B.Sc Chemistry

II YEAR

Major II – PHYSICAL CHEMISTRY – 1

Main Author : **Dr. S. R. BRINTHA**
HOD &Associate professor Of Chemistry
Annai Velankanni College
Tholayavattam -629157.

Co- Authors : **Dr.M. JAYARAJAN**
Assistant Professor of Chemistry
Annai Velankanni College , Tholayavattam.

Dr. R. Britto Dominic Rayan
Associate professor of Chemistry
St.Philomina’s College ,
Mysore- 570015.

B.Sc Chemistry

II YEAR

Major II – PHYSICAL CHEMISTRY – 1

SYLLABUS

UNIT – I GASEOUS AND SOLID STATE.

Types of molecular velocities and their inter relations – most probable velocity , average velocity and root mean square velocity.

Maxwell’s distribution of molecular velocities , statement of equation and explanation (no derivation) – graphical representation.

Crystalline and amorphous solids – crystal lattices – iaws of crystallography.

Bragg’s equation . derivation and applications.

Imperfections in a crystal – Schottky defects , Frenkel defects.

UNIT – II SOLUTIONS

Types of solutions – methods for expressing concentration – molarity , molality , mole fraction, normality , mass fraction , parts per million. Solubility of gases in liquids – Henry’s law – Solutions of liquid in liquid – Binary liquid mixture – Ideal and non ideal solutions – Raoult’s law. Fractional distillation – Azeotropic distillation.

UNIT – III PHOTO CHEMISTRY

Photochemical reactions – primary and secondary reactions – Laws of photochemistry, Grotthus – Draper law , Stark – Einstein law – Quantum efficiency – experimental determination of quantum yield.

Qualitative description of fluorescence , phosphorescence – chemiluminescence . bioluminescence and photosensitization.

UNIT – IV THERMODYNAMICS - I

Statement of first law – meaning of the terms internal energy and enthalpy – relation between E and H – heat capacities at constant volume (C_v) and at constant pressure (C_p) , relationship between C_p and C_v – calculation of work for the expression of an ideal gas under reversible isothermal condition.

Statement of second law of thermodynamics.

Entropy : Definition – entropy as function of T and V – entropy changes in isothermal transformation – physical significance of entropy.

UNIT – V THERMODYNAMICS – II

Free energy : Work and free energy functions – definition – physical significance of dA and dG – variation of G during isothermal change – Gibbs Helmholtz equation.

Van’t Hoff isotherm and isochore – Clapeyron equation – Clapeyron – Clausius equation – Applications of Clapeyron – Clausius equation . Third law of thermodynamics : statement of III law and applications . Exception to third law – experimental verification of the law – The concept of chemical potential – variation of chemical potential with T and P – Gibbs Duhem equation.

REFERENCES

1 . Principles of physical chemistry – Puri , Sharma and Pathania

2 . Test book of Physical chemistry – P.L.Soni , O.P.Dharmarha and U.N.Dash.

3 . Essentials of physical chemistry – B.S. Bahl , Arun Bahl &G.D.Tuli.

4 . Thermodynamics for students of chemistry – Rajaram and Kuriacose.

5. Thermodynamics for chemists – Samuel Glasstone.

6 . A test book of physical chemistry – A.S.Negi and S.C.Anand

CONTENTS

UNIT – 1 GASEOUS AND SOLID STATE

CONTENTS

UNIT – I

GASEOUS AND SOLID STATE

1.1 OBJECTIVES

- To know about the different types of molecular velocities and the relationship between them.
- To understand the Maxwell's distribution of molecular velocities.
- To learn the laws of crystallography
- To study the imperfections in crystals.

1.2 INTRODUCTION

Matter is anything that has mass and occupies space . All matter exist in three states : solid , liquid and gas. A substance may be made to exist in anyone of the state by varying the temperature or pressure or both . For example water exists as liquidat ordinary temperature and pressure and can be converted into solid state (ice) by cooling at 0^0C at atmospheric pressure and may be changed into gaseous state (steam) by heating to 100^0C at atmospheric pressure.

A substance is considered to be a gas if under atmospheric pressure , its boiling point is below the room temperature ; to be a liquid if under atmospheric pressure , its freezing point is below the room temperature and to be a solid if , under atmospheric pressure its melting point is above the room temperature.

Differences between solids , liquids and gases

S.No	Property	Solid	Liquid	gas
1	Shape	Definite shape	No definite shape	No definite shape
2	Arrangement of molecules	particles are closely packed in an orderly arrangement.	Particles are loosely packed compared to solids in a disordered manner.	Particles are loosely packed in random arrangement.
3	Intermolecular attraction	Force of attraction between molecules is strong.	Force of attraction between molecules is intermediate.	Force of attraction between molecules is less.
4	Volume	Definite volume	Definite volume	Indefinite volume
5	compressibility	Cannot be compressed	Cannot be compressed	Can be compressed
6	K.E of particles	K.E of particles is minimum	K.E of particles is more than solid.	K.E of particles is maximum.
7	Density	Highest density	Density lower than	Lowest density

			solid	

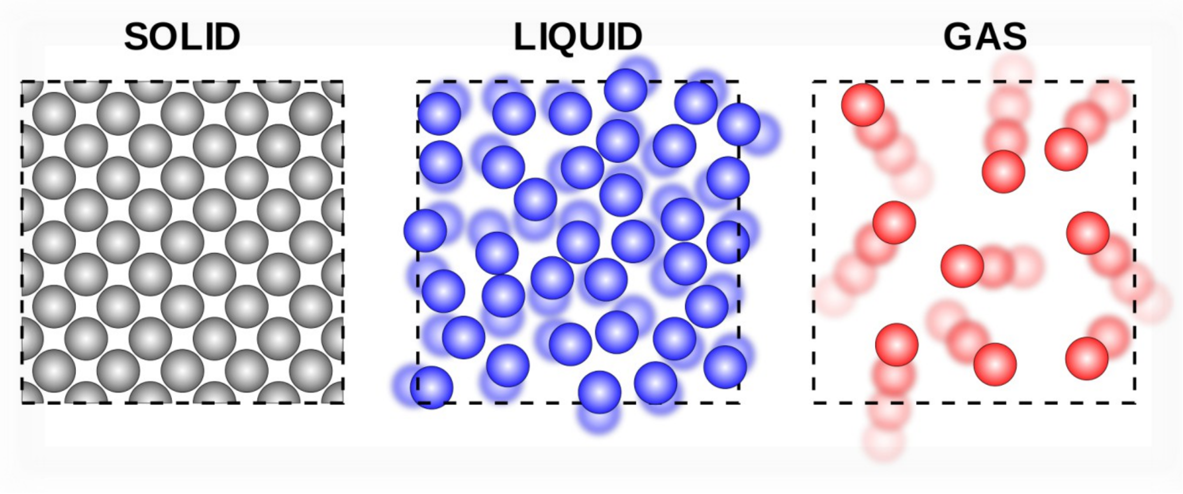


Fig : Molecular representation of solid , liquid and gaseous state

Molecules in all states of matter are in a state of constant motion. In solid state only vibratory motion exists, in liquid state vibratory and rotator motions and in gaseous state, all the three types of motion, namely , vibratory , rotator and translator motions. Molecules therefore possess energy of motion or kinetic energy. It is for this reason that the theory which describes the behaviour of gases is called the Kinetic theory of gases.

1.3 Maxwell’s Law of Distribution of Molecular Velocities

All the molecules in a given sample of a gas do not have the same velocity. The molecules are colliding with one another frequently and hence their velocities keep on changing. Since the number of molecules is very large , a fraction of molecules will have the same particular velocity. The distribution of molecules between different possible velocities was worked out by Maxwell by applying probability considerations. He showed that the distribution of molecular velocities is given by the expression

$$\frac{dN}{N} = 4\pi C^2 \left[\frac{M}{2\pi RT}\right]^{3/2} e^{\frac{-MC}{2RT}} dc$$

Where dN - number of molecules having velocities between C and (C + dc)

N - Total number of molecules.

M - Molecular mass

R - Gas constant

T - Temperature

The relation stated above is called **Maxwell's law of distribution of velocities**. The ratio dN/N gives the fraction of the total number of molecules having velocities between C and (C + dc). Maxwell plotted such fractions against velocity possessed by the molecules. The curves so obtained illustrate the salient features of Maxwell distribution of velocities.

1.3.1 Graphical representation of Maxwell's distribution of molecular velocities

The fraction of molecules $(\frac{1}{N}\cdot\frac{dN}{dC})$ having velocities greater than zero increases with an increase in velocity , reaches a maximum and then falls off towards zero again at higher velocities.

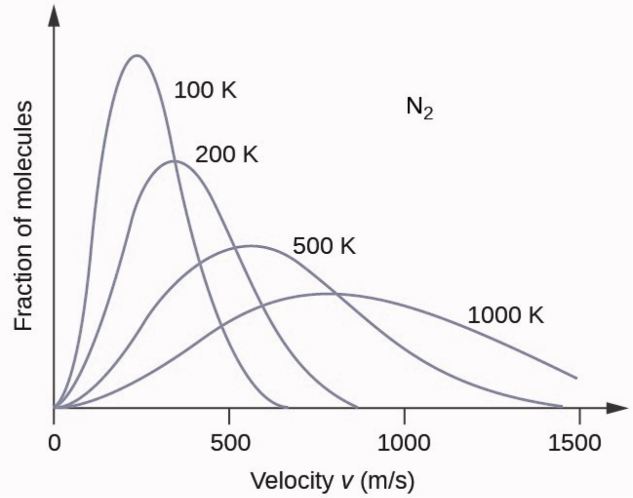


Fig: **Maxwell's distribution of molecular velocity of a gas at different temperature**

Important features

1. The number of molecules having very low or very high velocities is very small.
2. Most molecules possess velocities close to an average velocity represented by the peak of the curve. ie., the velocity possessed by maximum number of molecules of the gas at a given temperatute . This velocity is called the **most probable velocity**.
3. At higher temperature , the whole curve shifts to the right. This shows that at higher temperature more molecules have higher velocities and fewer molecules have lower velocities.

1.4 Types of molecular velocities

On the basis of kinetic theory of gases , there are three different kinds of molecular velocities. They are

1. The Average velocity (c_{av})
2. The Root Mean Square velocity (c_{rms})
3. The Most Probable velocity (c_{mp})

1.4.1 The Average Velocity

It is the average of the velocities of all the molecules present in the gas. If there are n molecules of a gas having individual velocities c_1, c_2 , c_3 ..... c_n , then

$$C_{av} = \frac{c1 + c2 + c3 \ldots\ldots cn,}{n}$$

Using Maxwell’s distribution law

$$C_{av} = \sqrt{\frac{8\,KT}{\pi\, m}} \quad \text{or} \quad \sqrt{\frac{8\,RT}{\pi\, M}}$$

1.4.2 Root Mean Square Velocity or RMS velocity (C_{rms})

It is the root of the mean of the square velocities of all the molecules present in the gas. If there are ‘ n’ molecules with velocities c_1, c_2 , c_3 ..... c_n , then

$$C_{rms} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \ldots\ldots\ldots c_n^2}{n}}$$

Using Maxwell’s distribution law ;

$$C_{rms} = \sqrt{\frac{3\,RT}{M}}$$

1.4.3 Most probable velocity (C_{mp})

It is the velocity possessed by maximum number of molecules in the gas.

$$C_{mp} = \sqrt{\frac{2\,RT}{M}}$$

1.4.4 Relationship between RMS velocity , Average velocity and Most probable velocity

The RMS velocity and Average velocity are given by the expression

$$C_{rms} = \sqrt{\frac{3RT}{M}}$$

$$C_{av} = \sqrt{\frac{8RT}{\pi M}}$$

$$C_{av} / C_{rms} = \sqrt{\frac{8RT}{\pi M}} \text{ X } \sqrt{\frac{M}{3RT}} = \sqrt{\frac{8}{3\pi}}$$

$$= 0.9213$$

Therefore , $C_{av} = 0.92 \text{ X } C_{rms}$

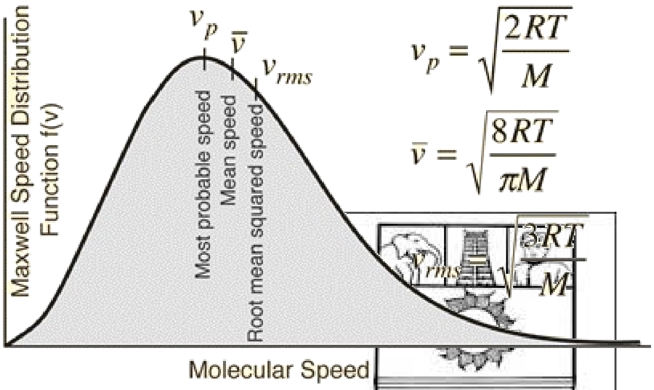
The expression for most probable velocity is

$$C_{mp} = \sqrt{\frac{2RT}{M}}$$

$$C_{mp} / C_{rms} = \sqrt{\frac{2RT}{M}} \text{ X } \sqrt{\frac{M}{3RT}} =$$

$$\sqrt{\frac{2}{3}} = 0.8165$$

Or , $C_{mp} = 0.82 \times C_{rms}$



Problem:

Calculate the RMS , average velocity and most probable velocity of hydrogen gas at 0^0C.

Given T = 0^0C = 273 K

Molecular mass of $H_2 = 2.016 \times 10^{-3}$ Kgmol^{-1}

$$C_{rms} = \sqrt{\frac{3\,RT}{M}} = \sqrt{\frac{3\,X\,8.314\,X\,273}{2.016\,X\,10-3}} = 1.84 \times 10^3 \text{ m/s}$$

$$C_{av} = \sqrt{\frac{8\,RT}{\pi\,M}} = \sqrt{\frac{8\times 8.314\times 273}{3.14\times 2.016\times 10-3}} = 1.69 \times 10^3$$

m/s

$C_{mpv} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2\times 8.314\times 273}{2.016\times 10-3}} = 1.5 \times 10^{3}$ m/s

1.5 Solids

In solids ,atoms ,ions and molecules are held together by relatively strong chemical forces – ionic bond , covalent bond or by intermolecular vanderwaal's forces. The molecules do not move but they vibrate to some extent in their fixed position.They are rigid and have definite shape.

Solids are of two types

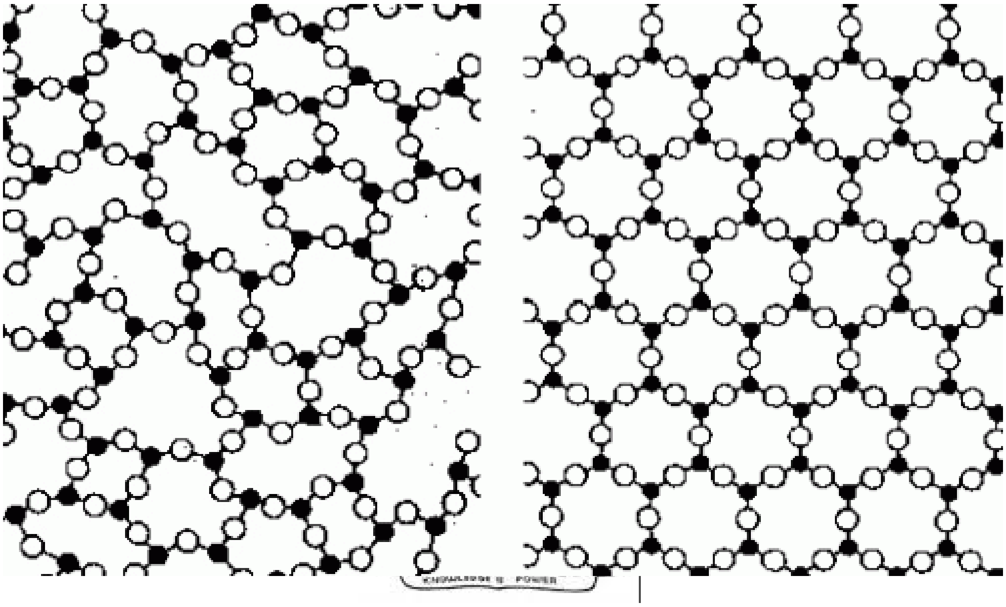
1. Crystalline solid
2. Amorphous solids

Crystalline solids:

In crystalline solids the atoms , molecules or ions are arranged in regular orderly arrangement. They have definite shape and sharp melting point. The constituent particles (atoms , molecules or ions) are arranged in long- range order. Crystalline solids have crystal symmetry. They possess anisotropic property . Examples are sodium chloride , sugar etc.

Amorphous solids:

In amorphous solids , the atoms , molecules or ions are arranged in random. So they do not have definite shape. They donot possess sharp melting point. The constituent particles are arranged in a short- range order. They do not have symmetry . They possesss isotropic property. Glass , rubber , plastic etc are examples of amorphous solids.



(a) (b)

Fig : (a) Amorphous solid (b) Crystalline solid

Differences between Crystalline and Amorphous solids

Crystalline Solids	**Amorphous Solid**

1)	They have a regular three dimensional arrangement of atoms, ions or molecules. So they have definite shape.	They do not have regular arrangement of particles, so they do not have definite shape.
2)	They have long range order	They have short range order
3)	They have sharp melting point i.e., they melt at a particular temperature.	They do not have sharp melting point i.e., they melt over a range of temperature.
5)	They are anisotropic, i.e., they have different properties in different directions.	They are isotropic, i.e., they have same properties in all directions.
6)	They possess elements of symmetry.	They do not possess elements of symmetry.

Some common terms used in crystallography:

- **Faces** : The crystals are bounded by a numbr of flat surfaces called faces. A cube has six faces.
- Edge : An edge is formed by the intersection of two adjacent faces. A cube has 12 edges.
- Interfacial angle : The angle between any two successive faces or planes in a crystal is known as interfacial angle. The interfacial angle is 90^0 for a cube.
- Crystal lattice or Space lattice : A space lattice is an array of points showing how molecules , atoms or ions are arranged in three –dimensional space.
- Unit cell : A unit cell is the smallest repeating unit in space lattice that represents the entire crystal.

1.6 Laws of crystallography

There are three important laws . They are

1. Law of constancy of interfacial angle.
2. Law of rational indices.
3. Law of symmetry

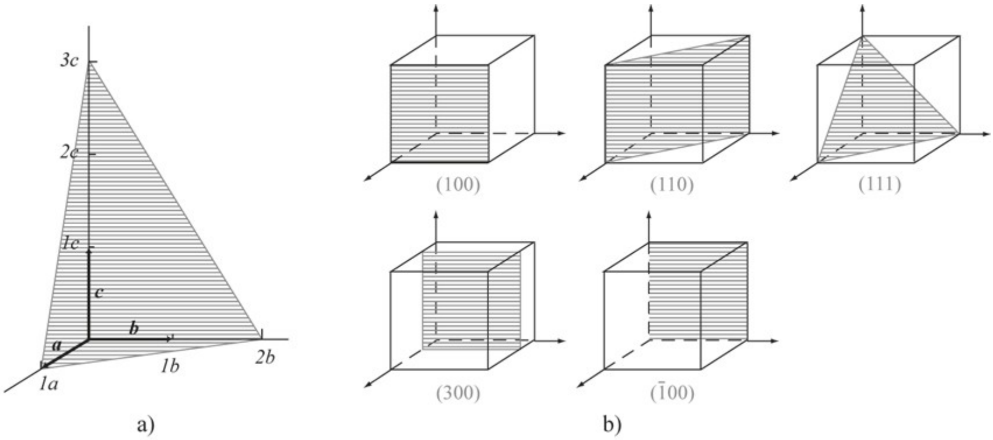
Law of constancy of interfacial angle:

The law states that , “ the interfacial angles between any two corresponding faces of the crystal remain invariably the same throughout”.

Law of rational indices (Hauy’s law):

This law states that ,“ the intercepts of any plane of a crystal along the crystallographic axes are small integral multiples of the intercepts made by the unit plane”.

Let OX, OY and OZ represent the three crystallographic axes and let ABC be a unit plane. The unit intercept will then be a, b and c. Then the intercept of any plane LMN will be a simple whole number multiple of a,b and c respectively. The intercepts may be la : mb : nc .



Law of symmetry:

According to this law , “ all crystals of the same substance possess the same elements of symmetry”.

1.6.1 Symmetry elements in crystals

There are three types of symmetry elements in crystals. These are called the Elements of symmetry.

1 . Plane of symmetry :

It is an imaginary plane that passes through the crystal and divide it into two parts such that one part is an exact mirror image of the other. A cube has 9 planes of symmetry (3 rectangular and 6 diagonal planes of symmetry).

2 . Centre of symmetry :

It is a point at the centre of the crystal so that any line drawn through it will intersect the surface of the crystal at equal distances in both directions. A cube has only one centre of symmetry.

3 **. Axis of symmetry:**

It is an imaginary line drawn through the crystal such that during rotation of crystal through 360^0 , the crystal presents exactly the same appearance more than once.

If the same appearance occurs twice during the complete rotation it is known as two-fold or diad axis . If the similar appearance occurs thrice during the complete rotation , then it is three-fold or triad axis and if it occurs four times , it is known as four-fold axis of symmetry.

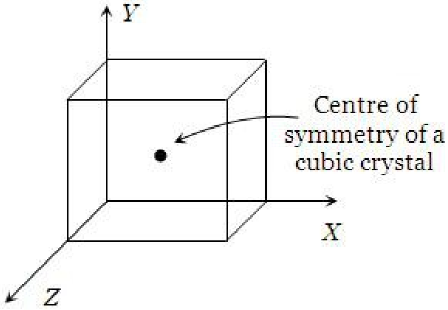
A crystal has 13 axis of symmetry (6 two-fold , 4 three-fold and 3 four-fold axis of symmetry).

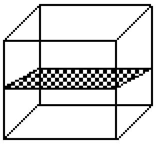
Totally a cube has 23 elements of symmetry. They are

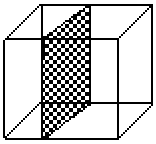
1 . Planes of symmetry -9

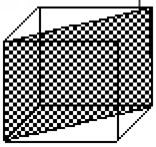
2 . Centre of symmetry – 1

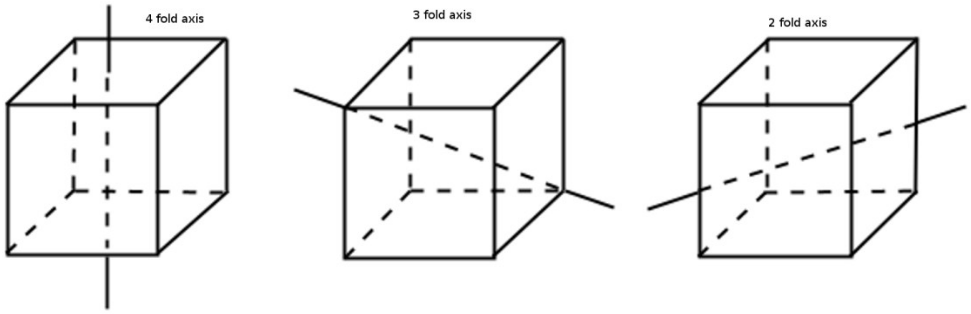
3 . Axis of symmetry - 13




Plane of symmetry


Rectangular plane of symmetry


Diagonal plane of symmetry



1.7 Bragg's Equation

W.H.Bragg worked out a mathematical relation to determine interatomic distances from x-ray diffraction. This relation is called the Bragg's equation .

$$n \lambda = 2 d \sin \theta$$

where n – order of reflection

λ - wavelength of x-rays

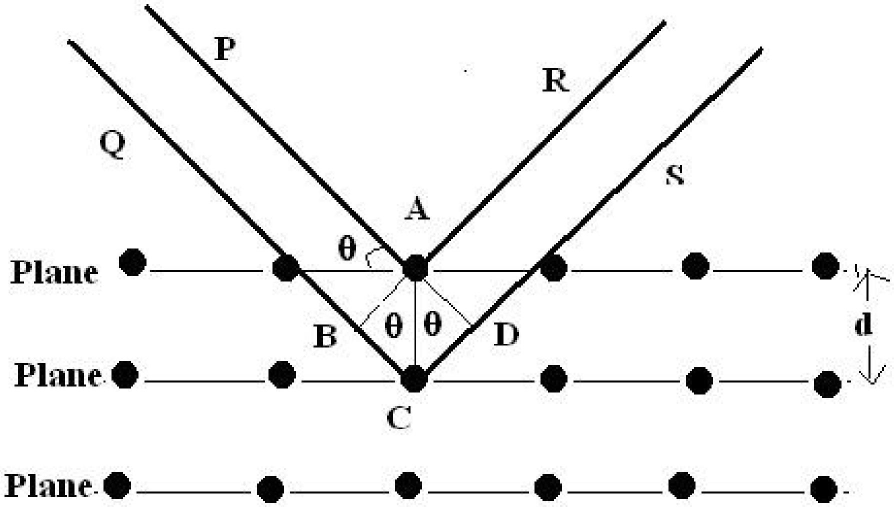
d – interplanar distance

glancing angle or diffraction angle

Derivation

Consider a beam of x-rays of wavelength λ falling on the crystal surface with an angle of incidence θ . Some of the rays are reflected with the same angle.Let 'd' be the distance between two successive crystal planes . The ray PA is reflected from the first plane along AR.The second beam gets reflected from the second plane and it has to travel a longer distance than first beam.this path difference is equal to BC + CD .For maximum reflection the path difference between the two rays must be equal to an integral multiple of wavelength.

ie., $BC + CD = n\lambda$ ………….. (1)



consider Δ BAC , $\sin\theta = \frac{BC}{AC}$

$\sin\theta = \frac{BC}{d}$ (since AC = d)

$d \sin\theta = BC$ .... (2)

From figure BC = CD

Substituting the values in Equ (1)

$d\sin\theta + d\sin\theta = n\lambda$

$$\mathbf{n\lambda = 2d\sin\theta}$$

This equation is known as **Bragg's equation.** The reflection corresponding to n = 1 is called the first order reflection and for n = 2 is second order reflection and so on.

Significance of Bragg's equation

Bragg's equation is used to determine the interplanar distance (d) in crystals.

$$d = \frac{n}{2\, sin\theta}$$

Problems:

1 . Find the interplanar distance in a crystal in which a series of planes produce a first order reflection from a copper x-ray tube (λ = 1.539Å) at an angle 22.5^0C.

Given n = 1 , $\theta = 22.5^0$C and λ = 1.539Å = $1.539 \text{ X } 10^{-10}$ m

Bragg's equation is $n\lambda = 1.539 \text{ X } 10^{-10}$

So, $$d = \frac{n}{2\sin\theta}$$

$$= \frac{1.539\, X\, 10-10}{2\, dsin(22.5)}$$

$= 2.01 \times 10^{-10}$ m

1.8 Imperfection in crystals

An ideally perfect crystal is one which has orderly arrangement of atoms or ions through out the crystal. But crystals are never actually perfect . The term imperfection or defect is used to describe any deviation from this orderly arrangement of atoms or ions in the crystal.The defects generally occur in crystals are point defects , line defects and plane defects

Point defects occurs due to missing atoms or dislocated atoms from its proper position.Such defects may occur due to imperfect packing or from thermal vibrations of atoms at elevated temperatures. The most common point defects are Schottky and Frenkel defects.

1.8.1 Schottky defects

Schottky defect is also known as ion vacancy. This defect arises due to missing of ions from the crystal lattice. One positive ion and one negative ion is missing. The ions left its position causing a vacancy or hole.

Schottky defect occurs in compounds which have

- High coordination number.
- Positive and negative ions are of similar size.
- Examples are NaCl , KCl , CsCl etc.

The number of Schottky defects (n) formed in a crystal at a given temperature is given by the Boltzmann's relation

$$n = N e^{-(E/2KT)}$$

where N – total number of atoms in the crystal.
E – Energy required to form Schottky defect
K – Boltzmann constant
T – Absolute temperature.

Consequences:

Because of Schottky defect

- the crystal is able to conduct electricity.
- The density of the crystal is low.

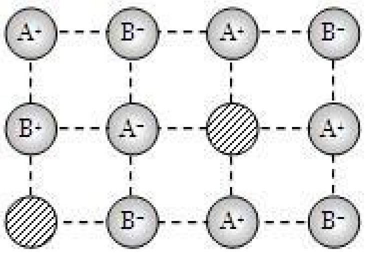


Fig : Schottky defect

1.8.2 Frenkel defect

Frenkel defect arises when an ion moves from its proper position to interstitial position. This also produces a hole or vacancy in the crystal.

Frenkel defect occurs in compounds which have

- Low coordination number.
- Anions are larger in size than cations.
- Examples are ZnS , AgCl etc.

The number of Frenkel defects (n) present in a crystal at a given temperature is given by the Boltzmann relation

$$n = (NN_i)^{1/2} e^{-(E / 2KT)}$$

where N_i – total number of interstitial position

N – total number of atoms or ions

E - energy required to form Frenkel defect

K - Boltzmann constant

T - Absolute temperature

Consequences : Frenkel defect leads to

- Increase in dielectric constant.
- Conductivity in crystals.

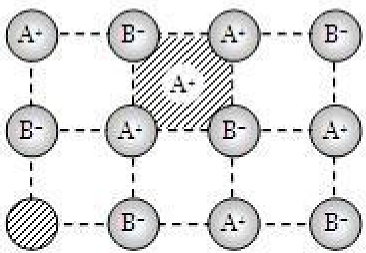


Fig : Frenkel defect

1.9 Self Evaluation

1 . According to Maxwell , the fraction of molecules moving with velocities zero and infinity is

(a) Zero (b) infinity (c) low (d) very high

2.At higher temperature the molecular velocity is

(a) Lower (b) higher (c) remains same (d) none

3.The total elements of symmetry of a cube is

(a) 15 (b) 32 (c) 23 (d) 9

4.The example for Frenkel defect is

(a) AgCl (b) NaCl (c) KCl (d) none

5.The value of average velocity is

(a) 0.72 x C_{rms} (b) 0.62xC_{rms} (c) 0.82 x C_{rms} (d)0.92x C_{rms}

Answers

1. (c) 2.(b) 3. (c) 4. (a) 5. (c)

Answer the following

1. State and explain Maxwell's distribution of molecular velocities.
2. Explain the different types of molecular velocities. How they are related to each other?
3. Derive Bragg's equation. Give its significance.
4. State and explain the laws of crystallography.
5. Write a short note on Schottky defect.

……

UNIT – II

SOLUTIONS

CONTENTS

UNIT – II

SOLUTIONS

2.1 OBJECTIVES

- To know the basic meaning of solution, solute and solvent. The classification of solutions and methods of expressing its concentration.
- To study Henry’s law that explains the solubility of a gas in liquid

- To study what is a binary liquid mixture and its classification
- To study Raoult's law for a binary liquid solution, classification as Ideal and non-ideal solutions and their characteristics,
- To study the classification of binary liquid mixtures as Type-I, Type-II and Type-III on the basis of their vapour pressure versus composition relationship and the principles behind the fractional distillation of these types and Azeotropes.

2.2 INTRODUCTION

The very fact that most of the chemical reactions done at different levels of science are mostly in solutions makes the study of it an important area in chemistry. It requires a comprehensive study starting from its components, classification, characteristics, laws that govern its behaviour, its relation with other phenomenon and its properties. This chapter gives a brief outline of solutions, especially binary liquid solutions so that the further interest of student in this area is made lucid.

2.3.1 Solution

A homogeneous mixture of two or more chemically non-reacting substances, whose relative amounts may be changed within certain limits, is called a *solution.*

2.3.2 Solute

The component which is present in lesser proportion in a solution is known as solute.

2.3.3 Solvent

The component which is present in larger proportion, and whose physical state is the same as that of the solution, is known as *solvent*.

2.3.4 Types of Solutions

The common binary solutions that we come across are those where the solute is a solid and the solvent is a liquid. Depending on the type of the physical states of solute and solvents there are seven types of solutions.

	Solute	**Solvent**	**Example**
1.	Gas	Gas	Air
2.	Gas	Liquid	Oxygen in water
3.	Gas	Solid	Adsorption of H_2 by Palladium
4.	Liquid	Liquid	Ethyl alcohol in water
5.	Liquid	Solid	Mercury in Zinc amalgam
6.	Solid	Liquid	Common salt in water
7.	Solid	Solid	

			Metal alloys

2.3.5 Methods for expressing concentration

There are several ways of expressing the concentration of a solution:

1. **Molarity (M)**

   It is the number of moles of a solute present in 1 dm^3 of a solution. If n moles of solute are present in V dm^3 of a solution , then

$$\text{Molarity} = \frac{\textit{Number of moles of the solute}}{\textit{Volume of the solution} \in dm\,3}$$

$$M = \frac{n}{V} \quad \text{mol dm}^{-3} \text{ or mol L}$$

$$= \frac{w}{MV} \qquad (\text{since } n = \frac{w}{M})$$

where w is the mass of the solute

M is the molar mass of the solute and

V is the volume of the solution in dm^{-3} (L)

2. **Molality (m)**

   It is the number of moles of a solute present in 1 kg of a solvent.

$$\text{Molality} = \frac{\textit{Number of moles of the solute}}{\textit{Mass of the solvent} \in Kg}$$

$$m = \frac{n}{w} \text{ mol Kg}^{-1}$$

If w_2 is the mass of solute dissolved in w_1 mass of solvent , then

$$m = \frac{w2}{Mw1}$$

3. Normality (N)

It is the number of gram equivalents of a solute present in 1 dm^3 of a solution.

$$\text{Normality} = \frac{Number\ of\ gram\ equivalent\ of\ solute}{Volume\ of\ solution \in dm3}$$

$$N = \frac{n}{V}$$

4. Mole Fraction(χ)

It is the number of moles of the solute or solvent present in a solution.

$$\text{Mole fraction } (\chi) = \frac{Number\ of\ moles\ of\ a\ consituent}{Total\ number\ of\ all\ constituents}$$

e.g. For a two component system containing A and B, The mole fraction of A is given as $\chi_A = \frac{nA}{nA+nB}$

The mole fraction of A is given as $\chi_B = \frac{nA}{nA+nB}$

where n_A and n_B are the number of moles of A and B respectively.

Hence $\chi_A + \chi_B = 1$

5. Mass Fraction*(w)*

Mass fraction of a constituent in a solution is the mass of that constituent divided by the total mass of all the constituents.

$$\text{Mass fraction} = \frac{\textit{Mass of a constituent}}{\textit{Total mass of all constituents}}$$

e.g. For a two component system containing A and B,

The mass fraction of A is given as $w_A = \frac{WA}{WA+WB}$

The mass fraction of B is given as $w_B = \frac{WB}{WA+WB}$

where w_A and w_B are the mass fraction of A and B respectively.

Hence $w_A + w_B = 1$

6. Parts Per Million (ppm)

It is the number of parts by mass of the solute in a million parts by mass of the solution.

$$\text{Number of ppm of solute} = \frac{\textit{Mass of solute}}{\textit{Mass of solution}} \text{ X } 10^6$$

e.g. For a solution containing a solute A and solvent B

No of ppm of A is given as $ppm_A = \frac{WA}{WA+WB} \times 10^6$

2.4 SOLUBILITY OF GASES IN LIQUIDS

2.4.1 Henry's law of gas solubility

Henry's law states as, "The mass of a gas dissolved in a given volume of the liquid at constant temperature is directly proportional to the pressure of the gas present in equilibrium with the liquid".

Mathematically, $m \propto p$

or $m = k\,p$

where m = mass of the gas dissolved in a unit volume of the solvent.

p = pressure of the gas in equilibrium with the solvent.

k = Henry's law constant, characteristic of the nature of the gas, solvent and temperature.

2.5 SOLUTIONS OF LIQUID IN LIQUID

2.5.1 Binary liquid solutions or mixtures

It is a solution containing two liquids.

2.5.2 Classification of binary liquid mixtures

Depending on the relative solubility of one liquid in another liquid there are three types of binary mixtures.

1. **Completely miscible liquids**

   In this type the two liquids are miscible in each other in all proportions.

   e.g. Benzene in toluene and ethyl alcohol in water.

2. **Partially miscible liquids**

   In this type a liquid is soluble in another to a partial extent.

   e.g. Phenol in water and nicotine in water.

3. **Immiscible liquids**

   In this type the two liquids do not dissolve in each other and remain separated.

   e.g. Benzene and water, carbon tetra chloride and water.

2.6.1 Raoult's law for a binary liquid solution

"The partial vapour pressure of any volatile component of a solution is equal to the product of mole fraction of that component in the solution and the vapour pressure of the pure component at that temperature".

Considering a binary solution of two liquids, A and B, consisting of n_A moles of A and n_B moles of B.

Then, partial vapour pressure of A is given by

$$P_A = \frac{nA}{nA+nB} \, .P^0_A \quad \text{or} \quad P_A = = \chi_A \, . \, p^0_A$$

The partial vapour pressure of B is given by,

$$P_B = = \frac{nB}{nA+nB} \, .P^0_B \quad \text{or} \quad P_B = = \chi_B \, . \, p^0_B$$

where p^0_A and p^0_B represent the vapour pressures of pure A and B at that temperature.

Therefore the total vapour pressure of the solution

$$P = P_A + P_B$$

2.6.2 Ideal and non-ideal solutions

In a binary solution of two liquids there are two types: Ideal solutions and Non-ideal solutions.

1. **Ideal solutions:** A solution of two (or more) liquids which obeys Raoult's law at all concentrations

and temperatures is called an ideal solution.

e.g. Benzene + Toluene, Ethyl bromide + ethyl iodide.

2. Non-ideal solutions: A solution of two (or more) liquids which do not obey Raoult's law is called non-ideal solution.

e.g. Ethyl alcohol + water, HCl + water.

2.6.3 Characteristics of ideal and non-ideal solutions

Ideal solution	Non-ideal solution
1. The forces of molecular interactions of the components in the solution are the same as in the pure components.	1. The forces of molecular interactions of the components in the solution are different from those in the pure components.
2. There is no change in volume on mixing the components. $\Delta V_{mix} = 0$.	2. There is a change in volume on mixing the components. $\Delta V_{mix} \neq 0$.
3. There is no change in enthalpy on mixing the components. $\Delta H_{mix} = 0$.	3. There is change in enthalpy on mixing the components. $\Delta H_{mix} \neq 0$.
4. Component obeys Raoult's law at all temperature and concentration. $p_A = \chi_A \cdot p^0_A$, $p_B = \chi_B \cdot p^0_B$	4. Component does not obey Raoult's law. $p_A \neq \chi_A \cdot p^0_A$, $p_B \neq \chi_B \cdot p^0_B$

2.7 BINARY MISCIBLE LIQUID MIXTURES

2.7.1 Classification

Based on boiling point-composition curves, the completely miscible binary liquid mixtures are classified into three types:

1. Distillation of solution **Type-1**: Ideal system obeying Raoult's law.
2. Distillation of solution **Type-II:** Non-ideal system showing positive deviation from Raoult's law.
3. Distillation of solution **Type-III:** Non-ideal system showing negative deviation from Raoult's law.

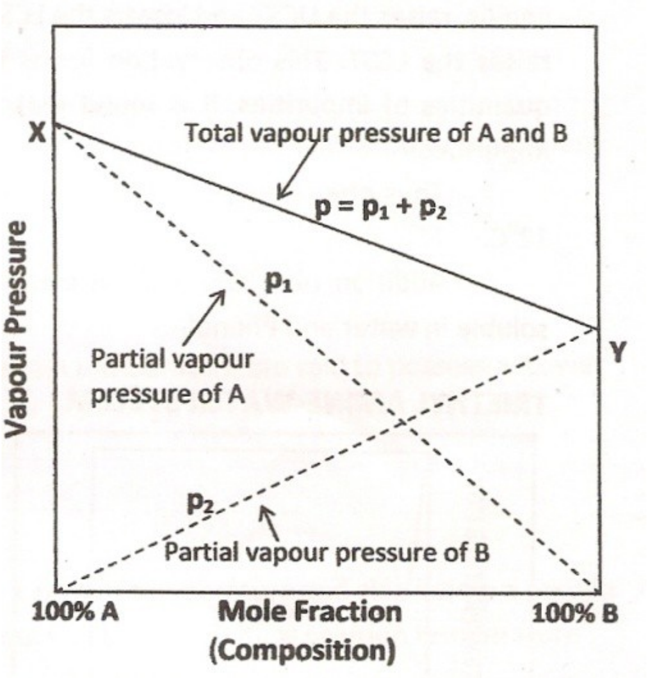
2.7.2 TYPE-I: System obeying Raoult's law - Ideal type of system

e.g. Benzene and Toluene, Benzene and Carbon tetrachloride.

The vapour pressure-composition curve for the binary mixtures, **A** and **B**, obeying Raoult's law is a straight line. The line **XY** gives the total vapour pressure of **A** and **B** in the mixture.

For the liquid mixtures, which obeys Raoult's law, the total vapour pressure lie between the vapour pressures of the pure liquids. The total vapour pressure of the mixture over the solution will be the sum of the partial vapour pressure of the components , A and B. Thus, $\mathbf{p = p_1 + p_2}$

Such a mixture leads to a system in which there is no enthalpy change on mixing ($\Delta H_{mix} = 0$) and there will be no change in volume ($\Delta V_{mix} = 0$)



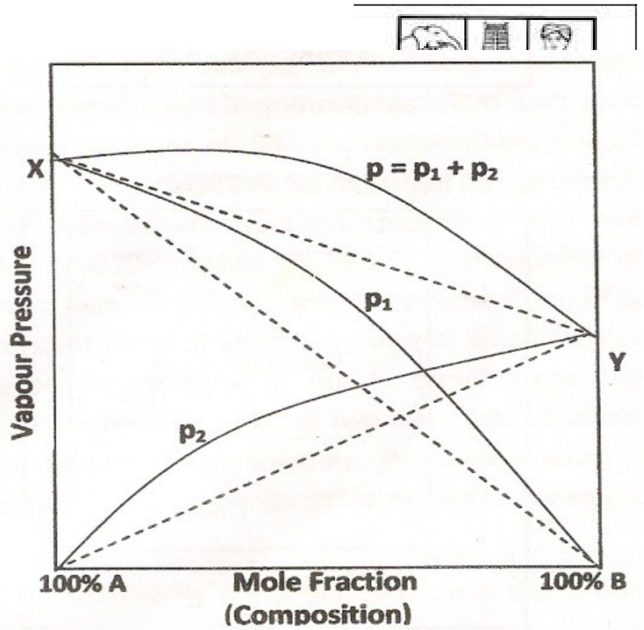
2.7.3 TYPE-2: System showing positive deviations from Raoult's law – Non-ideal type of system

e.g. Ethyl alcohol and water, Ethyl alcohol and chloroform

In this case, the vapour pressure-composition curve for the binary mixtures, **A** and **B**, and the two components lie above to those of ideal curves, i.e. they curve upwards. The dotted straight-line plots included in the graph are for ideal solution.

Here the total pressure of the solution is more than the total pressure of the solution if it were ideal. This means that the tendency for the molecules to escape from the solutions is more than from the pure liquids. This indicates that in such solutions, the inter-molecular forces of attraction between the molecules of the solution(**A-B**) are weaker than those of either of the pure components (**A-A** or **B-B** attractions)

Such a behaviour is associated with an increase in volume (**ΔV > 0**) and absorption of heat (**ΔH > 0**) on mixing.

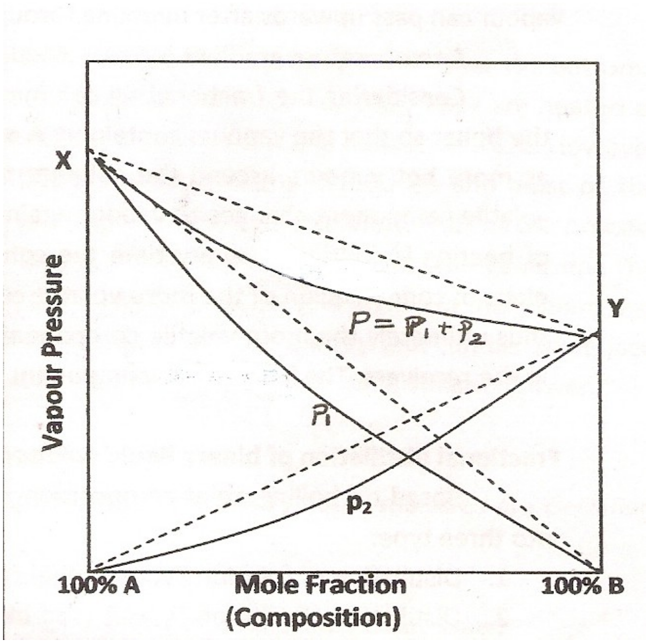


2.7.4 TYPE-3: System showing negative deviations from Raoult's law – Non-ideal type of system

e.g. Water and hydrochloric acid.

In this case, the vapour pressure-composition curve for the binary mixtures, **A** and **B**, and the two components lie below to those of ideal curves, i.e. they curve downwards. The dotted straight-line plots included in the graph are for ideal solution.

Such a behaviour is associated with a decrease in volume (**ΔV < 0**) and liberation of heat (**ΔH < 0**) on mixing.



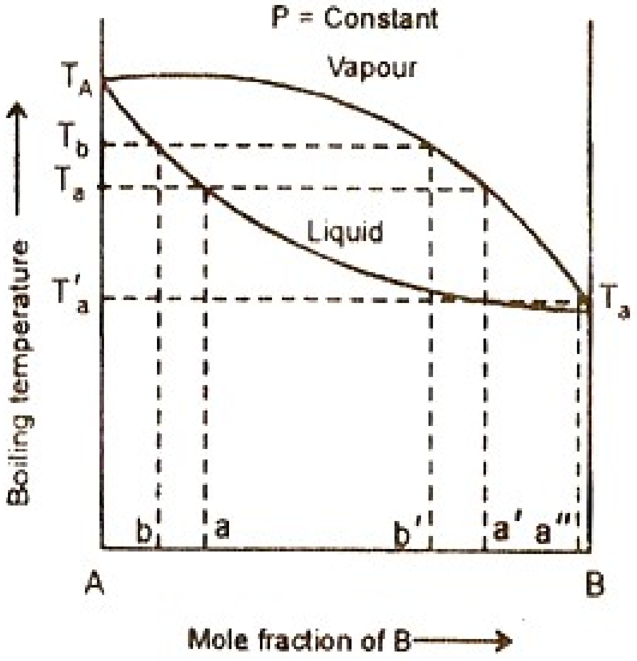
Here the total pressure of the solution is less than the total pressure of the solution if it were ideal. This means that the tendency for the molecules to escape from the solutions is less than from the pure liquids. This indicates that in such solutions, the inter-molecular forces of attraction between the molecules of the solution(**A-B**) are stronger than those of either of the pure components (**A-A** or **B-B** attractions)

2.8 FRACTIONAL DISTILLATION OF BINARY LIQUID MIXTURES (OR SOLUTIONS) - PRINCIPLES

2.8.1 Distillation of solution of Type-I: Ideal system obeying Raoult's law e.g. Benzene and Toluene

The boiling temperature-composition diagram for a solution of this type involving the liquids **A**(Toluene),less volatile, and **B**(Benzene), more volatile, is as given.

Suppose we have a solution corresponding to composition **a**. No boiling will start until temperature T_a is reached. The composition of the vapour phase at this stage will be **a'** i.e., it is richer in the component B (because **a'** > **a**). The residue, therefore, must become richer in **A** i.e., the composition of the residue shifts towards **A**, say it becomes equal to **b**. Now if the liquid mixture is heated, it will boil only when the temperature becomes equal to $\mathbf{T_b}$. The vapour will have composition corresponding to **b’** i.e., again it is richer in B and consequently the composition of the residue will be further enriched in **A**.



Thus if the process of heating the residue is continued, the boiling point of the solution will rise from the initial boiling point $\mathbf{T_a}$ towards the boiling point $\mathbf{T_A}$ of the pure liquid **A**. Moreover, every time the residue becomes richer in **A** than the original solution. This means that if the process is continued sufficiently long time, a final residue of pure **A** can be obtained.

Further, the vapour obtained in the first stage are condensed, a liquid mixture corresponding to **a’** is obtained. Now if this liquid mixture is distilled, it will boil when the temperature becomes $\mathbf{T_a}$’. The composition of the vapours coming off will correspond to the point **a”** i.e. the vapours have become richer in **B** than the original solution. This means that if the process of condensing the vapour and redistilling the liquid mixture is continued, until a distillate of pure **B** is obtained.

Thus a liquid mixture of Type-I can be separated completely by fractional distillation.

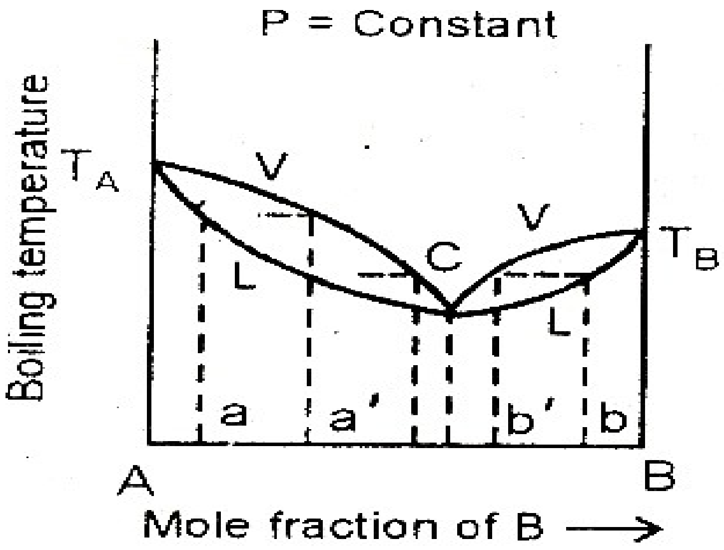
2.8.2 Distillation of solution of Type-II: Non-ideal system showing positive deviation from Raoult’s law.

e.g. Ethyl alcohol and water

The boiling temperature-composition diagram for the solutions of this type involving the liquids **A**(Water),less-volatile, and **B**(Ethyl alcohol),more volatile, is as shown.

The boiling point- composition curves of the liquid and vapour meet at the minimum point **C**. At the point **C**, both liquid and vapour have the same composition. The liquid mixture represented by the point **C** will boil at constant temperature and will distill completely without change of composition. This mixture is known as ***azeotropic mixture***. It is not possible to separate the components from such a mixture by distillation.

Considering the distillation of a mixture of composition **a**.



Then the first fraction obtained will have a composition shown by **a'**. The mixture is richer in the constant boiling mixture. The composition of the residual liquid, therefore, will shifts towards **A**. As the distillation proceeds, the composition of the distillate changes towards **C** and that of the residual solution towards **A**. Ultimately by repeated fractional distillation, the mixture of the minimum point of composition **C** will be obtained as distillate and the pure liquid **A** will be left as residue in the distillation flask.

If, on the other hand, a mixture of composition **b** is distilled, the composition of the first fraction will be represented by **b'**. Evidently, it will be richer in the constant boiling mixture. Therefore, the composition of the residual liquid will be richer in **B**. As the distillation proceeds, the successive fractional distillates will become increasingly rich in the constant boiling mixture while the residual liquid will increasingly rich in the pure component **B**. Ultimately by repeated fractional distillation, the mixture of the minimum point of composition **C** will be obtained as distillate and the pure liquid **B** will be left as residue in the distillation flask.

Thus a liquid mixture of Type-II can be separated into azeotropic mixture, pure A and pure B, by fractional distillation.

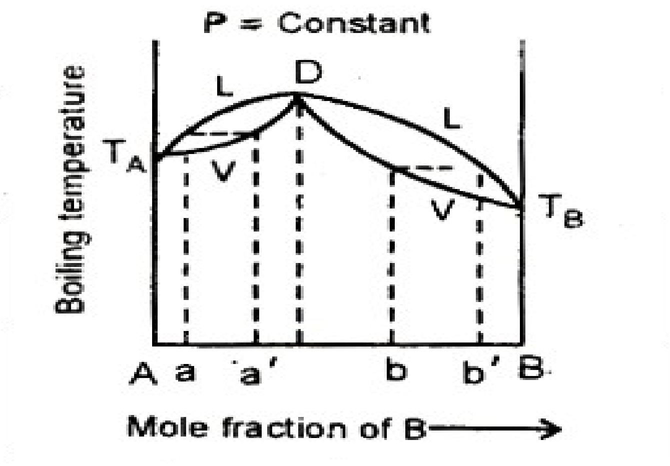
2.8.3 Distillation of solution of Type-III: Non-ideal system showing negative deviation from Raoult's law.

e.g. Water and hydrochloric acid

The boiling temperature-composition diagram for the solutions of this type involving the liquids **A**(Water),less-volatile, and **B**(hydrochloric acid),more volatile, is as shown.

The boiling point- composition curves of the liquid and vapour meet at the maximum point **D**. At the point **D**, both liquid and vapour have the same composition. The liquid mixture represented by the point **D** will boil at constant temperature and will distils completely without change of composition. This mixture is known as ***azeotropic mixture***. It is not possible to separate the components from such a mixture by distillation.

Considering the distillation of a mixture of composition **a**. Then the first fraction obtained will have a composition shown by **a'**. The mixture is richer in the constant boiling mixture.



The composition of the residual liquid, therefore, will shifts towards **A**. As the distillation proceeds, the composition of the distillate changes towards **D** and that of the residual solution towards **A**. Ultimately by repeated fractional distillation, the mixture of the maximum point of composition **D** will be obtained as distillate and the pure liquid **A** will be left as residue in the distillation flask.

If, on the other hand, a mixture of composition **b** is distilled, the composition of the first fraction will be represented by **b'**. Evidently, it will be richer in the constant boiling mixture. Therefore, the composition of the residual liquid will be richer in **B**. As the distillation proceeds, the successive fractional distillates will become increasingly rich in the constant boiling mixture while the residual liquid will increasingly rich in the pure component **B**. Ultimately by repeated fractional distillation, the mixture of the maximum point of composition **D** will be obtained as distillate and the pure liquid **B** will be left as residue in the distillation flask.

*Thus a liquid mixture of Type-III can be separated into azeotropic mixture, pure **A** and pure **B**, by fractional distillation.*

2.8.4 Azeotropic Mixtures:

Mixtures of liquids which boil at constant temperature like a pure liquid such that the distillate has the same composition as the liquid mixture are called constant boiling mixtures or azeotropic mixtures or simply azeotropes.

These azeotropes are of two types:

1. **Minimum boiling point azeotropes:**

   These azeotropes are formed by those liquid pairs, which show positive deviation from ideal behavoiur. Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is the highest and hence the boiling point is the lowest. Such azeotropes have boiling points lower than that of the pure components.

   e.g. *Ethyl alcohol*(B.P. = 78.3^{0}C) and *water* (B.P. = 100^{0}C) combine in a composition of 95.57% and 4.43% respectively to form an azeotropic mixture with a constant boiling point of 78.15^{0}C.

2. **Maximum boiling point azeotropes:**

   These azeotropes are formed by those liquid pairs, which show negative deviation from ideal behavoiur. Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is the minimum and hence the boiling point is the maximum. Such azeotropes have boiling points lower than that of the pure components.

e.g. Hydrochloric acid (B.P. = -85^{0}C) and *water* (B.P. = 100^{0}C) combine in a composition of 20.3% and 79.7% respectively to form an azeotropic mixture with a constant boiling point of 110^{0}C.

2.9 SELF EVALUATION

2.9.1 Fill in the blanks

1. Normality is the number of ……………. of a solute present in 1 dm^3 of a solution.
2. Nicotine and ……….. is an example of partially miscible liquids.
3. According to Henry's law of gas of solubility of gases, 'the mass of the gas that is soluble in a liquid is directly proportional to the …….. of the gas.
4. Mixtures of liquids which boil at constant temperature is called as ………
5. The azeotropic mixture of ethyl alcohol and water contains …..% of ethyl alcohol.

Answers: (1) gram equivalents (2) water (3) pressure (4) Azeotropic mixture (5) 95.57%

2.9.2 Answer the following

1. Define molarity
2. Calculate the normality of a solution containing 4 g of NaOH in a 100 cm^3 solution.

3. What is an ideal solution?
4. State the differences of between ideal and non-ideal solution.
5. State Raoult’s law of binary mixture.
6. What are maximum boiling point azeotropes? Explain with suitable example.
7. Explain the principle behind the fractional distillation of Type-I binary liquid mixture.

UNIT III

PHOTOCHEMISTRY

CONTENTS

UNIT – III

PHOTOCHEMISTRY

3.1 Objectives

- To know the laws of photochemistry.
- To understand the photochemical reactions.
- To study the quantum yield of various photochemical process and to determine it experimentally.
- To learn the various photophysical processes such as fluorescence and phosphorescence.

3.2 Introduction

The branch of chemistry which deals with the study of photochemical reactions is called **photochemistry.** It deals with the study of chemical reactions caused by absorption of light radiations in the visible and UV regions. The light radiations of the visible and ultraviolet regions lying between 8000Å to 2000Å wavelengths are chiefly concerned in bringing photochemical reactions. The light radiations in this region will have sufficient energy to raise the atoms or molecules from the ground state to the excited electronic state. In the excited state the atoms or molecules undergo chemical reaction easily.

The reactions which are caused by heat and in the absence of light are called **thermal or dark reactions**. The reaction that takes place by absorption of visible and ultraviolet radiations are called **photochemical reactions.**

Comparison between photochemical reactions and thermochemical reactions

THERMOCHEMICAL REACTIONS	**PHOTOCHEMICAL REACTIONS**
These reactions involve absorption or evolution of heat.	These reactions involve absorption of light.
They can take place even in absence of light i.e. dark.	The presence of light is the primary requisite for the reaction to take place.
Temperature has significant effect on the rate of a thermochemical reaction.	Temperature has very little effect on the rate of a photochemical reaction
The free energy change ΔG of a thermochemical reaction is always negative.	The free energy change ΔG of a photochemical reaction may not be negative.
They are accelerated by the presence of a catalyst.	Some of these are initiated by the presence of a photosensitizer

	.
Rate of reaction depends on concentration of reactants.	Rate of reaction depends on intensity of light.

3.2.1 Beer- Lambert's law

Statement :

When light is passed through a transparent medium , the rate of decrease of intensity with the thickness of the solution is proportional to the intensity of incident light and concentration of the solution.

$$-\frac{dI}{dl} \quad \alpha \quad I\,c$$

$$-\frac{dI}{dl} = kIc \quad \text{-------------} \quad (1)$$

Where k is a constant called molar absorption co-efficient.

C is the concentration of solution in moles/ litre

I is the intensity of radiation

$$\therefore \quad \frac{dI}{I} = kc\,dl \text{ ------------------ } (2)$$

Integration of equation (2) gives

$$\int_{I0}^{I} \frac{dI}{I} = -kc \int_{0}^{t} dl$$

$$\log \frac{I}{I0} = -\frac{kcl}{2.303} \quad \text{-----------------} \quad (3)$$

or , $$\log \frac{I0}{I} = \frac{kcl}{2.303} = \varepsilon c\, l$$

or, **$A = \varepsilon c\, l$**

where ε - molar extinction co-efficient

A - Absorbance or optical density

l - Cell length

C - concentration

3.3 Photochemical reactions

Photochemical reactions are defined as those reactions which occur by absorption of light radiations (*photons)*. The photons supply the necessary energy to the reactants enabling them to react to yield products.

The energy of the photon is given by the expression

$$E = h\nu$$

Where ν is the *frequency* and h is *Planck's constant*.

But, *frequency* $\nu = c/\lambda$ where c is the *velocity of light*.

$$E = hc / \lambda$$

The energy value of a photon is sometimes expressed in terms of *wave number* (v^{1})
which is defined as the number of wavelengths per centimetre. Wave number is the reciprocal of *wavelength* (λ) and is expressed in centimetres.

$$v^{1} \quad ¿1/¿$$

Hence energy associated with a photon may also be written as

$$E = hc \quad v1$$

It can be emphasized that a photochemical reaction requires absorption of photons of definite energy, by the reactants.

3.3.1 Primary and Secondary processes

The overall photochemical reaction may consist of

(i) Primary reaction
(ii) Secondary reaction

Primary reaction : *is one in which light radiation is absorbed by an atom or a molecule giving rise to the formation of an excited atom or an excited molecule.*

$$A \quad + \quad h\,v \quad \text{------------>} \quad A^{*}$$

Atom /molecule one quantum of light Excited atom/ molecule

Secondary reaction: *Reaction which involves the excited atom or molecules produced in the primary reaction.* The secondary process can take place in dark.

A^* ---------------→ product

Example : the decomposition of HBr occurs as follows

HBr + h ν ----------------→ H + Br primary reaction

HBr + H ----------------→ H_2 + Br secondary reaction

Br + Br ----------------> Br_2 secondary reaction

Evidently , the primary reaction only obeys the law of photochemical equivalence .The secondary reaction have no concern with the law.

3.4 Laws of Photo chemistry

There are two basic laws governing photochemical reactions.

(i) *Grotthus –Draper law*
(ii) *Stark-Einstein's law* of photochemical equivalence

3.4.1 Grotthus-Draper law

This law, first discovered by *Grotthus i*n 1818 and rediscovered by Draper in 1839.

Statement : *Only those radiations which are absorbed by a reacting system are effective in producing a chemical reaction.*

The **significance** of this law is that

- Photochemical reactions result only from the absorption of radiations. However , it does not mean that all the light radiation that is absorbed can be effective in bringing about a chemical reaction.
- In many cases , the light energy that is absorbed is merely converted into kinetic energy.
- In several other cases , the light energy that is absorbed is re-emitted as light radiation of same or some other lower frequency. This phenomenon of absorption of light radiation of one frequency and re-emission of radiation of same or lower frequency is known as fluorescence.
- The *Grotthus-Draper* law is so simple and self-evident . But it is purely qualitative in nature. It gives no idea of the relation between the absorbed radiation and the molecules undergoing change.

3.4.2 Stark- Einstein’s law of photochemical equivalence

Stark and Einstein (1905) studied the quantitative aspect of photochemical reaction by application of *Quantum theory of light*.

Statement *: Each molecule taking part in a photochemical reaction absorbs one quantum of radiation .*

One quantum of energy absorbed by molecule is

$$E = h\nu$$

Where, h is Planck's constant = 6.626×10^{-34} Js ,

ν = frequency of light

The quantum of energy absorbed per mole of reacting substance is given by

$$E = Nh\nu$$

Where N = Avagadro number

$$\text{Now}\ ,\quad \nu = c/\lambda$$

Where c is the velocity of light (3×10^{10} cm/ sec) and

λ is the wavelength of radiation absorbed

$$\mathbf{E = Nhc/\lambda}$$

3.5 Quantum yield or Quantum efficiency

Statement:

The number of molecules reacted or formed per photon of light absorbed is called as quantum yield (ϕ).

$$\phi = \frac{Number\ of\ molecules\ reacted \vee formed}{Number\ of\ photons\ absorbed}$$

$$\phi = \frac{Number\ of\ moles\ reacted \vee formed}{Number\ of\ Einstein's\ absorbed}$$

- For reactions that obey Einstein's law the quantum yield $\phi = 1$, ie., one molecule decomposes per photon.
- When two or more molecules are decomposed per photon , $\phi > 1$ and the reaction has a high quantum yield.
- If the number of molecules decomposed is less than one per photon , $\phi < 1$ and the reaction has a low quantum yield.

Examples of high quantum yield

1.Decomposition of HI

In the primary reaction, a molecule of HI absorbs a photon of light and dissociates to produce H and I. This is followed by secondary steps.

$HI + h\nu \longrightarrow H + I$ .... (1) primary process

$H + HI \longrightarrow H_2 + I$ .... (2) secondary process

$I + I \longrightarrow I_2$ .... (3) secondary process

$2HI + h\nu \longrightarrow H_2 + I_2$ overall reaction

In the overall reaction , two molecules of HI are decomposed for one photon of light absorbed. Thus the quantum yield is 2.

2.Hydrogen – chlorine reaction:

This is a well known example of a photochemical chain reaction. In the primary step , a molecule of chlorine absorbs a photon and dissociates into two Cl atoms. This is followed by the secondary reaction.

$Cl_2 + h\nu \longrightarrow 2Cl$ .... (1) primary reaction

$Cl + H_2 \longrightarrow HCl + H$ ....(2) secondary process

$H + Cl_2 \longrightarrow HCl + Cl$ .... (3) secondary process

The Cl atom used in step (2) is regenerated in step (3) . Thus the steps (2) and (3) gives a self-propagating chain reaction .This produces two molecules of HCl in each cycle . Thus one photon of light absorbed in step (1) forms a large number of HCl by repetition of reaction (2) and (3). The quantum yield of the reaction is very high and it varies from 10^4 to 10^6 .

Example of low quantum yield

Combination of H_2 and Br_2

When a mixture of hydrogen and bromine is exposed to light, hydrogen bromide is formed.

Br_2 + h ν ---------- ▭ 2 Br ....(1)

primary process

Br + H_2 -------- ▭ HBr + H ....(2) Secondary process

H + Br_2 -------- ▭ HBr + Br .... (3) “

H + HBr ------- ▭ H_2 + Br .... (4) “

Br + Br -------- ▭ Br_2 .... (5) “

The reaction (2) is extremely slow. Reactions (3) ,(4) and (5) depends on (2) and is slow. So most of Br produced in primary process recombine to form Br_2 . Thus the HBR molecules produced by absorbing one quantum is small and the quantum yield of the reaction is 0.01.

3.5.1 Experimental determination of Quantum yield

Quantum yield = $\frac{\text{Number of molecules reacted} \vee \text{formed}}{\text{Number of quantum of light absorbed}}$

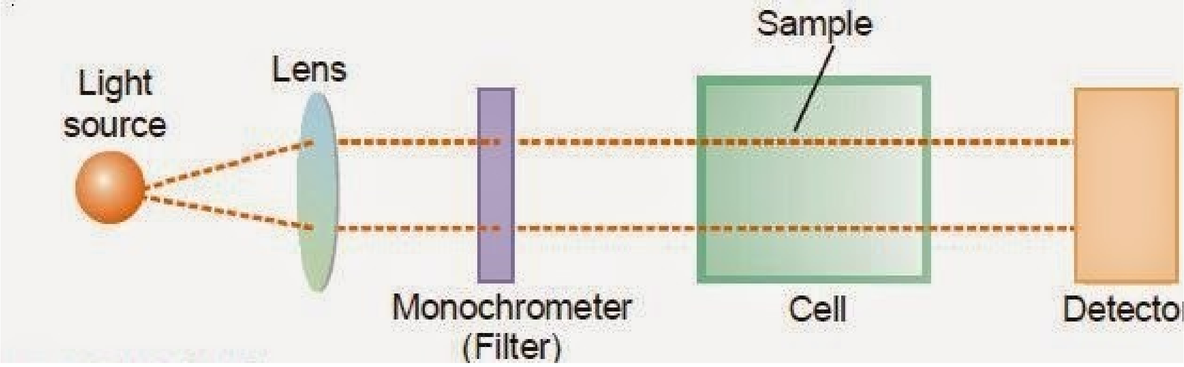
Quantum yield of a photochemical reaction is determined by knowing

(i) The number of molecules reacted in a given time and

(ii) The number of quantum of light absorbed at the same time.

The number of moles reacting in a given time can be determined by the usual analytical techniques used in chemical kinetics.

The number of quantum of light absorbed is measured using chemical actinometer



,.Fig . 1 Schematic diagram of apparatus used for measurement of light intensity

Light beam from a suitable source (tungsten filament or mercury vapour lamp) is made parallel by the lens and then passed through a filter which yield a monochromatic light. The monochromatic light then enters the reaction cell made of quartz. The unabsorbed light strikes the detector. The intensity of the light is first measured with the empty cell and then the cell filled with reaction sample. The difference gives the absorption intensity. The detector used is the **chemical actinometer**.

Uranyl oxalate actinometer contains 0.05 M oxalic acid and 0.01 M uranyl sulphate in water .When it is exposed to radiation , oxalic acid is decomposed to CO_2 ,CO and H_2O.

$$UO_2^{2+} + h\nu \longrightarrow (UO_2^{2+})^*$$

$$(UO_2^{2+})^* + \underset{\text{Oxalic acid}}{H_2C_2O_4} \longrightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

The amount of oxalic acid decomposed is determined by titration with std. $KMnO_4$ .From this the intensity of light absorbed is estimated. Thus quantum yield is calculated.

3.6 Photophysical processes

If the radiation absorbed by the substance is not used to cause a chemical reaction , it is re-emitted as light of longer wavelength .Two such photophysical process are *fluorescence and phosphorescence*. They are best explained with the help of *Jablonski diagram* .

On absorption of a photon of light , the electron from singlet ground state (S_0) goes to singlet excited states S_1 , S_2 ,S_3 etc.

Non-radiative transitions

The transition from higher excited state (S_3 ,S_2 or T_3 , T_2) to first excited state (S_1 or T_1) do not involve emission of radiation and this process is called *internal conversion (IC)* .Transition from sinslet excited state S_1 to triplet excited state T_1 is also non-radiative and is called *inter system crossing (ISC)*.

Radiative transitions

Transition from singlet excited state (S_1) to singlet ground state (S_0) is called fluorescence. Transition from triplet state (T_1) to singlet ground state (S_0) is phosphorescence,

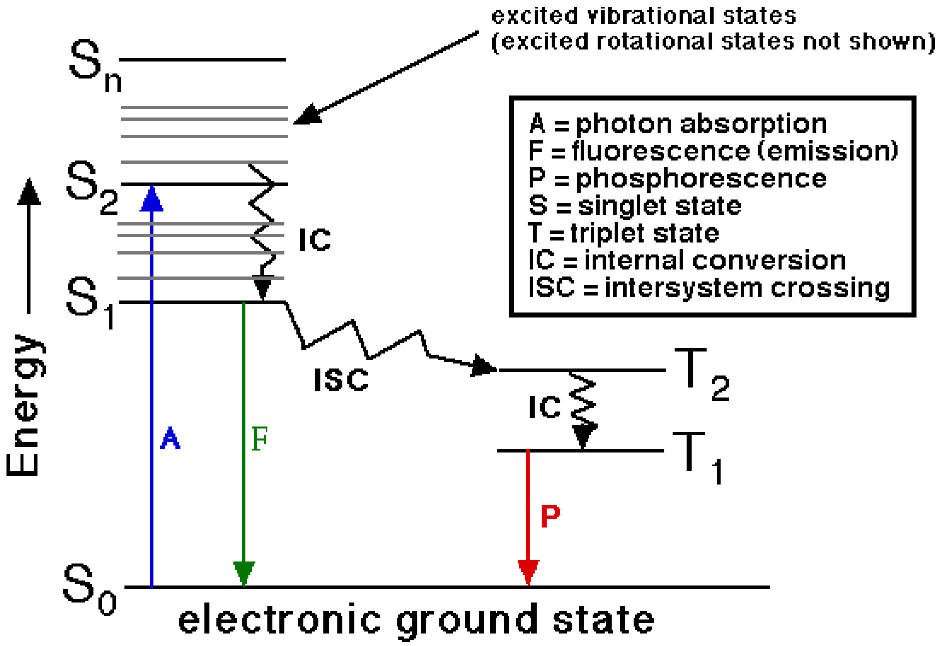


Fig : 2 Jablonski diagram

3.6.1 Fluorescence

Statement

When a beam of light is incident on certain substances , the absorbed light may be re-emitted almost instantaneously. This phenomenon is known as fluorescence and the substances that exhibit fluorescence are called fluorescent substances. Fluorescence stops as soon as the incident light is cut off.

Examples

(i) A solution of chlorophyll in ether shows blood red fluorescence.

(ii) A solution of quinine sulphate on exposure to visible light exhibits blue fluorescence

(iii)Chlorophyll , petroleum , fluoroscein , ultramarine , uranyl sulphate etc.

Explanation :

When a molecule absorbs high energy radiation , it is excited to higher energy states. Then it emits excess energy through several transitions to the ground state. Thus the excited molecule emits light of longer frequency. The colour of fluorescence depends on the wavelength of light emitted.

Chracteristics:

i) It is a rapid process and occurs within 10^{-8} seconds.
ii) It involves singlet – singlet transition.

Uses :

i) Fluorescent dyes are used in chemical diagnosis.
ii) Used as reflectors in automobiles, signals etc.

3.6.2 Phosphorescence

Statement

When a beam of light is incident on certain substances they emit light continuously even after the incident light is cut off. This phenomenon is known as phosphorescence . The substances that shows phosphorescence are called phosphorscent substances or phosphors.

Phosphorescence is generally shown in solids and it is caused by UV and visible light.

Examples:

i) Sulphides of barium , calcium and strontium exhibit phosphorescence.
ii) Organic substances like aspirin , cocaine , nicotine etc.

Charecteristics:

i) It is a slow process and occurs in 10^{-3} sec .
ii) It involves triplet – singlet transition.
iii) It is also known as delayed fluorescence.
iv) It emits light radiation at longer wavelength.

Uses :

i) Phosphorescent materials are used in colour television tubes.
ii) A paste of radium with zinc sulphide is used in watch dials, meter dial etc.

Comparison of fluorescence and phosphorescence

Fluorescence	**Phosphorescence**
When light is absorbed by a substance , the absorbed light is re-emitted instantaneously.	The absorbed light is re-emitted slowly.

Emission of light stops as soon as the incident light is cut off.	Emission of light continues for sometime even after the incident light is cut off.
It is a rapid process and occurs within 10^{-8} s of light absorption.	It is a slow process and occurs within 10^{-3} s .
It invoves singlet- singlet transition which is is spctroscopically allowed.	It involves singlet – triplet transition which is spectroscopically forbidden.
It emits light energy of longer wavelength.	It also emits light energy at longer wavelength.

3.6.3 Chemiluminescence

Statement

The emission of visible light as a result of chemical reaction is called chemiluminescence . The light emitted in a chemiluminescent reaction is also called as cold light because it is produced at ordinary temperature.

Examples :

i) The glow of phosphorus and its oxides.

ii) The oxidation of 5-amino phthalic cyclic hydrazide (luminol) by H_2O_2 in alkaline solution, producing bright green light.

iii) Many Grignard reagents exhibit chemiluminescence when oxidised by air or oxygen.

Explanation :

In a chemiluminescent reaction , the energy released in the reaction makes the product molecule electronically excited . The excited molecule then gives up its excess energy as visible light when returning to ground state.

$$4\,P + 5O_2 \text{ ------------}\rightarrow 2P_2O_5^*$$

$$P_2O_5^* \text{ ------------}\rightarrow P_2O_5 + h\nu \quad \text{(visible light)}$$

3.6.4 Bioluminescence

Statement

Bioluminescence is the emission of light by a living organism as a result of biochemical reaction.

Examples :

i) Light emitted by firefly and glow worm.
ii) Luminescence observed at night in ocean due to jelly – fish.
iii) Fox – fire in marshy places.

Explanation :

The light emitted by fireflies and glow worm is due to the aerial oxidation of luciferon (a protein) by enzyme luciferase.

3.6.5 Photosensitization

statement

When the reactant molecules are unable to absorb light , addition of a suitable light sensitive material stimulates the photochemical reaction. This process is known as photosensitization. The substance which can absorb and transfer the light to the reactant molecule are called photosensitizer.

The important photosensitizers are mercury , cadmium , zinc, benzophenone , SO_2 etc.

Example:

Reaction between H_2 and O_2 is photosensitized by mercury vapour.

$Hg + h\nu \dashrightarrow Hg^*$ primary absorption

$Hg^* + H_2 \dashrightarrow 2H + Hg$ Energy transfer

$H + O_2 \dashrightarrow HO_2$ Reaction

$HO_2 + HO_2 \dashrightarrow H_2O_2$ Reaction

3.7 Self Evaluation

Fill in the blanks

1. The emission of light by a firefly is due to ....

2. The photosensitizer used in the chemical actinometer is ....
3. The quantum yield for the photochemical combination of hydrogen and chlorine is ....
4. An example of photosensitizer is ....
5. The transition from triplet to singlt state is ....

Answers : 1) Bioluminescence 2) Uranyl ion 3) $\phi > 1$ 4) Hg 5) phosphorescence

Questions

1. Compare photochemical and thermal reactions.
2. State the laws of photochemistry.
3. Explain quantum yield. What are primary and secondary processes?
4. Write a short note on chemiluminescence.
5. Explain the experimental determination of quantum yield.

UNIT – IV

THERMODYNAMICS - I

Contents

4.9 Entory

4.10 Entropy us function of T and V:

4.11 Entropy changes of an ideal gas during isothermal reversible process:

4.12 Physical significance of entropy:

UNIT- IV

THERMODYNAMICS - I

Objectives:

- To learn to Internal energy and Enthalpy
- To measure changes in internal energy and enthalpy.
- To relate E and H
- To relate C_p and C_v
- To learn Entropy and physical significance

4.1 Introduction

The term **thermodynamics** is derived from Greek word, **‘Thermos'** meaning heat and **‘dynamics'** meaning flow. Thermodynamics deals with the inter-relationship between heat and work. It is concerned with the interconversions of one kind of energy into another without actually creating or destroying the energy. **Energy** is understood to be the capacity to do work. It can exist in many forms like electrical, chemical, thermal, mechanical, gravitational etc. Transformations from one to another energy form and prediction of the feasibility (possibility) of the processes are the important aspects of thermodynamics.

4.2 Statements of First law

First law of thermodynamics is also known as the law of conservation of energy which may be stated as follows:

"Energy may be converted from one form to another, but cannot be created or be destroyed".

There are many ways of enunciating the first law of thermodynamics. Some of the selected statements are given below:

(i) "Energy of an isolated system must remain constant although it may be changed from one form to another".

(ii) "The change in the internal energy of a closed system is equal to the energy that passes through its boundary as heat or work".

(iii)"Heat and work are equivalent ways of changing a system's internal energy".

(iv)"Whenever other forms of energies are converted into heat or vice versa there is a fixed ratio between the quantities of energy and heat thus converted".

Significance of first law of thermodynamics is that, the law ascertains an exact relation between heat and work. It establishes that ascertain quantity of heat will produce a definite amount of work or vice versa. Also, when a system apparently shows no mechanical energy but still capable of doing work, it is said to possess internal energy or intrinsic energy.

4.3 Internal Energy (E)

In chemical systems, there are two types of energy available. The energies acquired by the system like electrical, magnetic, gravitational etc. and termed as external energies of the system. The internal energy is generally referred to as the energy (E) of a thermodynamic system which is considered to be made up of mainly by P.E. and K.E.

4.3.1 Characteristics of energy (E) are:

(i) E is a state function. Its value depend on the initial and final states of the system.

(ii) E is an extensive property. Its magnitude depend on the quantity of material in the system.

(iii) E is not a path function. Its value remains constant for fixed initial and final states and does not vary even though the initial and final states are connected by different paths.

In S.I. system the unit of energy is Joules `J' or kJ.

4.4 Enthalpy

In chemistry most of the chemical reactions are carried out at constant pressure. To measure heat changes of system at constant pressure, it is useful to define a new thermodynamic state function called Enthalpy `H'.

H is defined as sum of the internal energy ‘E' of a system and the product of Pressure and Volume of the system.

That is,

$$H = E + PV$$

4.4.1 Characteristics of H

Enthalpy, H depends on three state functions E, P, V and hence it is also a state function. H is independent of the path by which it is reached. Enthalpy is also known by the term `heat content'.

4.5 Relation between enthalpy ‘H' and internal energy ‘E'

When the system at constant pressure undergoes changes from an initial state with H_1, E_1, V_1, P parameters to a final state with H_2, E_2, V_2, P parameters the change in enthalpy ΔH, is given by,

$$\Delta H = (H_2 - H_1) = (E_2 - E_1) + P(V_2 - V_1)$$

$$ie., \Delta H = \Delta E + P\,\Delta V$$

Considering $\Delta E = q - w$ or $q - P\Delta V$ (assuming p – V work), $\Delta E + P\Delta V$ becomes equal to `$q_p$'. `q_p' is the heat absorbed by the system at constant pressure for increasing the volume from V_1 to V_2. This is so because, -w indicates that work is done by the system. Therefore volume increase against constant pressure is considered.

$\therefore$ eqn. becomes $q_p = \Delta E + P\Delta V = \Delta H$

or $\Delta H = q_p$

'q_p' is the heat absorbed by the system at constant pressure and is considered as the heat content of the system.

Heat effects measured at constant pressure indicate changes in enthalpy of a system and not in changes of internal energy of the system. Using calorimeters operating at constant pressure, the enthalpy change of a process can be measured directly.

Considering a system of gases which are chemically reacting to produce product gases with Vr and Vp as the total volumes of the reactant and product gases respectively, and n_r and n_p as the number of moles of gaseous reactants and products, then using ideal gas law we can write that, at constant temperature and constant pressure,

$$PV_r = n_rRT \text{ and } PV_p = n_pRT.$$

Then considering reactants as initial state and products as final state of the system,

$$P(V_p-V_r) = RT(n_p-n_r)$$

$$\therefore \; P\,\Delta V = \Delta n_g RT$$ where,

Δn_g refers to the difference in the number of moles of product and reactant gases. But, we already know that,

$$\Delta H = \Delta E + \Delta n_g RT$$

4.6 Molar heat capacities:

Molar heat capacity (C) of a system is defined as the amount of heat required to raise the temperature of one mole of the system by one degree.

$$C = \frac{dq}{dT} \quad \text{................ (1)}$$

where, dq is the small amount of heat absorbed and

dT is the small temperature difference

Heat capacity is not a state function. Therefore it is necessary to specify the process by which the temperature is raised.

The two important types of molar heat capacities are those (i) at constant volume and (ii) at constant pressure.

4.6.1 Molar heat capacity at constant volume 'C_v'

At constant volume $(dV=0)$ no external work is done by the system or on the system $(w=0)$. Hence from first law of thermodynamics $(q=dE-w)$,

$$q=dE$$

$$\text{then } C_v = \frac{dq}{dT} = \left(\frac{\partial E}{\partial T}\right)_v$$

Heat capacity at constant volume is defined as the increase in internal energy of the system per degree rise of temperature.

4.6.2 Molar heat capacity constant pressure : (C_p)

At constant pressure, there is a change of volume and some work is done. By convention, work done (w) by the system –PdV.

From first law of thermodynamics

$$q = dE - W$$

$$q = dE - (-PdV)$$

$$q = dE + PdV = dH$$

$$/\ C_p = \frac{dq}{dT} = \left(\frac{\partial E}{\partial T}\right)_p$$

Heat capacity at constant pressure is defined as the increase enthalpy of the system per degree rise of temperature.

4.6.3 Comparison of C_p and C_v ($C_p > C_v$)

When a gas is heated at constant volume, no external work is done by the gas. All the heat supplied to the gas is used to increase he internal energy. However, when a gas is heated at constant pressure the heat supplied is utilized in two ways (i) to increase the internal energy and ii) to perform work. Hence molar heat capacity at constant pressure(C_p) must be greater than molar heat capacity at constant volume C_v

/ $C_p > C_v$.

$C_p - C_v$ = work done by one mole of the gas in expansion when heated through 1 oC at constant pressure.

4.6.4 Thermodynamic derivation of relation between C_p and C_v:

By definition

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \quad \text{and } C_v = \left(\frac{\partial E}{\partial T}\right)_v$$

Since H = E+PV

$$C_p = \left\{\frac{\partial(E+PV)}{\partial T}\right\}_p$$

$$C_p = \left(\frac{\partial E}{\partial T}\right)_p + P\left(\frac{\partial V}{\partial T}\right)_v \text{ ------------------ (1)}$$

We know that, Internal energy E is a state function.

$$E = f(T,V)$$

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \text{ ------------------ (2)}$$

Dividing equation (2) by dT and imposing a condition of constant pressure, then.

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T . \left(\frac{\partial V}{\partial T}\right)_P \text{ ------------------ (3)}$$

Substituting the value of $\left(\frac{\partial E}{\partial T}\right)_P$ in eqn. (1)

$$C_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T . \left(\frac{\partial V}{\partial T}\right)_P + P . \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P = C_v + \left(\frac{\partial V}{\partial T}\right)_P . \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] \quad (/\ C_V = \left(\frac{\partial E}{\partial T}\right)_V) \text{ ---------}$$

(4)

For an ideal gas, $\left(\frac{\partial E}{\partial V}\right)_T = 0$

Eqn. (4) becomes

$$C_p = C_v + P.\left(\frac{\partial V}{\partial T}\right)_P \text{ ------------------ (5)}$$

For one mole of an ideal gas,

$$PV = RT$$

Differentiating with respect to temperature

$$PdV + VdP = RdT$$

$$P\frac{dV}{dT}+V\frac{dP}{dT}=R$$

At constant pressure dP = 0

$$P.\left(\frac{\partial V}{\partial T}\right)_P=R \text{ ----------------------- (6)}$$

Equation (5) becomes

$$C_p = C_v + R$$

$$C_p - C_v = R \text{ -------------------- (7)}$$

4.7 Work of Expansion

Consider an ideal gas enclosed in a cylinder (area of cross section Am^2) fitted with a movable piston. Let the external pressure on the piston is p_{ext}.

if the pressure (P) of the gas is greater than p_{ext}, the gas undergoes expansion. Let the piston moves through a distance ‘dl’, then the work done is given by.

work done = δw = force x distance

$$\delta w = -p_{ext} \,.\, A.dl$$

$$\delta w = -p_{ext} \,.\, dV \qquad (1)$$

(According to IUPAC recommendations, work done by the system is given a negative sign as the system loses energy)

For a finite change in volume V_1 to V_2 the total work(w) is obtained by integrating equations(1)

$$\int_1^2 \delta w = -P_{ext} \int_1^2 dV$$

$$w = -P_{ext}\left(V_2 - V_1\right)$$

$$w = -P_{ext}\Delta V \qquad \text{\_\_\_\_\_\_\_\_\_\_\_\_} (2)$$

During expansion, ΔV, is positive and hence work done by the system is negative.

Free expansion:

Expansion of a gas in vacuum is called free expansion. During expansion into vacuum $P_{ext} = 0$. Therefore $w = 0$.

4.8 Statement of Second Law of Thermodynamics

Second law of thermodynamics can be stated in many ways:

i) "It is impossible to construct an engine which operated in a complete cycle will absorb heat from a single body and convert it completely to work without leaving some changes in the working system".

This is called as the Kelvin – Planck statement of II law of thermodynamics.

ii) "It is impossible to transfer heat from a cold body to a hot body by a machine without doing some work".

This is called as the clausius statement of II law of thermodynamics.

iii) ‘A process accompanied by increase in entropy tends to be spontaneous”.

This statement is called as the entropy statement of II law of thermodynamics. Entropy is a measure of randomness or disorder of the molecules of a system and it is a thermodynamic state function. A system always spontaneously changes from ordered to a disordered state. Therefore entropy of a spontaneous process is constantly increasing.

iv) “Efficiency of a machine can never be cent percent”.

v) The heat Efficiency of any machine is given by the value of ratio of output to input energies. Output can be in the form of any measurable energy or temperature change while input can be in the form of heat energy or fuel amount which can be converted to heat energy.

$$\text{thus \% efficiency} = \frac{output}{input} \times 100$$

The machine can be a heat engine also. Consider a heat engine which has an initial temperature T1 and final temperature as T2, then if T1 >T2then when some amount of heat is being converted into work, T2 is the lowered temperature.

The efficiency ‘η’ is given by,

$$\% \text{ efficiency} = \left(\frac{T_1 - T_2}{T_1}\right) \times 100$$

4.9 Entopy

Clausius introduced a thermodynamic state function called entropy. It is represented by the symbol ‘S’. Entropy is a measure of randomness or disorderness in a molecular system. Entropy is also a measure of unavailable energy.

For a reversible process, taking place at a constant temperature T, entropy change dS is given by

$$dS = \frac{\delta q_{rev}}{T}$$

dq : amount of heat absorbed by the system.

Hence, entropy change (dS) is defined as the ratio of the heat adsorbed in the reversible process (δq_{rev}¿ and temperature 'T' on Kelvin scale.

Entropy is expressed in the units JK^{-1}

4.10 Entropy us function of T and V:

S = f(T,V)

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \text{ ------------------- (1)}$$

We know that

$$dE = TdS - PdV \text{ -------------------- (2)}$$

E = f(T,V)

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \text{ ---------------- (3)}$$

Comparing eqns. (2) and (3), we get

$$TdS - PdV = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

$$TdS = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV$$

$$TdS = \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] dV$$

$$dS = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] dV \text{ ------------- (4)}$$

Equating the coefficients of dT and dV in equation (1) and (4), we get

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V = \frac{C_v}{T} \text{ ---------------------- (5)}$$

$$\text{and } \left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] \text{ ------------------ (6)}$$

Equation (5) can be rewritten as

$$\left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Differentiating this w.r.t volume at constant temperature,

$$\frac{\partial^2 E}{\partial V\,\partial T} = T \cdot \frac{\partial^2 S}{\partial V\,\partial T} \quad \text{-------------------- (7)}$$

Equation (6) can be rewritten as

$$\left(\frac{\partial E}{\partial V}\right)_T + P = T\left(\frac{\partial S}{\partial V}\right)_T$$

(or) $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$

Differentiating w.r.t temperature at constant volume,

$$\frac{\partial^2 E}{\partial T\,\partial V} = T \cdot \frac{\partial^2 S}{\partial T\,\partial V} + \left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial P}{\partial T}\right)_V \quad \text{---------------- (8)}$$

From eqns. (7) and (8), we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{---------------------- (9)}$$

(since E is a state function)

Equation (6) can also be written as

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \quad \text{------------------- (10)}$$

Substituting the value of $\left(\frac{\partial S}{\partial V}\right)_T$ in eqn (10), we get

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad \text{------------------- (11)}$$

Eqn. (11) is known as thermodynamic equation of state.

4.11 Entropy changes of an ideal gas during isothermal reversible process:

For an isothermal process ($dT = 0$), $T_1 = T_2$

The entropy changes (ΔS) of an ideal gas during reversible process is,

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + n R \ln \frac{V_2}{V_1} \qquad \text{(eqn. 3)}$$

$$\text{or } \Delta S = nC_p \ln \frac{T_2}{T_1} - n R \ln \frac{P_2}{P_1} \qquad \text{(eqn. 4)}$$

Applying the isothermal condition, eqns. (3) and (4) becomes

$$(\Delta S)_T = nR\,\ell n\,\frac{V_2}{V_1} = 2.303\ nR\log\frac{V_2}{V_1}$$

$$\text{(or) } (\Delta S)_T = -\,nR\,\ell n\,\frac{P_2}{P_1} = -\,2.303\ nR\log\frac{P_2}{P_1}$$

4.12 Physical significance of entropy:

Entropy as a measure of disorder:

In spontaneous processes, there is always an increase in entropy. i.e. increase in the disorder of the system or randomness.

Thus, S is a measure of disorder, or random arrangement of molecules.

For examples:

In crystalline solid, the atoms or ions are arranged in a definite order. When this solid becomes liquid, the order is decreased and the disorder is increased. Therefore entropy is regarded as a measure of the disorder of a system.

Entropy and Probability:

A spontaneous or reversible process invariably taken place from a less probable to a more probable state.

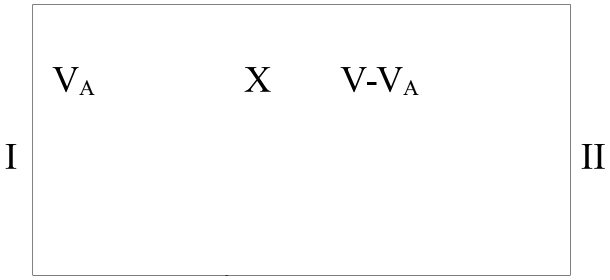
Therefore, the relation between entropy ‘S’ and the thermodynamic probability or complexion W is as follows

$S = k \ln W$ ------------------- (1)

where k-Boltzmann constant, i.e. R / N

Eqn. (1) is called Boltzmann equation.

Let us consider rectangular box of volume V, there is a partition wall x which divided the box in to two parts.



Suppose, there is a single molecule of an ideal gas in the box. The probability of finding the molecule in the volume

$$V_A = \frac{V_A}{V} \quad \text{-------------------------} \; (2)$$

If the box contains two molecules, the probability of finding both the molecules in V_A is $\left(\frac{V_A}{V}\right)^2$

Suppose we take one mole of an ideal gas, the probability of all the molecules in the volume.

$$w_A = \left(\frac{V_A}{V}\right)^N \quad \text{-------------------------} \; (3)$$

where, N is the Avogadro number

If the partition is removed, the probability of findings all the molecules in volume V is unity.

$$w = 1$$

$$/ \quad \frac{w_A}{w} = \left(\frac{V_A}{V}\right)^N$$

Taking logarithm on both sides.

$$\ell n \frac{w_A}{w} = N \ell n \frac{V_A}{V}$$

$$k \ell n \frac{w_A}{w} = k N \ell n \frac{V_A}{V}$$

$$/ \; k \ell n \frac{w_A}{w} = \frac{R}{N} . N \ell n \frac{V_A}{V}$$ (since $k = \frac{R}{N}$)

$$/ \; k \ell n \frac{w_A}{w} = R \ell n \frac{V_A}{V} \text{ ------------------- (4)}$$

Let S and S_A denotes entropy of gas in volume V and V_A

$S = k \ell n \, w$; $S_A = k \ell n \, w_A$

$$\Delta S = S - S_A = k \ell n \frac{w}{w_A} \text{ ------------------ (5)}$$

Comparing equations (4) and (5), we get

$$\Delta S = R \ell n \frac{V}{V_A}$$

Thus entropy is related to the probability.

Self Evaluation

Choose the Best Answer

1. Entropy (S) is a / an
   a) intensive property b) extensive property
   c) path function d) inexact differential
2. The entropy is expressed in
   a) calories b) calories per degree
   c) ergs d) none of the above
3. Entropy change for an adiabatic reversible process is
   a) +ive b) 0 c) –ve d) none
4. The driving force of a chemical reaction is most closely related to the concept of
   a) heat of reaction b) heat of formation c) entropy d) free energy
5. Entropy change for an adiabatic reversible process is
   a) +ve b) 0 c) –ve d) None

Answer the Following

1. State and explain the II law of thermodynamics. Discuss the need for II law.
2. Derive relation between C_p and C_v
3. Explain the physical significance of entropy
4. Give the relation between internal energy and enthalpy

5 . Explain variation of entropy with T and V.

UNIT - V

THERMODYNAMICS II

CONTENTS

UNIT –V

THERMODYNAMICS II

Objectives:

- To learn to Work, heat and free energy
- To study Van’t Hoff Isotherm and isochore
- To learn III law of thermodynamics
- To study classius-clapeyron equation
- To study Gibbs Duhem equation

5.1 Introduction

In chemistry, many reactions are encountered that can be utilised to provide heat and work along with the required products. At present thermodynamics is widely used in physical, chemical and biological sciences focussing mainly on the aspect of predicting the possibility of the processes connected with each sciences. On the other hand, it fails to provide insight into two aspects: Firstly, the factor of time involved during the initial to final energy transformations and secondly, on the quantitative microscopic properties of matter like atoms and molecules.

5.2 Work function (A) and Free energy function (G)

When a system reaches an equilibrium state, it possess some energy called free energy. It is the difference between initial state energy and equilibrium state energy.

Free energy = Initial state energy – Equilibrium state energy

If ‘q’ is the total amount of heat absorbed by a system at a constant temperature ‘T’, S is the entropy of the system, then TS represents the amount of heat degraded or not available for conversion in to work.

/ The amount of energy ‘FE’, that is available for conversion into work is given by

$$FE = q - TS$$

‘FE’ is called free energy.

If ‘q’ is the heat absorbed at constant volume, i.e. E, the free energy is called the Helmholtz free energy or work function.

i.e. $A = E - TS$

If ‘q’ is the heat absorbed at constant pressure i.e H, the free energy is called Gibbs free energy or free energy of Gibbs potential.

$$G = H - TS$$

G and A are state functions and dG and dA are exact differentials.

5.3 Significance of A and G

5.3.1 Helmholtz free energy ‘A’ as a work function:

We know that $A = E - TS$

For a given state of the system at constant temperature ‘T’, the three functions A, E, S becomes A_1, E_1 and S_1.

i.e. $A_1 = E_1 - TS_1$

For an appreciable change, the function changes to A_2, E_2 and S_2

$$A_2 = E_2 - TS_2$$

$/ \ A_2 – A_1 = (E_2 – E_1) – T (S_2 – S_1)$

$\Delta A = \Delta E – T \Delta S$ --------------------- (1)

where ΔA – change in Helmholtz free energy

ΔE – change in internal energy

ΔS – change in entropy

For a reversible isothermal process $T\Delta S = q_{rev}$ ------------------ (2)

From the I law of thermodynamics, $\Delta E = q_{rev} + w_{rev}$ ----------- (3)

Substituting the values from eqn (2) and (3) in eqn. (1),

we get

$\Delta A = w_{rev}$

(or) $- \Delta A = -w_{rev} = - w_{max}$

Thus the decrease in the Helmholtz function is equal to the maximum work done by the system during isothermal reversible condition.

Therefore, the function ‘A’ is called work function.

5.4 Variation of free energy with temperature and pressure

We know that

dG = VdP – SdT

At constant temperature, (dT = 0)

/ dG = VdP ------------------(1)

Integrating eqn. (1) with suitable limits

$$\int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} VdP$$

¿ $\int_{P_1}^{P_2} nRT \frac{dP}{P}$ (since V = $\frac{nRT}{P}$ for an ideal gas)

$$[G]_{G_1}^{G_2} = \text{nRT} \; [lnP]_{P_1}^{P_2}$$

$$G_2 - G_1 = nRT \ln \frac{P_2}{P_1} \quad \text{----------------} \; (2)$$

Eqn. (2) becomes

$$\Delta G = 2.303 \; nRT \log \frac{V_1}{V_2} \qquad \left(\text{Since} \quad \frac{P_2}{P_1} = \frac{V_1}{V_2}\right)$$

For 1 mole of an ideal gas,

$$\Delta G = 2.303 \; RT \log \frac{P_2}{P_1} = 2.303 \; RT \log \frac{V_1}{V_2}$$

5.5 Gibbs Helmholtz equation

For a closed system,

$$dG = VdP - SdT \quad \text{----------------------} \; (1)$$

At constant pressure, $dP = 0$

$$dG = SdT \; \text{-----------------} \; (2)$$

Suppose, G_1 is the free energy of a system in state 1 at a temperature, TK. If the temperature is changed by dT, the free energy becomes $G_1 + dG_1$ at the temperature. $T + dT$K.

Similarly, for the same system in state 2 the free energy becomes $G_2 + dG_1$ at the temperature T + dTK.

At constant pressure, $dG_1 = -S_1\, dT$

$$dG_2 = -S_2\, dT$$

/ $(dG_2 - dG_1)_P = -(S_2 - S_1)\, dT$

$$d\,(\Delta G)_P = -\Delta S dT$$

(or) $\left[\frac{\partial}{\partial T}(G)\right]_P =$ ¿ $- \Delta S$ ----------------- (3)

Substituting the value of $-\Delta S$ in equation, $\Delta G = \Delta H - T\Delta S$, we get

$$\Delta G = \Delta H + T \left[\frac{\partial}{\partial T}(G)\right]_P \quad \text{---------------} \ (4)$$

The expression (4) is known as Gibbs – Helmholtz equation.

Dividing eqn. (4) by – T^2, we get

$$\frac{-G}{T^2} = \frac{-H}{T^2} - \frac{1}{T}\left[\frac{\partial}{\partial T}(G)\right]_P$$

$$G\frac{\partial}{\partial T}\left(\frac{1}{T}\right)=\frac{-H}{T^2}-\frac{1}{T}\left[\frac{\partial(G)}{\partial T}\right]_P \mathit{Since}\,\frac{\partial}{\partial T}\left(\frac{1}{T}\right)=\frac{-1}{T^2}$$

$$(\text{¿})\,G\frac{\partial}{\partial T}\left(\frac{1}{T}\right)+\frac{1}{T}\left[\frac{\partial(G)}{\partial T}\right]_P=\frac{-H}{T^2}$$

$$\frac{\partial}{\partial T}\left[\frac{G}{T}\right]_P=\frac{-H}{T^2}\left(\mathit{Since}\,d(uv)=udv+vdu\right)$$

Since pressure is constant, u = ΔG   V = 1/T

$$d\left(\frac{G}{T}\right)=-H\left(\frac{dT}{T^2}\right)-----------(5)$$

Integrating eqn. (5), between the limits, we get

$$\frac{G}{T}=\int\frac{H}{T^2}dT+C--------------(6)$$

This is also Gibbs-Helmholtz equation, where C is integration constant.

5.5.1 Applications:

i) It is used to calculate the heat of reaction (ΔH) of a reversible electrochemical cell (E).

If E is the EMF of the cell, then electrical energy produced by the cell = nFE.

/ decrease in free energy, - ΔG = nFE

Substituting this value in the Gibbs Helmholtz equation,

we get, $nFE = -\Delta G + TnF\left[\frac{\partial E}{\partial T}\right]_P$

Thus knowing the temperature coefficient, $\left[\frac{\partial E}{\partial T}\right]_P$ ΔH can be calculated if E is known or viceversa.

ii) It is responsible for the development of the Nernst Heat theorem (precursor of third law of Thermodynamics)

iii) It is used to determine the equilibrium constant of a reaction at different temperature.

5.6 Van’t Hoff reaction isotherm:

Let us consider a reversible reaction

$$aA + bB \Rightarrow mM + Nn$$

where a, b, m, n are the stoichiometric coefficients of A, B, M, N respectively.

Free energy of the reaction,

$\Delta G_{r\,xn} = (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B)$ --------------- (1)

At equilibrium, $\Delta G_{r\,xn} = 0$ and substituting the value of

$\mu_1 = \square_1^0 + RT \ln p_1$ in eqn. (1), we get

$[m(\square_M^0 + RT \ln p_M) + n(\square_N^0 + RT \ln p_N)$

$- [a(\square_A^0 + RT \ln p_A) + b(\square_B^0 + RT \ln p_B)] = 0$

$$RT\left[\ln K_P\left(\frac{P_M^m P_N^n}{P_A^a P_B^b}\right)\right] = -G^0_{r\,xn}$$

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

(or) $\Delta G^0 = -RT \ln K_p$ -------------------- (2)

(or) $\Delta G^0 = - 2.303\ RT \log K_p$

Equation (2) is known as van't Hoff reaction isotherm.

5.6.1 Significance of Van't Hoff's isotherm:

i) van't Hoff's isotherm relates equilibrium constant and free energy change of a reaction. Hence it's an applications thermodynamics to law of mass action.

ii) The magnitude to K_p depends on the value of ΔG. More the –ve value of ΔG, more will be +ve value K_p.

iii) Using the reaction isotherm, we can workout the condition for maximum yield.

iv) Since ΔG is related to ΔS and ΔH as $\Delta G = \Delta H - T\Delta S$ The value of ΔS (increase in entropy) makes K_p (+ve) positive.

5.7 Van't Hoff isochore equation:

(Effect of temperature on chemical equilibria)

We know that

$$\Delta G^0 = - RT \ln K_p \quad ----------------(1)$$

where K$_p$ is the equilibrium constant at constant pressure.

Differentiating equation (1) w.r.t. temperature treating pressure as constant then

$$\left[\frac{\partial\left(G^0\right)}{\partial T}\right]_P=-Rln\,K_P-RT\left[\frac{\partial\left(ln\,K_p\right)}{\partial T}\right]_P----------(2)$$

(where d (uv) = udv + vdu)

Multiplying eqn. (2) by T, we get

$$T\left[\frac{\partial\left(G^0\right)}{\partial T}\right]_P=-RT\,ln\,K_P-RT^2\left[\frac{\partial\left(ln\,K_p\right)}{\partial T}\right]_P----------(3)$$

$$Since\,\Delta G^0=-RT\,ln\,K_P\wedge\left[\frac{\partial\left(G^0\right)}{\partial T}\right]_P=-\Delta S^0,$$

/ Eqn (3) becomes

$$-T\,\Delta S^0=\Delta G^0-RT^2\left[\frac{\partial\left(ln\,K_p\right)}{\partial T}\right]_P$$

$$(¿)RT^2+T\,\Delta S^0=RT^2\left[\frac{\partial\left(ln\,K_p\right)}{\partial T}\right]_P$$

$$(¿)\Delta H^0 = RT^2\left[\frac{\partial(\ln K_p)}{\partial T}\right]_P (since\,\Delta G^0 = \Delta h^0 - T\Delta S^0)$$

At constant pressure,

$$\Delta H^0 = RT^2\frac{d(\ln K_p)}{dT}$$

$$(¿)\frac{d(\ln K_p)}{dT} = \frac{H^0}{RT^2} ----------------- (4)$$

Since ΔH does not vary with pressure, hence $\Delta H^0 = \Delta H$,

$$\boxed{\frac{d(\ln K_p)}{dT} = \frac{H}{RT^2} ----------------- (5)}$$

The van’t Hoff equation is also written in terms of K_C and ΔE in the following form:

$$\frac{d(\ln K_c)}{dT} = \frac{E}{RT^2} ----------- (6)$$

Eqn (5) is known as van’t Hoff equation.

5.7.1 Integrated form of van’t Hoff equation:

On integrating equation (5) between the suitable limits, we get

$$\int_{1}^{2} d\left(ln K_p\right) = \frac{H}{R}\int_{T_1}^{T_2} \frac{dT}{T}$$

$$\left[ln K_p\right]_1^2 = \frac{-H}{R}\left[\frac{1}{T}\right]_{T_1}^{T_2}$$

$$ln\left[\frac{\left(K_p\right)_2}{\left(K_p\right)_1}\right] = \frac{-H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$2.303 \log\left[\frac{\left(K_p\right)_2}{\left(K_p\right)_1}\right] = \frac{-H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\log\frac{\left(K_p\right)_2}{\left(K_p\right)_1} = \frac{H}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] ---------------(7)$$

Eqn. (7) is known as integrated van't Hoff equation.

5.7.2 Significances:

i) It is possible to calculate the heat of reaction ΔH by measuring the values of the equilibrium constant at two different temperature.

ii) Van't Hoff's isochore gives the variation of equilibrium constant with temperature.

5.8 Clapeyron equation

Clapeyron derived a thermodynamic relation between the change of pressure with change of temperature of a system at equilibrium. This relationship is known as Clapeyron equation.

Consider any two phase (A and B) of a pure substance in equilibrium with each other at a constant temperature and at a constant pressure.

Phase A $\rightleftharpoons$ Phase B (at constant T and P)

At equilibrium

The free energy change for the process is zero.

(ie) $\Delta G = 0$

$G_B - G_A = 0$

(or) $G_B = G_A$ ----------------- (1)

where, G_B is the free energy per mole in the phase B and

G_A is the free energy per mole in the phase A.

If the temperature ‘T’ is raised to T + dT, the pressure is also changed from P to P + dP, in order to maintain equilibrium.

Let the free energies per mole of the two phases under new temperature and pressure be $G_A + dG_A$ and $G_B + dG_B$.

Since, the two phase A and B are still in equilibrium, hence

$G_A + dG_A = G_B + dG_B$ --------------------- (2)

$dG_A = dG_B$ (/ $G_A = G_B$) ------------------- (3)

The change of free energy with the change of temperature and pressure is expressed as

$$dG = VdP - SdT \text{ ------------------- } (4)$$

/ from eqn. (2) and eqn. (4), we get

$$V_A \, dP - S_A \, dT = V_B \, dP - S_B \, dT$$

$$(S_B - S_A) \, dT = (V_B - V_A) \, Dp$$

$$\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A} = \frac{S}{V} \text{-------------} (5)$$

where ΔV is the change in molar volume for the process.

For transition process,

$$\Delta S = \frac{H}{T}$$

where ΔH is the change in molar enthalpy for the reversible transformation at temperature T.

$$\frac{dP}{dT} = \frac{H}{TV} \text{-----------} (6)$$

Equation (6) is known as Clapyeron equation.

5.8.1 Applications:

It can be used to discuss the two-phase equilibria in one component system.

i) Liquid – Vapour equilibira (vaporization process)

Consider an equilibrium process.

Liquid $\rightleftharpoons$ Vapour

Applying Clapeyron equation (6), we get

$$\frac{dP}{dT}=\frac{H_{vap}}{T\left(V_g-V_l\right)}$$

where

ΔH_{vap} – molar enthalpy of vaporization

V_g – molar volume of substance in the vapour state

V_l – molar volume of substance in the liquid state

Since $V_g > V_l$ and ΔH_{vap} is positive,

$\therefore \frac{dP}{dT}$ will always be positive,

i.e with increase of P, there must be an increase in T.

ii) Solid – liquid equilibria (fusion process)

Consider an equilibria process

Solid $\rightleftharpoons$ Liquid

Applying Clapeyron equation, we get

$$\frac{dP}{dT} = \frac{H_{fus}}{T\left(V_l - V_s\right)}$$

where ΔH_{fus}, V_l, V_s – are molar enthalpy of fusion, molar volume of liquid and solid respectively. For majority of the substance (except water and bismuth metal)

$V_l > V_s$, ΔH_{fus} = positive

$\therefore \frac{dP}{dT}$ is positive

iii) Solid vapour equilibrium (Sublimation process)

Solid ⇌ Vapour

For this equilibrium process,

$$\frac{dP}{dT} = \frac{H_{\text{¿}}}{T\left(V_g - V_s\right)}$$

where ΔH_{sub} is molar enthalpy of sublimation and V_g, V_s and molar volumes of gas and solid respectively.

5.9 Clausuis – Clapeyron equation

When Clapeyron equation is applied to liquid – vapour equilibria with the assumption that the volume of the liquid phase is negligible as compared to that of vapour phase, then it is called Clausuis – Clapeyron equation.

$$\frac{dP}{dT} = \frac{H_v}{T\left(V_g - V_l\right)} ----------------(1)$$

Since V_g >>> V_ℓ eqn (1) becomes

$$\frac{dP}{dT} = \frac{H_v}{TV_g}$$

But $V_g = \frac{RT}{P}$ (Since V_g obeys ideal gas equation)

$$Hence \frac{dP}{dT} = \frac{H_v}{T} . \frac{P}{RT} = \frac{PH_v}{RT^2}$$

$$\frac{dP}{dT} = \frac{H_v}{R} . \frac{dT}{T^2} ----------------(2)$$

$$(¿) d(lnP) = \frac{H_v}{R} . \frac{dT}{T^2} ----------------(3)$$

Equation (3) is known as differential form of Clasius Clapeyron equation.

5.9.1 Integrated form of Clasius Clapeyron equation

On integrating eqn. (3), we get

$$\int d(lnP) = \frac{H_v}{R} \int \frac{dT}{T^2}$$

$$lnP = \frac{H_v}{R}\left[\frac{-1}{T}\right] + c$$

$$2.303 \log P = \frac{-H_v}{RT} + c$$

$$\log P = \frac{-H_v}{2.303\,RT} + c ---------(4)$$

$$where\; c \wedge c' = \frac{c}{2.303}\; are\; integration\; constants.$$

$$A\; plot\; of\; \log P\; against\; \frac{1}{T}\; gives\; a\; straight\; line\; of\; slope,$$

$$\frac{-H_v}{2.303\,R} \wedge intercept = c'$$

Thus ΔH$_v$ can be calculated,

Eqn. (3) can also be integrated between the limits, we get

$$\int_{P_1}^{P_2} d(lnP) = \frac{H_v}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$[lnP]_{P_1}^{P_2} = \frac{H_v}{R}\left[\frac{-1}{T}\right]_{T_1}^{T_2}$$

$$ln\frac{P_2}{P_1} = \frac{H_v}{R}\left[\frac{-1}{T_2} + \frac{1}{T_1}\right]$$

$$2.303 \log ln\frac{P_2}{P_1} = \frac{H_v}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\therefore \log\frac{P_2}{P_1} = \frac{H_v}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] --------(5)$$

Equations (4) and (5) are known as integrated form of Clausuis Clapeyron equation.

5.9.2 Applications (Signficance)

i) **Calculation of molar heat of vapourisation (ΔH_v)**

The molar heat of vapourisation, ΔH_v of a liquid can be calculated if its vapour pressures at two different temperatures are known.

ii) **Effect of temperature on vapour pressure of a liquid:**

If vapour pressure of a liquid at one temperature is known, then the vapour pressure at another temperature can be calculated.

iii) **Effect of pressure on boiling point:**

If the boiling point of a liquid at one pressure is known, then the boiling point at another pressure can be calculated.

iv) It is used to determinew the molar elevation constant (K_b), molar depression constant (K_f).

v) Clausius – Clapeyron equation is used in phase rule to study water and sulphur system.

5.10. Statements of third law of thermodynamics:

a) **Planck statement:**

The entropy of a solid or liquid becomes zero at absolute zero.

$$\underset{T \to 0}{¿} S=0$$

b) **Lewis and Randell statement:**

Every substance has a finite positive entropy. At absolute zero, the entropy may become zero and it does become zero for perfectly crystalline solids.

c) **Statement III:**

At 0 K, the entropy of a perfectly crystalline solid is equal to zero.

5.11. Experimental verification of the third law of thermodynamics

The third law of thermodynamics is verified using the heat capacity and enthalpy data on substances existing in two different crystalline forms.

For reversible isothermal transition, $\alpha \rightarrow \beta$

$$\Delta S = S_{\beta} - S_{\alpha} = \frac{H_{tr}}{T_{tr}} ----------- (1)$$

Where ΔH_{tr} and T_{tr} are the experimentally determined enthalpy of transition and the temperature of transition respectively.

$$\Delta S = S_0(\beta) + \int_0^{T_{tr}} \frac{C_{p,s}(\beta)}{T} dT$$

$$- S_0(a) - \int_0^{T_{tr}} \frac{C_{p,s}(\alpha)}{T} dT = \frac{H_{tr}}{T_{tr}} --------- (2)$$

If an experiment provs that

$$\int_0^{T_{tr}} \frac{C_{p,s}(\beta)}{T} dT - \int_0^{T_{tr}} \frac{C_{p,s}(\alpha)}{T} dT = \frac{H_{tr}}{T_{tr}} -------------(3)$$

then it will prove that

$$S_0(\beta) = S_0(a)$$

Thus, both the cry stalline modifications a and b would have equal entropies at OK, in accordance with III law.

In the case of phosphine,

$$DS_{tr} = \frac{H_{tr}}{T_{tr}} = \frac{185.7}{49.43} = 15.73\, J\, K^{-1}\, mol^{-1} ---------(4)$$

and the difference between the two integrals (eqn.3) is found to be

$$\int_0^{T_{tr}} \frac{C_{p,s}(\beta)}{T} dT - \int_0^{T_{tr}} \frac{C_{p,s}(\alpha)}{T} dT = 15.69\, J\, K^{-1}\, mol^{-1} ------(5)$$

From the difference between eqns (4) and (5) i.e. 0.04 JK^{-1} mol^{-1}, the third law is valid.

5.12 Exception to the third law:

i) CO:

In CO molecules the value of S_{spec} (spectroscopic entropy ie the value obtained on the basis of spectroscopic data by means of statistical formula) is greater than S_{cal} or thermal entropy (calculated using III law) by 4.5J. This can be explained on the basis of frozen in randomness of orientation in crystal.

When CO crystal grows in the presene of a liquid, the molecule is condensed with two equally probable orientations CO and OC.

CO OC CO OC
OC CO CO CO
CO OC CO OC

Hence the crystal does not have definite structure.

From Boltzman entropy equation,

$S = k \ln W$

Where W is the thermodynamic probability.

i.e. $S = k \ln 2^N$

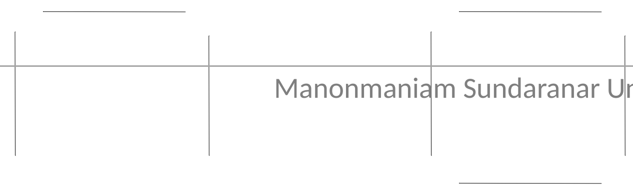
$= k.\, N \ln 2 = k \ln 2 = 8.314 \times 0.3010 \times 2.303$

$S = 5.76\ JK^{-1}\ mol^{-1}$

ii) NO (Nitric oxide)

It exists as a dimer N_2O_2. Two orientations are possible

N O O N



O ——— N N O

Since there are N/2 dimer molecule per mole of Nitric oxide.

$S = k\ln W = k\ln 2^{N/2}$

$$S=\frac{k.N}{2}ln2=\frac{Rln2}{2}=\frac{8.314\times2.303\times0.301}{2}=2.88\,JK^{-1}mol^{-1}$$

iii) Ortho and para hydrogen:

In hydrogen molecule, the difference between S_{cal} and S_{spec} is 11.5J. This is due to the fact that ordinary hydrogen at lower temperature is a mixture of two forms ortho and para hydrogen in the proportion 3 : 1. These two differ in their nuclear spin. Therefore the entropy of molecular hydrogen is larger then S_{cal} values.

iv) Ice:

In ice (H_2O), the entropy (S_{spec}) is higher than S_{cal} by 3.375 Joules. The is due to

i) rotational motion of molecule in the solid state.

ii) uncertainity of position of hydrogen bonding in the crystal.

5.13. Chemical potential (or) partial molar free energy μ_i or G_i

The partial molar free energy or chemical potential is represented as

$$\mu_i = \acute{G}_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j}$$

Chemical potential of i^th constituent (μ_i) may be defined as the rate of change of Gibbs free energy with no. of mole (n_i) under const, temperature, pressure and no. of moles other than $i(n_j)$.

We know that

$$G = f(T, P, n_1, n_2 \ldots\ldots n_i)$$

For a small change,

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P,N} dT + \left(\frac{\partial G}{\partial P} \right)_{T,N} dP + \left(\frac{\partial G}{\partial n_1} \right)_{T,P,n_1 \ldots\ldots n_i} d n_1$$

$$+ \left(\frac{\partial G}{\partial n_2} \right)_{T,P,n_1,n_3 \ldots\ldots n_i} d n_2 + \ldots + \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} d n_i ------(1)$$

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P,N} dT + \left(\frac{\partial G}{\partial P} \right)_{T,N} dP + \mu_1 d n_1 + \mu_2 d n_2 + \ldots + \mu_1 d n_i$$

where μ_1, μ_2 ….. are the chemical potential of the compounds respectively.

At const. T and P,

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \ldots + \mu_i dn_i ----------- (2)$$

On integrating eqn. (2), we get,

$$\int (dG)_{T,P} = \int \mu_1 dn_1 + \int \mu_2 dn_2 + \ldots + \int \mu_i dn_i$$

$$(G)_{T,P} = \mu_1 n_1 + \mu_2 n_2 + \ldots + \mu_i n_i ---------- (3)$$

From eqn. (3), chemical potential may be defined as the contribution per mole of each particular constituent of the mixture to the total free energy of the system under constant T and P.

5.14 Variation of chemical potential with temperature and pressure:

For an open system

$$dG = \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \mu_1 dn_1 + \ldots + \mu_i dn_i ----- (1)$$

In eqn (1), if there is no change in the number of moles of the variation constituents of a system, i.e. a closed system, then dn_1, dn_2 …… $dn_i = 0$

$$dG=\left(\frac{\partial G}{\partial P}\right)_{T,N} dP+\left(\frac{\partial G}{\partial T}\right)_{P,N} dT-----------(2)$$

For a closed system,

$$dG=VdP-SdT-----------(3)$$

Equating the coefficients of dP and dT in eqns. (2) and (3), we get

$$\left(\frac{\partial G}{\partial P}\right)_{T,N}=V\,and\left(\frac{\partial G}{\partial T}\right)_{P,N}=-S----------(4)$$

a) Variation of μ with temperature

We know that

$$\square_i=\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}--------(5)$$

Differentiating eqn. (5) w.r.t T and me other parameters being constant then

$$\left(\frac{\partial \square_i}{\partial T}\right)_{P,N}=\frac{\partial}{\partial T}\left[\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}\right]_{P,N}=\frac{\partial}{\partial n_i}\left[\left(\frac{\partial G}{\partial T}\right)_{P,N}\right]_{T,P,n_j}$$

(since G is a state function)

$$¿\frac{\partial}{\partial n_i}[-S]_{T,P,n_j} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j}, \therefore \left(\frac{\partial \square_i}{\partial T}\right)_{P,N} = -\acute{S}_i -----(6)$$

i.e. at constant pressure and composition, the rate of change of the chemical potential of a component ‘i’ with temperature is equal to the partial molar entropy of i $(\acute{S}_i)$.

Thus chemical potential decreases with increase in temperature since S is always positive.

b) Variation of ‘µ’ with pressure:

We know that

$$\square_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} ------(7)$$

Differentiating eqn (7) w.r.t P and the other parameters being constant, then

$$\left(\frac{\partial \square_i}{\partial P}\right)_{T,N} = \frac{\partial}{\partial P}\left[\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}\right]_{T,N} = \frac{\partial}{\partial n_i}\left[\left(\frac{\partial G}{\partial P}\right)_{T,N}\right]_{T,P,n_j}$$

(since G is a

state function)

$$¿\frac{\partial}{\partial n_i}[V]_{T,P,n_j}=\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j}$$

$$\left(\frac{\partial \square_i}{\partial P}\right)_{T,N}=\acute{V}_i----------(8)$$

i.e. at constant temperature and composition, the rate of change of the chemical potential of a constituent ‘i’ with pressure is equal to the partial molar volume of i $(\acute{V}_i)$.

5.15 Gibb’s Duhem equation

We know that

$(G)_{T,P} = \mu_1 n_1 + \mu_2 n_2 + \ldots + \mu_i n_i$ ------------------ (1)

The total differential is,

$dG = \mu_1\, dn_1 + n_1\, d\mu_1 + \mu_2\, dn_2 + n_2\, d\mu_2 \ldots\ldots + \mu_i\, dn_i + n_i\, d\mu_i$

$dG = (\mu_1\, dn_1 + \mu_2\, dn_2 + \ldots\ldots + \mu_i\, dn_i) + (n_1 d\mu_1 + n_2 d\mu_2 + \ldots + n_i d\mu_i)$

Since $\mu_1\, dn_1 + \mu_2\, dn_2 + \ldots + \mu_i\, dn_i = dG$ ----------------- (2)

/ eqn. (2) becomes

$dG = dG + (n_1\, d\mu_1 + n_2\, d\mu_2 + \ldots + n_i\, d\mu_i)$

(or) $n_1\, d\mu_1 + n_2\, d\mu_2 + \ldots + n_i\, d\mu_i = 0$ --------------- (3)

(or) $\sum n i d i = 0$ ------------------ (4)

This relationship is known as Gibbs-Duhem equation.

5.15.1 Siginficance:

For a system having only two components, the Gibbs Duhem equation reduces to

$n_1\, d\mu_1 + n_2\, d\mu_2 = 0$

$n_1\, d\mu_1 - n_2\, d\mu_2$

$(¿)\, d❑_1 = -\left(\frac{n_2}{n_1}\right) d_2$ ------------ (5)

From eqn. (4), if $d\mu_1$ is positive i.e. if μ_1 increase, then $d\mu_2$ must negative and μ_2 must decrease and vice versa.

Self Evaluation

Choose the Best Answer

6. The equation $\frac{\Delta H}{RT^2} = \frac{d(ln K_P)}{dT}$ is known as
   a) van’t Hoff equation
   b) van’t Hoff isochore

c) Gibb's equation
d) Gibbs Duhem equation

7. The equation $\frac{dP}{dT}=\frac{\Delta H}{T\left(V_2-V_1\right)}$ is called
a) Helmholtz equation
b) Kirchoff's equation
c) Clapeyron equation
d) Classius Clapeyron equation

8. The Clasius Clapeyron equation helps to calculate
a) latent heat of vapourisation
b) boiling point or freezing point
c) vapour pressure at one temperature, if at another
d) All the above

9. Van't Hoff reaction isotherm is
a) $\frac{\Delta E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$ b) $\frac{\Delta H}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$
c) $\frac{\Delta E}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$ d) $\frac{\Delta H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$

10. According to Clausius – clapeyron equation, increase of pressure of a liquid leads to
a) increase in boiling point b) decrease in boiling point
c) boiling point doubled d) no change in boiling point

11. Gibbs Duhem equation is
$a¿\sum_i \mu_i \partial \ni ¿0\, b¿\sum_i ¿\partial \mu_i \neq 0$

$c¿\sum_{i} ¿\partial\mu_i=0\,d¿\sum_{i}\mu_i\partial\ni\neq 0$

Answer the Following:

1. Drive the Gibbs-Helmholtz equation. Give its application.
2. Derive Van’t Hoff isochore from Van’t Hoff isotherm.
3. What are the exceptions of third law of thermodynamics.
4. Derive Gibbs-Duhem equation.
5. Derive clapeyron-clausius equation and write its applications.

6 . Discuss the exceptions of the third law of thermodynamics.