \frac{L^2}{2I}$$

Since total angular momentum of rotation is $L = \omega I$

Where $\omega =$angular velocity and I= moment of inertia about an axis passing through centre of gravity and normal to the line through masses. It is important to note that the direction of the moment of inertia is normal to the plane of rotation. The total angular momentum can be decomposed into components along x, y, and z i.e., $l^2 = l_x^2 + l_y^2 + l_z^2$.





Classically, we can know all three components simultaneously. Quantum mechanically, we'll see what happens........

Using the postulates of quantum mechanics, we construct the quantum mechanical Hamiltonian using operators for the classical componentsIf no external forces are acting on the system then V = 0, $mr^2 = m = I$ since r =1=constant.

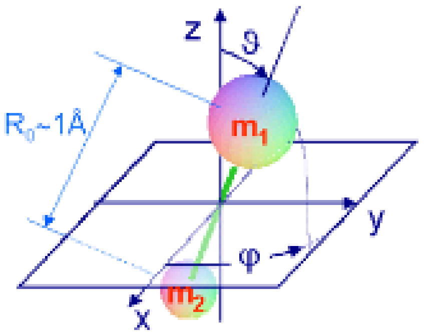
We have Schrodinger equation $\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0 - - - (1)$

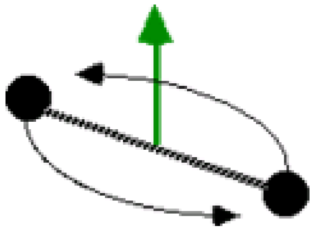
Therefore $\nabla^2 \psi + \frac{8\pi^2 I}{h^2} E\psi = 0 ....(2)$

Converting the equation (2) into polar co-ordinates $x = r\sin\theta\cos\phi,$ $y = r\sin\theta\sin\phi$ $z = r\cos\theta$ we will get

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2 IE}{h^2}\psi = 0 - - - - - - - - -(3)$$

A rigid rotator behaves like a single particle of mass I placed at a fixed distance equal to unity (since r=1) from the origin. The rotator is thus equivalent to a single particle of mass I moving on the surface of a sphere of radius unit





Solution in the form $\psi_{(\theta,\phi)}=\Theta_{(\theta)}\Phi_{(\phi)}$ or $\psi=\Theta\Phi$

Substitute $\psi=\Theta\Phi$ in (3) and divide by $\Theta\Phi$ and multiply by $\sin^2\theta$ we will get

$$\frac{\sin\theta}{\Theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right)+\frac{8\pi^2 IE}{h^2}\sin^2\theta+\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}=0 \text{ ----------------------------(4)}$$

To solve this equation, separate the wave function into a product of functions involving a single variable.

Solution of ϕ equation

put $\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\Phi^2}=-m^2$ or $\frac{\partial^2\Phi}{\partial\Phi^2}+m^2\Phi=0$ – – – – – – – – – – – – – – (5)

Solution of the above equation in the complex form is $\Phi=Ce^{\pm im\phi}$

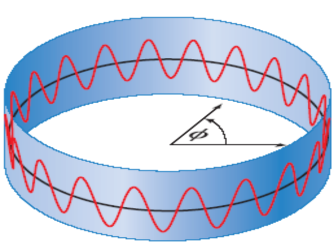
condition for an acceptable solution is that the function should be single valued i.e $e^{im\phi}=e^{im(\phi+2\pi)}$ since adding 2π to ϕ brings us back to the same point in space i.e function repeats itself after every 2π

$\Phi=Ce^{\pm im\phi}$ when $\phi=0$, $\Phi=C$, When $\phi=2\pi,\Phi=Ce^{\pm 2\pi mi}$

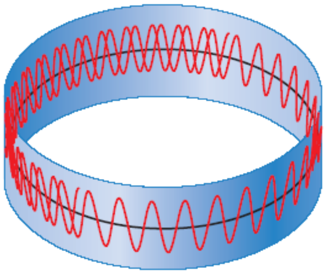
The two are equivalent i.e $C=Ce^{\pm 2\pi mi}$ or $e^{\pm 2\pi mi}=1$-------------(6)

i.e $\cos 2\pi m+i\sin 2\pi m=1$ This is time if m is zero or integer i.e m = 0, $\pm1,\pm2,\pm3$........

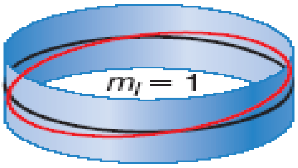
Where m_l = quantum number. We say that the energy levels with $m_l \neq 0$ are twofold degenerate.

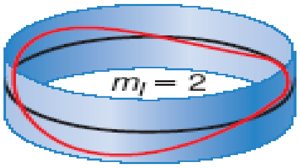


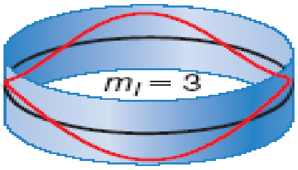
$m_l = \pm$integer

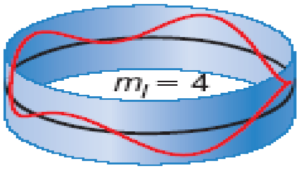


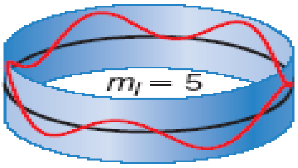
$m_l \neq \pm$integer

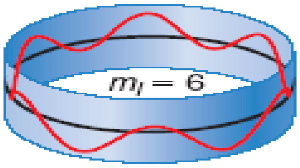












For normalization $\int_0 \phi\phi^{*} d\phi$ or $\int_0 \Psi^{2} d\phi = 1$

i.e $C^2 \int_0^{2\pi} e^{\pm im\phi} e^{\pm im\phi} d\phi = 1$ ------------------(7)

i.e $C^2 \int_0^{2\pi} d\phi = 1$ or $C^2(2\pi) = 1$ or $C = \frac{1}{\sqrt{2\pi}}$

$\therefore$ Normalized solution is $\Phi = \frac{1}{\sqrt{2\pi}} e^{\pm im\phi}$ ------------------(8)

In real form

$\Phi = c^1 \sin m\phi$ or $c^1 \cos m\phi$ ---------------(9) (obtained from linear combination of $e^{im\phi}$ and $e^{-im\phi}$

To find $C^1, \int_0^{2\pi} \Phi\Phi^* d\phi = 1$ i.e $\left(C^1\right)^2 \int_0^{2\pi} \sin^2 m\phi d\phi = 1$

$$\frac{(C^1)^2}{2}\int_0^{2\pi}(1-\cos 2m\phi)d\phi = \frac{\left(C^1\right)^2}{2}\left[\phi - \frac{1}{2m\phi}\sin 2m\phi\right]_0^{2\pi} = 1 ---------------(10)$$

$$i.e\frac{(C^1)^2}{2} X\, 2\pi = 1$$

$C^1 = \frac{1}{\sqrt{\pi}}$ so normalized solution

Is $\Phi = \frac{1}{\sqrt{\pi}}\sin m\phi$ or $\frac{1}{\sqrt{\pi}}\cos m\phi$ -------------------------------(11)

Solution of θ equation

Put $\frac{8\pi^2 IE}{h^2} = \beta$

Substitute $(-m^2)$ for ϕ term & divided by $\sin^2\theta$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(\beta - \frac{m^2}{\sin^2\theta}\right)\Theta = 0 ------------(12)$$

Put $S = \cos\theta$;

$$\frac{d\Theta}{d\theta} = \frac{ds}{d\theta}.\frac{d\Theta}{ds} = -\sin\theta.\frac{d\Theta}{ds}$$

Also $\sin\theta = \sqrt{1-s^2}$ in general $\frac{d}{d\theta} = -\sin\theta\frac{d}{ds}$

Again $\sin\theta\frac{d\Theta}{d\theta} = -\sin^2\theta\frac{d\Theta}{ds} = -(1-s^2)\frac{d\Theta}{ds}$

$$\frac{1}{\sin\theta}\frac{d}{d\theta} = -d/ds$$

$$\therefore -\frac{d}{ds}\left[-(1-s^2)\frac{d\Theta}{ds}\right]+\left[\beta-\frac{m^2}{(1-s^2)}\right]\Theta=0 ------------(13)$$

$$\frac{d}{ds}\left[(1-s^2)\frac{d\Theta}{ds}\right]+\left[\beta-\frac{m^2}{(1-s^2}\right]\Theta=0$$

$$(1-s^2)\frac{d^2\Theta}{ds^2}-2s\frac{d\Theta}{ds}+\left[\beta-\frac{m^2}{(1-s^2)}\right]\Theta=0 --------------(14)$$

Equation 14 standard mathematical form

$$\left(1-x^2\right)\frac{d^2y}{dx^2}-2y\frac{dy}{dx}+\begin{bmatrix} l(l+1) \\ -\dfrac{m^2}{1-x^2}\end{bmatrix}y=0 --------------(15) \text{ Legendre equation}$$

Differentiate m times we get

$$(1-x^2)\,{d^{m+2}y}\big/{dx^{m+2}}-2x(m+1)\frac{d^{m+1}y}{dx^{m+1}}+\left[l(l+1)-m(m+1)\right]\frac{d^my}{dx^m}=0$$

Introduce a new function $q=\dfrac{d_y^m}{dx^m}$

$$(1-x^2)\frac{d^2q}{dx^2}-2x(m+1)\frac{dq}{dx}+\left[l(l+1)-m(m+1)\right]q=0 -------------(17)$$

$$q=(1-x^2)^{\frac{-w}{2}}\rho\,\textbf{where}\;\rho=(1-x^2)^{\frac{m^2}{2}}\frac{d^my}{dx^m} ---------------------(18)$$

Substitute for P and after manipulation

$$(1-x^2)\frac{d^2p}{dx^2}-2x\frac{dp}{dx}+\left[l(l+1)-\frac{m^2}{(1-x^2)}\right]p=0 ----------------------(19)$$

Solution of (19) is $P_l^{|m|}(x)=(1-x^2)^{\frac{m}{2}}\dfrac{d^m}{dx^m}p_l(x) ---------------------(20)$

where $P_l(x)=\dfrac{1}{2^l l}\dfrac{d^l}{dx^l}(x^2-1)^l$

The final solution is $P_l^{|m|}(s)$ of equation (14)

So $\Theta = P_l^{|m|}(\cos\theta) = (\sin^2\theta)^{\frac{|m|}{2}} \frac{d^{|m|}}{d(\cos\theta)^{|m|}} P_l(\cos\theta)$

Where comparison of (14) & (19) gives possible energies

i.e $\frac{8\pi^2 IE}{h^2} = l(l+1)$

or $E = \frac{h^2}{8\pi^2 I} l(l+1) ----------------(21)$ Eigen values

we get the corresponding eif's corresponding to eiv's given by (21) by combining the two solution

$\psi_{l,m(\theta,\phi)} = Np_l^{|m|}(\cos\theta)\frac{1}{\sqrt{2\pi}}e^{\pm im\phi}$ Spherical harmonics $p_l^m(\cos\theta)$ remains finite in the range that $\cos\theta$ can cover if l is a non-negative integer and $l \geq |m|$. But m takes only integral values. So l is an integer i.e 0,1,2,3……….. and m = -l,-l+1………….-1,0,1………….l

Normalization of solution

$N^2\int_{-1}^{+1}\left[p_l^m(s)\right]^2 ds = 1$ **or** $N = \sqrt{\frac{2l+1}{2}\frac{l-|m|}{l+|m|}}$

Complete solution is $\psi = \sqrt{\frac{2l+1}{4\pi}\frac{l-|m|}{l+|m|}}p_l^m(\cos\theta)e^{\pm im\phi}$

Normalized spherical function

l	**m**	$\Theta_{l,m(\theta)}$	$\Phi_{(\phi)}$
0	**0**	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$
1	**0**	$\sqrt{\frac{3}{2}}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$
1	± 1	$\sqrt{\frac{3}{2}}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{\pm im\phi}$ **or** $\frac{1}{\sqrt{\pi}}\cos\phi$ **or** $\frac{1}{\sqrt{\pi}}\sin\phi$

Normalized eigen function and eigen values for a rigid rotator

l	**m**	$\Theta\Phi$	**E**

0	**0**	$\frac{1}{2\sqrt{\pi}}$	**0**
1	**0**	$\frac{\sqrt{3}}{2\sqrt{\pi}}\cos\theta$	
1	**+1**	$\frac{\sqrt{3}}{2\sqrt{\pi}}\sin\theta\cos\phi$	$\frac{2h^2}{8\pi^2 I} = \frac{h^2}{4\pi^2 I}$
1	**-1**	$\frac{\sqrt{3}}{2\sqrt{\pi}}\sin\theta\sin\phi$	
2	**0**	$\frac{\sqrt{5}\left[3\cos^2\theta - 1\right]}{4\sqrt{\pi}}$	
2	**1**	$\frac{\sqrt{30}\sin\theta\cos\phi\cos\theta}{2\sqrt{2\pi}}$	$\frac{6h^2}{8\pi^2 I} = \frac{3h^2}{4\pi^2 I}$
2	**2**	$\frac{\sqrt{15}\left[\sin^2\theta\cos^2\phi - \sin^2\theta\sin^2\phi\right]}{4\sqrt{\pi}}$	
2	**-1**	$\frac{\sqrt{30}\left[\sin\theta\cos\ \ \theta - \sin\phi\right]}{2\sqrt{2\pi}}$	
2	**-2**	$\frac{\sqrt{15}\left[\sin^2\theta\cos\phi - \sin\phi\right]}{2\sqrt{\pi}}$	

$$f = -\frac{Ze^2}{r^2} \Big/ V_{P.E} = -\int_{\infty}^{r} f\,dr = -\int_{\infty}^{r}\left(\frac{-Ze^2}{r^2}\right)dr$$

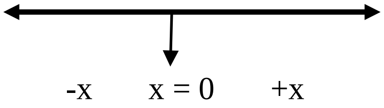
$$V = +Ze^2\int_{\infty}^{r}\frac{1}{r^2}\,dr = +Ze^2\int_{\infty}^{r} r^{-2}\,dr = +Ze^2\left(\frac{r^{-2+1}}{-2+1}\right) = \frac{r^{-1}}{-1} = -\frac{1}{r}$$

-ve sign indicates the decrease of P.E

10.9 Application of Schrodinger wave equation for Harmonic Oscillator

The harmonic oscillator is a fundamental problem in classical dynamics as well as in quantum mechanics. It represents the simplest model system in which attractive forces are present and is an important paradigm for all kinds of vibrational phenomena. For instance, the vibrations around equilibrium positions of a system of interacting particles may be described, via an appropriate coordinate transformation, in terms of independent harmonic oscillators known as normal vibrational modes. The same holds in quantum mechanics. The study of the quantum oscillator allows a deeper understanding of quantization and of its effects and of wave functions of bound states.

A vibrating diatomic molecules approximates to a harmonic oscillator



If the Harmonic oscillator executes simple harmonic motion, the restoring force proportional to displacement but is in the opposite direction i.e $f = -kx$ where x = displacement (amplitude of Vibration) and k = Hooke’s constant.

$$f = ma = m\frac{d^2x}{dt^2} = -kx$$

$$\therefore \frac{d^2x}{dt^2} = -\frac{k}{m}x \text{ or } \frac{d^2x}{dt^2} + \frac{k}{m}x = 0$$

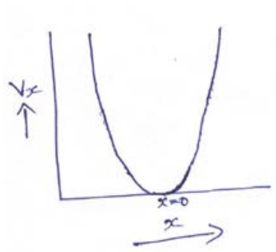
Solution of above equation is $x = A\cos\left(\frac{k}{m}\right)^{\frac{1}{2}}t$ If ν_0 is the classical frequency of the vibrating system $x = A\cos 2\pi\nu_0 t$

$$\left(\frac{k}{m}\right)^{\frac{1}{2}} = 2\pi\nu_0 \text{ or } \nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \text{ or } k = 4\pi^2\nu_0^2 m$$

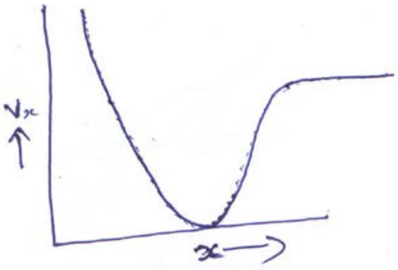
If V_x is the work done in achieving displacement x,

Then $V_x = \int_0^x - fdx = \int_0^x kxdx = \frac{1}{2}kx^2$ This is Hooke’s law potential

Locus is a parabola vibrations in a diatomic molecule are approximately simple harmonic.



But the potential energy curve slightly deviates from the theoretical curve



For a particle oscillating in x-direction only i.e, parallel to x-axis, co-ordinates of y & z remains constant

Then Schrödinger wave equation reduces to one dimensional form

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}(E-V_x)\psi=0 - - - - - (1)$$

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2 m}{h^2}\left(E-\frac{1}{2}\Re x^2\right)\psi=0$$

$$\frac{d^2\psi}{dx^2}+\left(\frac{8\pi^2 m}{h^2}E-\frac{4\pi^2 m\Re}{h^2}x^2\right)\psi=0$$

$$put\lambda=\frac{8\pi^2 mE}{h^2} and \alpha^2=\frac{4\pi^2 m\Re}{h^2}=\frac{4\pi^2 m.4\pi^2\vartheta_0^2 m}{h^2}=\left(\frac{4\pi^2 m\vartheta_0}{h}\right)^2$$

So $\frac{d^2\psi}{dx^2}+\left(\lambda-\alpha^2x^2\right)\psi=0 - - - - - - (2)$

For every large values of x, $\lambda << \alpha^2 x^2$

$$\therefore \frac{d^2\psi}{dx^2}=\alpha^2x^2\psi$$

The solution is approximately $\psi_{as}=e^{\pm\frac{\alpha}{2}x^2}$ where ψ_{as} is the asymptotic solution.

For every large values of x

$$\frac{d\psi}{dx}=\pm\alpha x e^{\pm\frac{\alpha}{2}x^2};\frac{d^2\psi}{dx^2}=\pm\alpha x e^{\pm\frac{\alpha}{2}x^2}\pm\alpha^2x^2e^{\pm\frac{\alpha}{2}x^2}$$

For very large values of x, first term is ignored

$$\therefore \frac{d^2\psi}{dx^2} = \alpha^2 x^2 e^{\pm\frac{\alpha}{2}x^2}$$

Since $\psi \to 0$ as $x \to \infty$

The correct solution is $\psi = f(x)e^{-\frac{\alpha}{2}x^2}$ $-------(3)$ since $e^{-\infty}$ =0

General solution is $\psi = f(x)e^{-\frac{\alpha}{2}x^2}$ $--------(3)$

Where $f(x)$ is function of x

I term is dominant at low values of x

II term is dominant at high values of x

Differentiating equation (3) we will get

$$\frac{d\psi}{dx} = \frac{df(x)}{dx}e^{-\frac{\alpha}{2}x^2} - f(x)\alpha x e^{-\frac{\alpha}{2}x^2}$$

$$\frac{d^2\psi}{dx^2} = \frac{d^2 f(x)}{dx^2}e^{-\frac{\alpha}{2}x^2} - \frac{df(x)}{dx}e^{-\frac{\alpha}{2}x^2} - f(x)\alpha e^{-\frac{\alpha}{2}x^2} - \frac{df(x)}{dx}\alpha e^{-\frac{\alpha}{2}x^2} + \alpha^2 x^2 f(x)e^{-\frac{\alpha}{2}x^2}$$

$$\frac{d^2\psi}{dx^2} = e^{-\frac{\alpha}{2}x^2}\left[\frac{d^2 f(x)}{dx^2} - 2\alpha x\frac{df(x)}{dx} + (\alpha^2 x^2 - \alpha)f(x)\right]$$

Substituting for $\frac{d^2\psi}{dx^2}$ in equation 2 and simplifying

$$\therefore \frac{d^2 f(x)}{dx^2} - 2\alpha x\frac{df(x)}{dx} + (\lambda - \alpha)f(x) = 0 -----(4)$$

Change $f(x)$ to $H(\xi)$, where $\xi = \sqrt{\alpha}x$

i.e $\frac{d\xi}{dx} = \sqrt{\alpha}$ or $\xi^2 = \alpha x^2$ or $\xi^{\frac{2}{2}=\frac{1}{2}\alpha x^2}$

Then equation (3) becomes

$$\psi = cons\tan t\ e^{-\xi^{\frac{2}{2}}}H(\xi) ----------(5)$$

$$\psi = N_n e^{-\xi^{\frac{2}{2}}} H(\xi)$$

$$f(x) = H(\xi), \frac{df(x)}{dx} = \frac{dH}{dx} = \frac{dH}{d\xi}, \frac{d\xi}{dx} = \sqrt{\alpha}\,\frac{dH}{d\xi}$$

$$\frac{d^2 f(x)}{dx^2} = \frac{d^2 H}{dx^2} = \alpha \frac{d^2 H}{d\xi^2}$$

$$\alpha \frac{d^2 H}{d\xi^2} - 2\alpha \frac{\xi}{\sqrt{\alpha}} \sqrt{\alpha}\,\frac{dH}{d\xi} + (\lambda - \alpha)H = 0$$

$\div \alpha$

$$\frac{d^2 H}{d\xi^2} - 2\xi \frac{dH}{d\xi} + (\frac{\lambda}{2} - 1)H = 0 ---------- (6)$$

Equation 6 is the standard Hermites differential equation. Solution in the form of a series (Hermites polynomial)

$$H(\xi) = a_0 + a_1\xi + a_2\xi^2 + a_3\xi^3 + -----$$

$$\frac{dH}{d\xi} = a_1 + 2a_2\xi + 3a_3\xi^2 + 4a_4\xi^3 + -----$$

$$\frac{d^2 H}{d\xi^2} = 2a_2 + 6a_3\xi + 12a_4\xi^2 + 20a_4\xi^2 + -----$$

Substitute in equation (6)

$$\left[1.2a_2 + 2.3a_3\xi + 3.4a_4 + 4.5a_5\xi^3 + -------\right] -$$
$$\left[2.1a_1\xi + 2.2a_2\xi^2 + 2.3a_3\xi^3 + ---\right] +$$
$$\left(\frac{\lambda}{2} - 1\right)a_2\xi^2 + \left(\frac{\lambda}{2} - 1\right)a_3\xi^3 + -------- a_3\xi^3 + ---------- = 0 ------- (7)$$

Science equation 7 is zero for every value of ξ ,it follows that the sum of coefficient of each power of ξ must be zero

$$\xi^0;1.2a_2+\left(\frac{\lambda}{2}-1\right)a_0=0$$

$$\xi^1;2.3a_3-2.1a_1+\left(\frac{\lambda}{2}-1\right)a_1=0$$

$$\xi^2;3.4a_4-2.2a_2+\left(\frac{\lambda}{2}-1\right)a_2=0$$

$$\xi^{\vartheta};(\vartheta+1)(\vartheta+2)a_{\vartheta+2}-2\vartheta a_{\vartheta}+\left(\frac{\lambda}{2}-1\right)a_{\vartheta}=0-------(8)$$

So From (8)

$$a_{\vartheta+2}=\frac{-\left(\frac{\lambda}{2}-2\vartheta-1\right)a_{\vartheta}}{(\vartheta+1)(\vartheta+2)}--------------------(9)$$

Equation 9 is called the recursion formula (RF). RF determines values of a_{ν} provided we know that first co-efficient of the series. It connects only terms that differ in index by 2.

Two possible choices if a_0 and a_1 which leads to power series consisting either entirely of even powers of ξ or of add powers of ξ

Even solution	a_0 finite	a_1=0
Odd solution	a_0 =0	a_1 is finite

If the series given by equation 9 does not terminate after a finite number of terms, the wave function given by equation 5 will not be satisfactory, because value of series increases too rapidly as x or ζ increases, with the result that the total function in equation 5. Though it includes the negative exponential factor increases without limit as x increases. So we must terminate the series after a certain value ν_f leaving a polynomial. This yields a satisfactory wave function, because the negative exponential factor $e^{-\frac{\xi^2}{2}}$ will cause the function to approach zero for large values of |ζ|. The condition for terminating the series is,

$$\left(\frac{\lambda}{2}-2\nu-1\right)=0 \text{ for any value of } \vartheta_f$$

i.e $\left(\frac{\lambda}{2}-2\nu_f-1\right)=0$ or $\frac{\lambda}{2}=(2\nu_f+1)$

or $\lambda = \left(2\nu_f + 1\right)\alpha$ substitute for α and λ

$$\frac{8\pi^2 mE}{h^2} = (2\nu_f + 1)\frac{4\pi^2 m\vartheta_0}{h} \quad \text{Where } \nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

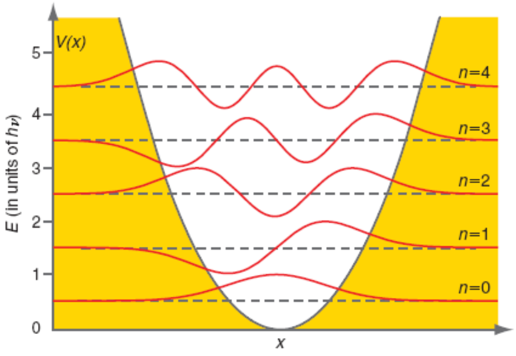
$$E = \frac{\left(2\nu_f + 1\right)}{2}h\nu_0 \text{ , put } \nu_f = n$$

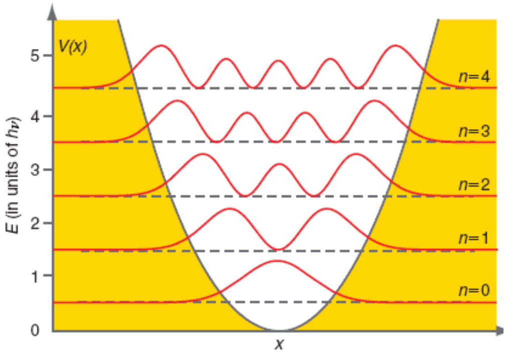
$$E_n = \left(n + \frac{1}{2}\right)h\nu_0 \text{ n is an integer}$$

$$E_n = \left(n + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{m}}$$

Thus, the positive values of energy depend on the values of n. Even when n = 0, $E_0 = ½ h\nu_0$ which is the zero point energy of the system in its lowest state (direct consequence of uncertainty principle)

A few Hermite polynomials	Solution
$H_0(\xi) = 1$	$\psi_0 = N_0 e^{-\frac{\xi^2}{2}}$
$H_1(\xi) = 2\xi$	$\psi_1 = N_1(2\xi)e^{-\frac{\xi^2}{2}}$
$H_2(\xi) = \left(4\xi^2 - 2\right)$	$\psi_2 = N_2\left(4\xi^2 - 2\right)e^{-\frac{\xi^2}{2}}$
$H_3(\xi) = \left(8\xi^2 - 12\xi\right)$	$\psi_3 = N_3\left(8\xi^3 - 12\xi\right)e^{-\frac{\xi^2}{2}}$
$H_4(\xi) = \left(16\xi^4 - 48\xi^2 + 12\right)$	$\psi_4 = N_4\left(16\xi^4 - 48\xi^2 + 12\right)e^{-\frac{\xi^2}{2}}$
$H_5(\xi) = \left(32\xi^5 - 160\xi^3 + 120\xi\right)$	$\psi_5 = N_5\left(32\xi^5 - 160\xi^3 + 120\xi\right)e^{-\frac{\xi^2}{2}}$





Polynomial $H(\xi)$ obtained are known as Hermite polynomials

The Wavefunctions for harmonic oscillator are given by

$\psi_{n(x)} = N_n e^{-\frac{\xi^2}{2}} H_n(\xi)$ where N_n is a Normalization Constant

$H_n(\xi)$ represent a Hermite polynomial of degree n

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n e^{-\xi^2}}{d\xi^n}$$

To find N_n

$$\int_{-\infty}^{+\infty} \psi_n^* \psi_n dx = \int_{-\infty}^{+\infty} N_n^2 H_n^2(\xi) d\xi = 1$$

$$N_n = \left[\left(\frac{\alpha}{\pi} \right)^{\frac{1}{2}} \frac{1}{2^n \underline{\lfloor n}} \right]^{\frac{1}{2}}$$

Where $\xi = \sqrt{\alpha}x; \alpha = \frac{4\pi^2 \vartheta_0 m}{h}$ and $\vartheta_0 = \frac{1}{2\pi}\sqrt{\frac{\Re}{m}}$

For the lowest vibration level (n=0) ψ_0 can be calculated

$$\psi_0 = \left(\frac{\alpha}{\pi} \right)^{\frac{1}{4}} e^{-\frac{1}{2}\xi^2} = \left(\frac{\alpha}{\pi} \right)^{\frac{1}{4}} e^{-\frac{\alpha}{2}x^2}$$

Similarly

$$\psi_1 = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} 2\sqrt{\alpha}xe^{-\frac{\alpha}{2}x^2}$$

$$\psi_2 = \frac{1}{\pi^{\frac{1}{4}}}\left(\frac{\sqrt{\alpha}}{2}\right)\left(-1+2\alpha x^2\right)e^{-\frac{\alpha x^2}{2}}$$

10.10 Summary of the unit

The ground state probability distribution is spherically symmetric i.e. the probability of finding the electron at a point depends on the distance from the nucleus but not on the angular orientation relative to it. All states of the formΨ_{n00}, (e.g.,Ψ_{100}, Ψ_{200}.....) have spherically symmetric shape and are called s state. The ground state Ψ_{100} having the lowest energy E_1 is the 1s state. Ψ_{200} is the 2s state. The 2 indicates that it is a state with energy E_2. The “s” indicates the azimuthal quantum number l is zero. States of the form Ψ_{n1m} (azimuthal quantum number) are called p states. The basic 2p states are, Ψ_{21-1}, Ψ_{210}, and Ψ_{211}. The Eigenfunctions Ψ_{200}, Ψ_{210}, Ψ_{211} and Ψ_{21-1}, , and Ψ_{211} all four have the same energy E_2 = -3.4 eV

The fact that the energy levels of a hydrogen atom depend only on *n*, and not on *l* and *m*, implies that the energy spectrum of hydrogen atom is highly degenerate: i.e., there are many different states which possess the same energy. The excited energy levels E_2, E_3….are all degenerate. There is more than one eigenstate producing each energy level of excited states. The stationary states of the hydrogen atom are orthonormal.

10.11 Key words

Degeneracy; Schrödinger wave equation for hydrogen atom; Eigen Function; probability distribution; Schrodinger wave for Rigid Rotator; Schrodinger wave equation for Harmonic Oscillator.

10.12 References for further studies

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3) Quantum Mechanics:Theory and Applications; Ajoy K. Ghatak, S. Lokanathan; *Macmillan*, **2004**.

4) Introduction to Quantum Mechanics with Applications to Chemistry; Linus Pauling, E. Bright Wilson; *Courier Dover Publications*; **2012**.

5) Quantum Mechanics and Spectroscopy; Gupta Tandon; *Galgotia Publications*.

10.13 Questions for self understanding

(1) Set up the S equation for H atom.

(2) Convert from Cartesian to polar co-ordinates.

(3) Separate the polar equation into 3 parts.

(4) Acceptance solution of ϕ equation present an by for certain values of parameter m, $m = 0,\pm1,\pm2,\pm3$...........

(5) Introducing the solution of ϕ equation it is found that θ equation possess acceptable solutions only for certain values of by where $\beta = l(l+1)$ i.e l=|m|, |m|+1, |m|+2………… m=-l to +l

(6) Introducing the result in r equation it is found that the r equation possess acceptable solution only for certain values of E.

(7) Multiply the three solution to get ψ the total wave function.

Unit -11

Structure

11.0 Objectives of the unit
11.1 Introduction
11.2 Approximate methods
11.3 General theory of perturbation method
11.4 Solution of I order perturbation technique
11.5 Application of perturbation method to Helium atom
11.6 Calculate the first ionization potential of the He atom
11.7 Calculation of binding energy
11.8 Summary of the unit
11.9 Key words
11.10 References for further study
11.11 Questions for self understanding

11.0 Objectives of the Unit

After studying this unit your are able to

- Recognize the advantage of Approximation methods
- Derive the general theory of perturbation method
- Find the solution of 1st order perturbation technique
- Apply the perturbation theory to He atom and solve the wave equation
- Calculate the binding energy of He molecule using Perturbation theorem
- Calculate the 1st and 2nd ionization energies of He atom using Perturbation theorem

11.1 Introduction

Theoretical physics hardly provides a mathematically exact answer to realistic questions. There are a small number of situations where an exact solution of a basic equation gives a remarkably accurate account of the data, but eventually refinement of experimental technique or previously overlooked effects will require a more complicated theoretical description that no longer yields to an exact analytical solution. This was true from the start in celestial mechanics, and has been true of quantum physics. Inded, the evaluation of effects which are known to be small or hoped to be small has always occupied a large portion of the life of most physicist.

There is an enormous arsenal of approximation methods for solving quantum mechanical problems. Before invention of powerful computers, great effort was devoted to analytical methods, and these are still of great importance. They are often though certainly not always the basis for numerical computations vastly most elaborate and precise than was original imaginable and they continue to be indispensable for gaining a quantitative and often even a quantitative understanding. These analytic approximation technique also play an essential role in quantum mechanical thinking and talking about phenomena from the mundane to the astonishing.This unit describes the rudiments of perturbation theorym, when it is assumed that the Hamiltonian is a sum of two terms $H = H_0 + \lambda H_1$

11.2 Approximate methods

The exact solution of the wave equation is possible only when the system contains a single electron (example; for H-atom). It is not feasible to obtain a complete solution of the wave equations if several electrons are involved (as is the case in most problems of chemical interest). In such circumstances the best that can be done is to employ an approximate procedure. Several methods have been suggested of which two are widely employed. These are known as approximate methods and they are

i) Perturbation method

ii) Variation method

Both the methods lead to achieve the same result, but the variation method is simple than perturbation method. The perturbation method is employed by using an already solved problem close to the present problem. The variation method is based on variation theorem.

11.3 General theory of perturbation method

Consider the solution to the problem of motion of a system whose Hamiltonian operator H is only slightly different from the Hamiltonian operator H_0 of some problem which has already been solved.

For H_0 we have a set of eigen values $E_1^0, E_2^0, E_3^0, -----E_n^0$------,and the corresponding Eigen functions are $\Psi_1^0, \Psi_2^0, \Psi_3^0 ----- \Psi_n^0 ----$, satisfying the Schvodoiger equation. $H_0\Psi_n^0 = E_n^0\Psi_n^0$------------- (1)

Since H is only slightly different from H_0, we can write $H = H_0 + \lambda H'$ ------------ (2)

Where λ is some parameter and λH^1 is called "perturbation" and λH^1 is small in comparison to H_0

Substituting for H in equation 1 using HΨ = EΨ

$(H_0 + \lambda H')\psi_n = E_n\psi_n$ ------------ (3)

E_n and Ψ_n are Eigen value and Eigen function associated with H (from $H\ \Psi_n = E_n\Psi_n$)

Equation 3 represents the Schrodinger equation for the exponential system.

∴ E_n and Ψ_n refers to the exponential system.

If λ = 0 in equation 3 then $\psi_n \rightarrow \psi_n^0$ and $E_n \rightarrow E_n^0$,

Then equation 3 reduces to equation 1

Therefore for small values of λ the solution of equation 3 will lie close to equation 1. i.e., the effect of perturbation λH^1 will be to change slightly the unperturbed eigen values E_n^0 and eigen functions ψ_n^0.

Further it is assumed that no two values of E_n^0 are equal (i.e., $E_1^0 \neq E_2^0 \neq E_3^0 \neq E_4^0$------)

Since Ψ$_n$ and E$_n$ are functions of λ we can expand them in the form of the following power series.

$\psi_n = \psi_n^0 + \lambda\psi_n^{'} + \lambda^2\psi_n^{''} + ---$ ----------- (4)

Similarly $E_n = E_n^0 + \lambda E_n^1 + \lambda^2 E_n^{11} + ---$-------(5)

Where $E_n^{'}$ is called the 1st order perturbation energy.

$E_n^{''}$ is called the 2nd order perturbation energy.

Similarly $\psi_n^{'}$ and $\psi_n^{''}$ is called I and II order permutation corresponds to the wave function ψ_n,

$E_n^{'}$ $E_n^{''}$, $\psi_n^{'}$ and $\psi_n^{''}$ are independent of λ.

Substituting ψ$_n$ and E$_n$ in equation 3

$$(H_0 + \lambda H^{'})\psi_n = E_n\psi_n$$

$$\left(H_0 + \lambda H^{'}\right)\left(\psi_n^0 + \lambda\psi_n^{'} + \lambda^2\psi_n^{''} + ----\right) = \left(E_n^0 + \lambda E_n^1 + \lambda^2 E_n^{11} + ----\right)\left(\psi_n^0 + \lambda\psi_n^{'} + \lambda^2\psi_n^{''} + --\right)$$

Multiplying and rearranging

$$H_0\psi_n^0 + \lambda\left(H^{'}\psi_n^0 + H_0\psi_n^{'}\right) + \lambda^2\left(H^{'}\psi_n^{'} + H_0\psi_n^{''}\right) + ------- = E_n^0\psi_n^0 + \lambda\left(E_n^1\psi_n^0 + E_n^0\psi_n^1\right) +$$
$$\lambda^2\left(E_n^{''}\psi_n^0 + E_n^{'}\psi_n^{'} + E_n^0\psi_n^{''}\right) + -------- (6)$$

In order that equation 6 may be satisfied for all values of λ, the co-efficients of the various powers of λ on the two sides of the equation must be equal. Equating the co-efficients of the various powers of λ gives the series of equations.

For λ^0, $H_0\psi_n^0 = E_n^0\psi_n^0$ ------------ (7)

For λ^1, $\left(H_0 - E_n^0\right)\psi_n^{'} = E_n^{'}\psi_n^0 - H^{'}\psi_n^0$ ------- (8)

For λ^2, $\left(H_0 - E_n^0\right)\psi_n^{''} = E_n^{''}\psi_n^0 + E_n^{'}\psi_n^{'} - H^{'}\psi_n^{'}$ ---------- (9)

Note that Equation 7 refers to Schrödinger wave equation for unperturbed system and by assumption method it is already solved.

Substituting these solved values equation 8, it is possible to get the values of E_n^1, ψ_n^1 and H^1,

Similarly if we solve equation 9 we get E_n^{11} and ψ_n^{11} i.e.; this gives 2nd order perturbation values, hence n principle upto nth order perturbation values can be obtained.

11.4 Solutionof eqquation 8 (I order perturbation technique)

From eq 8 we have $\left(H_0 - E_n^0\right)\psi_n^{'} = E_n^{'}\psi_n^0 - H^{'}\psi_n^0$

Expand $\psi_n^{'}$ in terms of unperturbed ψ_n^0

$\psi_n^{'} = A_1\psi_n^0 + A_2\psi_2^0 + - - - - - - - - + A_n\psi_n^0$ -------------- (10) Where the A$_n$'s are to be determined.

Similarly $H_1\psi_n^0$ is expressed as

$H_1\psi_n^0 = H_{1n}^{'}\psi_1^0 + H_{2n}^{'}\psi_2^0 + - - - - - - H_{mn}^{'}\psi_{mn}^0$ ------------------ (11)

Where $H_{mn}^{'} = \int \psi_m^{0*} H^{'}\psi_n^0 d\tau$ known as element of interaction of ψ_n^0 & ψ_n under perturbation.

Substituting in equation 8 for ψ_n^1 & $H^1\psi_n^0$ from equation 10 and equation 11 respectively, we can write $\left(H_0 - E_n^0\right)\left(A_1\psi_1^0 + A_2\psi_2^0 + - - - - - -\right) = E_n^1\psi_n^0 - H_{1n}^1\psi_1^0 - H_{2n}^2\psi_2^0$ --------- (12)

From 7 we have

$H_0\psi_n^0 = E_n^0\psi_n^0$

i.e., $H_0\psi_1^0 = E_1^0\psi_1^0$ ------- (7a)

$H_0\psi_2^0 = E_2^0\psi_2^0$ -------- (7b)

$H_0\psi_3^0 = E_3^0\psi_3^0$ ------ (7c)

Simplifying equation 12 and then substitute in equation12 we get

$$\begin{aligned}&\left(E_1^0 - E_n^0\right)A_1\psi_1^0 + \left(E_2^0 - E_n^0\right)A_2\psi_2^0 + - - - - - - - - \left(E_n^0 - E_n^0\right)A_n\psi_n^0 + - - - - - -\\ &= E_n^{'}\psi_n^0 - H_{1n}^{'}\psi_1^0 - H_{2n}^{'}\psi_2^0 - - - - - - - H_{mn}^{'}\psi_n^0\end{aligned} \text{ --------(13)}$$

Equating the coefficients of ψ_n^0 on both sides

$\left(E_n^0 - E_n^0\right) = \left(E_n^{'} - H_{mn}^{'}\right) = 0$ or $E_n^1 = H_{mn}^1$ --------------- (14)

The first order perturbation energy has thus been determined to be

$E_n^{'} = H_{mn}^{'} = \int \psi_m^{0*} H^{'}\psi_n^0 d\tau$ ---- (14a)

Similarly starting from eq 9 $E_n^{''}$

$E_n^{''} = \sum \frac{H_{mn}^{'}H_{nm}^{'}}{E_n^0 - E_m^0}$ --------- (14c)

$$H'_{nm} = \int \psi_n^0 H' \psi_m^0 d\tau$$

Where

$$H'_{mn} = \int \psi_m^0 H' \psi_n^0 d\tau$$

$$\psi'_n = \frac{\sum H'_{nm}}{(E_n^0 - E_m^0)} \psi_m^0 \qquad (m \neq n) \text{ ------- (14b)}$$

We can also show that

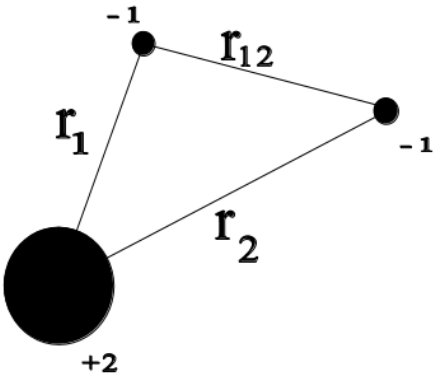
$$A_m = \frac{H'_{mn}}{(E_n^0 - E_m^0)} \text{ -------- (14d)}$$

From equation 14d, all the coefficients except A_n can be calculated. The coefficient A_n can be determined by the normalization requirement of ψ_n .

11.5 Application of perturbation method to Helium atom

We now turn to the helium atom, first multi-electron atom. If we consider the He atom with two electrons the potential energy term will contain not only the effect of the nucleus on each of the electron but also the coulombic repulsion between the two electrons. The nucleus is placed at the again of the coordinate system and the co-ordinates of the two electrons are x_1, y_1, z_1 and x_2, y_2, z_2 .

The helium atom consists of two electrons moving in the field of a nucleus with charge +2. We call the distance between the nucleus and the first electron r$_1$, between the nucleus and the second electron r$_2$, and the distance between the two electrons r$_{12}$. As always the Hamiltonian for this problem is the sum of the kinetic energy and potential energy



∇_1^2 – Linear operation for electron 1

∇_2^2 – Linear operation for electron 2

The Potential energy is given by

$$V = -\frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$$

where $r_{12} = |r_1 - r_2|$. Thus the overall Hamiltonian is

Total energy $H = -\frac{h^2}{8\pi^2 m}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}}$ -------- (1)

Transform to atomic units in terms of a_0 which expresses all distances.

$$r_1 = a_0 R_1, r_2 = a_0 R_2, r_{12} = a_0 R_{12}$$

$$\therefore H = -\frac{h^2}{8\pi^2 m} - \frac{1}{a_0^2}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{a_0 R_1} - \frac{Ze^2}{a_0 R_2} + \frac{e^2}{a_0 R_{12}}$$

$$\boxed{a_0 = \frac{h_2}{4\pi^2 me^2}}$$

In units of

$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{R_1} - \frac{Z}{R_2} + \frac{1}{R_{12}}$ ---------- (2)

For simplicity we will consider only the ground state energy only. If we consider the interelectronic repulsion term $\frac{e^2}{4\pi\varepsilon_0 r_{12}}$, to be the perturbation , then the unperturbed wave fnctions and energies are the hydrogenlike quantities.

From perturbation theory the Hamiltonian is split into two parts

$$H = H_0 + H^{'}$$

Where $H_0 = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{Z}{R_1} - \frac{Z}{R_2}$ ----------- (3)

And $H^{'} = \frac{1}{R_{12}}$ -------- (4) $H^{'}$ is the perturbation.

H_0 is known and corresponds to the Schrödinger equation,

$H_0\psi^0 = E^0\psi^0$ --------- (5)

ψ^0 is zeroth order of eigen function $\psi^0 = \psi_1^0\psi_2^0$ and $E^0 = E_1^0 E_2^0$

Equation 5 can be separsted into two parts

$\frac{1}{2}\nabla_1^2\psi_1^0 + (E_1^0 + \frac{Z}{R_1})\psi_1^0 = 0$ ------ (6a)

$$\frac{1}{2}\nabla_2^2\psi_2^0 + (E_2^0 + \frac{Z}{R_2})\psi_2^0 = 0 \text{ ------ (6b)}$$

Equations 6a and 6b correspond to 2 H atoms or H like atoms

$$\therefore \psi_{(1s)} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}.e^{-\frac{Zr}{a_0}}$$

Or $\psi_1^0 = \frac{1}{\sqrt{\pi}}Z^{\frac{3}{2}}.e^{-ZR_1}$ in terms of a_0 ground state wave function for H like atom

$$\psi_2^0 = \frac{1}{\sqrt{\pi}}Z^{\frac{3}{2}}.e^{-ZR_2}$$

$$\psi^0 = \psi_1^0\psi_2^0 = \frac{Z^2}{\pi}.e^{-Z(R_1+R_2)} \text{ ------------------- (7a)}$$

$$E^0 = E_1^0 + E_2^0 = Z^2.E_{H(1s)} + Z^2E_{H(1s)}$$

$$= 2Z^2E_{H(1s)} \text{ ------------------ (7b)}$$

$E_{H(1s)} = -\frac{e^2}{2a_0}$ is the energy of the ground state of hydrogen atom

To calculate $E,'$ the I order correction to energy

From perturbation theory

$$\left(E_n^{'} = H_{nn}^{'} = \int \psi_n^0 H^{'} \psi_n^0 d\tau\right)$$

$$\therefore E^{'} = \iint \psi^0 H^{'} \psi_n^0 d\tau_1 d\tau_2$$

Substituting for ψ_n^0 from ψ^0 in equation 7a $\psi^0 = \frac{Z^3}{\pi}e^{-Z(R_1+R_2)}$

$$\therefore E^{'} = \iint \frac{Z^3}{\pi}e^{-Z(R_1+R_2)}\frac{1}{R_{12}}\frac{Z^3}{\pi}e^{-Z(R_1+R_2)}d\tau_1 d\tau_2$$

$$= \frac{e^2}{a_0}\frac{Z^6}{\pi^2}\iint \frac{e^{-2ZR_1}e^{-2ZR_2}}{R_{12}}d\tau_1 d\tau_2 \text{ --------- (8)}$$

The solution of this equation 8 can be obtained using Legendre polynomials

$$\therefore E^{'} = \frac{5}{8}\frac{Ze^2}{a_0} \text{ or } \frac{5}{8}Z\frac{e^2}{a_0}$$

$$= -\frac{5}{4}Z\left(\frac{-e^2}{2a_0}\right) = -\frac{5}{4}ZE_{H(1s)} \text{ -------- (8a)}$$

This is the first order correction for the energy of Helium atom

$\therefore$ Total energy of the atom is

$$E = E^0 + E^{'} = 2Z^2E_{H(1s)} - \frac{5}{4}ZE_{H(1s)}$$

$$E = \left(2Z^2 - \frac{5}{4}Z\right)E_{H(1s)}$$

This E is the total binding energy of Helium atom and Helium like atoms

11.6 Calculate the first ionization potential of the He atom

The first ionization potential of the He atom i.e., the energy required to remove one electron from the atom $E_{He} - E_{He^+}$

$$= \left(2Z^2 - \frac{5}{4}Z\right)E_{H(1s)} - Z^2E_{H(1s)}$$

$$IP = \left(Z^2 - \frac{5}{4}Z\right)E_{H(1s)}$$

For Helium Z = 2

$$\therefore IP = \frac{3}{2}E_{H(1s)}$$

but for Helium $E_{H(1s)}$ = 13.6 eV

$$\therefore IP = \frac{3}{2}X13.6 = 20.4eV$$

This value is from perturbation method and the experimental value is 24.58 eV. Hence the error is about 16%

11.7 Calculation of binding energy

The results are better in calculated and observed binding energies of the Helium atom

$$B.E = \left(2Z^2 - \frac{5}{4}Z\right)E_{H(1s)}$$

$= \left(8 - \frac{5}{4}\right)13.6 = 74.8eV$ and the observed value is 78.98 eV

Therefore error is 4.18 eV or about 5%

Atom	E^0(eV)	$E=E^0+E'$ (eV)	Emeasured (eV)
He	-108.28	-74.8	-78.98
Li^+	-243.54	-192.8	-197.14
Be^{2+}	-432.96	-365.31	-369.96
B^{3+}	-676.50	-591.94	-596.10
C^{4+}	-974.16	-872.69	-876.20

11.8 Summary of the unit

Perturbation theory is a method for continuously improving a previously obtained approximate solution to a problem, and it is an important and general method for finding approximate solutions to the Schrödinger equation. We discussed a simple application of the perturbation technique in this unit, with the Zeeman Effect.

We use perturbation theory to approach the analytically unsolvable helium atom Schrödinger equation by focusing on the Coulomb repulsion term that makes it different from the simplified Schrödinger equation that we have just solved analytically. The electron-electron repulsion term is conceptualized as a correction, or perturbation, to the Hamiltonian that can be solved exactly, which is called a zero-order Hamiltonian. The perturbation term corrects the previous Hamiltonian to make it fit the new problem. In this way the Hamiltonian is built as a sum of terms, and each term is given a name. For example, we call the simplified or starting Hamiltonian, H_0, the zero order term, and the correction term H_1, the first order term. In the general expression below, there can be an infinite number of correction terms of increasingly higher order,

$$H = H_0+H_1+H_2+\cdots$$

11.9 Key words

Approximate methods; Perturbation method; I order perturbation technique; Helium atom; Binding energy; Ionization potential

11.10 References for further study

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11.11 Questions for self understanding

1) Write a note on approximation methods
2) Derive the general theory of perturbation method
3) Find the solution of 1st order perturbation technique
4) Solve the wave equation for He atom by apply the perturbation theory
5) Calculate the binding energy of He molecule using Perturbation theorem
6) Calculate the 1st and 2nd ionization energies of He atom using Perturbation theorem

Unit -12

Structure

12.0 Objectives of the unit
12.1 Introduction
12.2 Variation theorem – Statement and proof
12.3 Application of variation method
12.4 Application of variation method to ground state of He atom
12.5 Calculation of binding energy of the He atom
12.6 Application of various theorems to practice in a box problem (one-dimenction)
12.7 Application of variation theorem to a simple harmonic oscillator
12.8 Application to H-atom
12.9 Summary of the unit
12.10 Key words
12.11 References for further study
12.12 Questions for self understanding

12.0 Objectives of the unit

After studying this unit you are able to

- Write the statement of variation theorem
- Verify the proof of variation theorem
- Apply the variation theorem ground sate He atom
- Apply the variation theorem to simple harmonic oscillator
- Calculate the binding energy of He atom using variation theorem
- Apply the variation theorem to H- atom

12.1 Introduction

A very useful approximation method is known as the variational method. This is the basis of much of quantum chemistry, including Hartree-Fock theory, density functional theory, as well as variational quantum Monte Carlo. The underlying theorem of the method is the Ritz theorem, which states that, given a time-independent Hamiltonian, *H*, with a set of eigenvalues, *En* and eigenvectors, $|\psi_n›$ satisfying $H|\psi_n\rangle = E_n|\psi_n\rangle$

The variation theorem states that given a system with a Hamiltonian H, then if Φ is any normalised, well-behaved function that satisfies the boundary conditions of the Hamiltonian, then $< \Phi |H| \Phi \geq E_o$, where E_0 is the true value of the lowest energy eigenvalue of H. This principle allows us to calculate an upper bound for the ground state energy by finding the trial wavefunction f for which the integral is minimised (hence the name; trial wavefunctions are varied until the optimum solution is found). Let us first verify that the variational principle is indeed correct.

12.2 Variation theorem – Statement and proof

A completely different method of approach for approximate solutions of the wave equation is based upon the following theorem known as variation theorem.

Statement : If ϕ is any function of class Q such that $\int \phi^* \phi d\tau = 1$ and if the lowest eigen value of the operator H is E_0 then $\int \phi^* H\phi d\tau \geq E_0$ --------(1)

Proof: Consider the integral $\int \phi^*\left(H - E_0\right)\phi d\tau = \int \phi^*\left(H - E_0\right)\phi d\tau = \int \phi^* H\phi d\tau - E_0 \int \phi^* \phi d\tau$

$= \int \phi^* H\phi d\tau - E_0$ -----------(2)

Expand ϕ in the form of a series of the eigen functions

$\psi_{1,}\psi_{2,} -------\psi_i --------$ of H

i.e., $\phi = C_1\psi_1 + C_2\psi_2 + -------- + C_i\psi_i = \sum_i C_i\psi_i$

We have

$$\int \phi^*\left(H - E_0\right)\phi d\tau = \int\left(\sum_i C_i^*\psi_i^*\right)\left(H - E_0\right)\left(\sum_i C_i\psi_i\right)d\tau$$

--------- (3)

Since ψ_i are eigen functions of H $\therefore H\psi_i = E_i\psi_i$, So equation 3 becomes

$$\int \phi^*\left(H - E_0\right)\phi d\tau = \int\left(\sum_i C_i^*\psi_i^*\right)\left(\sum_i \left(E_i - E_0\right)C_i\psi_i\right)d\tau$$

$$\sum\left(C_i^*C_i\right)\left(E_i - E_0\right)\int \psi_i^*\psi_i d\tau$$

$$\boxed{\int \psi_i^*\psi_i d\tau = 1}$$

$$\int \phi^*\left(H - E_0\right)\phi d\tau = \sum\left(C_i^*C_i\right)\left(E_i - E_0\right)$$

Now $C_i^*C_i$ is a positive number and by definition $E_i \geq E_0$,

Hence $\int \phi^*\left(H - E_0\right)\phi d\tau \geq 0$ ---------------- (4)

The equality sign can hold only when $\phi = \psi_0$ where ψ_0 (Ground state wave function) is the eigen function with the eigen value E_0.

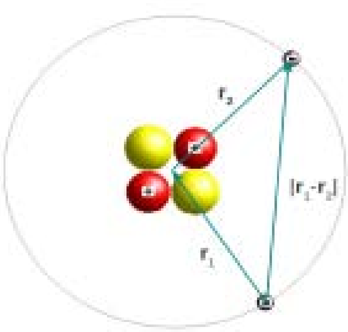
12.3 Application of variation method

The method of applying this theorem is equally simple in principle. A trial eigen function $\phi\left(\lambda_{1,}\lambda_{2,} ----\right)$ normalized to unity is chosen where ϕ is a function of number of parameters $\left(\lambda_{1,}\lambda_{2,} ----\right)$

Then the variational integral ie $J = \int \phi^* H\phi d\tau$ is doted. Therefore the result will be a function of the parameters $\left(\lambda_{1,}\lambda_{2,} ----\right)$ when J is minimized with respect to λ. The result obtained is an approximation to the lowest eigen value E and the corresponding ϕ is an approximation to the corresponding eigen function.

By taking a sufficiently large no of parameters in a function of well chosen form a very close approximation to the correct eigen value and eigen function be found.

12.4 Application of variation method to ground state of He atom



Helium atom

He atom is a 2 electron system. The potential energy (PE) is given by

$$V = -\frac{Ze^2}{r_1} - \frac{Ze^2}{r_1} + \frac{e^2}{r_{12}}$$

The zero order ground state is determined by 2H-like atoms.

For this system we can write

$\phi_{(r_1,r_2)} = U_{(r_1)} V_{(r_2)}$ and $E = E_1 + E_2$

For electron 1, $\left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}\right) U_{(r_1)} = E_1 U_{(r_1)}$

For electron 2, $\left(-\frac{1}{2}\nabla_2^2 - \frac{Z}{r_2}\right) U_{(r_2)} = E_2 V_{(r_2)}$

For the combined system the trial wave function $\phi = U_{r_1} V_{r_2}$

i.e., $U_{r_1} = \frac{\left(Z^1\right)^{\frac{3}{2}}}{\sqrt{\pi}} . e^{-ZR_1}$ $\quad V_{r_2} = \frac{\left(Z^1\right)^{\frac{3}{2}}}{\sqrt{\pi}} . e^{-ZR_2}$

z^1 is the effective nuclear charge and lies between 1 & 2 i.e., $Z^1 \neq Z$ for Helium atom.

For combined wave function $\phi = Ur_1 . Vr_2 = \frac{\left(Z^1\right)^{\frac{3}{2}}}{\pi} . e^{-Z\left(R_1 + R_2\right)}$ ------- (1)

ϕ is the corresponding wave function of the equation

$$H_0^{'} \phi = E_0^{'} \phi$$

$$H_0^{'} = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Z^{'}}{R_1} - \frac{Z^{'}}{R_2} \text{--------- (2)}$$

The corresponding energy of the system

$$E_0^{'} = 2\left(Z^{'}\right)E_{H(1S)}$$

One must evaluate the variational integral

$$E = \iint \phi^* H\phi d\tau_1 d\tau_2 \text{ ------------(3)}$$

H is the total Hamiltonian of the function

So $H = -\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Z}{R_1} - \frac{Z}{R_2} + \frac{1}{R_{12}}$ -----------(4a)

$$H\phi = \left\{-\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Z}{R_1} - \frac{Z}{R_2} + \frac{1}{R_{12}}\right\}\phi \text{ --------- (4b)}$$

Add and subtract $\frac{Z^{'}}{R_1}\phi$ and $\frac{Z^{'}}{R_2}\phi$ to 4(b) of RHS only and rearranging

$$H\phi = \left\{-\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Z}{R_1} - \frac{Z}{R_2} + \frac{1}{R_{12}}\right\}\phi - (Z - Z^{'})\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\phi + \frac{1}{R_{12}}\phi$$

$$\boxed{\because \left\{-\frac{1}{2}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{Z}{R_1} - \frac{Z}{R_2} + \frac{1}{R_{12}}\right\}\phi = \left(H_0^{'}\phi = E_0^{'}\phi\right)}$$

$$\therefore H\phi = E_0^{'}\phi - (Z - Z^{'})\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\phi + \frac{1}{R_{12}}\phi \text{ --------- (4c)}$$

$$\therefore H = E_0^{'} - (Z - Z^{'})\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \frac{1}{R_{12}} \text{ ---------- (4d)}$$

We know that the equation 3 is $E = \iint \phi^* H\phi d\tau_1 d\tau_2$ and substituting for H in 3 from 4d we get

$$\therefore E = \iint \phi^* \left[\left\{E_0^{'} - (Z - Z^{'})\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\right\} + \frac{1}{R_{12}}\right]\phi d\tau_1 d\tau_2$$

Since $\phi^* = \phi$

$$\therefore E = \iint \phi \left[\left\{E_0^{'} - (Z - Z^{'})\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\right\} + \frac{1}{R_{12}}\right]\phi d\tau_1 d\tau_2$$

$$i.e., \iint \phi E_0^{'}\phi d\tau_1 d\tau_2 - (Z - Z^{'})\left[\iint \frac{\phi^2}{R_1} d\tau_1 d\tau_2 + \iint \frac{\phi^2}{R_2} d\tau_1 d\tau_2\right] + \iint \frac{\phi^2}{R_{12}} d\tau_1 d\tau_2 \text{ ------- (5a)}$$

The value of $\iint \frac{\varphi^2}{R_1} d\tau_1 d\tau_2 = \frac{Z^1 e^2}{a_0}$

And $\iint \frac{\varphi^2}{R_2} d\tau_1 d\tau_2 = \frac{Z^1 e^2}{a_0}$

Also $\iint \frac{\varphi^2}{R_{12}} d\tau_1 d\tau_2 = \frac{5}{8} Z^1 \frac{e^2}{a_0}$

$$\therefore E = E_o^1 - \left(Z - Z^1\right)\left\{\frac{Z^1 e^2}{a_0} + \frac{Z^1 e^2}{a_0}\right\} + \frac{5}{8}\frac{Z^1 e^2}{a_0}$$

$$E = E_0^1 - 2Z^1\left(Z - Z^1\right)\frac{e^2}{a_0} + \frac{5}{8}\frac{z^1 e^2}{a_0}$$

$$= 2\left(Z^1\right)^2 E_{H(1s)} + 2Z^1\left(Z - Z^1\right)2E_{H(1s)} + \frac{5}{8}Z^1 2E_{H(1s)}$$

$$\therefore E = \left[-2\left(Z^1\right)^2 + 4ZZ^1 - \frac{5}{4}Z^1\right]E_{H(1s)} \text{ ------------ (6)}$$

Radius

$$a = \frac{4^2}{4\pi^2 \mu e^2}$$

$$\nabla_1^2 = L0\, fore_1^-$$

$$\nabla_2^2 = L0\, fore_2^-$$

$$r_1 = a_0 R_1$$

$$r_2 = a_0 R_2$$

$$r_{12} = a_0 R_{12}$$

The best approximation to a true value energy can be obtained by giving Z^1 the value which will make the energy a minimum this condition requires that

$$\frac{\partial E}{\partial Z^1} = \left(-4Z^1 + 4Z - \frac{5}{4}\right)E_{H(1s)} = 0$$

$$\therefore Z^1 = \left(Z - \frac{5}{16}\right)$$

$$\frac{4}{a}Z^1 - \frac{5}{4} = Z - \frac{5}{16}$$

$$Z^1 = Z - \frac{5}{16}$$

Substitute in (6) and simplify we obtain for the energy value E = $2Z^{12}$ $E_{H\,(1S)}$

$E = 2\left(Z - \frac{5}{16}\right)^2 E_{H(1S)}$ …….. E is the B.E of the He atom.

First ionization potential of He atom:

= Gs of He atom – Gs of He^+

$$=\left[2(Z-\frac{5}{16})^2-Z^2\right]E_{H(1s)}$$

If I .P He atom $=\left(2Z^2-\frac{5}{4}Z+2\left(\frac{5}{16}\right)^2-Z^2\right)E_{H(1S)}$

Put Z=2,

$$\therefore IP=\left[Z^2-\frac{5}{4}Z+2\left(\frac{5}{4}\right)^2\right]E_{H(1S)}$$

=1.695 $E_{H(1s)}$

First IP of He atom=1.695X13.6 ev = 23.05ev. The expected value is about 24.58ev, hence the error is about 1.53ev or about 6%

12.5 Calculation of binding energy of the He atom

B.E of the atom = $2(Z^1)^2$ $E_{H(1s)}$

$$=\left(Z-\frac{5}{16}\right)^2E_{H(1S)}=2\left(2-\frac{6}{16}\right)^2\times 13.6$$
$$=77.45ev.$$

Expected value is -78.98ev and 2% error is observed. Therefore by introducing more parameter into the trail Eigen function ϕ we can approach closer values to the expected value

12.6 Application of various theorem to practice in a box problem (one-dimenction)

Consider a particle in a box Length ‘l’ the wave function is zero outside the box and the boundary conditions are $\psi=0$ and x=0 and $\psi=0$ at x= l. The variation function must meet these two conditions simply function that has all these properties is given as $\phi=x(l-x)$ for $0\le x\le l$

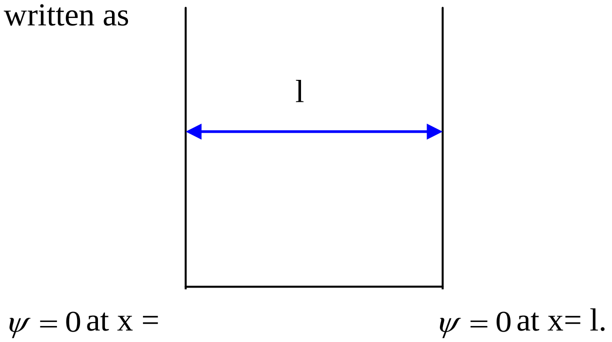
i.e $\phi=(lx-x^2)----(1)$

The Hamiltonian for the particle in a box (inside) can be written as

$$H=-\frac{h^2}{8\pi^2m}\frac{d^2}{dx^2}.........(2)$$

From variation theorem

$$E=\frac{\int\phi^*H\phi dT}{\int\phi^*\phi dT}........(3)$$



Substituting from equation (1) and (2) in equation (3) we can write for numerator as

$$\int \varphi^* H\varphi d\tau = \int_0^l \left(lx - x^2\right)\left\{-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}\right\}\left(lx - x^2\right)dx$$

$$= \int_0^l \left(lx - x^2\right)\left[-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2}\left\{lx - x^2\right\}\right]dx$$

$$= -\frac{h^2}{8\pi^2 m}(-2)\int_0^l \left(x^2 - lx\right)dx$$

$$= \frac{h^2}{4\pi^2 m}\left(l\frac{x^2}{2} - \frac{x^3}{3}\right) = \frac{h^2}{4\pi^2 m}\left(\frac{l.l^2}{2} - \frac{l^3}{3}\right)$$

$$= \frac{l^2}{4\pi^2 m}\left(\frac{l^3}{2} - \frac{l^3}{3}\right) = \frac{h^2}{4\pi^2 m}\left(\frac{l^3}{6}\right)$$

$$= \frac{h^2 l^3}{24\pi^2 m}$$

$$= -\frac{h^2}{8\pi^2 m}\int_0^l 2(lx - x^2)dx$$

$$= -\frac{h^2}{4\pi^2 m}\int_0^l (lx - x^2)dx$$

$$\int \phi^* H\varphi d\tau = \frac{h^2 l^3}{24\pi^2 m} ------(4)$$

Similarly considering the denominator

$$\int \varphi^* \varphi d\tau = \int_0^l (lx - x^2)(lx - x^2)dx = \frac{l^5}{30} --- (5)$$

$$\therefore E = \left(\frac{\frac{h^2 l^3}{24\pi^2 m}}{\frac{l^5}{30}} \right) = \frac{5h^2}{4\pi^2 l^2 m} = 0.12665 \frac{h^2}{ml^2} --- (6)$$

But the actual value obtained from SWE is

$$\frac{h^2}{8ml^2} = 0.125 \frac{h^2}{ml^2} = 0.125 \frac{h^2}{ml^2} ----- 7$$

$\therefore \%error = 1.3$ This error is due to very simple trial curve function move exact value can be obtained by choosing a trial curve function

$$\phi = x^k (l - x)^k$$

$$\frac{X^3}{3}(L^2 - 2L\frac{x^2}{2} + \frac{x^3}{3})$$

$$\frac{x^3 L^2}{3} - \frac{2Lx^5}{6} + \frac{x^6}{9}$$

$$\frac{x^3}{3}\left(L^2 - Lx^2 + \frac{x^3}{3} \right)$$

$$\frac{x^3}{3}\left(x^2 - x^3 + \frac{x^3}{3} \right)$$

$$\frac{x^5}{3} - \frac{x^6}{3} + \frac{x^6}{9} = \frac{x^5 - x^6}{3}$$

$$3x^5 - 3x^6 + x^6 = 3x^5 - 2x^6$$

$$\int x^2 \left(l^2 - 2lx + x^2 \right) dx = \int x^2 l^2 - 2.lx^3 + x^4$$

$$= \int \tfrac{x^3}{3} l^2 - 2\frac{x^4}{4} l + \frac{x^5}{5} = \tfrac{x^3}{3} l^2 - \frac{x^4}{2} l + \frac{x^5}{5}$$

$$\frac{l^5}{3} - \frac{l^5}{2} + \frac{l^5}{5} = \frac{10l^5 - 15l^5 + 6l^5}{30} = \frac{l^5}{30}$$

12.7 Application of variation theorem to a simple harmonic oscillator

For a simple harmonic motion one can write

$\frac{d^2\psi}{dx^2} = kx^2\psi$............(1) x- displacement and k -force constant . Suitable trial wave function can be written as

$$\phi = e^{-\beta x^2} ------(2)$$

It satisfies a condition where $x \rightarrow \pm\infty, \psi = 0$

Hamiltonian for simple harmonic oscillator is given by

$$H = \left[-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]...........(3)$$

From various theorem

$$E = \frac{\int \varphi^* H \varphi d\tau}{\int \varphi\varphi^* d\tau}............(4)$$

Substituting for ϕ and H in (4)

$$E = \frac{\int_{+\infty}^{-\infty}\left\{e^{-\beta x}\left[-\frac{h^2}{8\pi^2 m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right]e^{-\beta x^2}\right\}dx}{\int_{+\infty}^{-\infty}\left\{e^{-\beta x^2}e^{-\beta x^2}dx\right\}}......(5)$$

$$E = \frac{\int_{-\infty}^{+\infty} e^{-\beta x^2}\left[-\frac{h^2}{8\pi^2 m}\left(4\beta^2 x^2 e^{-\beta x^2}\right) - -\frac{h^2}{8\pi^2 m}(-2\beta e^{-\beta x^2}) + \frac{1}{2}kx^2 e^{-\beta x^2}\right]dx}{\int_{-\infty}^{+\infty} e^{-2\beta x^2}dx}.............(6)$$

$$E = \frac{\frac{h^2\beta}{4\pi^2 m}\left(\frac{\pi}{2\beta}\right)^{\frac{1}{2}} - \frac{h^2\beta}{8\pi^2 m}\left(\frac{\pi}{2\beta}\right)^{\frac{1}{2}} + \frac{k}{8\beta}\left(\frac{\pi}{2\beta}\right)^{\frac{1}{2}}}{\left(\frac{\pi}{2\beta}\right)^{\frac{1}{2}}}$$

$$= \frac{\left[\frac{h^2\beta}{8\pi^2 m} + \frac{k}{8\beta}\right]\left[\frac{\pi}{2\beta}\right]^{\frac{1}{2}}}{\left(\frac{\pi}{2\beta}\right)^{\frac{1}{2}}} = \left[\frac{h^2\beta}{8\pi^2 m} + \frac{k}{8\beta}\right]............(7)$$

Minimize E by differentiating the above equation and set equal to zero

$$\frac{dE}{d\beta} = \frac{d}{d\beta}\left[\frac{h^2\beta}{8\pi^2 m} + \frac{k}{8\beta}\right] = 0...........(8)$$

$$\frac{h^2}{8\pi^2 m} - \frac{k}{8\beta^2} = 0$$

$$\beta = \frac{\pi(mk)^{1/2}}{h} ----------- (9)$$

Substituting (9) in (7) for β

$$E_0 = \frac{h}{4\pi}\left\{\frac{k}{m}\right\}^{1/2} ------(10)$$

Equation 10 is exactly the same as obtained by solving SWE for a SHO

$E = (v + \frac{1}{2})hc\overline{w}$ ---- From SWE for SHO

For $E_0 = \frac{1}{2}hc\overline{w}$

$$\because v = 0$$

$$\overline{w} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

$$\therefore E_0 = \tfrac{1}{2}hc\frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

$E_0 = \frac{h}{4\pi}\sqrt{\frac{k}{\mu}}$ .... from SWE

12.8 Application to H-atom

This exam shows how powerful the variation method is and the exactness of the result when correct trial wave function is chosen. For H-atom, the wave function is of the form

$$\psi = e^{-ar} ------(1)$$

$$\& \, H = -\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{e^2}{r} ----- (2)$$

$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 - \frac{\partial}{\partial r}\right)$ In spherical co-ordinates ------- (3)

$$\nabla^2\psi = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 - \frac{\partial}{\partial r}\right)\times e^{-ar} -----(4)$$

$$= \left(a^2 - \frac{2a}{r}\right)e^{-ar} -------------(5)$$

From Variation method $E = \dfrac{\int \psi^* H\psi d\tau}{\int \psi^*\psi d\tau} ----(6)$

In spherical co-ordinates, $d\tau = 4\pi r^2 dr$

Substituting for ψ and H

$$E = \frac{\int_0^\infty e^{-ar}\left\{-\frac{h^2}{8\pi^2 m}\left(a^2 - \frac{2a}{r}\right)e^{-ar} - \frac{e^2}{r}e^{-ar}\right\}4\pi r^2 dr}{\int_0^\infty e^{-ar}.e^{-ar}.4\pi r^2 dr}$$

$$= \frac{\int_0^\infty \left(-\frac{h^2 a^2}{8\pi^2 m}\right) r^2 e^{-2ar} dr + \int_0^\infty \left(\frac{2h^2 a}{8\pi^2 m}\right) re^{-2ar} dr - \int_0^\infty e^2 re^{-2ar} dr}{\int_0^\infty r^2 e^{-2ar} dr}$$

$$E = \frac{-\frac{h^2 a^2}{8\pi^2 m}\left(\frac{2}{8a^3}\right) + \left(\frac{h^2 a}{4\pi^2 m}\right)\left(\frac{1}{4a^2}\right) - e^2\left(\frac{1}{4a^2}\right)}{\left(\frac{2}{8a^3}\right)}$$

$$\therefore E = \left\{\frac{h^2 a^2}{8\pi^2 m} - e^2 a\right\} -----------(7)$$

Differentiating w.r.t a and $\frac{dE}{da} = 0,$ The values corresponding to minimum energy is obtained

$$\frac{dE}{da} = \frac{2h^2}{8\pi^2 m}a - e^2 = 0$$

$$\therefore a = \frac{4\pi^2 me^2}{h^2} -----(8)$$

Substitute (8) in (7) we get

$$E\frac{h^2a^2}{8\pi^2m}-e^2\left(\frac{4\pi^2me^2}{h^2}\right)$$

$$E=\left(-\frac{2\pi^2me^4}{h^2}\right)-----(9)$$

This is exactly the same expression as obtained by solving S.W equation by variation method gives result in a much easier way however the wave function must be know exactly.

It is also interesting to know that 'a' as given by equation is exactly the same as the reciprocal of a_0,

The Bohr radius given by $a=\frac{1}{a^0}$

i.e $a^0=\frac{h^2}{4\pi^2me^2}$

$$E=\tfrac{1}{2}a.\mu.=0.5a.\mu$$

Suppose issued of using $\psi=e^{-ar}$, if we use $\psi=e^{-ar2}$, Then E= -0.424 $a.\mu$

More general function $\psi=e^{-cr}$ is used c =1, n =1, $\psi=e^{-r}$ (normalized wave function)

12.9 Summary of the unit

The variational method is the other main approximate method used in quantum mechanics. Compared to perturbation theory, the variational method can be more robust in situations where it's hard to determine a good unperturbed Hamiltonian (i.e., one which makes the perturbation small but is still solvable). On the other hand, in cases where there is a good unperturbed Hamiltonian, perturbation theory can be more efficient than the variational method.

The basic idea of the variational method is to guess a ``trial" wave function for the problem, which consists of some adjustable parameters called ``variational parameters." These parameters are adjusted until the energy of the trial wavefunction is minimized. The resulting trial wave function and its corresponding energy are variational method approximations to the exact wave function and energy.

Why would it make sense that, the best approximate trial wave function is the one with the lowest energy? This results from the Variational Theorem, which states that the energy of any trial wave function E is always an upper bound to the exact ground state energy E_0. This can be proven easily.

12.10 Key words

Variation theorem; Ground state; Practice in a box; Simple harmonic oscillator; H-atom

12.11 References for further study

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3) Quantum Mechanics:Theory and Applications; Ajoy K. Ghatak, S. Lokanathan; *Macmillan*, **2004**.

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5) Quantum Mechanics and Spectroscopy; Gupta Tandon; *Galgotia Publications*.

12.12 Questions for self understanding

1) Define statement variation theorem and verify its proof

2) Write a note o application of variation method

3) Apply the variation method to ground state of He atom

4) Calculation of binding energy of the He atom using variation method

5) Derive the equation for practice in a box problem (one-dimenction) by Applying variation o theorem

6) Using variation theorem derive the equation to a simple harmonic oscillator

7) Obtain the equation for H-atom by applying variation theorem.

Unit-13

Structure

13.0 Objectives of the unit
13.1 Introduction
13.2 Surface phenomena
13.3 Adsorption
13.4 Adsorption of Gases
13.5 Types of adsorptions
13.6 Langmuir adsorption isotherm (ideal adsorption)
13.7 Adsorption with dissociation
13.8 Competitive adsorption
13.9 Chemical Reactions on Surface
13.10 Mechanism of surface Reaction
13.11 Uni molecular surface reactions
13.12 Equation of uni-molecular surface reaction
13.13 Bimolecular surface reaction
13.14 Two special cases
13.15 Inhibition of unimolecular Surface Reaction
13.16 Activation Energies
13.17 Summary of the unit
13.18 Key Words
13.19 References for further study
13.20 Questions for self understanding

13.0 Objectives of the unit

After studying this unit you are able to

- Explain the different types of surface phenomena
- Illustrate the difference between adsorption and absorption
- Derive the expression for Langmuir adsorption isotherm
- Explain the Competitive adsorption
- Explain the different Chemical Reactions on Surface
- Derive the expression for Uni molecular surface reactions
- Derive the expression for Bimolecular surface reaction
- Derive the expression for Inhibition of unimolecular Surface Reaction

13.1 Introduction

The attraction and holding of one molecule, ion, or atom at the surface of a liquid or solid is called adsorption. There are several kinds of forces which cause adsorption. They may be physical in nature, such as unsatisfied intermolecular attractions (van der Waals forces), or they may be chemical such as hydrogen-bond formation, ion exchange, or covalent bond formation. Adsorption always occurs in such a way as to reduce the free energy of the surface involved. Since the free energy of a surface equals area times surface tension, a reduction in either area or surface tension results in a lessening of the free energy of the surface. In a homogeneous solution which has molecules of differing activities, the molecules orient themselves at the surface in such a way that their least active part is exposed, thus reducing the surface energy. This is similar to the behavior of the molecules in a solution, where those molecules with the least energy, producing the greater drop in surface tension, will concentrate at the surface.

13.2 Surface phenomena

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process.

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behavior of real gases.

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption.

Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent, with its pressure (if gas) or concentration (if liquid). One can find in literature several models describing process of adsorption, namely Freundlich isotherm, Langmuir isotherm, BET isotherm, etc.

13.3 Adsorption

Adsorption is a surface phenomena used to describe the existence of a higher concentration of any particular substance at the surface of a liquid or solid is present in the bulk of the medium. Therefore adsorption is called as an excess concentration of any substance at the surface whereas in absorption more or less uniform penetration of a given substance in to solid or liquid occurs.

Charcoal, silicagel, alumina are important adsorbing material and they are called Adsorbents.

The material which on given substance is adsorbed are called absorbent.

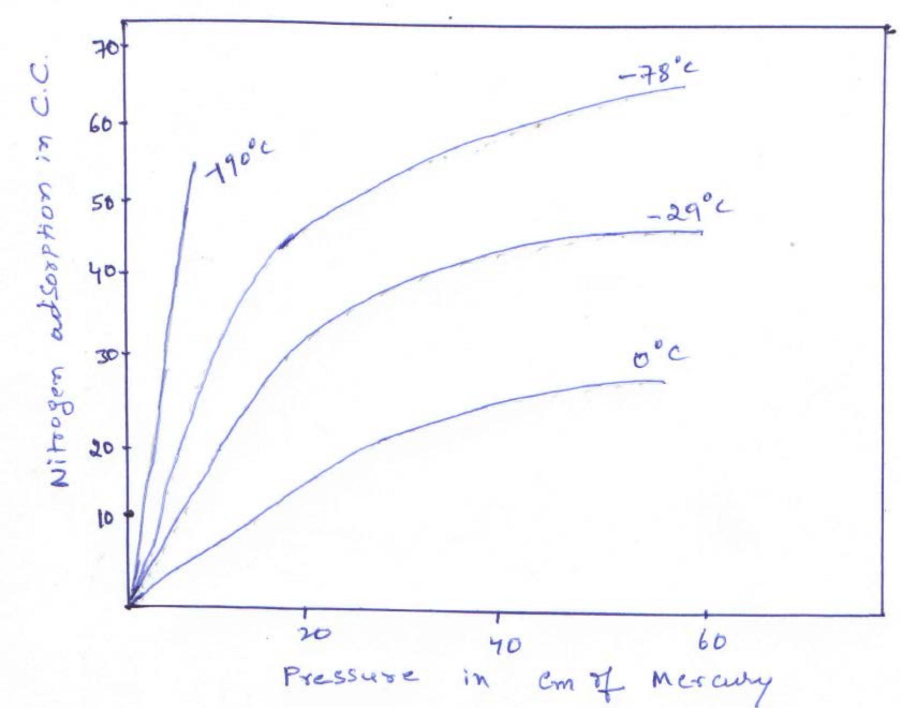
Chromium(III) oxide (Cr_2O_3) and Zinc oxide, metals such as platinum, Palladium, copper, nickel are used for adsorbing gases, example H_2

A given metal may adsorb one gas but not another. Thus hydrogen very strongly adsorbs on Ni but nitrogen is very poorly adsorbed on Ni.

To understand this adsorption phenomena it is convenient to treat adsorption of gases and adsorption from solution separately.

13.4 Adsorption of Gases

Increasing of pressure and decreasing of temperature increase the extent of the adsorption of a gas by solid



Adsorption isotherms of nitrogen by charcoal

Figure indicates the character of nitrogen gas adsorbed by 1gm of charcoal at various temperature and pressures

Adsorption process is usually studied through graphs known as adsorption isotherm. That is the amount of adsorbate on the adsorbent as a function if its pressure or concentration at constant temperature .The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials.

Each of the curves is called an adsorption isotherm, because it gives extent of adsorption at different pressure at constant temperature (specified temperature) so we can see that decrease in temperature and increase in pressure increases the adsorption

From the above we can predict that after saturation pressure Ps, adsorption does not occur anymore, that is there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached when all the sites are occupied and further increase in pressure does not cause any difference in adsorption process. At high pressure, Adsorption is independent of pressure.

Note: *adsorption decrease with increase of temperature becomes evolution of heat take place i.e adsorption of a gas is accompanied by a decrease of enthalpy and this is known as Heat of adsorption.* (for evergy gas and solid there is a definite heat of adsorption, if no gas is absorbed by the solid earlier)

This variation of gas adsorption with pressure at constant temperature can be represented over a limited range of pressure by an empirical equation commonly known as the Freundlich adsorption isotherm

i.e $a = kP^n$ ---------------------------------(1)

a = amount of gas adsorbed by unit mass.

P = pressure

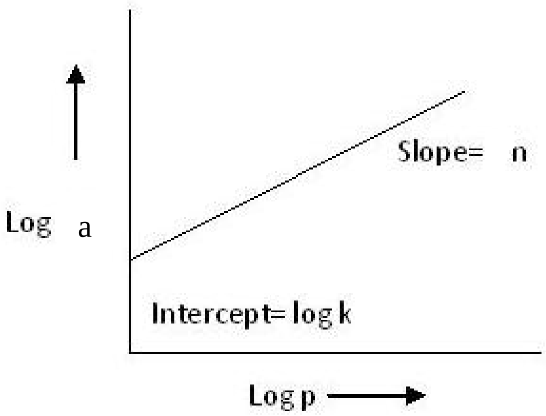
K and n are constant depends with adsorbate and adsorbent at the particular temperature.

n < 1 at moderate temperature and higher temperature for most of adsorbents and adsorbates so that increase of 'a' with pressure is less rapid

But as n→1, then a α P at least at low pressure then (1) become by taking logarithms

loga =log k + n log p-------- (2)

so that a plot graph of log a Vs log p should be straight line



Intercept = k

Slop =n

Off course experiment shows slight curvature especially at low temperature. Hence Freundlich adsorption isotherm regarded as approximate only i.e it is convenient to use over a short range of pressure.

13.5 Types of adsorptions

Depending on the nature of attractive forces existing between the adsorbate and adsorbent, adsorption can be classified mainly two types they are

(1) Physical adsorption or Vander Waal's adsorption
(2) Chemisorption

Physical adsorption or Vander Waal's adsorption

The force are of a physical nature i.e adsorption is relatively weak and the forces are assigned to be same as that of Vander Waal's force in the Vander Waal's equation of state of gases (Expect for certain atomic process) this is not important i connection with surface reactions. Usually the heat changes (heat of adsorption) formed with Vander Waal's adsorptions is less than 5 Kjols/mole

Chemisorption

In this type of adsorption, adsorbed molecules are held to the surface by strong valence forces similar to bound atoms in molecules and heat evolved be the same order as that formed with chemical reactions i.e 10 to 100 K cals/mole

i) Adsorption of molecules with the surface takes place forming chemi molecular layer and then become saturated. Then no further adsorption takes place. Even adsorptions take place means on the readily formed layer only. Therefore there is limitation for adsorption pressure.

ii) Taylor – chemisorptions associated with high activation energy (920kcal/mole) is slow process called some time Activated adsorption. Therefore at low temperature Vander Waal's adsorption is predominating than activated adsorption.

iii) All surfaces are not smoother – some surface will be more active than others and chemical process will occur predominately on the most active sites Taylor referred to as active centers
(Which depends on certain types of lattice defect)

iv) Also there are interactions usually repulsive forces, which exists between atoms or molecules adsorbed side by side on a surface

Comparison between Physisorption and Chemisorption

Physical adsorption	Chemisorption
Forces of attraction are Vander Waal's forces	Forces of attraction are chemical bond forces
Low enthalpy of adsorption (20-40Kj/mole)	High enthalpy of adsorption (200-400Kj/mole)
This process is observed under conditions of	This process takes place at high temperature

low temperature	
It is not specific	It is highly specific
Multi-molecular layers may be formed	Generally monomolecular layer is formed
This process is reversible	This process is irreversible

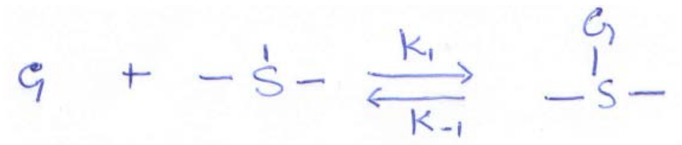
13.6 Langmuir adsorption isotherm (ideal adsorption)

The Freundlich isotherm equation is empirical one and the Langmeir theoretical equation is simplest, which applies to the ideal case of chemisorptions on a perfectly smooth surface with the interactions between adsorption between adsorbed molecules. Therefore Langmuri isotherm is looking similar to the ideal gas laws. Hence Langmeir adsorption isotherm are called ideal adsorption

The equations of ideal adsorption play an important role in surface kinetics and they will be derived with difference parts of views and for different situations

L adsorption Isotherm (without dissociation of molecule)

The simplest case is, the gas atoms or molecules occupy single sites on the surface and are not dissociates i.e the adsorption and decrease in pressure is represented by



Then if θ be the fraction of surface that is covered (used for adsorption)

(1-θ) is the fraction that is bare (remained)

the rate of adsorption = $k_1 p(1-\theta)$ --------------------(1)

Rate of desorption = $k_{-1}\theta$ --(2)

Where p is the gas pressure and $k_1 k_{-1}$ are rate constant

At equilibrium (1) = (2)

$k_1 \, p(1-\theta) = k_{-1}\theta$

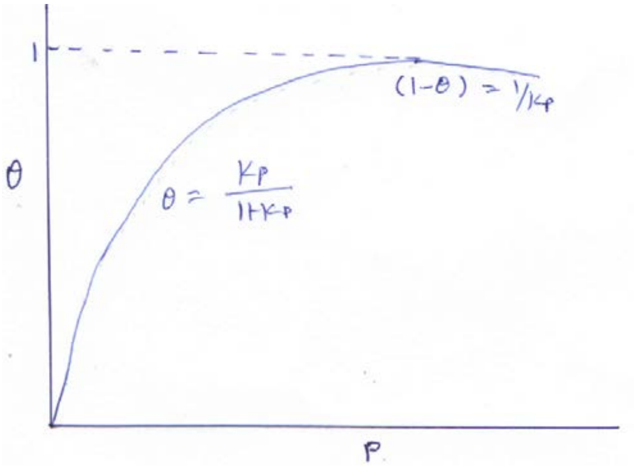
$$\frac{\theta}{1-\theta} = \frac{k_1}{k_{-1}} p = KP$$

$$\therefore \frac{\theta}{(1-\theta)} = KP -------------(3)$$

Equation (3)

$$\theta = \frac{kp}{1+KP} --(4)$$

So this equation gives the behavior of adsorption at low and high pressure



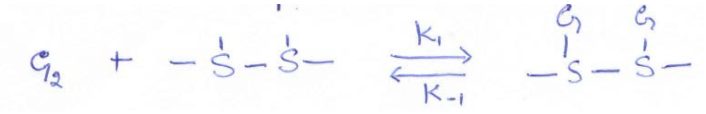
When p is low 1>>kp

i.e, θ = kp or θ α p

(When θ = 1, (1-θ) = 0 therefore no surface available as the pressure is increases i.e, reaches a maximum of adsorption)

13.7 Adsorption with dissociation

In certain case the process of adsorption takes place by the dissociation of the molecule on the surface



Example, hydrogen molecule is adsorbed on the surface of many metals in the form of hydrogen atoms which occupies a surface state

Similarly $2CH_4$ adsorbed on metals dissociated into CH_3, CH_2 and hydrogen atom

The process of adsorption must be take place between gas molecules and two surface sites

Then the rate of adsorption $q_1 = k_1 P(1-\theta)^2$ ---------(1)

Since descroption process take place between two adsorbed atoms, the rate proportional to square of the fraction of surface covered

$$q_{-1} = k_{-1}\theta^{2} \text{-----------------}(2)$$

At equilibrium (1) = (2)

Hence $k_1 p(1-\theta)^2 = k_{-1}\theta^2$

$$\frac{k_1}{k_1 p} = \left(\frac{\theta}{1-\theta}\right)^2$$

$$\therefore \frac{\theta}{1-\theta} = \left(\frac{k_1}{k_1} p\right)^{\frac{1}{2}}$$

$$\frac{\theta}{1-\theta} = K^{\frac{1}{2}} P^{1/2} -------------(3)$$

The above equation can be written as

$$\theta = \frac{KP^{\frac{1}{2}}}{1+K^{\frac{1}{2}}P^{\frac{1}{2}}} ----------------------(4)$$

When P is small then $K^{1/2}$ $P^{1/2} <<<<$ unity i.e., negligible

Therefore $\theta \ \alpha \ P^{1/2}$

When pressure is high equation 4 can be written as

$$1-\theta = \frac{1}{1+K^{\frac{1}{2}}P^{\frac{1}{2}}} ----------------------(5)$$

$$\boxed{1-\frac{k^{\frac{1}{2}}p^{\frac{1}{2}}}{1+k^{\frac{1}{2}}p^{\frac{1}{2}}} = \frac{1}{1+k^{\frac{1}{2}}p^{\frac{1}{2}}}}$$

Then $K^{1/2}P^{1/2} >>>> 1$

$\therefore (1-\theta)\alpha\frac{1}{p^{\frac{1}{2}}}$, i.e fraction of the surface that is base is inversely proportional to the square root of the pressure.

13.8 Competitive adsorption

These isotherm is with respect to when two gases adsorbed on the same surface is of considerable importance in connection with the kinetics of surface reactions within two substances

Let θ= fraction of surface corrected by molecules of type A.

θ^1= fraction of surface corrected by molecules of type B.

$\therefore$ Fraction base is=$1-\theta-\theta^1$

Assessing A and B adsorbed without dissociation.

The rate of adsorption of A

$$q_1 = k_1 p(1-\theta-\theta^1) \text{ ------------------------(1)}$$

P is partial pressure of A

The rate of desorption of A is

$$q_{-1} = K_{-1}\theta \text{ ------------------------------(2)}$$

At equation 1=2

$$K_1 p(1-\theta-\theta^1) = k_{-1}\theta$$

$$\frac{\theta}{1-\theta-\theta^1} = kp \text{ --------------------------(3)}$$

Similarly for B

$$\frac{\theta^1}{1-\theta-\theta^|} = K^| p^| \text{ ------------------------(4)}$$

Where $p^|$ = partial pressure of B

K and $K^|$ are equilibrium constant for the adsorption of A and B respectively

Similarly (3) and (4) are simultaneous equations, the solution for this equation

$$\theta = \frac{kp}{1+kp+k^| p^|} \text{ -----------------------(5)}$$

$$\theta' = \frac{K'P'}{1 + kp + k'p'} \text{ ------------------------(6)}$$

Equation (5) can be reduced to $\theta = \frac{kp}{1 + kp}$ if $p' = 0$ (B is absent) or $k' = 0$ (B is not adsorbed)

Similarly equation (6) can reduced to $\theta' = \frac{k'P'}{1 + k'P'}$ if p=0 (A is absent) or k =0 (A is not absorbed)

Form (5) and (6) it has been seen that "fraction of the surface covered by one gas is reduced if the presence of the other gas is increased" (i.e in (5) if P^1 increases then θ decreases and in (6) if p of A increases then θ' decreases.

i.e the molecule are competing with one another for a limited number of surface sites. Hence this case is called as competitive chemisorptions or competitive adsorption .

Sometimes (special cases) two gas may become adsorbed on two different sets of surface sites (A+B→S –

In which case there is no completion. The isocromes then lowering similar to that of two completely separate surfaces where in solved i.e $\theta = \frac{kp}{1 + kp}$ apply to each gas.

13.9 Chemical Reactions on Surface

The structure of solid surfaces and the chemical reactions that take place on surfaces are of fundamental importance to a wide variety of technological problems. For example, catalytic converters in automobiles have dramatically reduced the atmospheric pollutants in automobile exhaust. The chief component of automotive catalysts are precious metals such as platinum or rhodium and the key chemical reactions involved in the removal of pollutants such as carbon monoxide, unburned hydrocarbons, and nitrogen oxides, take place on the surfaces of the metal particles contained in the catalysts. This is an example of heterogeneous catalysis, a method that is widely used to promote desired chemical reactions. Other technological fields that require a detailed understanding of surface properties include nanoscience and nanotechnology, semiconductor manufacturing and processing, and various strategies for developing alternative energy sources. Prof. Trenary's laboratory contains an array of advanced surface science instrumentation for investigating fundamental aspects of the structure of solid surfaces as well as the chemical reactions that take place on the surfaces of metals and metal oxides.

13.10 Mechanism of surface Reaction

A reaction on surface in which following five consecutive steps may occur

1. Diffusion of the reacting molecules to the surface (from the gas phase)
2. Adsorption of the gases on the surface.
3. Reaction on the surface.
4. Desorption of the products.
5. Diffusion of the desorbed products into the main body of the gas.

At first it was through (1) or (5) is slowest process, but latter it was found diffusion process in which no activation energy i.e very rapid Langmuir also postulated if it so ((1) or (5) is state) a thick diffusion layer on the surface would be visible (But some time solid liquid reaction diffusion in solution is slower than in the gas)

It has been shown that adsorption or desorption steps are slow in heterogeneous reactions particularly for desorption steps activation energies are very high, so that this may be that rate determining step. But however in practice it is not possible to separate (3) and (4) because not possible to know the rate of desorption of products.

∴ To study this surface reaction the step (3) and (4) may considered as a single steps

This concept is used for the treatment of surface reactions by Langmuir and Hinshelwood calculation q rate

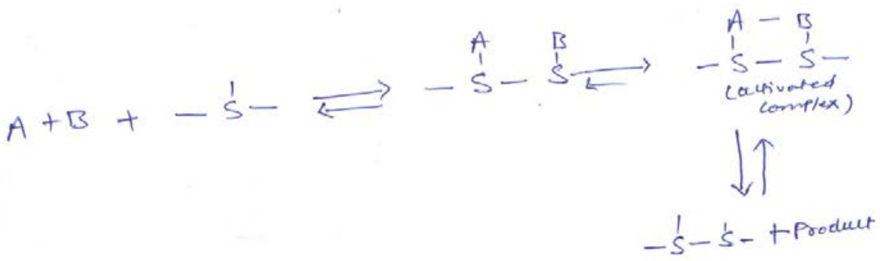
i) Expression for the concentration of reactant molecules on the surface is obtained

ii) Then the rate of formation of gaseous product is expressed in terms of these surface concentrations.

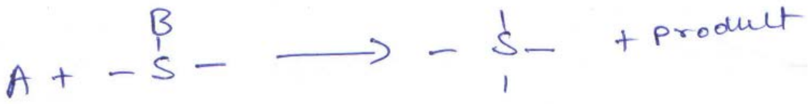
So that rate is then expressible in terms of the concentration of the gaseous reactants.

If only one reactant, the surface process is uni-molecular change

But if two A and B term adsorption at weakly binding surface sites take place



Another type



i.e reaction between gas molecules A and an adsorbed molecule i.e B which is already adsorbed. One of the important concept for classification of surface reactions is molecularity. i.e number of molecules taking part in the course of reaction (the no surface site is not considerable)

i.e reaction involving a single reacting substance usually unimolecular

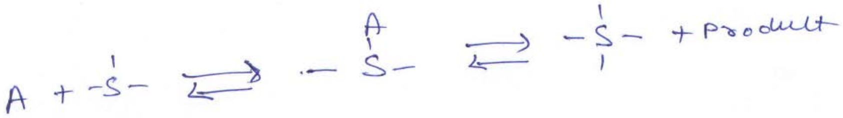
Example, Surface catalyzed ammonia decomposition on the over hand, if two molecule are adsorbed on neighboring surface sites.

Ex- decomposition of acetaldehyde on various surface is adsorbed two acetaldehyde molecule is bi molecular reactions.

Similarly nitric oxide and oxygen reactions on gases surface is bi molecular

13.11 Uni molecular surface reactions

Simplest case of Langmuir adsorption



For this reaction θ at p is given by

$$\theta = \frac{Kp}{1+Kp} \text{ ----------------------------- (1)}$$

Since rate of reaction proportional to θ, we can write θ α C α q (θ proportional concentration of molecules adsorbed on the surface)

$$q = k_2\theta \text{ -------------------------------- (2)}$$

$$q = \frac{k_2 KP}{1 + KP} \text{ ------------------------------ (3)}$$

k_2 is proportionality constant

Equation (3) is written with assumption that “the adsorption equilibrium is not disturbed by the occurrence of the surface reaction “ a condition which is equally satisfied. The reaction between rate and pressure seen to same as that of θ and pressure i.e surface coverage and pressure

At high pressure KP>>>1 then (3) become $q = k_2$ ---------------------(4)

i.e rate is independent of the pressure which means that the kinetics are zero order.

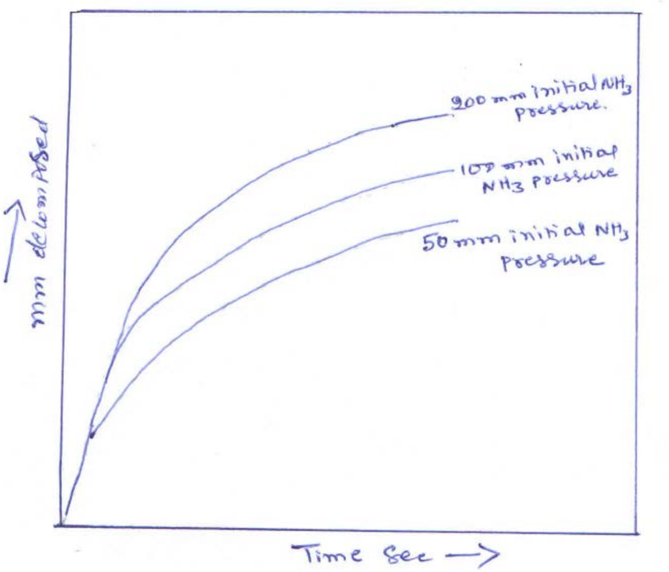
At low pressure KP<<<1 then

$q = k_2, KP$--(5)

i.e showing kinetics of first order.

13.12 Equation of uni-molecular surface reaction

Decomposition of NH_3- to nitrogen and hydrogen using tungsten and platinum surface



At 856^o C initial slopes are same with different concentration of NH_3, indicating zero order. Latter dissociation is due to kinetic approach first order behaving at lower partial pressure of ammonia on tungsten. No effect of added hydrogen is seen.

But with platinum it is found, the reaction was inhibited by the hydrogen produced in the reaction and by added hydrogen, the rate of lowering $q = \frac{k[NH_3]}{[H_2]}$

Decomposition of Phosphine

Phosphine on glass surface shows I order at low pressure and zero order at high pressure

Decomposition of Nitrous Oxide _Into nitrogen and oxygen $V = \frac{k[N_2O]}{1 + a(N_2O) + b(O_2)}$

Decomposition of formic acid

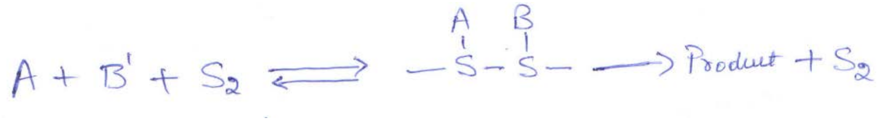
Glass , platinum, Ag, gold

$HCOOH \rightarrow Co + H_2O$ 16 kcal

$HCOOH \rightarrow CO_2 + H_2$ 28.0 kcal

13.13 Bimolecular surface reaction

Most surface reactions between two substances occur by reaction between two molecules which are adsorbed on neighboring surface sites i.e Langmuir – Hinshelwood mechanism



$$A + B' + S_2 \rightleftharpoons -\underset{}{\overset{A}{\overset{|}{S}}} - \overset{B}{\overset{|}{S}} - \longrightarrow \text{Product} + S_2$$

Then the rate of reaction proportional to probability that A and B are adsorbed on neighboring sites

i.e rate of reaction proportional to faction of the surface θ and $\theta^{|}$ by A and B

i.e $q = k_2\theta\theta^{|}$ ----------- (1)

$= \frac{k_2KK^{|}PP^{|}}{(1 + KP + K^{|}P^{|})^2}$ -------- (2)

$$\theta = \frac{kp}{(1 + kp + K^{|}P^{|})}$$

$$\theta^{|} = \frac{K^{|}P^{|}}{(1 + KP + K^{|}P^{|})}$$

If P^1 is kept constant and P is varied reaction the rate first increases, passes through a maximum and then decreases as shown in figure

The falling of the rate at high pressure because one reactant displaces the order as its pressure is increased.

The rate corresponds to maximum indicates the existence of the rate maximum number of neighboring A-B pairs on the surface (lll^{rly} they observed when p is kept constant)

13.14 Two special cases

Case-1

Sparsely covered surfaces

If both P and $P^|$ are sufficiently low then KP and K^1P^1 may be neglected

$\therefore$ becomes $q=k_2.KK^1PP^1$-------------------------(3)

$\therefore$ the reaction is second order being first order in both A and B

Ex- reaction between Nitric oxide and oxygen on glass

Case-2

One reactant very weakly adsorbed

Suppose if A is very weakly adsorbed then kp in the denominator in equation (2) is similar and may be neglected

Then $q = \dfrac{k_2KK^1PP^1}{(1+K^1P^1)^2}$ ---------------(4)

Rate is proportional to the pressure of A. But as the pressure of B increases the rate first increases passes through a maximum and then it decreases.

The decrease of rate may be as factor

Sine reactant B is sufficiently strongly adsorbed hence $K^1P^1 >> 1$ then

(4) become $q = \frac{k_2KK^1PP^1}{(K^1P^1)^2}$

$\therefore q = \frac{k_2Kp}{K^1P^1}$ -------------------------(5)

i.e rate is first order reaction with respect t0 p and A are inversely proportional to

When the gas is strongly adsorbed (Kinetics are Zero order) $k_P >> 1$

$$\theta = \frac{KP}{KP} = 1$$

$$q = k_3$$

$$i.e \frac{-dp}{dt} = k_2$$

$$-dp = k_2dt$$

$$-p = k_2t + C$$

When P = P_0 and t = 0 then constant = $-P_i$, P_i is the unit pressure of the gas and P is the pressure of the gas at any instance of time t

$\therefore -P = k_2t - P_i$

$$k_2 = \frac{p_i - p}{t}$$

This is equation for the uni molecular reactant which form zero order

Ex- decomposition of NH_3 on O_3, Decomposition of HI on Gold etc

When the gas is weakly adsorbed (Kinetic are 1st order)

Kp<<<1

$$\theta = Kp$$

$$Q = K_2KP$$

$$Let K = K_{2.}K$$

$$Q = K.P$$

$$\therefore \frac{dp}{dt} = kp$$

$$\frac{-dp}{p} = Kdt$$

$$\text{int}\, egrate$$

$$-\ln P = kt + C$$

When t=0, $P=P_1$

Then –ln P_i = constant

$\therefore$ $-\ln P = kt - \ln P_1$

$\ln P_i - \ln P = kt$

$kt = \ln \frac{P_l}{P}$ or $k = \frac{l}{t} \ln \frac{P_l}{P}$

This equation is idetical with the equation for first order homogeneous reaction.

P_1=initial pressure of gas and P=is the pressure of gas at any instant of time t

Ex- decomposition of PH_3 on glass, Decomposition of N_2O on gold. Decomposition of HI on Pt

When the gas is moderately adsorbed

$$q = k_2\theta$$

$$\theta = \frac{KP}{1+KP}$$

$$\therefore q = k_2\left(\frac{KP}{1+KP}\right)$$

$$q = \frac{kp}{1+KP}$$

This equation is approximates as

$$\frac{-dp}{dt} = kP^n$$

Where n is fractional

Ex- decomposition of (SbH_3) on Sb for which n = 0.

13.15 Inhibition of unimolecular Surface Reaction

One of the complication exits in this surface reaction effect of absorption foreign substance on the surface which reduce the reaction called Inhibitor (because of effective surface area)

Let us considered a substance A is undergoes uni molecular reaction on a surface and that a non reacting gaseous substance (I) or poison is also adsorbed.

θ = fraction of the surface core red by A

θ_I = fraction of the surface core red by I

Then the fraction corered by A is given By

$$\theta = \frac{KP}{1 + KP + K_i P_i} \text{ ---------------------- (6)}$$

Where P_i is partial pressure of the inhibitor and K_i its adsorption constant

$\therefore$ rate of reaction = $k_2\theta$

$$\text{Or } = \frac{k_2 KP}{1 + KP + K_i P_i} \text{ --------------------- (7)}$$

In the absence of Inhibitor this reduce to rate of reaction $= \dfrac{k_2 KP}{1 + KP + k_i p_i}$

A special integrating case is

When p is very small then KP<<<<1+K_iP_i

$$\text{Than } q = \frac{\Re_2 KP}{1 + K_i P_i} \text{ ------------------------- (8)}$$

So if the inhibitor is very strongly adsorbed then K_iP_i >>>1 then

$$q = \frac{k_2 KP}{K_i P_i} \text{ -- } (9)$$

Therefore in such cases the reaction is first order with respect to reactant and the rate is inversely proportional to the inhibitor pressure.

These special case arises when the inhibitor (I) is a product of the reactant

13.16 Activation Energies

Since the rate constant k_2 obeys Arrhenius law we can wrote

$$\frac{d}{dt}\ln k_2 = \frac{E}{RT^2} \text{ -------------------- } (10)$$

And from Van't Hoff relationship the temperature variation of the equation constant k is given by $\frac{d}{dt}\ln K = \frac{-\lambda}{RT^2}$ -------------------- (11)

Where λ= heat evolved /mole of reactent gas in the adsorption process

Then effect of temperature on rate can be considered with two cases

i) If the pressure is low the rate is given by (using $V=k_2k.P$) then the first order rate constant

$k^1 = k_2.k$ ---------------- (12)

$$\frac{d}{dt}\ln q = \frac{d}{dt}\ln k^1$$

$$But\,\frac{d}{dt}\ln k^1 = \frac{d}{dt}\ln k_2 + \frac{d}{dt}\ln K$$

Using (10) and (11)

$$\frac{d}{dt}\ln q = \frac{d}{dt}\ln k^1 = \frac{E}{RT^2} - \frac{\lambda}{RT^2}$$

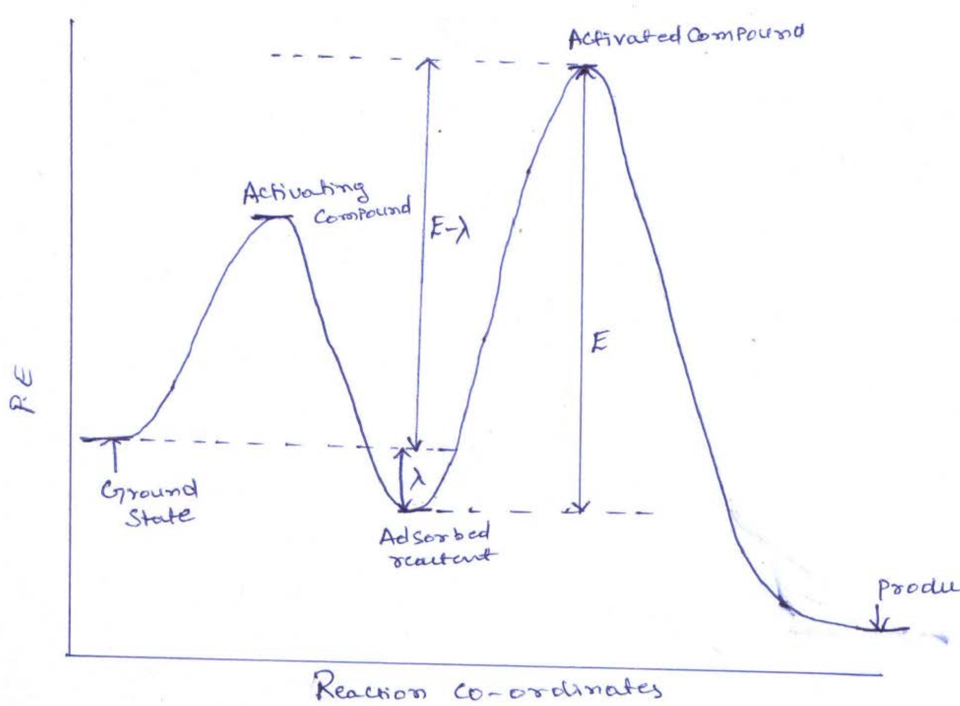
$$= \frac{E-\lambda}{RT^2} \text{ --------------------------------------- } (13)$$

(E-λ) is called appropriate activation energy E_a $\therefore$ it is given by "true" activation energy

E reduced by the value adsorption of the reactant.

If the pressure is high (equation 4 is $v = k_2$) applies then E_a is = true activation energy

This relationship may be explained by P.E diagram



The reaction, first passage of the system over an initial energy barrier to give the adsorbed state, during which energy is lower by λ then that of initial state. Then the system posses over a second barrier of height E

For this, if p is low

Then most of reactant molecules are in an adsorbed state so to pass to activate state it need only energy E-λ

Pressure

The equilibrium favors the adsorbed state and system need energy E in order to pass to the activation state.

If the reaction is inhibitated then activation energy is not same but is modified by the energy of adsorption (heat of adsorption) of the inhibitor

Secondary to (9) $q = \frac{k_2 Kp}{K_i P_i}$

For which the reactant is weakly adsorbed and the inhibitor strongly adsorbed

It follows that

$$\frac{d\ln q}{dT} = \frac{d\ln k_2}{dT} + \frac{d\ln k}{dT} - \frac{\ln k_i}{dT} \text{------------------ (14)}$$

Since variation of inhibition constant with temperature is given by Vant Hoff by

$$\frac{d\ln K_i}{dT} = \frac{-\lambda i}{RT^2} \text{--------------------------- (15)}$$

There λ_i = heat of adsorption of the poison (inhibitor)

$$\frac{d\ln q}{dT} = \frac{E}{RT^2} - \frac{\lambda}{RT^2} - \left(\frac{-\lambda}{RT^2}\right)$$

$$= \frac{E-\lambda+\lambda}{RT^2} \text{-------------------------- (16)}$$

Is apparent activation energy (in presence of inhibitor) is given by $E_a = E-\lambda+\lambda_i$ ----- (17)
i.e the activation energy is increased by λ_i because it is necessary for molecule of the inhibitor to be desorbed (so that) in order for a molecule of reaction to become adsorbed and un definite reaction.

13.17 Summary of the unit

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins and water purification.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favourable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption. Physisorption or physical adsorption is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions, which are also responsible for the non-ideal behaviour of real gases.

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physisorption.

13.18 Key Words

Surface phenomena; Adsorption; Langmuir adsorption isotherm; Competitive adsorption; Chemical Reactions on Surface; Uni molecular surface reactions; Bimolecular surface reaction; Inhibition of unimolecular Surface Reaction.

13.19 References for further study

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13.20 Questions for self understanding

1) What are surface phenomena? Explain the different types of surface phenomena

2) How adsorption is different from adsorption phenomenon?

3) Explain Adsorption of Gases and derive the expression for it

4) Derive the expression for Langmuir adsorption isotherm

5) Derive the expression for Adsorption with dissociation

6) Explain the Competitive adsorption

7) Explain the different Chemical Reactions on Surface

8) Derive the equation for Uni molecular surface reactions

9) Derive the equation for Bimolecular surface reaction

10) Derive the expression for Inhibition of unimolecular Surface Reaction

11) Write a note on Activation Energies.

Unit-14

Structure

14.0 Objectives of the unit
14.1 Introduction
14.2 BET (Brunauer Emmet Teller) Adsorption Isotherm
14.3 Assumptions in the BET theory
4.4 Derivation
14.5 Limitations of BET Isotherm
14.6 Determination of surface area
14.7 Brunauer, Emmett and Teller (BET) theory and specific surface area determination
    a) Multi-point measurement
    b) Single-point measurement
14.8 Adsorption Isotherms
14.9 Gibbs Isotherm
14.10 Gibb's Adsorption Isotherm
14.11 Applications of Adsorption
14.12 Summary of the unit
14.13 Key words
14.14 References for further study
14.15 Questions for self understanding

14.0 Objectives of the unit

After studying this unit you are able to

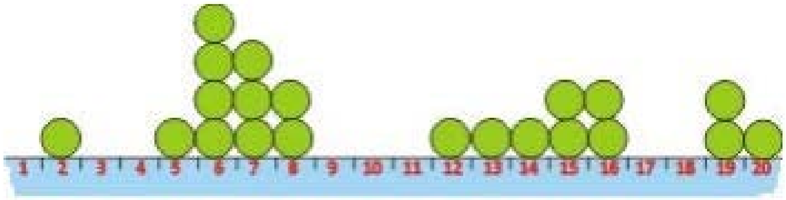
- Write the Assumptions in the BET theory
- Solve the derivation BET theory
- Explain the Limitations of BET Isotherm
- Explain the methods of Determination of surface area
- Explain the Adsorption Isotherms
- Solve the equation of Gibb's Adsorption Isotherm

14.1 Introduction

The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Physical adsorption results from relatively weak forces (van der Waals forces) between the adsorbate gas molecules and the adsorbent surface area of the test powder. The determination is usually carried out at the temperature of liquid nitrogen. The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure. The most widely used technique for estimating surface area (also the one we use) is the so-called BET method. BET analysis provides precise specific surface area evaluation of materials by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in m^2/g yielding important information in studying the effects of surface porosity and particle size in many applications

14.2 BET (Brunauer Emmet Teller) Adsorption Isotherm

Stephen Brunauer, Paul Emmet and Edward Teller published this theory in 1938. It is a theory for multi-layer physisorption and is of profound significance in the development of this field.



To derive the BET adsorption isotherm equation let us propose the following

i) Consider the surface of adsorbent to be made up $N_T$of sites (in the above figure = 20)

ii) Let number of sites which have adsorbed 0 molecules = N_0 (in the above figure = 8; viz. Site number 1, 3, 4, 9, 10, 11, 17, 18)

iii) Let number of sites which have adsorbed 1 molecule be = (in the above figure = 6; viz. Sites number 2, 5, 12, 13, 14, 20)

iv) Let number of sites which have adsorbed 2 molecules be = (in the above figure = 4; viz. sites number 8, 15, 16, 19) and so on……..

Let number of sites which have adsorbed molecules be = n_i

Therefore, total number of sites N_T has to be $N_T = \sum_{i=0}^{\infty} n_i$

In the above example it can be verified that 20 = 8 + 6 + 4 + 1 + 1 ($n_0 + n_1 + n_2 + n_3 + n_4$)

Also it is easy to note that the total number of molecules adsorbed is given by $N = \sum_{i=0}^{\infty} i.n_i$

In the above figure N = 0*8 + 1*6 +2*4 + 3*1 + 4*1 = 21 molecules (which can be verified bycounting)

14.3 Assumptions in the BET theory

While the Langmuir provides a simple picture for looking at surface adsorption, it is not accurate representation of how nitrogen actually adsorbs to the surface. This is because more than one nitrogen is actually adsorbed to each site on the surface. A brtter approximation for this process is to use BET Isotherm which allows for multiple nitrogen molecules to adsord to each surface site.

The assumptions used to derive the BET isotherm are

i) Gaseous molecules behave ideally

ii) Multilayer adsorption is possible to each site

iii) Each adsorbed gas molecules provides a site for the adsorption of the molecule in the layer above it (However, owing to the influence of the adsorbent, the van der Waals forces on the surface of the adsorbent will be stronger than the van der Waals forces between molecules of the gas phase. So the forces of adsorption are much higher for the first layer and constant for the subsequent layers. This implies that the heat of adsorption of the 1^{st} layer is greater than that of the 2^{nd} and higher layers. There is again no lateral interaction as in the case of Langmuir).

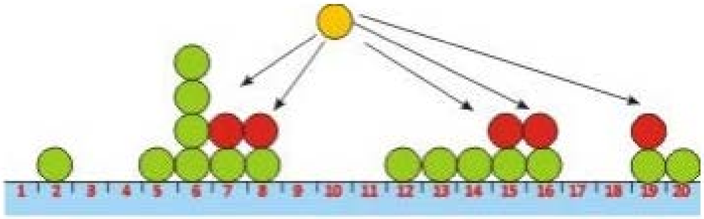
iv) All the sites on the surface are equivalent

v) No adsorbate-adsorbate interactions

vi) An adsorbed molecule is immobile

According to the BET theory, at equilibrium the rate of adsorption is equal to the rate of desorption. The rate of adsorption of the ith layer is proportional to the number of sites in the lower (i-1)th layer and the gas phase pressure.

The rate of desorption from the ith layer is proportional to the number of sites occupied by the ith layer but not occupied by molecules of higher layers (i.e there should be only i molecules on that site)



For instance, to form a layer i = 3, the molecule in gas phase have sites only with i = 2 molecules available for adsorption. Hence the rate for i = 3 is proportional to number of sites having i = 2 molecules.

At equilibrium, Rate of formation of ith layer = Rate of destruction of ith layer

What are the ways in which ith layer can be formed?

If adsorption takes place on (i-1)th layer, the Rate = $\left(k_a\right)_i n_{i-1} p$

If desorption takes place on (i+1)th layer, the Rate = $\left(k_d\right)_{i+1} n_{i+1}$

Assume rate constant for adsorption is k_a and for desorption is k_d

What are the ways in which an ith layer can be destroyed?

Adsorption takes place on ith layer, the Rate = $\left(k_a\right)_{i+1} n_{i+1} p$

Desorption takes place on ith layer, the Rate = $\left(k_d\right)_i n_i$

4.4 Derivation

Below figure shows a cartoon of what an surface would look like under the BET isotherm assumptions. We define θ_0, θ_1, θ_2, .=θn... where

θn = # of sites with n adsorbed molecules $\theta_n = \frac{No\ of\ sites\ with\ n\ adsorbed\ \ molecules}{total\ \ no\ of\ sites}$ -------- (1)

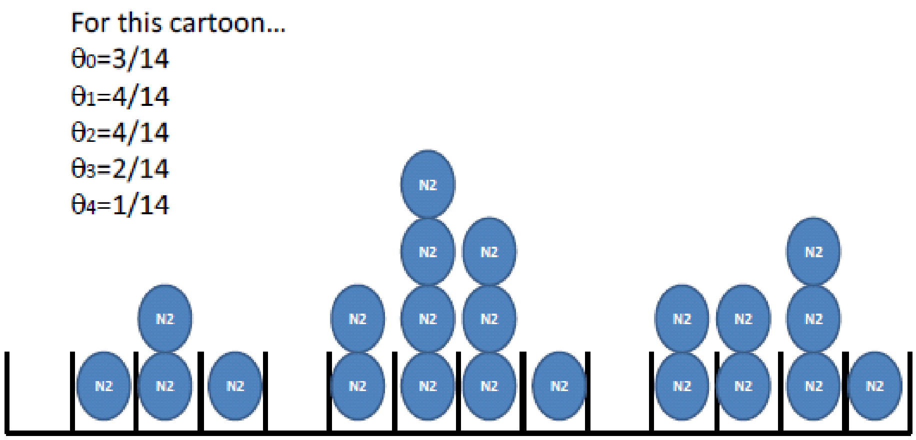
We can also define

k_n = rate of condensation to form the nth layer

k_{-n} = rate of evaporation to form the n^{th} layer

P = pressure above the surface

N = total number of sites



At equilibrium

$\frac{d\theta_n}{dt} = 0$ ----------- (2) for all n.

For the bare surface we can write

$\frac{d\theta_0}{dt} =$ rate of evaporation from 1^{st} layer i.e., rate of condensation onto bare surface

$$0 = k_{-1}N\theta_1 - k_1PN\theta_0$$

$\theta_1 = P\frac{k_1\theta_0}{k_{-1}}$ -------------- (3)

Where $N\theta_1$ is the number of sites with 1 layer of gas on it and

$N\theta_0$ is the number of sites with no gas is adsorbed. (Note this is the same for the Langmuir isotherm where $\theta_1=(1-\theta_0)$.)

For surface sites with only one molecule adsorbed we can write

$\frac{d\theta_1}{dt} =$ Rate of condensation onto bare surface + Rate of evaporation from 2^{nd} layer - Rate of condensation onto the 1^{st} layer - rate of evaporation from the 1^{st} layer. i.e.,

$0 = k_1PN\theta_0 + k_{-2}N\theta_1 - k_2PN\theta_1 - k_{-1}N\theta_1$ ----------- (4)

Combining equations 3 and 4 gives

$$k_{-2}\theta_2 = k_2 P\theta_1$$

$$\theta_2 = P\frac{k_2\theta_1}{k_{-2}}$$

$$= P^2 \frac{k_2}{k_{-2}}\frac{k_1\theta_0}{k_{-1}} \text{----------------- (5)}$$

For the second layer

$\frac{d\theta_2}{dt}$ = Rate of condensation onto 1st layer + Rate of evaporation from 3rd layer - Rate of condensation onto the 2nd layer - Rate of evaporation from the 2nd layer

$0 = k_2PN\theta_1 + k_{-3}N\theta_3 - k_3PN\theta_2 – k_{-2}N\theta_2$ -------- (6)

Plugging equation 5 to 6 gives

$$\therefore \theta_3 = P\frac{k_3\theta_2}{k_{-3}}$$

$$= P^3 \frac{k_3}{k_{-3}}\frac{k_2}{k_{-2}}\frac{k_1}{k_{-1}}\theta_0 \text{------------------ (7)}$$

Generalizing to the ith layer gives

$$k_{-i}\theta_i = k_i\theta_{i-1}P$$

$$\theta_i = \frac{k_i}{k_{i-1}}P\theta_{i-1}$$

$$= \frac{k_i}{k_{i-}}\frac{k_{i-1}}{k_{-(i-1)}}\frac{k_{i-2}}{k_{-(i-2)}} ------ \frac{k_1}{k_{-1}}P^i\theta_0 \text{--------- (8)}$$

Since for i > 1 the BET isotherm assumes the nitrogen is liquid like, we can also say that

$k_2 \cong k_3 \cong k_4 \cong k_i \neq k_1$

$k_{-2} \cong k_{-3} \cong k_{-4} \cong k_{-i} \neq k_{-1}$

Where ki is the rate of adsorption onto a gas surface and k-I is the rate of desorption off a gas surface. So if we define $x = Pk_i/k_{-i}$

$$\theta_i = x^{i-1}P\frac{k_1}{k_{-1}}\theta_0 = x^i\frac{1}{x}P\frac{k_1}{k_{-1}}\theta_0; i \neq 0,1 \text{-------------------- (9)}$$

And if we define $C = \frac{Pk_1}{xk_{-1}}$, we can say

$$\theta_i = x^i C\theta_0 ; i \neq 0,1 \text{------- (10)}$$

If we then define the total surface coverage θ such that

$$\theta = \frac{n_a}{n} = \frac{total\ \ no\ of\ molecules\ \ adsorbed}{total\ \ no\ of\ sites}$$

We can write $n_a = \sum_{i=0}^{\infty} i\theta_i N$

So that $\theta = \frac{\sum_{i=0}^{\infty} i\theta_i N}{\sum_{i=0}^{\infty} \theta_i N} = \frac{\sum_{i=1}^{\infty} i\theta_i}{\theta_0 + \sum_{i=1}^{\infty} \theta_i} = \frac{c\theta_0 \sum_{i=1}^{\infty} ix^i}{\theta_0 + c\theta_0 \sum_{i=1}^{\infty} x^i}$

If we use $\sum_{i=1}^{\infty} x^i = \frac{x}{1-x}$

Then $\sum_{i=1}^{\infty} ix^i = x\sum_{i=1}^{\infty} ix^{i-1} = x\sum_{i=1}^{\infty} \frac{d}{dx} x^i = x\frac{d}{dx}\sum_{i=1}^{\infty} x^i = x\frac{d}{dx}\frac{x}{1-x} = \frac{1}{(1-x)^2}$

Plugging this in for θwe obtain

$$\theta = \frac{c\theta_0 \frac{x}{(1-x)^2}}{\theta_0 + c\theta_0 \frac{x}{(1-x)}} = \frac{\frac{cx}{(1-x)^2}}{\frac{1-x+cx}{(1-x)}} = \frac{cx}{1-x}\frac{1}{1-x+cx} = \frac{cx}{(1-x)(1+(c-1)x)}$$

Making physical sense of the constants

The constant x was defined as $x = P\left(\frac{k_i}{k_{-i}}\right)$ where k_i and k_{-i} are the adsorption rate and desorption rate respectively, of a gas surface. If we consider a nitrogen surface in equilibrium with the gas state the condition for equilibrium is

$$k_i NP = k_{-i} N$$

Or

$$k_i P = k_{-i}$$

The equilibrium pressure for this system P is just the vapor pressure for the pure nitrogen, P_0 at the temperature the experiment is being done. Therefore x is just P/P_0 the pressure over the equilibrium vapor pressure of the nitrogen at the experimental temperature.

The constant c was defined as $\frac{Pk_i}{xk_{-1}}$ where k_1 is the rate constant of adsorption on to the bare surface and k_{-1} is the desorption off the surface. Plugging in what we known for x, c becomes $\frac{P_0k_i}{k_{-1}}$ a unit less number. Using this and equation 3, $c = \frac{\theta_1}{\theta_0}$ the ratio of the number of adsorbed molecules on the first layer to the number of empty sites. This ration should be

$$c = \frac{n_1}{n_0} = e^{\frac{\Delta_{des}H^0 - \Delta_{vap}H^0}{RT}}$$

Where $\Delta_{des}H^0$ is the enthalpy of desorption and $\Delta_{vap}H^0$ is the enthalpy of vaporization. The equation comes about because n_0, the number of bare spots, is proportional to $e^{-\frac{\Delta_{des}H^0}{RT}}$ (if desorption is energetically favorable ($\Delta_{des}H^0 <0$) ie, n_0 is larger) and the number of molecules in the first mono layer is proportional to $e^{\frac{-\Delta_{vap}H^0}{RT}}$ (if vaporization is energetically favorable ($\Delta_{vap}H^0 < 0$) ie, n_1 is larger). Notice that c is larger when the enthalpy of desorption from the monolayer is larger compared with the enthalpy of vaporization.

14.5 Limitations of BET Isotherm

The BET isotherm is accurate when P/P_0 is between ~ 0.05 and ~0.3, pressure at which only a few complete layer have formed. At low pressure the BET isotherm does not do a good job at decreasing adsorption because in deriving the isotherm it was assumed that all the sites on the surface are equivalent. This is not really the case and when only a few molecules have adsorbed, effects from inhomogeneities in the surface become more important. As more molecules adsorb these inhomogeneities average out. At high pressure, the cracks and roughness of the surface cause the BET isotherm to fall. This is especially true for very porous materials where the indents have a width of only a few monolayers. This is because the cracks can only hold a few monolayers and as the cracks fill up, the effective surface area of the solid where the nitrogen adsorb can change.

14.6 Determination of surface area

The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Physical adsorption results from relatively weak forces (van der Waals forces) between the adsorbate gas molecules and the adsorbent surface of the test powder. The determination is usually carried out at the temperature of liquid nitrogen. The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure.

14.7 Brunauer, Emmett and Teller (BET) theory and specific surface area determination

a) Multi-point measurement

The data are treated according to the Brunauer, Emmett and Teller (BET) adsorption isotherm equation.

$$\frac{1}{\left[V_a\left(\frac{P_0}{P}-1\right)\right]}=\frac{C-1}{V_mC}\,X\,\frac{P}{P_0}+\frac{1}{V_mC} \text{ ----------- (1)}$$

P = partial vapour pressure of adsorbate gas in equilibrium with the surface at 77.4 K (b.p. of liquid nitrogen), in pascals,

P_o = saturated pressure of adsorbate gas, in pascals,

V_a = volume of gas adsorbed at standard temperature and pressure (STP) [273.15 K and atmospheric pressure (1.013 × 105 Pa)], in millilitres,

V_m = volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, in millilitres,

C = dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample.

A value of V_a is measured at each of not less than 3 values of P/P_o. Then the BET value

$$\frac{1}{\left[V_a\left(\frac{P_0}{P}-1\right)\right]}$$

is plotted against P/Po according to equation (1). This plot should yield a straight line usually in the approximate relative pressure range 0.05 to 0.3. The data are considered acceptable if the correlation coefficient, r, of the linear regression is not less than 0.9975; that is, r^2 is not less than 0.995. From the resulting linear plot, the slope, which is equal to $(C - 1)/V_mC$, and the intercept, which is equal to $1/V_mC$, are evaluated by linear regression analysis. From these values, V_m is calculated as 1/(slope + intercept), while C is calculated as (slope/intercept) + 1. From the value of V_m so determined, the specific surface area, S, in $m^2 \cdot g^{-1}$, is calculated by the equation

$$S = \frac{V_m N_a}{mX\,22400} \text{ ----------- (2)}$$

N = Avogadro constant (6.022 × 1023 mol^{-1}),

a = effective cross-sectional area of one adsorbate molecule, in square metres (0.162 nm^2 for nitrogen and 0.195 nm^2 for krypton),

m = mass of test powder, in grams,

22400 = volume occupied by 1 mole of the adsorbate gas at STP allowing for minor departures from the ideal, in millilitres.

A minimum of 3 data points is required. Additional measurements may be carried out, especially when non-linearity is obtained at a P/P_o value close to 0.3. Because non-linearity is often obtained at a P/P_o value below 0.05, values in this region are not recommended. The test for linearity, the treatment of the data, and the calculation of the specific surface area of the sample are described above.

b) Single-point measurement

Normally, at least 3 measurements of V_a each at different values of P/P_o are required for the determination of specific surface area by the dynamic flow gas adsorption technique or by volumetric gas adsorption. However, under certain circumstances described below, it may be acceptable to determine the specific surface area of a powder from a single value of V_a measured at a single value of P/P_o such as 0.300 (corresponding to 0.300 mole of nitrogen or 0.001038 mole fraction of krypton), using the following equation for calculating V_m

$$V_m = V_a\left(1 - \frac{P}{P_0}\right) \text{--------- (3)}$$

The specific surface area is then calculated from the value of V_m by equation (2) given above.

The single-point method may be employed directly for a series of powder samples of a given material for which the material constant C is much greater than unity. These circumstances may be verified by comparing values of specific surface area determined by the single-point method with that determined by the multiple-point method for the series of powder samples. Close similarity between the single-point values and multiple-point values suggests that 1/C approaches zero. The single-point method may be employed indirectly for a series of very similar powder samples of a given material for which the material constant C is not infinite but may be assumed to be invariant. Under these circumstances, the error associated with the single-point method can be reduced or eliminated by using the multiple-point method to evaluate

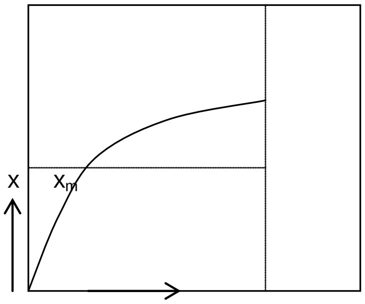
C for one of the samples of the series from the BET plot, from which C is calculated as (1 + slope/intercept). Then V_m is calculated from the single value of V_a measured at a single value of P/P_o by the equation

$$V_m = V_a\left(\frac{P_0}{P} - 1\right)\left[\frac{1}{C} + \frac{C-1}{C}\, X\, \frac{P}{P_0}\right] \text{-------------} \ (4)$$

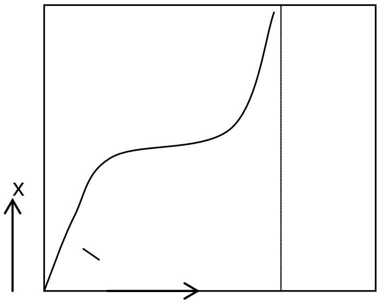
The specific surface area is calculated from V_m by equation (2) given above.

14.8 Adsorption Isotherms

A relation between the amount of adsorbate adsorbed on a given surface at constant temperature and the equilibrium concentration of the substrate in contact with the adsorbent is known as Adsorption Isotherm. Two types of typical adsorption isotherms are shown in the following Figures A & B. Figure A shows adsorption with monolayer formation at saturation point. Figure B shows a situation when several layers of adsorbate molecules are formed on the surface of the adsorbent (multilayer adsorption).



A. Monolayer adsorption



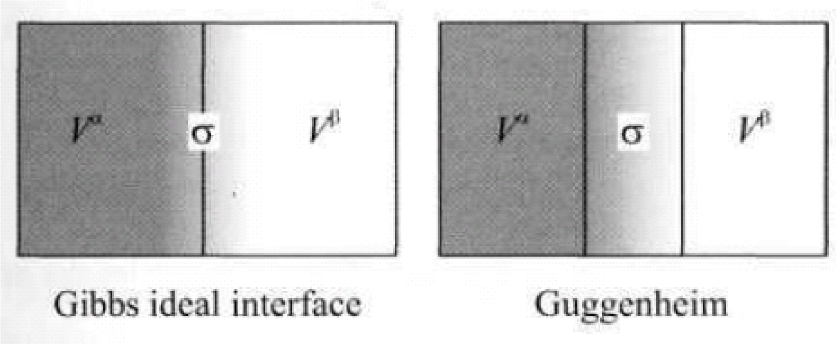
B. Multilayer adsorption

X_m is the amount of the substrate required to make a monolayer where as Po is the saturation equilibrium concentration of the substrate.

Arrangement of adsorbed molecules on the surface of the adsorbent could normally be monolayer in nature. Normally, chemisorption leads to monolayer adsorption whereas multilayer arrangement of substrate molecules is observed due to physisorption only. Multilayer formation is also possible due to chemisorption followed by physisorption

14.9 Gibbs Isotherm

The presence of an interface influences generally all thermodynamic parameters of a system. To consider the thermodynamics of a system with an interface, we divide that system into three parts: The two bulk phases with volumes V^α and V^β, and the interface σ.



In this first convention the two phases σ and β are thought to be separated by an infinitesimal thin boundary layer, the Gibbs dividing plane. This is of course an idealization and the Gibbs dividing plane is also called an ideal interface. There are alternative models. Guggenheim, for example, takes the extended interfacial region, including its volume, explicitly into account. We use the Gibbs model because in most applications it is more practical.

In the Gibbs model the interface is ideally thin ($V^\sigma = 0$) and the total volume is

$V = V^\alpha + V^\beta$--------------- (1)

All other extensive quantities can be written as a sum of three components they are

One of bulk phase α,

One of bulk phase β, and

One of the interfacial region σ.

Examples are the internal energy U, the number of molecules of the ith substance N^i, and the entropy S.

$U = U\alpha + U\beta + U\sigma$ --------------------(2)

$N_i^{\alpha} = N_i^{\beta} + N_i^{\sigma}$ ---------------------- (3)

$S = S^{\alpha} + S^{\beta} + S^{\sigma}$ -------------- (4)

The contributions of the two phases and of the interface are derived as follows.

Let u^{α} and u^{β} are the internal energies per unit volume of the two phases. The internal energies u^{α} and u^{β} are determined from the homogeneous bulk regions of the two phases. Close to the interface they might be different. Still, we take the contribution of the volume phases to the total energy of the system as $u^{\alpha}V^{\alpha} + u^{\beta}V^{\beta}$. The internal energy of the interface is

$U^{\sigma} = U - u^{\alpha}V^{\alpha} - u^{\beta}V^{\beta}$------------------(5)

At an interface, the molecular constitution is changes. The concentration (number of molecules per unit volume) of the ith material is, in the two phases, respectively c_i^{α} and c_i^{β}. The additional quantity that is present in the system due to the interface is

$N_i^{\sigma} = N_i - c_i^{\alpha}V^{\alpha} - c_i^{\beta}V^{\beta}$ ---------- (6)

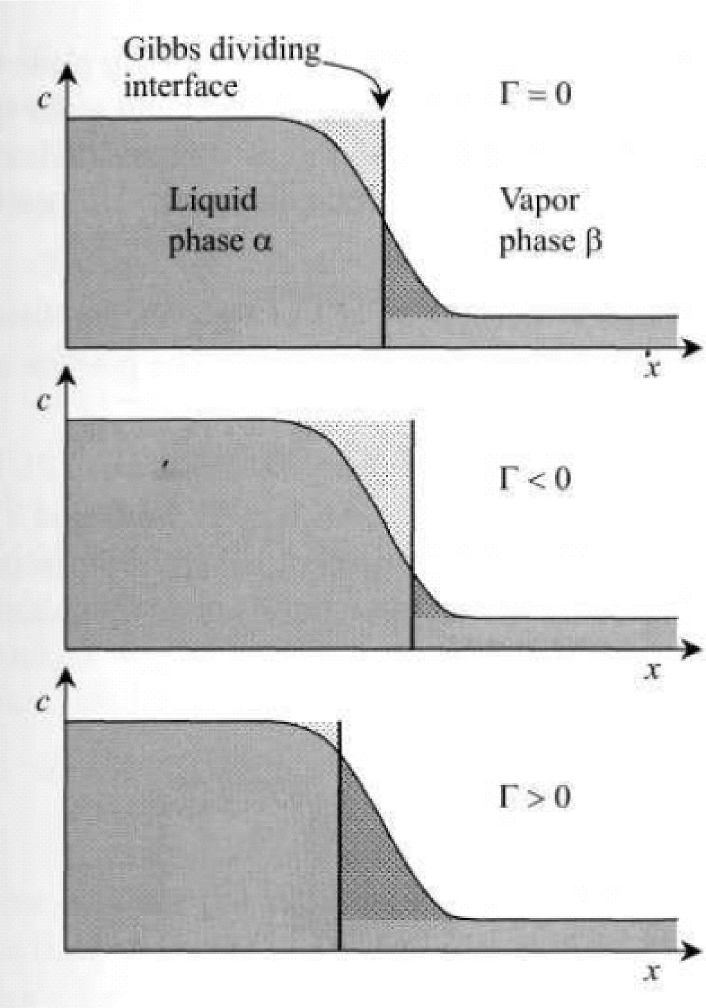
With Equation 6 it is possible to define something like a surface concentration, the so called *interfacial excess*

$\Gamma_i = \frac{N_i^{\sigma}}{A}$ -------------- (7)

'A' is the interfacial area. The interfacial excess is given as a number of molecules per unit area (m^{-2}) or in mol/m^2.

In the Gibbs model of an ideal interface there is one problem i.e, where precisely do we position the ideal interface? Let us therefore look at a liquid-vapor interface of a pure liquid more closely. The density decreases continuously from the high density of the bulk liquid to the low density of the bulk vapor. There could even be a density maximum in between since it should in principle be possible to have an increased density at the interface.

It is natural to place the ideal interface in the middle of the interfacial region so that $\Gamma = 0$. In this case the two dotted regions, left and right from the ideal interface, are equal in size. If the ideal interface is placed more into the vapor phase the total number of molecules extrapolated from the bulk densities is higher than the real number of molecules, $N < c^{\alpha}V^{\alpha} + c^{\beta}V^{\beta}$.Therefore the surface excess is negative. Vice versa: if the ideal interface is placed more into the liquid phase, the total number of molecules extrapolated from the bulk densities is lower than the real number of molecules, $N > c^{\alpha}V^{\alpha} + c^{\beta}V^{\beta}$ and the surface excess is positive.



Let us now turn to two- or multi-component liquids such as a solvent with dissolved substances. Substituting $V^{\alpha} = V - V^{\beta}$ we can write

$$N_1^{\sigma} = N_1 - c_1^{\alpha}V + \left(c_1^{\alpha} - c_1^{\beta}\right)V^{\beta} \text{ --------------- (8)}$$

for the first component which is taken to be the solvent. For all other components we get similar equations.

$$N_i^{\sigma} = N_i - c_i^{\alpha}V + \left(c_i^{\alpha} - c_i^{\beta}\right)V^{\beta} \text{ ----------------- (9)}$$

All quantities on the right side of the equations, except V^{β}, do not depend on the position of the dividing plane and are measurable quantities. Only V^{β}, depends on the choice of the dividing plane. We can eliminate V^{β} by multiplying Equation 8 by $\frac{c_i^{\alpha}-c_i^{\beta}}{c_1^{\alpha}-c_1^{\beta}}$ and subtracting Equation 8 form Equation 9

$$N_i^{\alpha}-N_i^{\alpha}\left(\frac{c_i^{\alpha}-c_i^{\beta}}{c_1^{\alpha}-c_1^{\beta}}\right)=N_i-c_i^{\alpha}V-\left(N_1-c_1^{\alpha}V\right)\frac{c_i^{\alpha}-c_i^{\beta}}{c_1^{\alpha}-c_1^{\beta}} \text{--------- (10)}$$

The right side of the equation does not depend on the position of the Gibbs dividing plane and thus, also, the left side is invariant. We divide this quantity by the surface area and obtain the invariant quantity

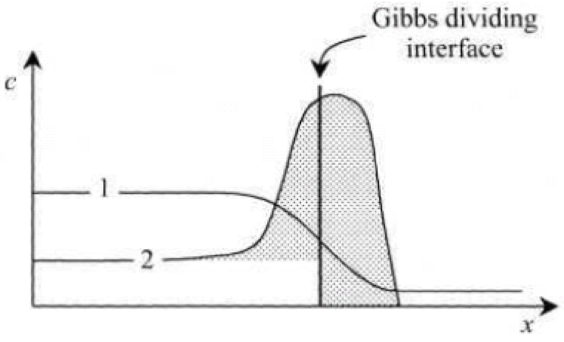
$$\Gamma_i^{(1)}\equiv\Gamma_i^{\sigma}-\Gamma_1^{\sigma}\frac{c_i^{\alpha}-c_i^{\beta}}{c_1^{\alpha}-c_1^{\beta}} \text{---------- (11)}$$

It is called *relative adsorption* of component *i* with respect to component 1. This is an important quantity because it can be determined experimentally.

For the case when component 1 is a solvent in which all other components are dissolved and thus have a much lower concentration than component 1, we choose the position of the dividing plane such that $\Gamma_1^{\sigma}=0$ and from Equation 11 we get

$$\Gamma_i^{(1)}=\Gamma_i^{\sigma} \text{------- 12}$$

In below figure the concentration profiles for solute 2 dissolved in liquid 1 are illustrated. We assume that the solute is enriched at the surface. The area of the dotted region corresponds to the surface excess $\Gamma_2^{(1)}$' of solute.



14.10 Gibb's Adsorption Isotherm

This isotherm normally considers the case when adsorbents are liquid and adsorbates are soluble or partially soluble in it e.g., surfactants / water or organic liquid / water system.

Considering a system having a plane interface between them the Gibb's free energy of a system containing two components could be written as follows:

$G = n_1\mu_1 + n_2\mu_2$ ------------------- (1)

Where n_1 and n_2 are the number of moles and μ_1 and μ_2 are the chemical potentials of the two components respectively. While dealing with the adsorption of one of the components on the surface of another, an additional term of surface energy has to be introduced, hence, equation 1 modifies to

$G = n_1\mu_1 + n_2\mu_2 + \gamma\sigma$ --------- (2)

where γ is the surface energy per unit area and σ is the surface area. It is now clear that equation 1 is for bulk while equation 2 will be applicable for the surface of the absorbent liquid. The complete differential of equation 2 may be written as

$dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 + \gamma d\sigma + \sigma d\gamma$ -------- (3)

We find that the total free energy G of the whole system depends on independent variables , namely , T,P,n_1,n_2 and б, thus,

$G = f(T, P, n_1, n_2, \sigma)$ and complete differential of G will be,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n_1,n_2,\sigma} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2,\sigma} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2,\sigma} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1,\sigma} dn_2 + \left(\frac{\partial G}{\partial \sigma}\right)_{T,P,n_1,n_2} d\sigma$$

or $dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma$ ----------- (4)

At constant temperature and pressure, above equation reduces to,

$dG = \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma$ ----------- (5)

Comparing equation 3 and 5, we get

$n_1 d\mu_1 + n_2 d\mu_2 + \sigma d\gamma = 0$ --------- (6)

A corresponding equation for the bulk of the system may be,

$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0$ ---------------- (7)

Where n_1^0 and n_2^0 are the number of moles of adsorbent liquid and solute in the bulk. From the equation 6 and 7, we get

$$-\frac{d\gamma}{d\mu_2} = \frac{(n_2 - n_1 n_2^0 / n_1^0)}{\sigma} \text{ ---------------------(8)}$$

Here, the term $\frac{(n_2 - n_1 n / n_1^{0})}{\sigma}$ represents the corresponding excess moles of solute per unit area on the surface of the adsorbent and now be represented by Γ_2

$$\therefore \qquad -\frac{d\gamma}{d\mu_2} = \Gamma_2$$

The chemical potential of solute $\mu_2 = \mu_2^0 + RT \ln a_2$

or $\quad d\mu_2 = RTd \ln a_2$

When solution is very dilute activity a_2 of solute could be replaced by its concentration.

$$\therefore \qquad \Gamma_2 = -\frac{c_2}{RT}\left(\frac{d\gamma}{\partial c_2}\right)_T$$

or, in general for any solute and liquid adsorbent,

$$\Gamma = -\frac{c}{RT}\left(\frac{\partial\gamma}{\partial c}\right)_T \text{ ----------------- (9)}$$

In the above equation γ is essentially surface energy per unit area, which may easily be replaced by surface tension (force/length).

The application of the above equation is as follows. If the detergent (solute or adsorbate) tends to accumulate at the interface its surface excess is positive, and so $\frac{d\gamma}{dc}$ is negative. This means surface tension decreases when a solute accumulates at the surface.

Example: the surface tension of the dilute solution of phenol in water at 27^oC were the following:

Mass % phenol	0.024	0.05	0.125	0.25	0.40
γ x 10^3/(Nm^{-1})	72.7	72.2	71.3	70.3	69.3

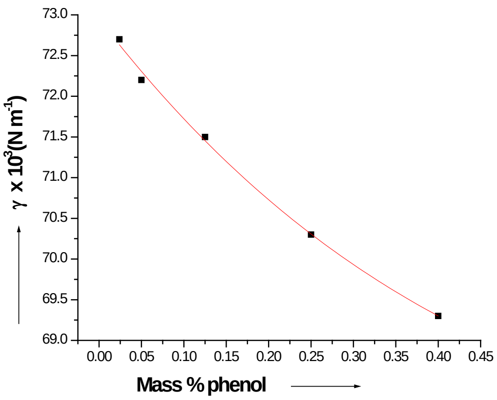
Calculate surface excess concentration (Γ) at a concentration of 0.15 mass of phenol. Comment on the significance of the observed value of Γ.

Solution : A plot of γ us mole of phenol gives a curvature with negative slope, for 0.15 mol of phenol slope is $-\frac{1.7}{0.1875}$, putting values in equation,

$$\Gamma = -\frac{C}{RT}\left(\frac{\partial\gamma}{\partial c}\right)_T$$

We get, $$\Gamma = -\frac{0.15}{8.31x300^0 k}\left(-\frac{1.7}{0.1875}\right)$$

$= \ 5.45 \text{ x } 10^{-4} \text{ mol m}^{-2}$



The positive value of Γ signifies that phenol is surface active and accumulates at the interface.

14.11 Applications of Adsorption

The process of adsorption is very important as it has many applications in domestic as well as in industrial processes, to name some of them are follows:

1. **In heterogeneous catalysis:** Surface active material are widely used as catalyst mostly due to adsorption processes. If the surface active materials (adsorbents) have different phase with that of substrates, then the catalysis is called heterogeneous catalysis. A system where both the catalyst and substrate are in same phase is called homogeneous catalysis.
2. **In removal of colouring material:** Many coloured materials or impurities are removed through adsorption by suitable surface active materials like charcoal. Activated charcoal has been extensively used for this purpose.
3. **In ion exchange resins:** Several polymeric materials are used for the separation of ionic substances in chromatography through ion-exchange.
4. **In adsorption indicators:** Several dyes like eosin and fluoresein are used as indicators in the titrations of Cl^-, Br^- etc. against Ag^+(Fajan's method).
5. **In gas masks**: Activated charcoal is used to remove toxic gases in gas masks.
6. **In dyeing of cloth:** Many substances work as mordants for dyeing of cloths. Several metal cyanogen complexes, alums work as efficient mordants in dyeing cloths.
7. **In de humidizers:** Many substances when they adsorb water change their colour. Silica and alumina gels are used as adsorbents for removing moisture. Silica is colourless but after adsorbing water becomes blue.Silica is colourless but after adsorbing water becomes blue.

14.12 Summary of the unit

In the present unit on surface chemistry, we began by distinguishing between physisorption and chemisorption and also between monolayer adsorption and multiplayer adsorption. The binding energies in physisorption are much smaller and in the range of 8 to 25 kJ/mole. A relation between the amount of adsorbate adsorbed on a given surface at constant temperature and the equilibrium concentration of the substrate in contact with the adsorbent is known as Adsorption Isotherm. We have outlined the main ingredients of some important isotherms such as the adsorption isotherms of Gibbs, Freundlich and Langmuir

Amultiplayer adsorption was characterized through the BET isotherm.

The heat of a reaction was obtained using an adsorption. We also outlined the mechanisms of unimolecular and bimolecular reactions at surfaces. The Langmuir – Hinshelwood mechanism and the Langmuir – Rideal mechanism of bimolecular surface reactions were described in detail. Towards the end, the role of adsorption in surface catalysis was highlighted and the other applications of adsorption were listed.

14.13 Key words

BET theory; Surface area; Multi-point measurement; Single-point measurement; Adsorption Isotherms; Gibb’s Adsorption Isotherm.

14.14 References for further study

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5) Principles of Colloid and Surface Chemistry, 3rd ed. Paul C. Hiemenz, Raj Rajagopalan; *CRC Press*, **1997**.

14.15 Questions for self understanding

1) Write a note on BET (Brunauer Emmet Teller) Adsorption Isotherm

2) Explain the Assumptions in the BET theory

3) Derive the Brunauer Emmet Teller Adsorption Isotherm

4) Explain the Limitations of BET Isotherm

5) Using Brunauer, Emmett and Teller (BET) theory explain the procedure for determination of specific surface area by a) Multi-point measurement b) Single-point measurement

6) What is Adsorption Isotherms

7) What is Gibbs Isotherm

8) Derive the equation for Gibb’s Adsorption Isotherm

9) Write a note on applications of Adsorption

Unit-15

Structure

15.0 Objectives of the unit
15.1 Introduction
15.2 Colloid System consists of two separate phases
15.3 Main difference between colloids and suspension
15.4 Nature of colloidal system
15.5 Types of colloids
  a) Based on physical state of dispersed phase and dispersion medium
  b) Classification on the basis of interaction between both phase and medium
    i) Lyophilic colloids (Lyophilic means solvent-loving)
    ii) Lyophobic Colloids (Lyophilic means solvent – hating)
  c) Classification based on the type of particles of the dispersed phase
    i) Multimolecular colloids
    ii) Macromolecular colloids like starch. Proteins and cellulose
    iii) Associated colloids (Micelles)
    iv) Mechanism of micelle formation
15.6 Preparation of lyophobic colloids
  a) Dispersion method
  b) Peptization
15.7 Purification of colloidal solutions (Sols)
  a) Electrodialysis
  b) Ultra- centrifugation
15.8 Properties of colloidal solutions
  a) Colligative properties of colloidal solutions
  b) Optical Properties (Tyndall effect)
15.9 Brownian movement
15.10 Presence of electrical charge on colloidal particles and stability of sols
15.11 Coagulation or flocculation
15.12 Summary of the unit
15.13 Key words
15.14 References for further study
15.15 Questions for self understanding

15.0 Objectives of the unit

After studying this unit you are able to

- Identify the main difference between colloids and suspension
- Recognize the nature of colloidal system
- Explain the different types of colloids
- Explain the different methods of preparation of colloids
- Explain the different methods of purification of colloidal solutions
- Explain the properties of colloidal solutions

15.1 Introduction

Colloids are a class of materials found in a wide range of products from cosmetics, food, paints to pharmaceuticals. The substance includes solids, emulsified liquids, clays, gels and paints. The colloid system consists of small particles dispersed in a continuous phase. Although they are aggregates of atoms or molecules, colloidal particles are not ordinarily seen by an optical microscope. It should however be noted that the size limits are somewhat arbitrary and some system may contain particles that are outside the size range. The extensive interface created between the particles and disperse phase is a predominant feature of colloidal system. The surface area is so much larger than an equal volume of particles. For example colloidal system is affected or related to the size of particles. Gold for example gives a red colour in a sol form but turns blue as the size increases. Antimony and arsenic trisulfides exhibit colour changes associated with the particle size of the colloidal system too. Different types of colloids are Foams, Milk, Fog, Smoke, Detergent, Aerogel, Blood, Paints, Cosmetics.

15.2Colloid System consists of two separate phases

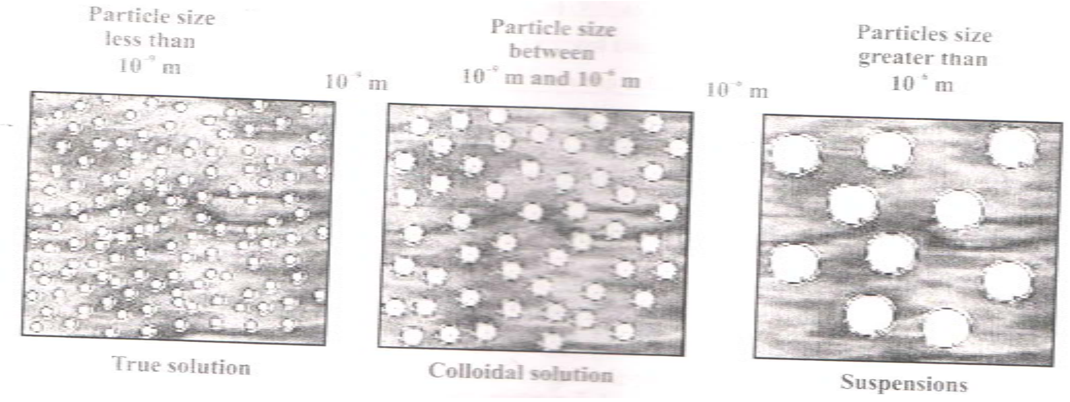
i) A dispersed Phase or also known as internal phase (for solute)

ii) A continuous phase or dispersion medium (for solvent)

iii) A colloidal system may be solid, liquid, or gaseous

Dispersion is a system in which a dispersed phase is distributed through a continuous phase. Dispersions may be molecular, colloidal or coarse. The classification of a particular dispersion into a particular sub-type is based on the particle size of the dispersed phase. Molecular dispersion are homogeneous and coarse dispersion are heterogeneous. A coarse dispersion may be either a suspension(dispersed phase is solid) or an emulsion(dispersed phase is a liquid). The properties of dispersed system depend on the 'bulk' surface properties of the components of the system.

Colloidal state is the state of matter in which the size of constituent particles is in between 1 to 1000 nm and they cannot pass through the animal or vegetable membrane**.** The non diffusibility colloids compared to true sol is due to difference in particle size. Science the constituent particles are bigger compare to true sol, hence they cannot pass through membrane. On the other hand the particles in colloids are smaller than the particle present in a suspension, hence they cannot precipitate like suspension.



15.3 Main difference between colloids and suspension

Properties	Colloid	Suspension
Particle size	1-1000 nm	More than 1000 nm.
Filterability	Pass through filter paper but cannot pass through animal membrane	Cannot pass through filter paper as well as animal membrane

Visibility	Particle can be observed by ultra microscope	Particles are visible
Appearance	Translucent	Opaque

15.4 Nature of colloidal system

Colloids are an intermediate type of mixture that has a particle size between those of true sols and suspensions. The particles do not settle out of the sol but they make the sol cloudy or opaque, Example of colloids include: fog, smoke, paint, milk, mayonnaise, shaving cream or clouds. It is not easy to give a precise definition of colloidal system. A definition that is frequently used is that it is a system comparing of two phases one of which consists of minute particles (disperse phase) which are dispersed uniformly throughout the second phase (continuous or dispersion medium). When one considers our everyday encounters, one can identify many systems that fit into the description just given. More specifically a colloidal system is defined on the basis of the system of particles of the dispersed phase.

15.5 Types of colloids

Colloids are characterized according to the state (solid, liquid, gas) of the dispersed phase and of the continuous phase (dispersion medium). Fog and smoke are aerosols, which are liquid droplets or solid particles dispersed throughout a gas. An emulsion consists of liquid droplets dispersed throughout another liquid. A sol consists of solid particles dispersed in a liquid. There are two phases in a colloidal system: Dispersed phase, the solute and dispersion medium, the solvent. Dispersion medium means the medium in which the substance dispersed in the form of colloidal particles and dispersed phase means the substance distributed in the dispersion medium in the form of colloidal particles.

For example in gel the dispersed phase is liquid and dispersion medium is solid

Colloids can be classified on the basis of :

1. Based on physical state of dispersed phase and dispersion medium.
2. Based on the nature of interaction between both phases.
3. Based on the type of particles of the dispersed phase.

d) Based on physical state of dispersed phase and dispersion medium

Out of three physical states, dispersed phase and dispersion can be any one. Hence there are nine possible combinations of these thee states of matter and each type colloid named as a certain type of colloid. But if both dispersed phase and dispersion medium are gases. They do not form colloid (homogeneous). Hence there are eight types of colloids.

Types of colloids and examples

Dispersed Phase	Dispersed medium	Type of collide	Example
Gas	Liquid	Foam	Whipped cream, froth, soap, lather
Gas	Solid	Solid sol	Pumice stone, foam rubber
Liquid	Gas	Aerosol of liquid	Fog, mist, Cloud, insecticide sprays.
Liquid	Liquid	Emulsion	Milk, cold-liver oil, hair cream
Liquid	Solid	Gel	Butter. Cheese, Jellies
Solid	Gas	Aerosol of solid	Smoke, dust
Solid	Liquid	Sol	Starch, protein, paints, cell, fluid
Solid	Solid	Solid sol	Ruby glass, alloys, gem stones, some coloured glass

b) Classification on the basis of interaction between both phase and medium

Colloids prepared under this heading can be of two types

i) Lyophilic colloids (Lyophilic means solvent-loving)

In such type of colloids there is more affinity between dispersion phase and dispersion medium. For example, gum, starch, etc. when mixed with dispersion medium like water, they directly from colloidal sol. This sol is also called as colloidal sol or Lyophilic sol. If water is present as a dispersion medium it termed as hydrophilic sol. Lyophilic sol are reversible in nature, i.e precipitate can be remix and convert to colloidal again. For such type of sol the viscosity is very high and surface tension is low. Lyophilic sol are quite stable due to affinity between dispersion phase and dispersion medium, hence not easily coagulated. Lyophilic colloids are colloids in which there is strong attraction between the particles and the dispersion medium, which results in a thermodynamically stable system. Many of the properties of this class are due to the attraction between the particles and disperse phase leading to salvation (attachment of solvent molecules to molecules in the dispersed phase). A hydrophilic colloid is one in which water is the dispersion medium. The attraction between the dispersed particle and water molecules leads to hydration of the particles, molecules or ions. Examples of Lyophilic colloids include gelatin, insulin, and albumin, which produce Lyophilic colloids in aqueous dispersion medium. Polystyrene and rubber can be dispersed in non-aqueous (organic solvent) medium.

ii) Lyophobhic Colloids (Lyophilic means solvent – hating)

When there is no affinity between dispersion phase and dispersion medium we cannot prepare sol by simple mixing but certain preparation methods required for that. Such type of colloids are termed as lyophobic colloids and if the medium is water then called as hydrophobic colloids. Since they do not have affinity between phase and medium, hence they are unstable and easily coagulated. They are irreversible in nature and cannot reform after precipitation. When a dispersion phase is added to dispersion medium to form lyophobic colloid there will be no charge in viscosity as well as surface tension. For ex- when substance like metal sulphide is mixed with dispersion medium, they form lyophobic colloids. If the dispersion medium is water they called as hydrophobic colloids. The particles in lyophobic system have ‘great dislike’ for the dispersion medium. There is a little attraction between the particles in the dispersion phase and dispersion phase. Typically, lyophobic colloids are composed of inorganic substance disperse in an aqueous medium, water Example include silver, gold, silver iodide and arsenous sulphide. The methods used to prepare lyophobic colloids are inherently different to those used for Lyophilic colloids.

	Lyophilic colloids	Lyophobic colloids
1	These are easily formed by direct mixing	These are formed by only under special methods.
2	These are reversible in nature	These are irreversible in nature
3	The particles of colloids are true molecules and are big in size	The particles are aggregates of many molecules
4	The particles are not easily visible even under microscope	The particles are easily detected under ultra microscope
5	These are very stable	These are unstable and require traces of stabilizers.
6	The addition of small amount of electrolyte causes precipitation (called	The addition of small amount of electrolyte has less effect. Larger quantities of electrolytes are

	coagulation) of colloidal sol	required to cause coagulation
7	The particles do not carry any charge, The particles may migrate in any direction or even under the influence of electric field	The particles move in specific direction i.e either towards anode or cathode depending upon their charge
8	The particles of colloids are heavily hydrated due to attraction for solvent	The particles of colloids are not appreciably hydrated due to hatred for the solvent.
9	The viscosity and surface tension of the sol are much higher than that of dispersion medium	The viscosity and surface tension are nearly the same as that of the dispersion medium.
10	They do not show Tyndall effect	They show Tyndall effect.

c) Classification based on the type of particles of the dispersed phase

Third type of classification based on the range of particle size of dispersed phase in given colloids. On the basis of particle size, colloids can be of three types.

(i) Multimolecular colloids

When a large number of small particles (dispersed phase) aggregate to form a large size molecular or particle having the size in the colloidal range, it is known as Multimolecular colloids. Here the atoms or particles are held together by weak van der walls force of attraction. For example gold sol contains particles of various sizes having several atoms. Another example is sulphur sol. When on dissol, atoms or smaller molecules of substance (having diameter less than 1nm) aggregate together to form particles of colloidal dimensions. They have usually lyophilic character.

(ii) Macromolecular colloids like starch. Proteins and cellulose

These colloidal sols are quite stable and resembles to the true sol in many respects. Macromolecular colloids are the substance having big molecules (called macromolecules) which on dissol form size in the colloidal range. These macromolecules forming the dispersed phase are generally polymers having very high molecular masses. Naturally occurring macromolecules are starch, cellulose, proteins, enzymes, gelatin, etc. Artificial macromolecules are synthetic polymers such as nylon, polythene, plastic, polystyrene etc. they have usually lyophobic character.

(iii) Associated colloids (Micelles)

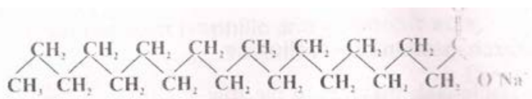
These colloidal sol are also known as micelles. In these colloids, when a dispersion phase is dissolved in dispersion medium at low concentration, they behave as normal strong electrolyte. But as the concentration increases, they show colloidal state in solutiokn. At high concentration, the van der wall's forces of attraction are strong between dispersion phase and dispersion medium. These aggregate particles are called as micelles and the temperature associated with formation of micelles is called Kraft temperature(T_k). The concentration at which the micelles formation starts is called as critical micelle concentration (CMC). The best example of associated colloids is soap and synthetic detergents in water. For soap the CMC is 10^{-14} to 10^{-3} mol L^{-1}.

Soap molecules can cluster together to form aggregates called micelles. These molecules have both a polar and hydrophobic component. Such molecules are known as surface active agents or surfactants or amphiphiles may be predominantly hydrophilic (water loving) or hydrophobic (water hating).

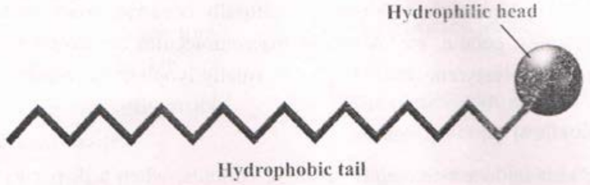
These are the substance which on dissol in a medium behave as normal electrolytes at low concentration but behave, as colloidal particles at higher concentration due to the formation of aggregated particles. Their molecules contain both Lyophilic and lyophobic groups. The common examples of micelles are soap and detergents. They are capable of forming ions. Micelles may contain as many as 100 molecules or more. For example sodium stearate is typical example of such type of molecules.

iv) Mechanism of micelle formation

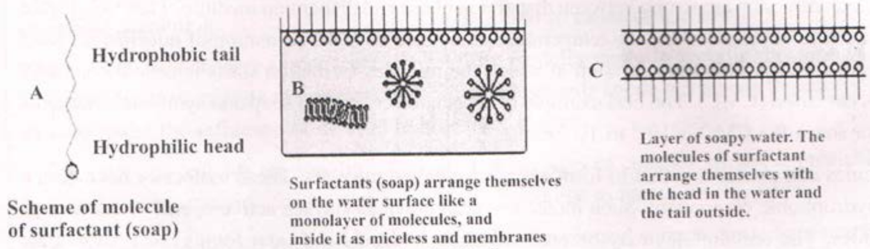
Surface active materials exhibit unusual properties. In dilute sol highly surface active substances act as normal solutes. At a fairly well defined concentration, their physical properties (examples, osmotic pressure, turbidity, electrical conductance and surface tension) charge abruptly. The abrupt change in physical properties are explained via the formation of aggregates known as micelles. Micelles are colloid- sized cluster of molecules in which the hydrophobic tails congregate in the interior and the hydrophilic component resides on the outerside towards the water as shown in the diagrams. The micelles that form are in the size of colloidal particles hence the term associated colloids. The following schemes indiacted the formation of surfactant mecelles.



(a) Structure of salt of saturated fatty acid, sodium stearate ($C_{17}H_{35}COO^{-}Na$)



(b) Two terminal ends of sodium stearate

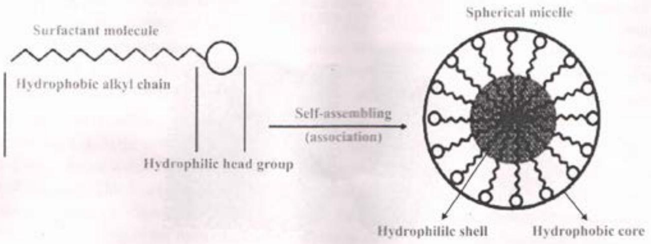


Scheme of molecule of surfactant (soap)

Surfactants (soap) arrange themselves on the water surface like a monolayer of molecules, and inside it as miceless and membranes tied by their hydrophobic tail. As the cohesion of these molecules is interior to that of the molecules of water, the surface tension of water is lowered.

Layer of soapy water. The molecules of surfactant arrange themselves with the head in the water and the tail outside.

Surfactant micelles



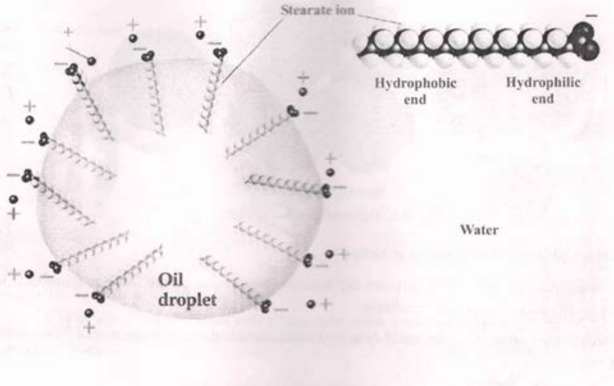


Fig. 24B Arrangement of stearate ions inside the bulk of water (ionic mecelle) at critical mecelle concentrations of soap

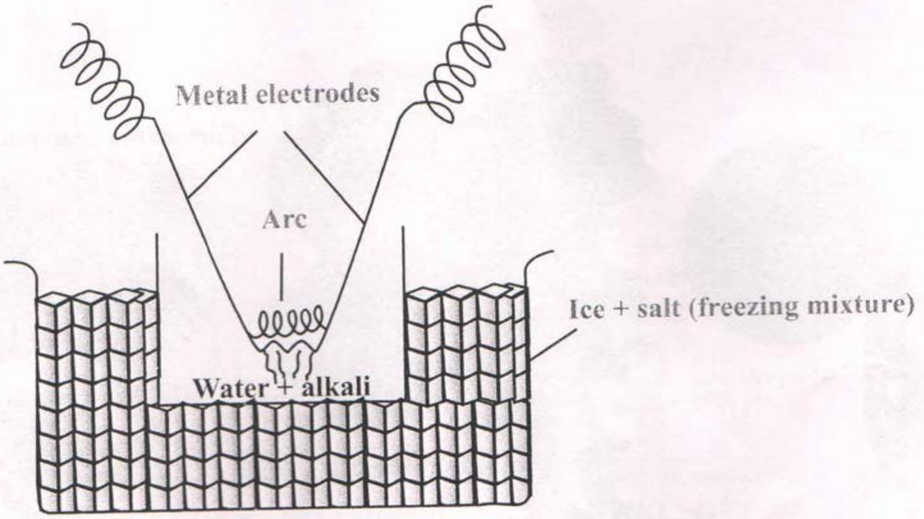
15.6 Preparation of lyophobic colloids

a) Dispersion method

Dispersion method may involve the use of high sonic generation in excess or 20,000 cycles per second or production of an electrical arc within a liquid.

Bredig’s arc method (Electric disintegration method)

This method is based on dispersion. This is the suitable method for the preparation of sol metals such as gold, silver, platinum, etc. In this method an electric arc is struck between the two electrodes of the metal immersed in the dispersion medium (say water). The dispersion medium is cooled by surrounding it with a freezing mixture. High temperature of the arc vaporized some of the metal. The vapour condenses to the particles of colloidal size on cooling. The colloidal particles thus formed get dispersed in the medium to form a sol of the metal. The alkali (KOH) present in the sol stabilizes the sol.



Bredig’s arc method

e) Peptization

In this method a freshly prepared precipitate of the substance is made to pass into the colloidal state by the addition of suitable electrolyte. The process of dispersing a freshly prepared precipitate into colloidal form by using a suitable electrolyte is called peptization. The electrolyte added is called peptizing agent.

Some example of peptization are given below

(a) When a small amount of ferric chloride solution is added to the freshly precipitated ferric hydroxide a reddish brown coloured colloidal solution of ferric hydroxide is obtained. This occurs due to the adsorption of Fe^{+3} ions over ferric hydroxide particles which causes them to disperse into the solution due to the electrostatic repulsion between the similarly charged particles.

(b) When a freshly prepared precipitate of silver iodide is shaken with a dilute solution of silver nitrate colloidal solution of silver iodide is obtained.

Condensation methods (Aggregation method)

In condensation methods the smaller particles of the dispersed phase are aggregated to form larger particles of colloidal dimensions. Some important condensation methods are described below

In condensation methods smaller particles of dispersed phase are condensed suitably to be of colloidal size. This is done by the following methods.

(a) ***By oxidation***

A colloidal solution of sulphur can be obtained by bubbling oxygen (or any other oxidation agent) through a solution of hydrogen sulphide in water. Sulphur is obtained by bubbling H_2S gas through the solution of an oxidizing agent like HNO_3 or $\mathbf{Br_2}$ in water according to the following equation.

$$SO_2 + 2H_2S \longrightarrow 3S(sol) + 2H_2O$$

$$Br_2 + H_2S \longrightarrow S + 2HBr$$

$$HNO_3 + H_2S \longrightarrow H_2O + NO_2 + S$$

(b) By reduction

A number of metals such as silver, gold and platinum have been obtained in colloidal state by treating the aqueous solution of their salts, with a suitable reducing agent such as formaldehyde, phenyl hydrazine stannous chloride, etc. The gold sol, thus prepared has a purple colour and is called purple of cassius. Silver colloids are prepared by ,passing H_2 through a saturated aqueous solution of silver oxide at 65^0 C

$$2AuCl_3 + 2HCHO + 3H_2O \longrightarrow 2Au(sol) + 3CHCOOH + 6HCl$$

(c) ***By hydrolysis***

Many salt solutions are rapidly hydrolysed by boiling dilute solutions of their salts. For example ferric hydroxide and aluminum hydroxide sols are obtained by boiling solutions of the corresponding chlorides. Similarly silicic acid sol is obtained by the hydrolysis of sodium silicate. Dark brown $Fe(OH)_3$ colloidal solution is prepared by adding $FeCl_3$ into boiling water.

$$FeCl_3+3H_2O \longrightarrow Fe(OH)_3(sol)+3HCl$$

(d) ***By double decomposition***

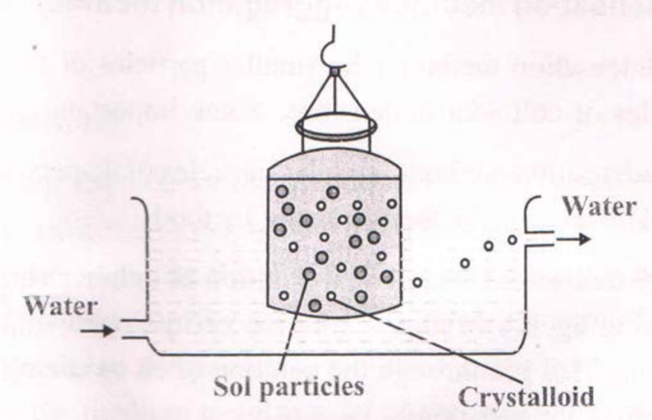
A sol of arsenic sulphide is obtained by passing hydrogen sulphide through a cold solution of arsenious oxide in water.

$$S_2O_3+3H_2S \longrightarrow As_2(sol)+3H_2O$$

15.7 Purification of colloidal solutions (Sols)

Colloidal solutions usually contain the impurities of electrolytes. The presence of electrolytes in the smaller concentration stabilizes a sol but their presence in large concentration tends to destabilize the colloidal solution. Therefore it is necessary to purify colloidal solutions by removing the impurities of electrolytes present in them. Following methods are generally used for the purification of colloidal solutions.

Dialysis: We known that an animal membrane allows the passage of crystalloids but retains the larger colloidal particles. This property of animal membrane is utilized for the purification of sols. The process involved is called dialysis. It may be defined as follows.

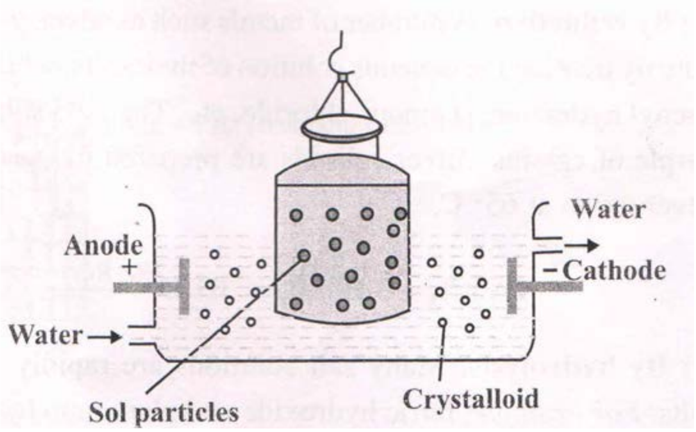


The process of separating the impurity particles of true solution dimensions (crystalloids) from an impure sol by means of diffusion through a suitable membrane such as parchment paper or cellophane membrane is called dialysis

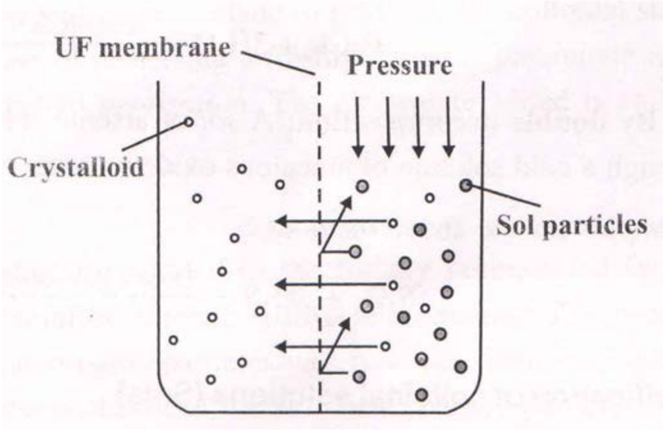
The apparatus used in this method is called dialyser. It consists of a bag made of parchment or cellophane. The bag is filled with the impure sol to be purified and is suspended in a tank through which pure water is circulated. The impurities of electrolytes present in the sol diffuse out of the bag leaving behind pure sol in the bag.

a) Electrodialysis

Dialysis is a low process. However it can be expedited by applying an electric field, the impurity ions move faster to the oppositely charged electrodes and the process gets quickened. This process is referred to as electrolysis.



Ultra filtration: The pores of an ordinary filter paper are large enough to allow the passage of both impurity particles as well as colloidal particles Sol particles directly pass through ordinary filter paper because their pores are larger (more then or) than the size of sol particles (less then). Therefore an ordinary filter paper cannot be used for removing the impurities of electrolytes from an impure sol. However if the pore size of ordinary filter paper is redxuced it can be used for separating the impurities from impure sols. This is achieved by treating an ordinary filter paper with collodion or gelation followed by its hardening by dipping it in formaldehyde solution. This treatment reduces the pore size and enables it to check the passage of colloidal particles through it. Filter papers thus obtained are called ultrafilters. Filtration through ultrafilters is called ultra filtration. In ultra filtration, the ultra filter is supported over a wire mesh and impure sol is poured over it. The impurity particles (electrolytes) pass through the ulrafilter while the larger colloidal particles are retained. The process is very slow. However it can be expedited by applying pressure on sol side or by using a suction pump on the filtrate side. By using a series of graded ultra filters, impurities of different size can easily be removed and it is even possible to separate colloidal particles of different size from one another. This process is illustrated in fig



b) Ultra- centrifugation

Ultra-centrifugation involves the separation of colloidal particles from the impurities by centrifugal force. The impure sol is taken in a tube and the tube is placed in an ultra- centrifuge. The tube is rotated at high speeds. On account of this, the colloidal particles settle down at the bottom of the tube and the impurities remain in the solution. this solution is termed as Centrifugate. The settled colloidal particles are removed from the tube and are mixed with an appropriate dispersing medium. Thus the pure sol is obtained.

15.8 Properties of colloidal solutions

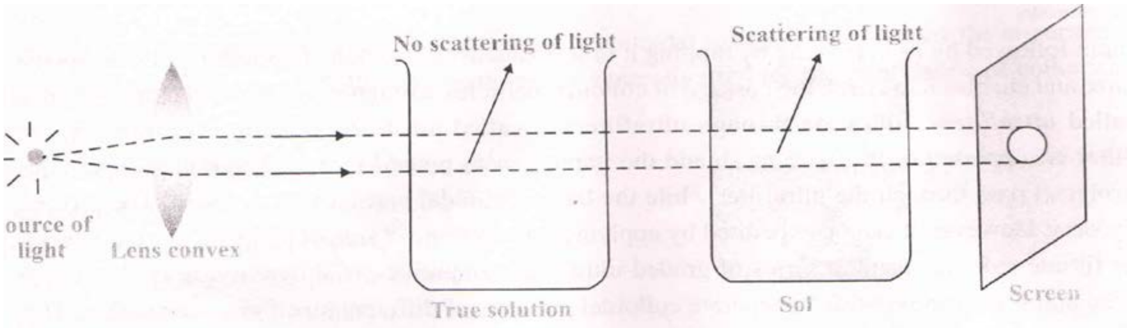
a) Colligative properties of colloidal solutions

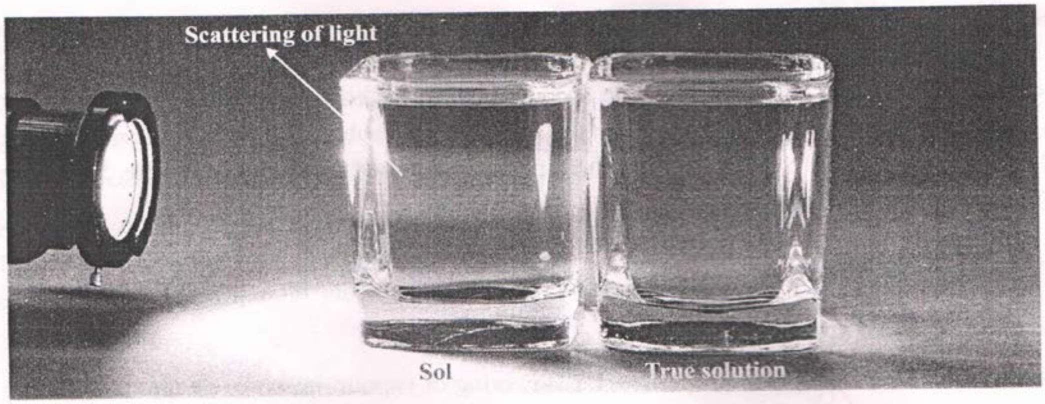
Colloidal solution exhibits colligative properties i.e lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure in the same way as the true solutions of electrolytes and non electrolytes do. Due to formation of associated molecules (aggregates), observed values of colligative properties like relative decrease in vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure are smaller than expected. For a given colloidal sol, the number of particles will be very small as compared to the solution. for a given mass of the substance, the number of colloidal particles present in the colloidal solution of the substance will be much less than the number of particles present in its true solutions. Since a colligative property as compared to that exhibited by a true solution having the same mass of the same substance.

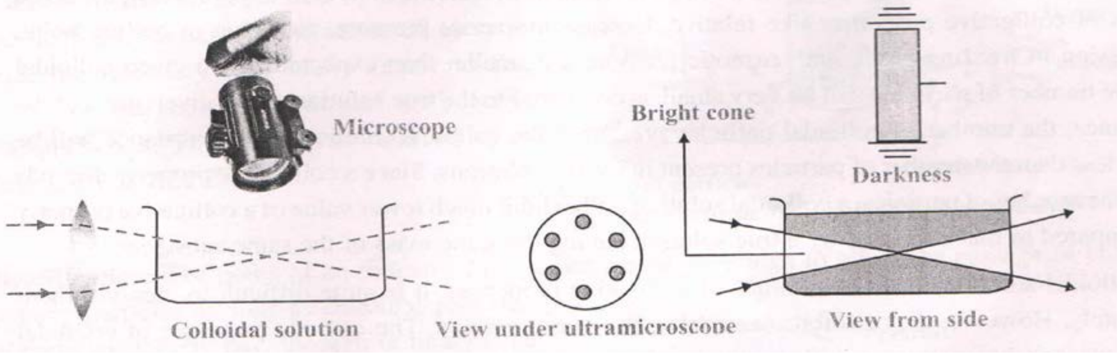
As colloidal solution have low values of colligative properties, it is quite difficult to measure them accurately. However they exhibit measurable osmotic pressures. The osmotic pressures of colloidal solutions can be measured with a reasonable degree of accuracy. This property is used for the determination of the average molecular masses of the colloids.

b)Optical Properties (Tyndall effect)

When an intense converging beam of light is passed through a colloidal solution kept in dark, the path of the beam gets illuminated with a bluish light. This phenomenon is called Tyndall effect and the illustrated path is known as Tyndall Cone. The phenomenon was observed by Tyndall in 1869







The Tyndall effect is due to the scattering of light by colloidal particles. Since the dimension of colloidal particles are comparable to the wavelength of ultraviolet and visible radiation, they scatter these radiations get illuminated. Tyndall observed that the zone of scattered light is much larger than the particle itself. This is why colloidal particles look like bright spots when viewed with a micro scope at right angles to beam of light as shown in fig Thus Tyndall effect may be defined as the scattering of light by colloidal particles present in a colloidal solution.

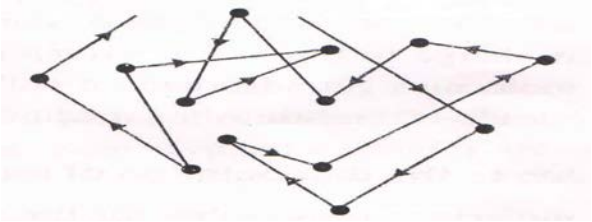
Tyndall effect is not exhibited by true solution. this is because the particles (ions or molecules) present in a true solution are too small to scatter light. Thus Tyndall effect can be used to distinguish a colloidal solution from a true solution. The phenomenon has also been used to device an instrument known as ultra microscope. The instrument is used for the detection of the particles of colloidal dimensions. Tyndall effect also establishes the fact that colloidal system are heterogeneous in nature.

Some examples of Tyndall effect are as follows

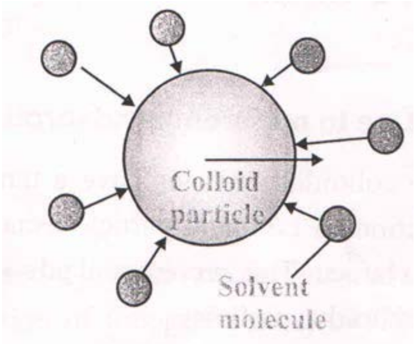
i) Tails of comets is seen as a Tyndall cone due to the scattering of light by the tiny solid particles left by the comet in its path.
ii) Due to scattering the sky looks blue.
iii) The blue colour of water in the sea is due to scattering of blue light by water molecules.
iv) Visibility of projector path and circus light.
v) Visibility of sharp ray of sunlight passing through a slit in dark room.

15.9 Brownian movement

Colloidal particles exhibit erratic random motion. The motion has been ascribed to the bombardment of the particles by molecules in the dispersion medium. The motion is affected by size and also the viscosity of the medium, smaller particles have higher random motion whilst high viscosity reduces Brownian motion.



The zig-zag movement of colloidal particles continuously and randomly results Brownian movement. This Brownian motion arises due to the uneven distribution of the collisions between colloidal particles and the solvent molecules



This type of similar motions could be seen in smoke or dust particles suspended in air and other fluids. This motion is ascribed to the thermal motion of the molecules of the fluid. These molecules are in constant irregular, erratic motion with a velocity proportional to the square root of the temperature. The idea that molecules of a fluid are constantly in motion is a key part of the kinetic theory of gases. Brawnian motion is observed for particles about 1 μm in diameter. The velocity of the particles increases with decreased particle size.

15.10 Presence of electrical charge on colloidal particles and stability of sols

One of the most important properties of colloidal solutions is that colloidal particles possess a definite type of electrical charge. In a particular colloidal solution all the colloidal carry the same type of charge, while the dispersion medium has an equal but opposite charge. Thus the charge on colloidal particles is balanced by that of the dispersion medium and the colloidal solution as a whole is electrically neutral. For example in a ferric hydrox ide sol the colloidal ferric hydroxide particles are positively charged while the dispersion medium carries an equal and opposite negative charge.

The stability of a colloidal solution is mainly due to the presence a particular type of charge on the colloidal particles present in it. Due to the presence of similar and equal charges, the colloidal particles repel one another and are thus unable to combine together to form large particles. This keeps them dispersed in the medium and the colloidal system remains stable. This is why sol particles do not settle down even on standing for a long time.

15.11 Coagulation or flocculation

The stability of a sol is due to the charge present on the colloidal particles. Due to similar charges colloidal particles repel one another and are unable to combine together to form larger particles, However if the charge on colloidal particles is destroyed they are free to come nearer and grow in size. When the particles become sufficiently large they are get precipitated. This phenomenon is termed as coagulation of flocculation. The process of settling of colloidal particles is called coagulation or precipitation. The coagulation of colloidal solution can be achieved by the addition of an electrolyte. It is to be noted that a small amount of electrolyte is necessary for the stability of a sol because the ions of the electrolyte get adsorbed on the colloidal particles and import them some charge. However when an electrolyte is added in substantial amount the positively charged ions of the electrolyte neutralize the charge on the colloidal particles and compel the sol to get coagulation.

Fog and smoke are aerosols which are liquid droplets or solid particles dispersed throughout a gas. An emulsion consists of liquid droplets dispersed throughout another liquid (for example particles of butterfat dispersed through homogenized milk). A sol consists of solid particles dispersed in a liquid.

5.12 Summary of the unit

Colloids and colloidal systems are essential to life. They function in everybody cell, in the blood, and in all body fluids, especially the intercellular fluids.

Suspension is a heterogeneous fluid containing solid particles that are sufficiently large for sedimentation. In this Particle size is > 1 mm. Dispersion is made by mechanical agitation (sand in the water). Aerosol is a suspension of liquid droplets or a suspension of fine solid particles in a gas. Example: smoke, air pollution, smog, etc. Emulsion is a mixture of two or more immiscible liquids one liquid (the dispersed phase) is dispersed in the other (the continuous phase). Prepared by shaking – oil/water (milk), water/ oil (butter).

Collides is a solution in which a material is evenly suspended in a liquid. In other words, a colloid is a microscopically small substance that is equally dispersed throughout another material. The particle size in 1 – 1000 nm. Particles have very large surface area. There are two types of colloidal system they are Homogenous colloidal system (lyophilic dispersion) and Heterogenic colloidal system (lyophobic dispersion). Lyophilic particles are mixed with the suitable solvent. Particles have high affinity to the solvent. Lyophobic colloid particles do not have affinity to the molecules of solvent. Diffusion is the spontaneous mixing of two substances with different concentrations over a semi-permeable membrane. The reason of diffusion is the thermal motion of molecules.The bulk of diffusion is characterized by diffusion coefficient (D)

D = amount of diffusing substance per time unit through 1 cm^3, at a concentration gradient equal to 1 . Concentration gradient is $D = \Delta c/l$, c – concentration, l - membrane thickness

15.13 Key words

Colloids; Suspensions; Lyophilic colloids; Lyophobic Colloids; Dispersion method; Peptization; Electro dialysis; Ultra- centrifugation; Tyndall effect; Brownian movement; Coagulation.

15.14 References for further study

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15.15 Questions for self understanding

1. What is adsorption?
2. Define desorption.
3. What is sorption?
4. Define term colloid.
5. What is catalysis?
6. What is auto catalysis?
7. What is catalytic position?
8. What is the effect of a positive catalyst on rate of a reaction?
9. Distinguish between the meaning of the term adsorption and absorption. Give one example each.
10. What is the difference between physisorption and chemisorption?
11. Give reason why a finely divided substance is more effective as an adsorbent?
12. What are factors which influence the adsorption of gas on a solid?
13. What is an adsorption isotherm? Describe Freundlich adsorption isotherm.
14. What do you understand by activation of adsorbent? How is it achieved?
15. What role does adsorption play in heterogeneous catalysis?
16. Why is adsorption always exothermic?

17. How are the colloidal solutions classified on the basis of physical states of the dispersed phase and dispersion medium?
18. Discuss the effect of pressure and temperature on the adsorption of gases on solids.
19. What are Lyophilic and lyophobic sols? Give one example of each type. Why are hydrophobic sols easily coagulated?
20. What is the difference between Multimolecular and macromolecular colloids? Give one example of each. How are associated colloids different from these two types of colloids?
21. What are enzymes? Write in brief the mechanism of enzyme catalysis.
22. How are colloids classified on the basis of:

(i) Physical states of components

(ii) Nature of dispersion medium and

(iii) Interaction between dispersed phase and dispersion medium?

23. Explain what is observed:
    (i) When a beam of light is passed through a colloidal sol?
    (ii) An electrolyte, NaCl is added to hydrated ferric oxide sol.
    (iii) Electric current is passed through a colloidal sol.
24. What is emulsion? What are their different types? Give example of each type.
25. What is de-emulsification? Name two de-emulsification
26. Action of soap is due to emulsification and micelle formation. Comment
27. Give four example of heterogeneous catalysis
28. What do you mean by activity and selectivity of catalysts?
29. Describe some feature of catalysis by zeolites.
30. What is shape selective catalysis?
31. Explain the following terms.
    (i) Electrophoresis (ii) Coagulation.
    (iii) Dialysis (iv) Tyndall effect.
32. Give four uses of emulsion
33. What the term with suitable examples:

(I) Alcosol (ii) Aerosol (III) Hydrosol

34. What is micelles? Give one example of a micellers system
35. Comment on the statement that “colloidal is not a substance but a state of substance”.

Unit-16

Structure

16.0 Objectives of the unit
16.1 Introduction
16.2 Electro kinetic Phenomena
16.3 Electro osmosis
16.4 Streaming potential
16.5 Electrophoresis
16.6 Moving Boundary Electrophoresis
16.7 Toepler “Sechlieren” Method
16.8 Paper Electrophoresis
16.9 Zone electrophoresis
16.10 Gel electrophoresis
16.11 Stabilizers
16.12 Summary of the unit
16.13 Key words
16.13 References for further study
16.15 Questions for self understanding

16.0 Objectives of the unit

After studying this unit you are able to

- Explain the electro osmosis phenomenon
- Explain the streaming potential
- Explain the Electrophoresis
- Explain moving boundary electrophoresis
- Explain paper Electrophoresis
- Explain zone electrophoresis
- Explain gel electrophoresis

16.1 Introduction

There are several views regarding the origin of charge on colloidal particles. According to these views colloidal particles acquire charge due to the following reasons.

(a) Due to dissociation of the adsorbed molecular electrolytes

Colloidal particles have a strong tendency to adsorb reactant or product molecules. The molecules thus adsorbed on the surface of colloidal particles may undergo dissociation or ionization and may impart charge to them. For example during the preparation of sulphide sols (ex- AS_2S_3 sol), H_2S molecules get adsorbed on colloidal particles. H_2S molecules thus adsorbed undergo ionization and release H^+ ions into the medium. Consequently colloidal particles are left with negative charge.

(b) Due to the dissociation of molecules forming colloidal aggregates

The molecules responsible for the formation of aggregates of colloidal dimensions may themselves undergo dissociation or ionization resulting in the development of charge on the colloidal particles formed by their aggregation. For example the soap molecules (RCOONa) dissociates to give $RCOO^-$ and Na^+ ions. $RCOO^-$ ions aggregate together to form micelles to form micelles which carry negative charge as explained earlier.

(c) Due to preferential adsorption of ions from solutions

The colloidal particles have a tendency to preferentially adsorb a particular type of ions from the solution. A colloidal particle usually adsorbs those ions which are in excess and are common to its own lattice. This preferential adsorption of a particular type of ions imparts a particular type of charge to colloidal particles.

The phenomenon of flow of solvent from a dilute solution to concentrated solution “across a semipermeable membrane, till the system attains equilibrium is called Osmosis. The movement of solvent molecule from solvent side to solution side (sugar) increases the hydrostatic pressure on right side so that the level of the liquid in solution side increases. Their hydrostatic pressure difference before osmosis and after osmosis is referred as the osmotic pressure or excess of pressure applied to stop the flow of solvent through the semipermiable membrane is referred as osmotic pressure

16.2 Electro kinetic Phenomena

The rate and relative movement of a solid in liquid or liquid with solid accompanying with certain electrical phenomena is referred as electro kinetic effect.

When a solid is bought in contact with a liquid an electrical double layer is formed as

Then the potential difference produced at solid liquid interface (because of charge separation) is called electronegative potential or zeta potential ($\xi - potential$)

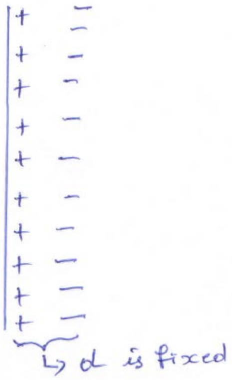
Three theorems of electrical double layer

(1) Helmoltz previews theory

(2) Gossy champion theory

(3) Stern theory

According to Helmoltz theory, it consists of dielectric parallel plate condenser the distance between two layers is fixed. Then the potential at the interface



$$\xi = \frac{4\pi\sigma\, d}{D}$$

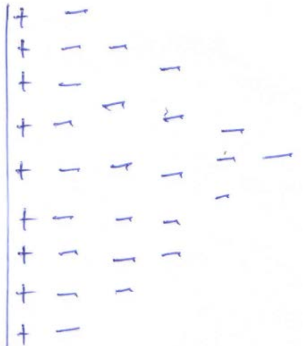
$where$

$D = di\ electric\, current\, of\ the\, medium$

$\sigma = change\, density$

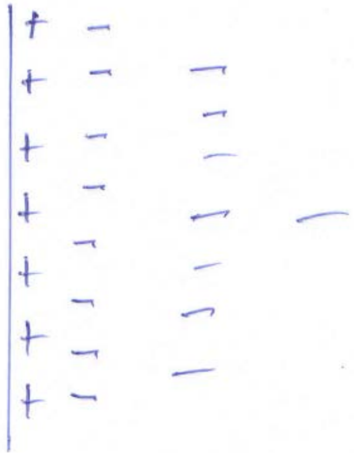
Gossy champion difference layer

Charges on the solution side is not fixed, but the diffused from the solution side



Stern Model

Some changes are fixed (H.P) some changes are diffused (G.C). Therefore stern model is combination of H.P and G.C model



Under electro kinetic phenomena we have 4 types

(1) Electro osmosis.

(2) Streaming potential

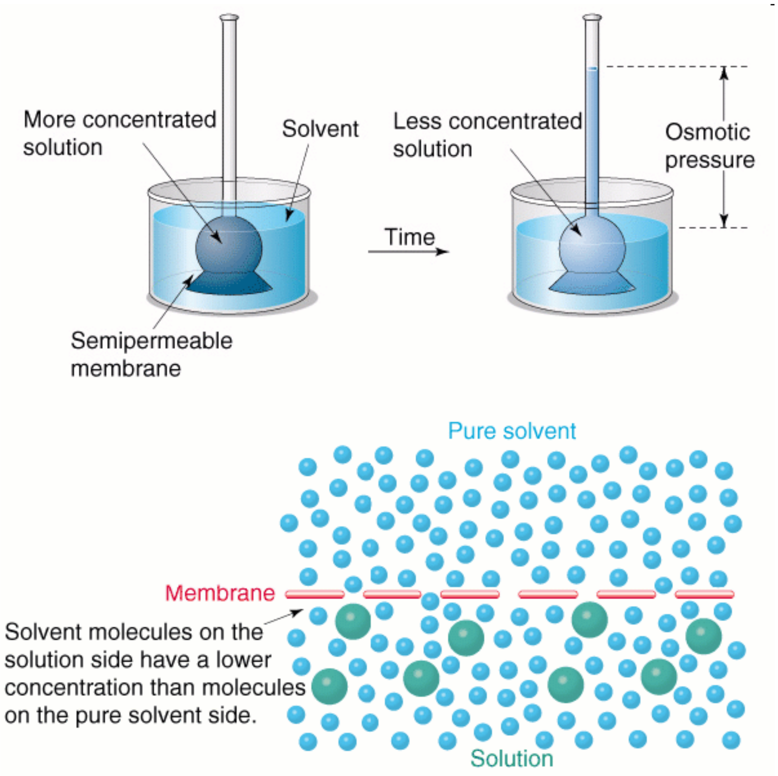
(3) Electro phrases

(4) Dorn effect or sedimentation potential

16.3 Electro osmosis

"The movement of a liquid through the pores of a diaphragm of a solid under the influence of an applied E.M.F is called electro osmosis or electro endosmosis.

Ex- if two portion of water (any solvent) are separated by a diaphragm of a porous non-conducting material and metal electrode are connected to a surface of E.M.F in each side of a diaphragm then if E.M.F is applied the liquid will tend to flow through the pores of the diaphragm if the solid phase is fixed and direction of the flow depend on the sign of the charge it with respect to that of solid.



Initially if the liquid level is same after electro osmosis starts the level is decreased at one side and another side it is increased so that a pressure difference is caused because of electro osmotic pressure.

If the level of the liquid maintained same in the capillary tube the liquid will flow outside continuously because of applied E.M.F

Let us consider the liquid placed in a capillary tube separated by a pours diaphragm when a liquid is allow to flow through diaphragm in presence of applied E.M.F then the rate of flow depends with two forces

i) Electro osmosis force

If v= applied potential gradient.

σ = charge density/ liquid boundary at which the liquid moves then the electrical force $= v\sigma$ -------(1)

ii) Frictional force for movement of liquid layer(and the wall)

i.e if

u=uniform velocity with which liquid moves in the double layer.

d= effective thickness of the double layer.

η=viscosity of the solvent (liquid)

Then force due to friction $= \frac{\eta u}{d} -------(2)$

Therefore at the stationary state 1=2

$\eta u = d v \sigma$ ------ (3)

Or $d = \frac{\eta u}{v\sigma}$ ----- (4)

we know from H.P theory

$$\xi = \frac{4\pi\sigma d}{D} -----$$

Substituting 4 in 5

$$\xi = \frac{4\pi\sigma}{D}\frac{\eta u}{v\sigma}$$

$$\xi = \frac{4\pi\eta^4}{DV}$$

If v=unity i.e e.s unit potential/e.s

Then
$$\xi = \frac{4\pi\eta U_0}{D}$$
$$or\, U_0 = \frac{\xi . D}{4\pi\eta}$$

U_o is called electro- osmotic mobility

If ν :the total area of cross section of all the pores

U=velocity of the liquid flow

Then volume of liquid from potential/see

Electro somatically $\vartheta = \nu u ---(8)$

$$\therefore u = \frac{v}{\vartheta} ----(9)$$

9 in 6 given

$$\xi = \frac{4\pi \eta}{Dv}\frac{\vartheta}{v} -------(10)$$

$$\vartheta = \frac{\xi v Dv}{4\pi\eta} -------- (11)$$

$if\ \theta\ and\ r\ is\ the\ radius\ the\ tube\ then\ \vartheta = \pi r^2$

$12\ \ in\ \ 10\ \ gives \qquad \vartheta = \frac{\xi r^2 Dv}{4\eta} ------(13)$

Also if ν is the volume of liquid flowing/sec in the viscosity η, through a capillary tube length l and radius r, By poiseuille equation

$$\nu = \frac{\pi r^4 p}{8nl} ---------14$$

P: difference of pressure (e.o pressure) between the ends of tube.

Therefore 14 and 13

$$p = \frac{\nu.8nl}{\pi r^4}$$

$$= \frac{\xi r^2 D \nu}{4\eta} \quad \frac{8\eta l}{\pi r^4}$$

$$p = \frac{2\xi D \nu\, l}{\pi r^2} = \frac{2\xi D\nu l}{\nu}$$ --------------- (15)

If electrode are placed at the ends of the tube

For v = potential gradient

l= length of the tube

then v.l = E (applied EMF)-------------- (16)

Therefore $p = \frac{2\xi DE}{\nu} - - - - - 17$

For a given tube v is constant therefore P is proportional to applied EMF which is formed in the e To determine ξ

$$\xi = \frac{Pu}{2DE} = \frac{P\pi r^2}{2DE}$$

P=dynes/sqcm

u=sqcm

E=volts

If p is in atmosphere pressure then

$$\xi = \frac{P\pi r^2}{2DE} \times 9 \times 1.013 \times 10^{10}\, volts$$ xperiment

Example; Electro osmosis of H_2O through a galas capillary tube of r = 0.037cm , D = 80, and

P/E = 2 X 10^{-8} atm/ Volt. Then zeta potential between water ans glass = 0.049 volt

16.4 Streaming potential

If the relative moment of the two phases i.e movement of liquid phases is brought about mechanically (no electric field) then displacement of charged layers with respect to each other produce a difference of potential between any two points in the direction of rotation this resulting potential is known as the streaming potential

Ex- liquid is forced through a porous material live clay diaphragm or a capillary tube

Therefore streaming potential is considered as the reverse to the electro osmosis

Let us consider the liquid is flowing through capillary tube.

Let d is the thickness of electrical double layer if the liquid is force to flow mechanically and the liquid layer is moved to displace r from one center to the tube then r-d is moving part of double layer length of the tube then poiseuille's equation

$D[r^2-(r-d)^2$ ---- (1)

16.5 Electrophoresis

Electro phoresis is the migration of solid ,particles (changed particle) or molecules in a medium under the influence of an applied electric field.

This is one of the important method to determine

i) Number of components

ii) Amount of component

iii) Zeta potential

iv) Separation of component in a mixture.

Almost all particles in solvent Eg- red blood cells , bacteria, peptides, proteins, nucleic acid etc. acquire either +ve or –ve charges. Then the mobility depends on charge on the molecule i.e the basis in charge/mass ratio.

similar to argument electro osmosis, hence the solid particles are moving of liquid, experiences two forces

i) The electro phohetic force is electric force acting on the particle =Vσ

ii) Frictional force $\frac{\eta u}{d}$

$\frac{\eta u}{d} = V\sigma$ and $\xi = \frac{4\pi\sigma d}{D}$

We get $\xi = \frac{4\pi n^4}{DV}$ -------- (1)

If V=unit/

$u_e = \frac{\xi D}{4\pi\eta}$ -------- (2)

Equation (2) is applicable to cylindrical ,particle solid liquid or gases suspended in a liquid)

However later it is proposed that u_e depends with particle size and surface

Delye and Hukel modified equation 2 to

$u_e = \frac{\xi D}{6\pi\eta}$ -------------- (3)

Applied to small particles

For larger particles it is modified by

$u_e = \frac{\xi D}{6\pi\eta}\frac{3k_e}{2k_e + k_e'}$ ------------- (4)

Here k_e and k_e' are the specific conductance of liquid and the particle respectively if the particle is non conductor

4 become 1

$$u_e = \frac{\xi D}{4\pi\eta}$$

The test of equation 1 is done by determining u_0 and u_e for some particle and liquid so that

$$\frac{u_0}{u_e} = 1$$

However for some particle $\frac{u_0}{u_e} = 1.5$ according to 3

If potential gradient is volts per cm

$$\xi = e.s\,unit$$

$$\xi = \frac{4\pi\eta u_e}{D} \times \theta \times 10^4\ volt$$

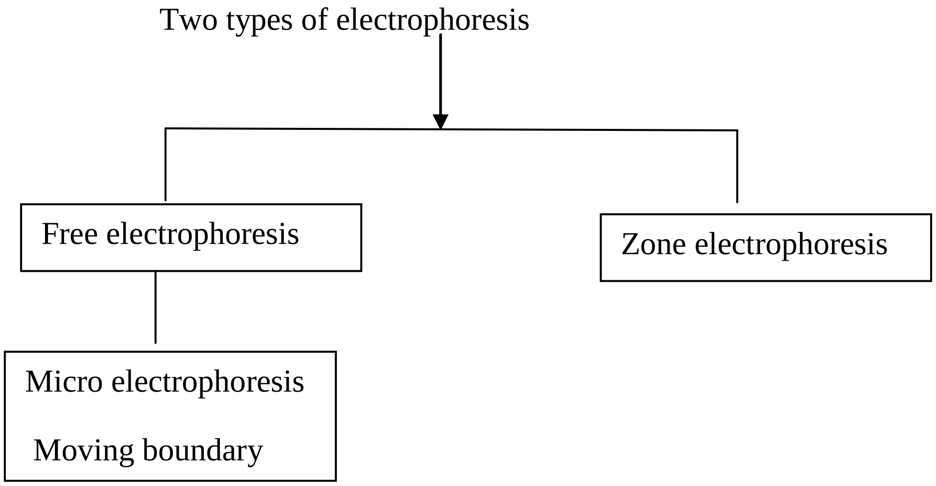
High charge in the particle : high u_e

U_e is large for spherical particle

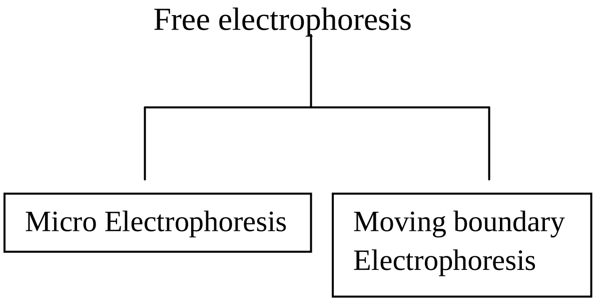
U_e is small for needle shape

Globular protein u_e > fibrous proteins

Medium pH always influence the u_e i.e, u_e increasing or decreasing with pH



Two types of electrophoresis



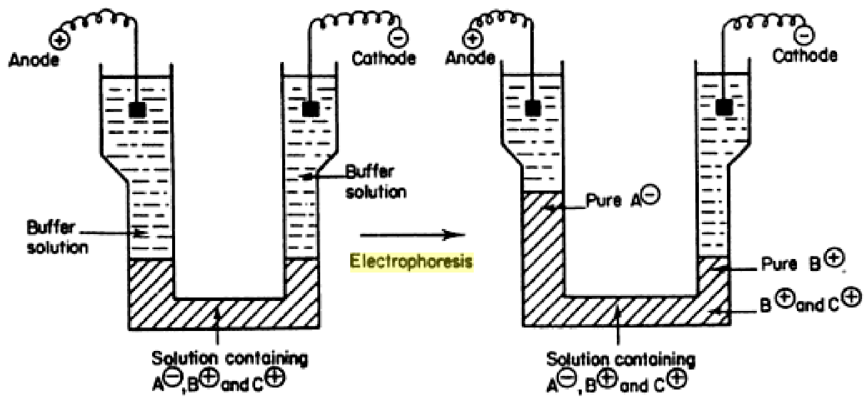
When the observation of small particle motion in an electric field through a micro slope

The suspension is placed in closed heat system of the wall section through with observation

Ex- R.B cells, neutrophils, bacterial etc.

16.6 Moving Boundary Electrophoresis

Moving boundary electrophoresis was used quite widely and various designs of equipement for this technique become available commercially. The principal use was in protein research were it provided valuable information. The equipment used consists of a U-shaped cell with a rectangular cross section as shown in figure. In moving boundary electrophoresis a buffered solution of macro molecules (proteins) is placed under a layer of pure buffer solution in a U-shaped observation cell



Before Electrophoresis After Electrophoresis

Equipment is partially filled with the protein solution of interest and over it is layered a buffer solution. Eelectrodes are immersed in the bath. When a voltage is applied, charged molecules migrate towards the appropriate electrodes. If several components are present in the sample, and if their electrophoretic mobilities differ, their migration can be as multiple moving boundaries in the system. Since the protein solution has refractive index a little higher than that of the buffer, there will be a local charge in refractive index at the protein boundary in the U-tube and this can be detected by optical methods, usually using Schleiren optics.

After electrophoresis is complete, fractions can be obtained that contain separated components of the original sample and these can be analyzed chemically and biologically as appropriate. In this way biologically active substances present in concentrations too low to be detected by optical means may be determined.

For separation of proteins the cell is placed at constant temperature bath. Once the electric field is applied, the species bearing –ve charge will move towards +ve electrode depending upon the charge.

Example; two proteins one having –ve charge and another having +ve charge. Then we can separate because one is moving towards +ve chamber formed –ve but came faster.

Therefore a buffer is chosen in such a way that all the compounds forms same types of charges –ve or +ve. Then the separation is achieved depending on the rate of migration.

For example; in X Y Z proteins, X is fast moving, Z is slow moving and y is intermediate then X can be separate because it coming out first. Y remains in the middle and Z remains in the right hand side so that separate them. A boundary is formed depending on the sensity and refractive index of the different types of compounds.

A major drawback of moving boundary electrophories is that only the slowest and more rapidly moving components of a mixture can be obtained in pure form. However it has been a useful method for the determination of the complexity of heterogeneous sample.

To get good boundaries

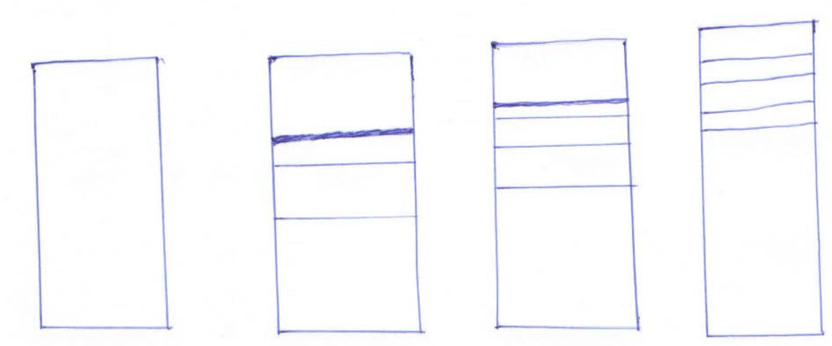
i) The tubes of rectangular section provides maximum amount of wall area and facilitate the removal of heat to the surroundings (otherwise the conditions near the wall and center of the tube is not uniform and boundary disturb)

ii) Temperature is low (3^0 – 10^0 C) so that variation of density of the liquid with respect to temperature is small

iii) Suitable buffer is selected depending on the substance.

16.7 Toepler "Sechlieren" Method

Toepler "Schlieren method technique depends on changes of relative index and density i.e the boundaries absents of shadow which can be as such on a ground glass screen or they can be recorded photographically

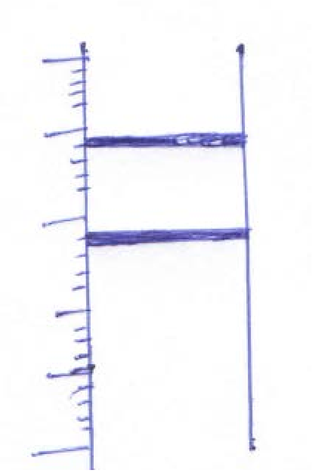


'schlieren' photographs of blood serum with time

By taking observations offer various intervals of time the rate of movement of the boundary the u_e can be evaluated

Another method is "scale method'

In which a photograph of the tube which contained graduated scale is taken for the movement of the boundary. The displacement of the boundary due to changes of relative index given an indication of the portion of the boundary at any time hence u_e can obtained



Tissaliys electrophoresis and schlieren techniques application for separation of constituents of a mixture of their u_e is different. This is used to indicate how many components present in particular system. Where as it is homogeneous or contain more than two proteins.

If two or more boundaries present (substance) schlieren photograph shows one shadow region to each constituents.

Ex- human blood serum at pH 8.06 at intervals of 20 min

Then further moving boundary album in constituents $u_{e\,=}$ 6 x 10^{-5} cm/see

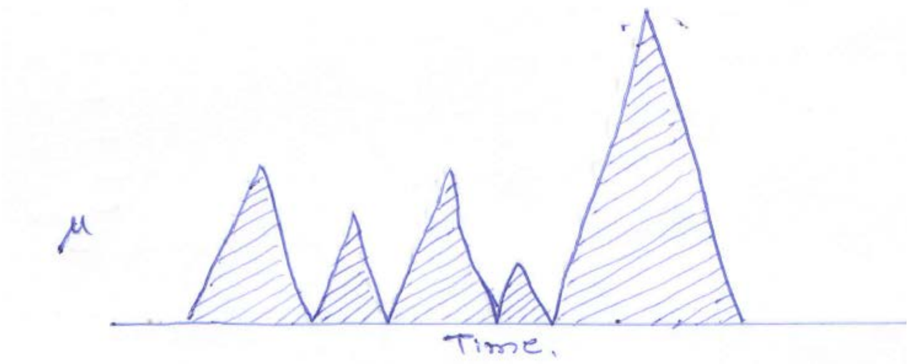
α-globins:4.3 x 10^{-5} cm/see

β-globins:2.8 x 10^{-5} cm/see

Therefore qualitative study can be

However "schlieren Scanning" technique is used for quantitative purpose and separation. i.e this gives amounts of the various substance present

The schlieren scanning photographs is obtained as shown in figure with respect to relative of the substance present in the system with internal of time.



Ex- normal blood plasma

A: albumia boundary

α: α-globulin

β: β-globins

γ : γ-globins

ϕ: fibrinogen

Therefore until the components is present, we observed the boundary area and one is removed it is absent)

Further the areas under the respective peaks are proportional to the quantities (ampont) of various substances present and we can easily evaluate. Hence qualitative separation and quantitative analysis is possible.

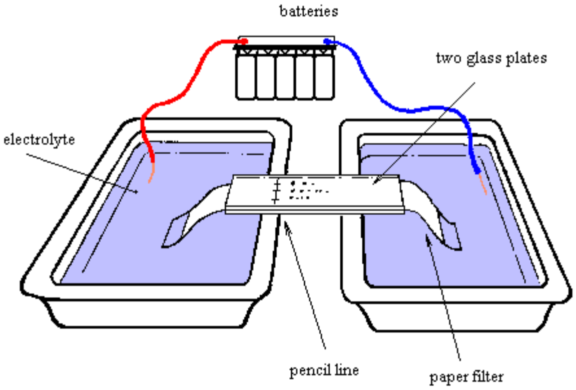
16.8 Paper Electrophoresis

Filter paper as stabilizing medium is very popular for the study of normal and abnormal plasma proteins. Paper of good quality contains 95% α- cellulose with very slight adsorption capacity is used. Chromatography paper is very suitable.

There are two types of Paper electrophoresis they are

1) Horizontal paper electrophoresis
2) Vertical paper electrophoresis

Horizontal paper electrophoresis



Apparatus for paper electrophoresis.

The buffer reservoir separated in to two sections, one section containing the electrode and the curves is in contact with the supporting medium (paper wicks), and wicks are having contact with buffer reservoir. (Wicks are made up of several layers of filter paper). The electrodes are usually platinum electrode. Depending upon sample amino acids, proteins etc. particular buffer is selected (pH). Current should be controlled otherwise over heating may lead to

It can be avoided by keeping relative unit in a cold room

Experiment

The sample may be applied as a spot (≈ 0.5 cm in diameter). The current is switched on for 2 hours, and then paper is removed directly in vacuum over 110^0 C

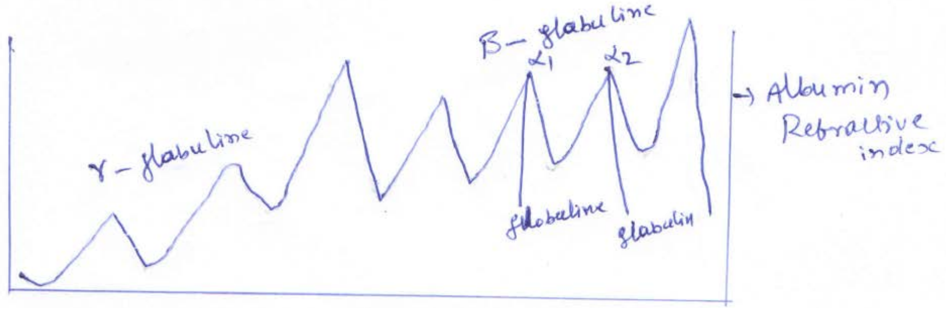
To identity unknown components the electrophoretogram may be compared with standard electrophoretogram (Just like chromatography)

i) Fluorescence: staining with ethidium bromide or densyl chloride of this electrophoretogram getting fluorescence we can be visualized using fluorospectra. We can detect DNA, RNA amino acid peptides etc.

ii) Similarly with U.V 260-280 nm proteins, peptides, nucleic acids.

iii) Staining with different dyes, color develops from which we can detect the component

Quantitative estimation is obtained by removing the different zones obtained and compare with the standards of known quantity otherwise the electrophoretogram

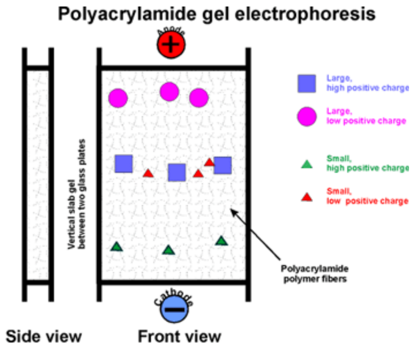


Proteins separation blood/plasma

16.9 Zone electrophoresis

Separation in presence of inert stabilizing media like paper, gel etc.

This supporting medium through the adsorption difference with different particle or pores present is allows some particle or porse present is allows some particles and not allows some particles or decrease the rate of migration when it entering the pores medium is responsible to from different bands or zones separation between on component to others. This principle used to identify or separation of the species present in the macro molecules compare to free electrolyte this is more advantage as the free electrolysis sometimes due to concentration overlapping of but in zone electrophoresis a sharp, clear different boundary separation is occur which makes easy to separate.



16.10 Gel electrophoresis

Gel electrophoresis is a basic biotechnology technique that separates macromolecules according to their size and charge. It is frequently used to analyze and manipulate samples of DNA, RNA, or proteins. In this laboratory activity, agarose gel electrophoresis will be used to separate and characterize colored dye molecules of various sizes and charges.

Gel electrophoresis mainly through the pores.

Ex- starch gel, A gas gel,

$$T = \frac{[a+b]}{v} \times 100\%$$

a = acrytamide in grms

b = bis acrytamide in grms

v = volume of buffer in Cm^3

T =3 % to 30% then pore size 0.2 nm to 0.5nm

The gels are pores and the size of the pores is responsible of movement of molecules through the gel. Hence the separation not only depends on the charge on the molecules but also on its size. Therefore resolution if sample is sharper and better in a gel than in any other types of medium.

Ex- starch gel, Agar Gel, polyacrylamide gel etc.

Starch gel: contain micro organisms hence not good. The pore size is not easy to control.

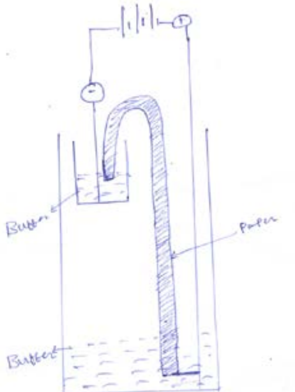
Agar has high pure size hence used to separate high molecular weight macro molecules like proteins and nucleic acids.

The mobility of a molecule during gel electrophoresis also depends on its molecular size and shape. The small pores of the gel matrix act as a sieve that provides great resolving power. Small molecules maneuver more easily through the pores than larger molecules and therefore travel relatively quickly. Large molecules encounter more resistance as they make their way through the tiny pores and therefore travel at a slower rate.

Size and net charge are factors that together determine how quickly molecules will travel through the gel, and thus what their migration distance will be. Small size and strong charge increase a molecule’s migration rate through the gel. Large size and weak charge decrease the migration rate.

In gel electrophoresis, samples to be separated are applied to a porous gel medium made of a material such as agarose. Agarose is a purified form of agar, a gelatinous substance extracted from red algae. Agarose gels are made by first adding powdered agarose to liquid buffer and boiling the mixture until the agarose dissolves. This molten agarose is then cooled to about 55–60°C, poured into a gel mold called a casting tray, and allowed to solidify. Before solidification occurs, a comb is placed in the casting tray to create a row of wells into which samples are loaded once the comb is removed from the solidified gel.

One of the best gels used is acrylamide gel whose pore size is adjusted. The compound is eluted using appropriate solvent. Then the colour is extracted and the colour density of the solution is measured and the compare with slandered. This may gives fairly accurate data.



Vertical electrophoresis.

The pore size and electrophoresis mobility is related by

$\log E = \log E^1 - Kr\,\varsigma$.

where

E is the electrophoretic mobility.

E^1 is the mobility in solution

K_r retradition co efficient.

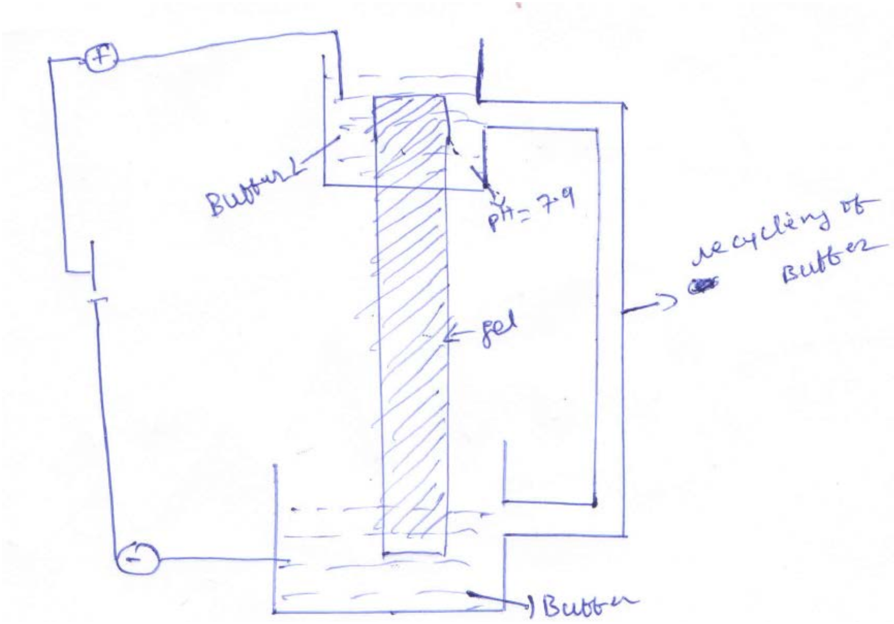
ς= is the total gel concentration.

$K_r = c(R+r)$

C is the constant

R mean radius of the macro molecules

r= radius of gel Fiber.



16.11 Stabilizers

Some time to separate subunits (to get zones)

RNA : α,β, and β^1 then some solubility agent are added to get 3 zones instead of one zone

Ex- SDS sodium dodecyl sulphate.

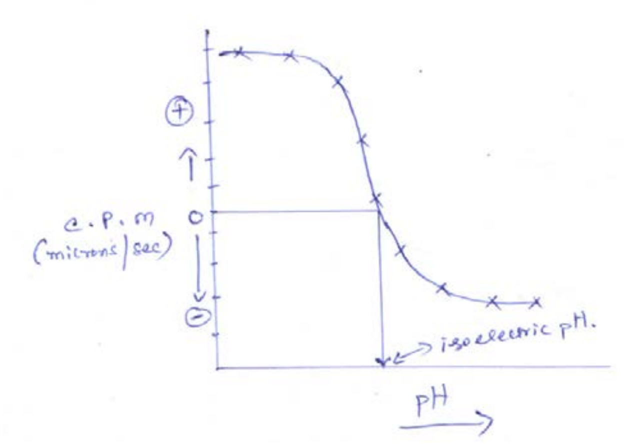
Determination of iso electric point of proteins

To determine the iso electric point (PI) of proteins (poly peptides)

i) Measure the mobility of protein at several pH

ii) Plot the mobility values V/s pH values

The pH where the proteins interseets zero mobility line is taken



At isoelectric point all the anions on the proteins are exactly balanced by number of cations. The net charge is zero and the protein does not more in the electric field.

Ex- peptides (glycotonic acid, aspoctic acid) P^H=1

Histones P^H= 12

Solubility of proteins is zero at pH = 1 helps in the separation of proteins

pH	e.p.p microns/see
4.03	0.6
4.36	0.356
5.66	-0.487
5.86	-0.75
6.52	-1.0 pH is high

16.12 Summary of the unit

A solid surface in contact with a solution of an electrolyte usually carries an electric charge. This gives rise an electric potential, at the surface, and a decreasing potential as we move through the liquid away from the surface, and in turn this effect the distribution of ions in the liquid. There are two regions for this. The Stern Layer immediately adjacent to the surface where ion size is important; and outside this is a diffuse layer.

Because of difference in charge between the diffuse layer and the solid surface, movement of one relative to the other will cause charge separation and hence generate a potential difference, or alternatively, application of an electrical potential will cause movement of one relative to the other. The relative movement of the solid surface and the liquid occurs at a surface of shear.

The potential at the shear plane is known as the zeta potential and its value can be determined by measurement of electrokinetic phenomena. Zeta potential is almost identical with the Stern potential thus gives a measure of the potential at the beginning of the diffuse layer. The isoelectric point is the pH at which the zeta potential is zero. It is usually determined by pH titration, measuring zeta potential as a function of pH. The point of zero charge is the pH at which the positive and negative charges of a zwitteric surface are balanced.

16.14 Key words

Electro osmosis; Streaming potential; Electrophoresis; Moving Boundary Electrophoresis; Paper Electrophoresis; Zone electrophoresis; Gel electrophoresis.

16.15 References for further study

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16.15 Questions for self understanding

1) Explain electro osmosis phenomenon

2) What is streaming potential?

3) Explain the Electrophoresis

4) Explain moving boundary electrophoresis

5) Explain paper Electrophoresis

6) Explain zone electrophoresis

7) Explain gel electrophoresis