BSCCH- 303

B. Sc. III YEAR
PHYSICAL CHEMISTRY

DEPARTMENT OF CHEMISTRY
SCHOOL OF SCIENCES
UTTARAKHAND OPEN UNIVERSITY

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UNIT- 1 ELEMENTARY QUANTUM MECHANICS

CONTENTS:

1.1 OBJECTIVES

In this chapter you will learn the following:

- The inadequacy of classical mechanics
- Birth of quantum mechanics
- Basic formalism of quantum mechanics
- Introduction to quantum mechanical operators

1.2 INTRODUCTION

The concepts and formulation of quantum mechanics are not elementary in the sense that they are easily understood. They are based on the outcome of considerable theoretical research supported by experimental evidence. The quantum mechanical approach to physical problems cannot be explained in simple non-mathematical terms.

Simple and elegant mathematical techniques have been used to elucidate the physical concepts. There are two approaches to quantum mechanics. One is to follow the historical development of the theory from the first indications that the whole fabric of classical mechanics and electrodynamics should be held in doubt to the resolution of the problem in the work of Planck, Einstein, Heisenberg, Schrodinger, and Dirac. The other is to stand back at a point late in the development of the theory and to see its underlying theoretical structure. The first is interesting and compelling because the theory is seen gradually emerging from confusion and dilemma. We see experiment and intuition jointly determining the form of the theory and, above all, we come to appreciate the need for a new theory of matter. The second, more formal approach is exciting and compelling in a different sense: there is logic and elegance in a scheme that starts from only a few postulates, yet reveals as their implications are unfolded, a rich, experimentally verifiable structure.

1.3 BLACK BODY RADIATION

Black-body radiation is the thermal electromagnetic radiation within or surrounding a body in thermodynamic equilibrium with its environment, or emitted by a black body (an opaque and non-reflective body). It has a specific spectrum and intensity that depends only on the body's temperature, which is assumed for the sake of calculations and theory to be uniform and constant. The thermal radiation spontaneously emitted by many ordinary objects can be approximated as black-body radiation. A perfectly insulated enclosure that is in thermal equilibrium internally contains black-body radiation and will emit it through a hole made in its wall, provided the hole is small enough to have negligible effect upon the equilibrium.

A black-body at room temperature appears black, as most of the energy it radiates is infrared and cannot be perceived by the human eye. Because the human eye cannot perceive color at very low light intensities, a black body, viewed in the dark at the lowest just faintly visible temperature, subjectively appears grey (but only because the human eye is sensitive only to black and white at very low intensities - in reality, the frequency of the light in the visible range would still be red, although the intensity would be too low to discern as red), even though its objective physical spectrum peaks in the infrared range.When it becomes a little hotter, it appears dull red. As its temperature increases further it eventually becomes blue-white.

Although planets and stars are neither in thermal equilibrium with their surroundings nor perfect black bodies, black-body radiation is used as a first approximation for the energy they emit. Black holes are near-perfect black bodies, in the sense that they absorb all the radiation that falls on them. It has been proposed that they emit black-body radiation (called Hawking radiation), with a temperature that depends on the mass of the black hole.

Equations for Black-body radiation

1. Planck's law of black-body radiation

Planck's law states that

$$B_\nu(T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

Where,

B_ν (T) is the spectral radiance (the power per unit solid angle and per unit of area normal to the propagation) density of frequency ν radiation per unit frequency at thermal equilibrium at temperature T;h is the Planck constant;c is the speed of light in a vacuum;k is the Boltzmann constant;ν is the frequency of the electromagnetic radiation and T is the absolute temperature of the body.

2. Wien's displacement law

Wien's displacement law states that the black body radiation curve for different temperatures peaks at a wavelength inversely proportional to the temperature. The shift of that peak is a direct consequence of the Planck radiation law which describes the spectral brightness of black body radiation as a function of wavelength at any given temperature. However, it had been discovered by Wilhelm Wien several years before Max Planck developed that more general equation, and describes the entire shift of the spectrum of black body radiation toward shorter wavelengths as temperature increases.

Formally, Wien's displacement law states that the spectral radiance of black body radiation per unit wavelength peaks at the wavelength λ_{max} given by:

$$\lambda_{max} = \frac{b}{T}$$

Where T is the absolute temperature in Kelvin; b is a constant of proportionality called Wien's displacement constant, equal to $2.8977729(17) \times 10^{-3}$ m·K or more conveniently to obtain wavelength in micrometers, b ≈ 2900 μm·K.

Wien's displacement law shows how the spectrum of black-body radiation at any temperature is related to the spectrum at any other temperature. If we know the shape of the spectrum at one temperature, we can calculate the shape at any other temperature. Spectral intensity can be expressed as a function of wavelength or of frequency.

Planck's law was also stated above as a function of frequency. The intensity maximum for this is given by

$$\upsilon_{max} = T \bullet 58.8\ \text{GHz/K}$$

1.4 PLANCK'S RADIATION LAW

Planck's law describes the spectral density of electromagnetic radiation emitted by a black body in thermal equilibrium at a given temperature T (Fig1).The spectral radiance of a body, Bν, describes the amount of energy it gives off as radiation of different frequencies. It is measured in terms of the power emitted per unit area of the body, per unit solid angle of emission, per unit frequency. Planck showed that the spectral radiance of a body for frequency ν at absolute temperature T is given by

$$B_\nu(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{k_B T}} - 1}$$

Where, $k_B$is the Boltzmann constant, his the Planck constant and c isthe speed of light in the medium, whether material or vacuum. The spectral radiance can also be measured per unit wavelength λ instead of per unit frequency. In this case, it is given by;

$$B_\lambda(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

The law may also be expressed in other terms, such as the number of photons emitted at a certain wavelength, or the energy density in a volume of radiation. The SI units of $B_\nu$are $W \cdot sr^{-1} \cdot m^{-2} \cdot Hz^{-1}$, while those of B_λ are $W \cdot sr^{-1} \cdot m^{-3}$.

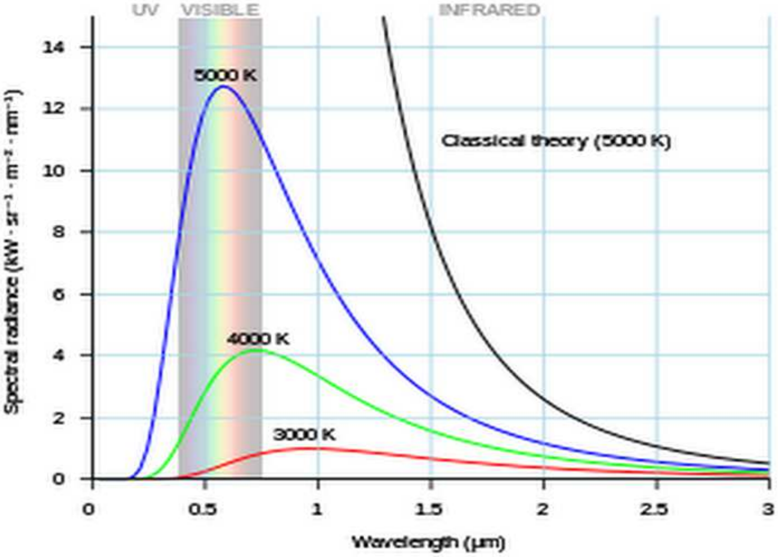

Fig1: Planck's law (colored curves) accurately described black body radiation and resolved the ultraviolet catastrophe (black curve).

1.5 PHOTOELECTRIC EFFECT

The photoelectric effect is a phenomenonin which electrically charged particles are released from or within a material when it absorbs electromagnetic radiation. In a broader definition, the radiant energy may be infrared, visible, or ultraviolet light, X rays, or gamma rays; the material may be a solid, liquid, or gas; and the released particles may be ions (electrically charged atoms or molecules) as well as electrons. in 1887 by the German physicist Heinrich Rudolf Hertz.Further research showed that the photoelectric effect represents an interaction between light and matter that cannot be explained by classical physics, which describes light as an electromagnetic wave. One inexplicable observation was that the maximum kinetic energy of the released electrons did not vary with the intensity of the light, as expected according to the wave theory, but was proportional instead to the frequency of the light.

Consideration of these unexpected behaviours led Albert Einstein to formulate in 1905 a new corpuscular theory of light in which each particle of light, or photon, contains a fixed amount of energy, or quantum, that depends on the light's frequency. In particular, a photon carries an energy E equal to hf, where f is the frequency of the light and h is the universal constant that the German physicist Max Planck derived in 1900 to explain the wavelength distribution of blackbody radiation that is, the electromagnetic radiation emitted from a hot body. The relationship may also be written in the equivalent form $E = hc/\lambda$, where c is the speed of light and λ is its wavelength, showing that the energy of a photon is inversely proportional to its wavelength.

Theory of Photoelectric Effect

In order to study the effect, a metal plate and collecting electrode are placed in a volume. A variable source of potential difference is placed across the electrodes. A sensitive current measuring device is placed in series with the collector. Light is allowed to strike the surface and the current at the collector is noted as a function of the potential difference. According to the above discussion the following conclusion can be obtained;

1) If the frequencyof the light is constant, the photoelectric current increases with increasing intensity of the light.
2) The photoelectrons are releasedwithin less than 10^{-9} sec after the surface is illuminated by the light. The emission is essentially instantaneous with illumination.
3) For a given photosensitive surface, the emission of the photoelectrons takes placeonly if the frequency of the light is equal to a greater than a certain minimumfrequency υ_o, sometimes called the threshold frequency. The value of $\upsilon_o$is different for different materials.
4) The maximum kinetic energy (k_{max}) of the photoelectrons is independent of theintensity of incident radiation (I).
5) The maximum kinetic energy (k_{max})of the photoelectrons depends on the frequency of the incident light.
6) The relationship between k_{max} and $\upsilon_o$is linear.

Explanation of photoelectric effect:

According to the quantum theory, the radiation consists of energy packets known as photon or quanta of energy $h\upsilon$, where h is Planck's constant and υ is frequency of the incident light. When a photon of energy $h\upsilon$ falls on the metal surface its energy is used in two ways:

1) A part of its energy is used in ejecting the electrons just out of the surface; the energy depends on the metal and is called as work function (ϕ_0).

2) The rest part of the energy is used up in imparting the kinetic energy ½ $h\upsilon^2$ to the ejected electrons, thus-

$$h\upsilon = \phi_0 + \frac{1}{2}mv^2$$

$$\phi_0 = h\upsilon_0$$

Where, υ_0 = Threshold frequency

$$h\upsilon = h\upsilon_0 + \frac{1}{2}mv^2$$

$$h\upsilon - h\upsilon_0 = +\frac{1}{2}mv^2\ (KE)$$

$$KE = h\,(\upsilon - \upsilon_0)$$

We know that;

$$\upsilon = \frac{c}{\lambda}$$

$$KE = h\,(\frac{c}{\lambda} - \frac{c}{\lambda_0})$$

Where,λ_0= Threshold wavelength

$$KE = h\upsilon\,(\frac{1}{\lambda} - \frac{1}{\lambda_0})$$

$$KE = h\upsilon\,(\frac{\lambda_0 - \lambda}{\lambda\lambda_0})$$

1.6 BOHR'S MODEL OF THE HYDROGEN ATOM AND ITS DEFECTS

Bohr's model of the Hydrogen atom started from the planetary model, but he added one assumption regarding the electrons, what if the electronic structure of the atom was quantized? Bohr's suggested that perhaps the electroncould only orbit the nucleus in specific orbit or shells with a fixedradius.Only those shells with a radius provided by the equation below were allowed, and it was impossible for electrons to exist between these shells. Mathematically, the allowed value of the atomic radius is given by the equation

$$r(n)=n^2\times r(1)$$

Where n is a positive integer and r(1) is the smallest allowed radius for the hydrogen atom also known as the Bohr's radius. The Bohr's radius has a value of r(1)=0.529×10−10m.

By applying his postulates and the classical laws of physics Bohr workout on various expressions for uni-electronic species like H, $H^{+,}$ $Li^{+,\ -}$, these expressions are given for radius of n^{th} orbit velocity and energy of an electron which is revolving around the n^{th} orbit. He also derived an expression for the frequency (υ)andwavelength (λ)of the spectral line estimated when an electron falls from a high energy orbit to low energy orbit.

Expression for the Radius of n^{th} Orbit of Hydrogen Atom and Hydrogen like Species:

Let us consider Hydrogen like species whose atomic number equal to **Z**;suppose an $\bar{e}$ofcharge **e** is revolving around the nucleus and its charge on the nucleus is equal to **Ze**; suppose **n** is equal to distance between the revolving electron and nucleus in the mass of electron and **v** is the velocity of the electron. Now the revolving electron is being acted upon simultaneously by the two types of forces:

1. Electrostatic Force of Attraction (centripetal force): This force exists between the nucleus and the electron which is revolving around the nucleus, this force of attraction tends to attract the electron towards the nucleus.

This force is equal to Ze^2/r^2
While in SI system this force is equal to

$$= \frac{1}{4\pi\epsilon o} x \frac{ze^2}{r^2}$$

Where$\bullet_0$ is a constant called permittivity of medium and its value is;8854$\bullet$ 10^{12} $J^{-1}C^2m^{-1}$

2. Force of Repulsion (Centrifugal Force):
This force acts outwards from the nucleus and hence tries to keep the revolving electron away from its orbit. In both systems of units, this force is equal to

$$\frac{mv^2}{r}$$

Both the above forces work on opposite direction w.r.t the electron revolving around the nucleus. Then from the above two assumptions, it is clear that these forces must be equal.

Bohr's Radius (r_H): The radius of the first orbit whennis equal to one (n-1)ofH-atom (ʊ - 1) is known as Bohr's radius which is represented as (r_H), the value can be calculated as:

(a) In c.g.s System: we know that in c.g.s system the value of r_n is given by:

$$r_n = \frac{h^2}{4\pi^2 me^2} \bullet \frac{n^2}{z}$$

If the value ofn=1(for $(r_1)_H$andz = 1,putting it in the above equation we get;

$$(r_1)_H = \frac{h^2}{4\pi^2 me^2} \bullet \frac{(1)^2}{1}$$

Putting the value of h = 6.626$\bullet 10^{-27}$ ergs, π = 3.14, m = 9.108 $\bullet 10^{-28}$g, e = 4.8$\bullet 10^{-10}$ esu

$$(r_1)_H = \frac{6.626 \times 10 - 27 \text{ ergs}^2}{(4.3.14)^2 \times (9.108 \times 10^{-28})^2 \times (4.8 \times 10^{-10}\, esu)^2}$$

$(r_1)_H = 0.529 \bullet 10^{-8}$

Or

$(r_1)_H = 0.529$ $A^{\bullet}$

The value of Bohr's Radius for hydrogen atom is 0.529 $A^{\bullet}$.

Defects of Bohr's Model:

- Bohr's model doesn't work well for complex atoms.
- It couldn't explain why some spectral lines are more intense than others.
- It could not explain why some spectral lines split into multiple lines in the presence of a magnetic field.
- The Heisenberg's uncertainty principle contradicts Bohr's idea of electrons existing in specific orbits with a known radius and velocity.

Although the modern quantum mechanical model and the Bohr model may seem vastly different, the fundamental idea is the same in both. Classical physics isn't sufficient to describe all the phenomena that occur on an atomic level. But, Bohr was the first to realize the quantization of electronic shells by fusing the idea of quantization into the electronic structure of the hydrogen atom and was successfully able to explain the emission spectra of hydrogen as well as other one-electron systems.

1.7 COMPTON EFFECT

In 1923,A. M. Compton found that when X- Rays of high energy are allowed to fall on solid matter like carbon block or some other light elements, an electron is ejected from the carbon block and X-Rays are scattered from their original path. In this process a proton from the incident X-Ray collides while the loosely bound electron in the carbon block. After receiving an impact from the photon, the electronwhich was initially at restgain some velocity and hence moves below the direction of incident X-Rays while the photon is deflected above.According to the above discussion we see that X-Rays are scattered from their original path and as a result collision takes place between photon which is moving and electron at rest. It has been found that scatteredX-Rays have longer wavelength than the incident X-Rays (Fig2).

If the wavelength of incident X-Ray and scattered X-Ray are λ and λ' respectively then hc/λ and hc/λ' are the energy associated with the photon of incident and scattered reflect respectively thus the decrease is energy is equal to-

$$\frac{hc}{\lambda} - \frac{hc}{\lambda'}$$

Then this energy $\frac{hc}{\lambda} - \frac{hc}{\lambda}$ is transmitted to the electron at rest and therefore the electron gains some velocity and move from its path in this process.

"*This phenomenon in which there is a change in the wavelength of the scattered X-Ray is called as Compton effect*".

The angle through which the incident X-Rays are deflected from their original path is known as angle of scattering and is denoted by **θ.**

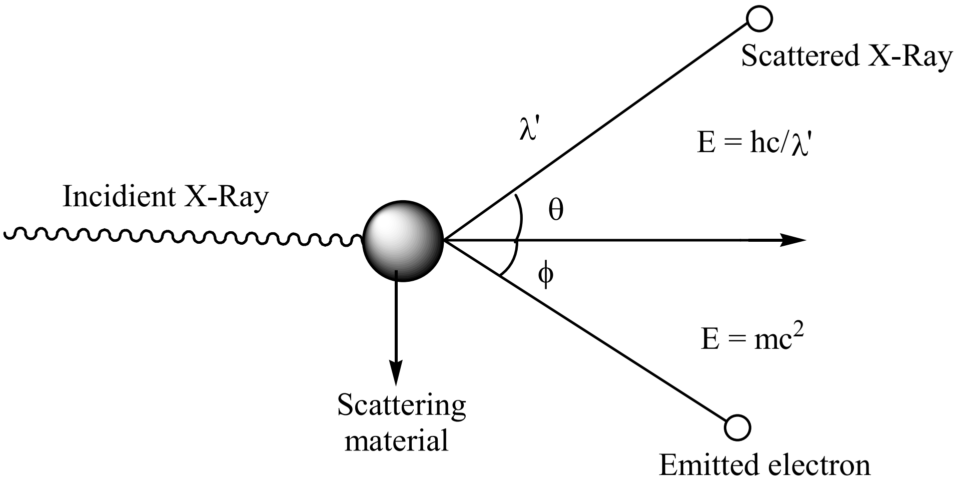

Fig2: Compton Effect of X-Ray Photons

By applying the conservation of energy and momentum and by assuming that the X-Ray is composed of photon each of which has energy equal to hυ. Compton shows that the wavelength λ' of the scattered X-Ray and the wavelength λ of incident X-Ray are related to each other by the relation.

$$\lambda - \lambda' = \frac{h}{mc}(1 - Cos\theta)$$

Where h is the Planck's constant, m is the rest mass of the electron and c is the velocity of light. The difference in λ and λ' is called Compton wavelength shift and is denoted by Δλ.

$$\lambda - \lambda' = \frac{h}{mc}(1 - Cos\theta)\text{……………..(1)}$$

$$\{1\text{-}\cos\theta = \frac{2\sin^2\theta}{2}\}$$

$$\Delta\lambda = \frac{h}{mc}\frac{2\sin^2\theta}{2}$$

$$\Delta\lambda = \frac{2h}{mc}\frac{\sin^2\theta}{2}\text{………………(2)}$$

In equation (1) $\frac{h}{mc}$ = constant = 0.2424 x 10^{-11} m or 0.2424 A^0

From the above relation following cases are obtained:

Case -1 When $\theta = 0^0$

$$\Delta\lambda = \frac{h}{mc}\ 1 - Cos\ 0^0$$

$$\Delta\lambda = 0$$

Case -2 When $\theta = 90^0$

$$\Delta\lambda = \frac{h}{mc}\ 1 - Cos\ 90^0 = 0.2424A^0$$

Case -2 When $\theta = 180^0$

$$\Delta\lambda = \frac{h}{mc}\ 1 - Cos\ 180^0 = 0.4848A^0$$

1.8 de-BROGLIE HYPOTHESIS

Einstein in 1905 suggested that light shows dual character, i.e. particle as well as wave nature. de-Broglie in 1923 extended Einstein's view and said that all the forms of matter like electrons, protons, neutrons, atoms, molecules, etc. also show dual character, he further said that wavelength (λ) of the moving particles of mass m and velocity vis given by

$$\lambda = \frac{h}{mv}$$

Where, h = Planck 's constant

m = mass of electron

υ = velocity of electron

This equation is called as de-Broglie's wave equation and λ is called de-Broglie's wavelength.

Derivation of de-Broglie's equation:

We know that the energy (E) of a photon is given by E = hv ……….(1)

i.e $\upsilon = \frac{c}{\lambda}$

Putting the value of υ in equation number (1)

$E = h\frac{c}{\lambda}$……….. (2) (According to Planck's Quantum theory).

According to Einstein's equation

$E = mc^2$ ………….. (3)

Here, **c** = velocity of light

λ = wave length

m = mass of proton

On combining the above equation (2) and (3) we get

$$mc^2 = h\frac{c}{\lambda}$$

$$mc = \frac{h}{\lambda}$$

$$h = \lambda mc$$

$$\lambda = \frac{h}{m \times c} \text{……………} (4)$$

Thus for another particle moving with a velocity $\boldsymbol{\upsilon}$ then,

$$\lambda = \frac{h}{m \times v}$$

We know that m • v = ρ

$$\lambda = \frac{h}{\rho} \text{………..} (5)$$

Where ρ = momentum of the particles.

The equation (4) is known as de-Broglie's wave equation.

Experimental verification of de-Broglie's wave equation:

If an electron of charge **e** is accelerated by an applied potential, **v** (ES units), i.e. kinetic energy (KE) is given by:

$$KE = V_e \text{……….} (1),$$

Also the magnitude of KE of an electron moving with a velocity $\boldsymbol{\upsilon}$ is also given by;

$$KE = \frac{1}{2} mv^2 \text{………} (2)$$

On combining these two relations we have,

$$KE = V_e = \frac{1}{2} mv^2$$

Or

$$\upsilon = \sqrt{ve/m}$$

Now on putting the value of $\boldsymbol{\upsilon}$ obtained as above in de- Broglie's equation –

$$\lambda = \frac{h}{mv}$$

We get, $\lambda = \frac{h}{\sqrt{\frac{2ve}{m}}}$

On putting the value of h = 6.624•10^{-34} Js, e = 1.602 × 10^{-31} kg, the above equation becomes

$$\lambda = \frac{12.26}{\sqrt{V\ volts}}\ A^0 \quad \text{(de- Broglie's equation)}$$

If a potential difference of 10 volts is applied the wavelength λ of the e^- wave emerging out would be equal to 3.877 A^0. Similarly if the potential difference is varied between 10 and 10000 volts, λwould vary between 3.877 A^0 and 0.1226 A^0. It is well-known that X- Rays have the wavelength in this range.

1.9 HEISENBERG'S UNCERTAINTY PRINCIPLES

According to this principle it is not possible to determine simultaneously and precisely both the position and momentum (or velocity) of a microscopic moving particle like electron, proton etc.Thus from the above discussion Heisenberg gives a mathematical treatment which can be expressed as:

$$\boxed{\bullet x\ X \bullet p}\boxed{\geq \frac{h}{4\,\pi}} \ ....(1)$$

Where $\bullet x$ = uncertainty position, $\bullet p$ = uncertainty momentum and h = Planck's constant, the sign≥ means that the product of $\bullet x$ and $\bullet p$ is equal and greater than $\frac{h}{4\,\pi}$ but never less than$\frac{h}{4\,\pi}$.

The above equation shows $\bullet x$ and$\bullet p$ are inversely proportional to each other which means that$\bullet x$ is very small,$\bullet p$ would be large.

Similarly if an attempt is made to measure the momentum (velocity) of the particle exactly, the uncertainty in the measurement of its position becomes large.

So the equation (1) can be written as:

$$\bullet x\ X \bullet p = \frac{h}{4\,\pi} \ ....(2)$$

We know that, $\Delta p = m\ X \bullet v$;

Where m = mass of moving particle,

Δv = change in velocity

The equation (2) is also written as

$$\bullet x\ X\ m\ X \bullet v = \frac{h}{4\,\pi}$$

$$\bullet x\ X \bullet v = \frac{h}{4\,\pi m}$$

1.10 SCHRODINGER WAVE EQUATION (WITH DERIVATION)

In quantum mechanics, the Schrödinger equation is a mathematical equation that describes the changes over time of a physical system in which quantum effects, such as wave–particle duality, are significant. The equation is a mathematical formulation for studying quantum mechanical systems. It is considered as central result in the study of quantum systems and its derivation was a significant landmark in developing the theory of quantum mechanics. It was named after Erwin Schrödinger, who derived the equation in 1925 and published it in 1926, forming the basis for his work that resulted in Schrödinger being awarded the Nobel Prize in Physics in 1933. The equation is a type of differential equation known as a wave-equation, which serves as a mathematical model of the movement of waves.

The equation can be given as:

$$\frac{\delta^2\varphi}{\delta x^2}+\frac{\delta^2\varphi}{\delta y^2}+\frac{\delta^2\varphi}{\delta z^2})\frac{8\pi^2 m}{h^2}\ (E-V)\varphi=0$$

$$\left(\frac{\delta^2}{\delta x^2}+\frac{\delta^2}{\delta y^2}+\frac{\delta^2}{\delta z^2}\right)\varphi\ \frac{8\pi^2 m}{h^2}\ (E-V)\varphi=0$$

$$\boldsymbol{\nabla^2\ \varphi+\frac{8\pi^2 m}{h^2}\ (E-V)\varphi=0}$$

Where ∇ = Laplacian operator

φ = Wave function which gives the amplitude of wave around the nucleus of any point

m = Mass of particle

Derivation of the Schrodinger wave equation:

According to wave length relationship de- Broglie

$$\lambda = \frac{h}{mu}\text{……………… (1)}$$

Let us consider the wave equation of the stationary wave associated with the particle in term of the certain Cartesian axis at any time can be given as:

$$\varphi = \varphi^0\ Sin\ 2\pi\vartheta t\text{……………… (2)}$$

Since the differential wave equation of motion can be written in classical way as follow-

$$\frac{\delta^2\varphi}{\delta t^2} = u^2\ \left(\frac{\delta^2}{\delta x^2}+\frac{\delta^2}{\delta y^2}+\frac{\delta^2}{\delta z^2}\right)\varphi$$

$$\frac{\delta^2\varphi}{\delta t^2} = u^2\ \nabla^2\varphi\text{………………….. (3)}$$

Now differentiating equation (2) with respect to‘t’

$$\frac{\delta\ \ \varphi}{\delta t} = \varphi^0 Cos\ 2\pi\vartheta t.\,2\pi\vartheta$$

We know that $\frac{\delta}{\delta t}\ Sin\ x\ = Cos\ x = \ -Sin\ x$

$$\frac{\delta\ \ \varphi}{\delta t} = -\varphi^0 2\pi\vartheta.\,Cos\ 2\pi\vartheta t\text{………………….. } \mathit{(4)}$$

Double differentiating **of equation (4),**

$$\frac{\delta^2\varphi}{\delta t^2} = -\ \varphi^0 2\pi\vartheta\ Sin 2\pi\vartheta t.\,2\pi\vartheta$$

$$\frac{\delta^2 \varphi}{\delta t^2} = -\varphi^0 4\pi^2 \vartheta^2 . Sin2\pi\vartheta t$$

From equation (2)$\varphi = \varphi^0 Sin2\pi\vartheta t$, **on putting the value of** $\varphi^0\, 2\pi Sin2\pi\vartheta t = \lambda$**i** in equation (2)

$$\frac{\delta^2 \varphi}{\delta t^2} = -4\pi^2\vartheta^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$\vartheta = \frac{v}{\lambda} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Putting the value of ϑ equation (5)

$$\frac{\delta^2 \varphi}{\delta t^2} = -\frac{4\pi^2\vartheta^2}{\lambda^2}\varphi \ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Equating the equation (3) and (7)

$$u^2\ \nabla^2\varphi = -\frac{4\pi^2 u^2}{\lambda^2}\varphi$$

$$\nabla^2\varphi = -\frac{4\pi^2}{\lambda^2}\varphi \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Now putting the value of equation (1) to (8)

$$\nabla^2\varphi = -\frac{4\pi^2\ m^2 u^2}{h^2}\varphi \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

We know that, $E = KE + V$

$$E = \frac{1}{2}m\vartheta^2 + V$$

$$(E - V) = \frac{1}{2}m\vartheta^2$$

$$2(E - V) = m\vartheta^2$$

Multiplying by m on both side,

$$2m(E - V) = m^2\vartheta^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Putting the value of $m^2\vartheta^2$ in equation (9)

$$\nabla^2\varphi = -\frac{4\pi^2\, 2m\ (E - V)}{h^2}\ \varphi$$

$$\boxed{\nabla^2\ \varphi + \frac{8\pi^2 m}{h^2}\ (E - V)\varphi = 0} \ldots\ldots\ldots\ldots\ \mathbf{(11)}$$

Equation (11) is known as time independent wave equation of Schrodinger.

1.11 PHYSICAL INTERPRETATION OF THE WAVE FUNCTION

In Schrodinger's wave equation, wave function φ represents the amplitude of the spherical wave. According to the theory of propagation of light and sound waves, the square of the amplitude of the wave is proportional to the intensity of sound and light. A similar concept, modified to meet the requirement of uncertainty principle, has been developed for the physical interpretation of wave function φ.

This may be stated as the probability of finding an electron around the nucleus. It is proportional to the square of the function φ^2 at that point. If wave function φ is imaginary, φ φ* become a real quantity where φ* is complex conjugate of φ. This quantity represents the probability φ^2 as a function of x, y and z coordinate of the system, and it varies from one space region to another. Thus the probability of finding an electron around the nucleus is different in different region.

In Schrodinger wave equation, the symbol φ represents the amplitude of the spherical wave. For hydrogen atom, Schrodinger wave equation gives the wave function of the electron situated at a particular distance ‘r’, so that:

$$\varphi = C_1 e\ –C_2 r$$

Where, C_1 and C_2 are constants. The square of the amplitude (φ^2) is proportional to the density of the wave. The wave of energy or the cloud of negative charge is denser in some part than others. Max Born proposed the wave equation on the basis of probabilities. The space characteristic of an electron is best described in term of distribution function given by,

$$D = 4\pi^2 \varphi 2$$

The numerical value of ‘D’ denotes the probability or chance of finding the electron in a shell of radius r and thickness dr, or volume $4\pi r^2\, dr$.

1.12 OPERATOR

Operators are commonly used to perform a specific mathematical operation on another function. The operation can be to take the derivative with respect to a particular term, or to multiply, divide, add or subtract a number or term with regard to the initial function. Operators are commonly used in physics, mathematics and chemistry, often to simplify complicated equations such as the Hamiltonian operator, used to solve the Schrödinger equation.The result of an operator on a function gives another function.

(Operator) x (Function) = Another function

1.12.1 Hamiltonian Operator:

From the fundamental wave equation of Schrodinger:

$$\nabla^2\varphi + \frac{8\pi^2 m}{h^2}(E - V)\varphi = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (1)$$

The potential energy $v = \frac{q_1\, q_2}{r}$

$$v = \frac{e-(-e)}{r} = -e^2/r$$

Putting the value of v in equation 1-

$$\nabla^2\varphi + \frac{8\pi^2 m}{h^2}\left(E - \frac{e^2}{r}\right)\varphi = 0$$

$$\nabla^2\varphi + \frac{8\pi^2 m}{h^2}E\varphi + \frac{e^2\varphi}{r} = 0$$

$$E\varphi + \frac{e^2\varphi}{r} = -\nabla^2\varphi \; X \; \frac{h^2}{8\pi^2 m}$$

$$E\varphi = -\nabla^2\varphi \; X \; \frac{h^2}{8\pi^2 m} - \frac{e^2\varphi}{r}$$

$$E\varphi = (-\nabla^2\frac{h^2}{8\pi^2 m} - \frac{e^2}{r})\varphi$$

We know that,

$$(-\nabla^2\frac{h^2}{8\pi^2 m} - + \frac{e^2}{r})\varphi = H\varphi$$

Since,

$$\boxed{E\varphi = H\varphi}$$

Where, Hφ is called as Hamiltonian operator. In this equation, φ is called Eigenfunction and E is called Eigenvalue.Such an equation is, therefore, called Eigenvalue equation. Thus for Schrodinger wave equation, we can write as given:

(Energy operator) x (wave function) = (energy) x (wave function)

1.12.2 Laplacian operator:

This is a very common operator used in quantum mechanism. It is represented by $\nabla^2$and is defined as:

$$\nabla^2 = \frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2}$$

Schrodinger wave equation;

$$\frac{\delta^2\varphi}{\delta x^2} + \frac{\delta^2\varphi}{\delta y^2} + \frac{\delta^2\varphi}{\delta z^2} + \frac{8\pi^2 m(E-V)}{h^2}\varphi = 0$$

The above equation may also write as:

$$\boxed{\nabla^2\varphi + \frac{8\pi^2 m(E-V)}{h^2}\varphi = 0}$$

1.13 POSTULATES OF QUANTUM MECHANICS

The postulates of quantum mechanism which can generate the derivation of Schrodinger wave equation are given as:

1.The state of a quantum mechanical system is completely specified by a function ψ (r,t) that depends on the coordinates of the particle**s** and time. This function, called the wave function or state function, has the important property thatψ^***(**r,t) ψ(r,t) **dt**is the probability that the particle lies in the volume element dt located at **r** at time **t**.

The wave function must satisfy certain mathematical conditions because of this probabilistic interpretation. For the case of a single particle, the probability of finding it somewhere is **1**, so that we have the normalization condition

$$\int_{-\infty}^{\infty} \Psi^*(\mathbf{r}, t)\Psi(\mathbf{r}, t)\, d\tau = 1$$

It is customary to also normalize many particle wave functions to **1.** The wave function must also be single valued, continuous, and finite.

2. To each observable quantity in classical mechanics, like position, velocity, momentum, energy etc., there is a corresponding certain mathematical operator in quantum mechanics, the nature of which depends upon the classical expression for the observable quantity. Some common operators occurring in quantum mechanics are collected in given Table 1.

Table 1: Physical observables and their corresponding quantum operators

Observable Name	**Observable Symbol**	**Operator Symbol**	**Operator operation**
Position	R	$\hat{\mathbf{r}}$	Multiply by r
Momentum	P	$\hat{\mathbf{P}}$	$-i\hbar\left(\hat{i}\frac{\partial}{\partial x}+\hat{j}\frac{\partial}{\partial y}+\hat{k}\frac{\partial}{\partial z}\right)$
Kinetic energy	T	$\hat{T}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$
Potential energy	V(r)	$\hat{V}(\mathbf{r})$	Multiply by V(r)
Total energy	E	$\hat{H}$	$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V(\mathbf{r})$
Angular momentum	l_x	$\hat{l}_x$	$-i\hbar\left(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}\right)$
	l_y	$\hat{l}_y$	$-i\hbar\left(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}\right)$
	l_z	$\hat{l}_z$	$-i\hbar\left(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\right)$

3. If ψ is a well behaved function for the given state of a system and A is a suitable operator for the observable quantity, then the operation on ψ by the operator A gives ψ multiplied by a constant value of the observable property i.e.,

$$\hat{A}\Psi = a\Psi$$

This postulate cover the central point of quantum mechanics, the values of dynamical variables can be quantized (although it is still possible to have a continuum of Eigenvalues in the case of unbound states). If the system is in an eigenstate of Â with Eigen value **a**, then any measurement of the quantity (A) will yield (a).

4. If a system is in a state described by a normalized wave function ψ, then the average value of the observable corresponding to Â is given by-

$$< A >= \int_{-\infty}^{\infty} \Psi^* \hat{A} \Psi d\tau$$

5. The wave function or state function of a system evolves in time according to the time dependent Schrödinger equation-

$$\hat{H}\Psi(\mathrm{r},t) = i\hbar\frac{\partial\Psi}{\partial t}$$

6. The total wave function must be antisymmetric with respect to the interchange of all coordinates of one fermion with those of another. Electronic spin must be included in this set of coordinates.

1.14 SCHRODINGER WAVE EQUATION FOR HYDROGEN LIKE ATOM

We know that in case of Hydrogen atom, one proton, one electron, and the electrostatic (Coulomb) potential that holds them together.The potential energy in this case is simply;

$$V = -\frac{e^2}{4\pi\varepsilon_0 r}$$

This is the attractive potential between charges of +e and -e separated by a distance r.

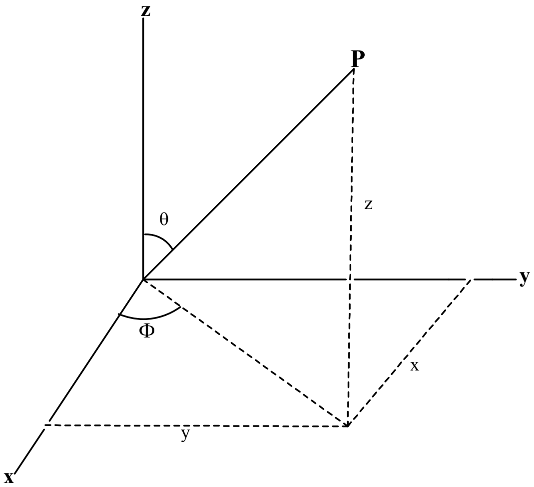

Fig3: spherical polar coordinates, r is the length of the radius vector from the origin to a point (xyz)

(a) Wave equation in Cartesians coordinates (x, y, z):

On putting $V = -\frac{e^2}{r}$ in Schrodinger wave equation, we get:

$$\left(\frac{\delta}{\delta x^2}+\frac{\delta}{\delta y^2}+\frac{\delta}{\delta z^2}\right)\varphi\ \frac{8\pi^2 m}{h^2}\ (E+\frac{e^2}{r})\varphi = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

This is Schrodinger wave equation for H atom in Cartesian coordinates (x, y, z). In this equation the wave function ψ is a function of x, y and z.

(b) Wave equation in polar coordinates (r, θ, ϕ):

When three Cartesians coordinates (x, y, z) appearing in equation (1) are converted in to polar coordinates (r, θ, ϕ) with the help of relations z = r cos θ, y = r sin θ sin ϕ and x = r sin θ cos ϕ, equation (1) gets converted in to given equation (2) which is Schrodinger wave equation for H atom in polar coordinates.

$$\left[\frac{\delta}{\delta r}\left(r^2\frac{\delta}{\delta r}\right)+\frac{1}{sin\theta}\frac{\delta}{\delta\theta}\left(sin\theta\frac{\delta}{\delta\theta}\right)+\frac{1}{sin^2\theta}\frac{\delta^2}{\delta\emptyset^2}\right]\varphi+\frac{8\pi^2 m r^2}{h^2}\left(E+\frac{e^2}{r}\right)\varphi = 0 \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In equation (2) φ is a function of polar coordinates (r, θ, ϕ) instead of Cartesians coordinates (x, y, z).

Solution of Schrodinger wave equation for H- atom:

In the above Schrodinger wave equation for H -atom in polar coordinates is written as:

$$\left[\frac{\delta}{\delta r}\left(r^2\frac{\delta}{\delta r}\right)+\frac{1}{sin\theta}\frac{\delta}{\delta\theta}\left(sin\theta\frac{\delta}{\delta\theta}\right)+\frac{1}{sin^2\theta}\frac{\delta^2}{\delta\emptyset^2}\right]\varphi+\frac{8\pi^2 m r^2}{h^2}\left(E+\frac{e^2}{r}\right)\varphi = 0 \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The value of ψ appearing in the above equation can be made only when ψ is written in the form-

$$\Psi(r, \theta, \phi) = R(r)\ \Theta(\theta)\ \Phi(\phi) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

In the equation (2), R(r) is a function which depends on r only but is independent of the other two polar coordinates *viz*., θ and ϕ. Θ (θ) is a function which depends on θ and is independent of r and ϕ. Same way Φ (ϕ) is a function which is dependent on ϕ only but is independent of r and θ.

In the above equation (2), the function R(r) is called radial wave function while the other two wave functions viz., Θ (θ) and Φ (ϕ) are called angular wave function. Ψ(r, θ, ϕ) is called complete or total wave function.

When we assume Ψ(r, θ, ϕ) equal to R(r) Θ (θ) Φ (ϕ) in equation (1), this equation is converted in to a complicated equation. This equation is divided into following three equations which are given below.

(a) $\frac{1}{R}\cdot\frac{\delta}{\delta r}\left(r^2\frac{\delta R}{\delta r}\right)+\frac{8\pi^2 m r^2}{h^2}\left(E+\frac{e^2}{r}\right) = l\ (l+1)$

The above equation is a function of r only and on solution gives the value of R(r). When this equation is solved for R(r), we get many values of R(r). The value of R(r) beside dependingon r also depends on two constants *n* and *l*. R(r) is, therefore, generally written as $R_{n,\ l}$**(r)**, n and l are called quantum numbers since they represent the quantization of definite physical properties about the electron in the atom.

The values of radial wave function, $R_{n,\ l}$for 1s, 2s and 2p states for hydrogen atom are given below:

For 1s state (*n* = 1, *l* = 0), $R_{1,0}$ or $R_{1s} = [Z/a_0]^{3/2}\ e^{-\sigma/2}$

For 2s state (*n* = 2, *l* = 0), $R_{2,0}$ or $R_{2s} = 2^{-3/2}\ [Z/a_0]^{3/2}\ (2-\sigma)\ e^{-\sigma/2}$

For 2p state (*n* = 2, *l* = 1), $R_{2,1}$ or $R_{2p} = 2^{-1} \times 6^{-1/2}\ [Z/a_0]^{3/2}\ \sigma \times e^{-\sigma/2}$

Where, a_0 = Bohr's radius, Z = atomic number and σ = Zr /n a_0

(b) $\frac{\sin\theta}{\Theta}\frac{\delta}{\delta\theta}\left(\sin\theta\ \frac{\delta\Theta}{\delta\theta}\right) + \ l(l+1)\sin^2\theta\ = m^2$

This equation is a function of Θ only and on solution gives the value of Θ (θ). When this equation is solved for Θ (θ), we get many value of Θ (θ). Each value of Θ (θ) beside depending on the angle θ, also depends on two constant *l* and *m*. Θ (θ) is, therefore, generally represented as $\Theta_{l,\,m}$ (θ). The value of *m* depends on the value of *l*. For a given value of *l, m* = 0, ± 1, ± 2….. ± *l*. Thus m has (2*l* + 1) values for a given value of *l*, m is called magnetic quantum number.

If the values of *l* and *m* are known for a given orbital, the value of the angular wave function, $\Theta_{l,\,m}$ for that orbital can be written as given below:

(i) $\Theta_{0,0}(l = 0, m = 0)\ = \frac{1}{\sqrt{2}}(s - orbitals)$

(ii) $\Theta_{1,0}(l\ = 1, m\ = 0)\ = \sqrt{\frac{3}{2}}\cos\theta;\ \Theta_{1,\pm1}\ (l = 1, m = \pm1) = \sqrt{\frac{3}{2}}\sin\theta\ \ (p - orbitals)$

$\Theta_{2,0}(l = 2, m = 0)\ = \sqrt{\frac{5}{8}}(3\ \cos^2\theta - 1$

(iii) $\Theta_{2,\pm1}(l = 2, m = \pm1)\ = \sqrt{\frac{15}{4}}(\sin\theta\ \cos\theta)$ (d -orbitals)

$\Theta_{2,\pm2}(l = 2, m = \pm2)\ = \sqrt{\frac{15}{16}}\sin^2\theta$

(c) $\frac{1}{\Phi}.\frac{\delta^2\Phi}{\delta\text{Ø}^2} = m^2$

This equation is a function of m only and on solution gives the value of Φ (Ø), we get many values of Φ (Ø). Each values of Φ (Ø) depending on angle Ø and also depends on the constant *m*. Hence the angular wave function Φ (Ø) is also represented as Φ_m(Ø) or $\Phi_{m.}$

1.15 INTERPRETATION OF QUANTUM NUMBERS

The three quantum numbers which arise in a natural way during search of acceptable solution of the Schrodinger wave equation may be express as follow:

n =1, 2, 3, …………..
l = 0, 1, 2,…………...
m_1 = 0, ±1, ±2……….., ±*l*

We can interpret these quantum numbers in the following way:

To interpret *n*, we note that according to the Schrodinger's theory of uni-electronic species, the total energy of the bound states of the atom can have only following values:

$$E_n = -\frac{2\pi^2\mu Z^2 e^4}{n^2 h^2}$$

These Eigen values depend only on the quantum number n, are the same as obtained by old quantum theory. They are in excellent agreement with experiment. Thus n quantizes the total energy of the atom. Hence n is called the total or principal quantum number.

To explain *l, we consider the radial wave equation*

$$\frac{1}{R}\cdot\frac{\delta}{\delta r}\left(r^2\frac{\delta R}{\delta r}\right)+\frac{8\pi^2 m r^2}{h^2}\left(E+\frac{e^2}{r}\right)=l\ (l+1)$$

$$\frac{1}{r^2}\cdot\frac{\delta}{\delta r}\left(r^2\frac{\delta R}{\delta r}\right)+\left[\frac{8\pi^2 m}{h^2}\left(E+V(r)\right)-\frac{l(l+1)}{r^2}\right]R=0$$

The total energy E of the atom consist of the kinetic energy K and potential energy V of its electron. The kinetic energy K has two parts K_{radial} due to electron motion towards or away from the nucleus and $K_{orbital}$ due to the motion around the nucleus. Thus

$$E = K_{radial} + K_{orbital} + V\ (r)$$

Putting the value of E in the radial equation, we obtained,

$$\frac{1}{r^2}\cdot\frac{\delta}{\delta r}\left(r^2\frac{\delta R}{\delta r}\right)+\left[\frac{8\pi^2 m}{h^2}\left(E_{radial}+K_{orbital}-\frac{h^2}{8\pi^2\mu}\frac{l(l+1)}{r^2}\right)\right]R=0$$

This radial equation is concerned only with the radial motion of the electron, hence it must be free from $K_{orbital}$. This is possible only when the last two terms cancel out each other, i.e when

$$K_{orbital}=\frac{h^2}{8\pi^2\mu}\frac{l(l+1)}{r^2}$$

Since the quantum number *l* is restricted to the values 0, 1, 2,……..(*n*-1), the electron can have only discrete values of the angular momentum. Thus like total energy E, the orbital angular momentum is also quantized and this quantization is described by *l*. Hence *l* called the orbital quantum number. The representation for the angular momentum is identical to that obtained in Bohr-Somerfield theory.

The interpretation of m_l comes when the atom is placed in an external magnetic field. We know that an electron revolving around the nucleus is a minute counter loop and behave like a magnetic dipole in an external magnetic field. Its magnetic moment and its potential energy depend upon the magnetic moment and its orientation with respect to the field. But the magnitude and direction of the magnetic moment depends upon the magnitude and direction of the angular momentum of the electron which, therefore, determine the magnetic potential energy.

As we see that the direction of the angular momentum is quantized with respect to an external magnetic field. If the field is along the z-axis, the component of angular momentum in this direction is:

$$l_z = m_l \frac{h}{2\pi}$$

Where m_l are the values 0, ±1, ±2,…….±l. Thus m_l describe the quantization of the orientation of angular momentum in a magnetic field and hence the quantization of the magnetic energy of the electron. Hence m_l is called the magnetic quantum number.

Thus each of the eignfunctions of one electron atom is specified by three quantum numbers *n, l* and m_l; in which *n* determines the total energy, *l* determine the angular momentum and m_l determine the z- component of the angular momentum of the electron. But for a given value of *n,* there are various possible values of *l* and $m_{l.}$

1.16 SUMMARY

In this chapter the historical development of quantum mechanics has been discussedseveral effects like photoelectric, Compton, black body radiation, Heisenberg Uncertainty principle. The postulates of quantum mechanics along with the basicterms involved are also discussed. The Schrödinger's wave equation has been derivedand the properties and its physical significance also are given indetail. Schrodinger wave equation has been applied to several simple systems andalso being solved to get wave function and the respective energy values. The quantum numbersare also described.

1.17 TERMINAL QUESTIONS

1. What is black body? Discuss the energy distribution for black body radiationat different temperatures.
2. Discuss photoelectric effect.
3. What do you understand by de Broglie hypothesis?
4. State and explain Heisenberg's uncertainly principle. Derive the equation forit. Write its applications also.
5. Discuss Compton Effect. Write its physical significance.
6. What are operators? Discuss the algebra of operators.
7. Write a brief note on physical significance of ψ and ψ^2.
8. Write the Schrödinger wave equation for hydrogen atom in spherical polarcoordinates.Separate the variables of this equation to expression forindividual one.
9. How do the three quantum numbers follow from the solution of Schrodinger wave equation?
10. Derive the Plank's radiation law. How can it be verified experimentally?

11. Explain briefly de-Broglie hypothesis related to the dual nature of matter. Derive de-Broglie wave equation.
12. What are the main postulates of Bohr's atomic model?
13. State and explain Heisenberg's Uncertainty principle.
14. What is an operator? Give the types of operators.
15. Write a short note on:
    a) Compton effect
    b) Black body radiation
    c) Wien's Displacement law
    d) Photoelectric effect
    e) Heisenberg's Uncertainty principle

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UNIT- 2 FUNDAMENTALS OF SPECTROSCOPY

CONTENTS

2.1 OBJECTIVES

The main objectives of this chapter are:

(1) To understand the basics of spectroscopy.
(2) Explain the importance of spectroscopy.
(3) Know the relationship between wavelength, frequency and the energy of transition.
(4) Differentiate various region of the electromagnetic spectrum.
(5) Describe the basic features of different spectrometer.
(6) Compare the atomic and molecular spectroscopy.
(7) Identify the absorption and emission spectra.
(8) Understand Born-Oppenheimer Approximation.

2.2 INTRODUCTION OF SPECTROSCOPY

Spectroscopy deals with the transitions induce in a chemical species by its interaction with the photons of electromagnetic radiation. Spectroscopic methods are generally used to measure the energy difference between various molecular energy levels and to determine the atomicand molecular structures. The instruments used in such studies, called spectrophotometers, are devised to measure the relative energy that is emitted or reflected in the infrared, visible or ultraviolet regions, as a function of wavelength or wavenumber. Special devices are incorporated in these instruments for the automatic recording of spectra. The spectrum of a molecule is thus presented as a continuous graph obtained by plotting either absorption or transmittance of electromagnetic radiation as a function of wavelength or wavenumber over a particular range.

The term spectrometry is quite different from usual spectroscopic techniquesdepending upon the absorption or emission of electromagnetic radiation.Mass spectrometry involves the interaction of charged species with magnetic and/or electric fields,giving rise to a mass spectrum. In mass spectrometry, the photographic plate is calibrated to measure various values of m/z. In most branches of spectroscopy, the system interacts with electric field. However, in case of magnetic resonance spectroscopy, it interacts with the magnetic field.This type of spectroscopy depends on the physical quantity measured. Normally, the quantity that is measured is intensity, either of energy absorbed or produced. Electromagnetic spectroscopy involves interactions of matter with electromagnetic radiation, such as light. Electron spectroscopy involves interactions with electron beams. Acoustic spectroscopy involves the frequency of sound. Dielectric spectroscopy involves the frequency of an external electrical field.Mechanical spectroscopy involves the frequency of external mechanical stress, e.g. a torsion applied to a piece of material.

2.3 IMPORTANCE OF SPECTROSCOPY

Spectroscopic techniques are used widely in all technical fields of science and technology. UV-Visible spectroscopy is used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds. Infrared spectroscopy is widely used in industry as well as in research. It is a simple and reliable technique for measurement, quality control and dynamic measurement. It is also used in forensic analysis in civil and criminal analysis. IR spectroscopy has major role in the identification of functional groups and structure elucidation, identification of substances, studying the progress of the reaction, detection of impurities, etc.

Circular dichroism (CD) spectroscopy is a type of absorption spectroscopy that can provide information on the structures of many types of biological macromolecules specifically chiral or asymmetric molecules because they absorb left and right handed polarized light to different extent. CD spectroscopy is mainly used to monitor secondary structures, conformational changes, environmental effects, protein folding and denaturation, etc.

Raman spectroscopy is commonly used in chemistry since vibrational information is very specific for the chemical bonds in molecules. It provides a fingerprint by which the molecule can be identified. Raman spectroscopyhas many practical applications, such as they are used inpharmaceuticals and cosmetics for the monitoring of compounds, in geology and mineralogy for the identification of gemstone and minerals, for characterization of semiconductors, their purity, alloy composition, contamination identification, doping effects, etc.

Mass spectrometry (MS) is an analytical technique that ionizes chemical species and sorts the ions into a spectrum based on their mass-to-charge ratio.It is widely used in forensic testing, environmental monitoring, pharmaceutical testing, archeological studies (isotope ratios), medical research and biological studies. Electron paramagnetic resonance is used in solid state physics, for the identification of radicals in chemistry to identify reaction pathways, as well as in biology and medicine for tagging biological spin probe. NMR Spectroscopy has applications in a widerange of disciplines, and developmentof newly applied methods for NMRis an activearea of research. Common applications of NMR spectroscopyincludestructureelucidation, chemical composition determination,mixture analysis, quality assurance and control, quantitative analysis, compound identification and confirmation, analysisof inter- and intramolecular exchange processes, reaction kinetics examination, reaction mechanism investigation, etc.

2.4 THE ELECTROMAGNETIC RADIATION

Earlier it was believed that light travels in a straight line. But it was not true because this could not explain some important phenomenon such as Interference, Refraction, and Diffraction etc. later light is supposed to travel in the form of wave. Visible light is the form of energy which can be described by two complementary theories, the wave theory and the corpuscular theory. Neither of these theories alone can explain all the properties of light. We shall consider wave theory here and see the propagation of light by light waves involves both electric and magnetic forces. Electromagnetic radiation is the form of energy propagates through free space or through material in the form of electromagnetic waves. Electromagnetic radiations have electric and magnetic fields that simultaneously oscillate in plane which are mutually perpendicular to each other. Electromagnetic radiation has dual nature it exhibits wave properties and particulate (photon) properties.

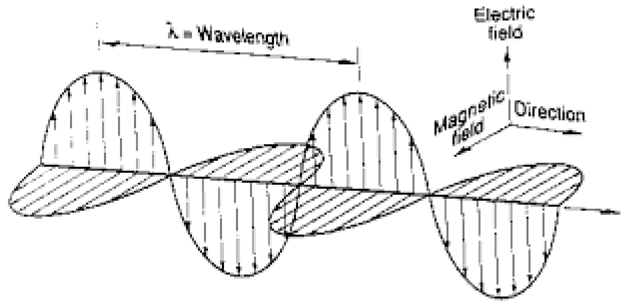


Fig 1: Planes of electromagnetic waves

General Properties of all electromagnetic radiation:

1) Electromagnetic radiation can travel through empty space (vacuum). Most types of waves travel through some sort of substance. For example, sound waves need either a gas, solid, or liquid to pass through in order to be heard.
2) The speed of light is always a constant and no medium is required for their propagation (Speed of light: 2.99792458×10^{8} ms^{-1}).
3) These are characterized by their wavelength or frequencies or wave numbers.
4) Electromagnetic waves are not deflected by electric or magnetic field.
5) Wavelengths are measured between the distances of either crests or troughs. It is usually characterized by the Greek symbol λ (Fig 1).
6) The direction of electric field and magnetic field perpendicular to each other and both perpendicular to the direction of wave propagation.
7) Electromagnetic waves are transverse waves.

8) Electromagnetic waves have the characteristic properties of reflection, refraction and polarization.

Characteristics of Electromagnetic Spectrum

(1) **Wavelength:**Any of the parts of the wave that are pointing up like mountains are called crests. Any part that is sloping down like a valley is a trough (Fig 2).

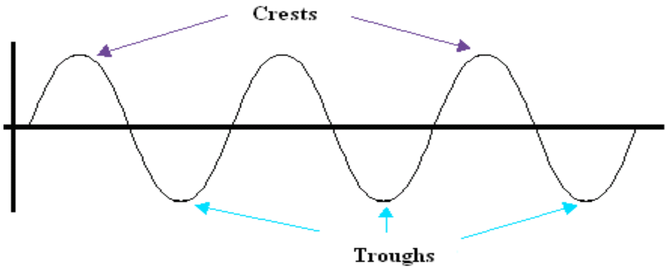


Fig 2: Crests and Trough in a wave

Wavelength is the distance between the two adjacent crests or troughs in a particular wave. It is denoted by the letter λ (lambda).

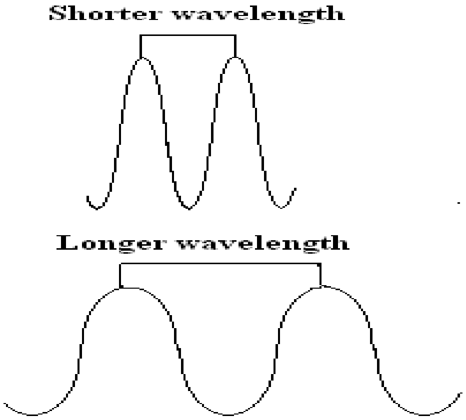


Fig 3: Wave motion

Wavelengths are usually expressed in the metric or SI system, since having multiples of 10 are more convenient (Table 1 and Table 2). Wavelengths can range from many kilometers long to extremely short lengths or fractions of a meter (Fig 3).

Table 1: Unit expression for wavelength

Name	**Meters**	**Exponent**
1 km (kilometer)	1000 m (meters)	$1x10^{3}$ m
1 m	1 m	1 m
1 cm (centimeter)	0.01 m	$1x10^{-2}$ m
1 mm (millimeter)	0.001 m	$1x10^{-3}$ m

1 µm (micrometer or micron)	0.000001 m	$1x10^{-6}$ m
1 nm (nanometer)	0.000000001 m	$1x10^{-9}$ m
1 Å (Angstrom)	0.1 nm	$1x10^{-10}$ m

Table 2:Common Wavelength units for Electromagnetic radiation

Unit	**Symbol**	**Wavelength(m)**	**Type of radiation**
Picometer	Pm	10^{-12}	Gamma ray
Angstrom	Å	10^{-10}	X-ray
Nanometer	Nm	10^{-9}	X-ray, UV
Micrometer	Mm	10^{-6}	Infrared
Millimeter	Mm	10^{-3}	Infrared
Centimeter	Cm	10^{-2}	Microwave
Meter	M	10^{0}	radio wave

(2) **Frequency:** Frequency refers as the number of times an event occurs. For example, someone who enjoys computers may frequently visit the computer home web page. It is defined as the number of waves which can pass through a point in one second. **Example:**If an alternating current is said to have a frequency of 3 Hz, that indicates its waveform repeats 3 times in 1 second.It is expressed as ν (nu) in cycle per second or in Hertz (Hz) where 1Hz = 1 cycle sec^{-1}. Other major units of frequency are given in table 3 below.

Table 3:Unit expression for frequency

Unit	**Equivalent**
Hertz (Hz)	1 Hz
Kilohertz(kHz)	10^{3} Hz
Megahertz(MHz)	10^{6} Hz
Gigahertz(GHz)	10^{9} Hz
Terahertz(THz)	10^{12} Hz

(3) **Wavenumber:** It is defined as the total number of waves per unit distance of radiant energy of a given wavelength. It is reciprocal of wavelength and expressed in per centimeter (cm^{-1}), represented asv.

Relation between wavelength and frequency:

The equation that relates wavelength and frequency for electromagnetic waves is:

$\nu = c / \lambda$

Where λ is the wavelength, ν is the frequency and c is the speed of light.

Relation between wavelength and wavenumber:

The equation that relates wavelength and frequency for electromagnetic waves is:

$$\tilde{\upsilon} = 1 / \lambda$$

Where ν is wave number and λ is wavelength.

Relation between frequency and wave number:

The equation that relates wavelength and frequency for electromagnetic waves is:

$\nu = c\,\tilde{\upsilon}$

Relation between energy and frequency:

The equation that relates energy and frequency for electromagnetic waves is:

$$E = h\nu$$

Where h is Planck's constant and E is energy.

2.5 REGIONS OF SPECTRUM

Electromagnetic waves can be classified and arranged according to their various wavelengths/frequencies; this classification is known as the electromagnetic spectrum. The following figure 4 and table 4 shows us this spectrum, which consists of all the types of electromagnetic radiation that exist in our universe.

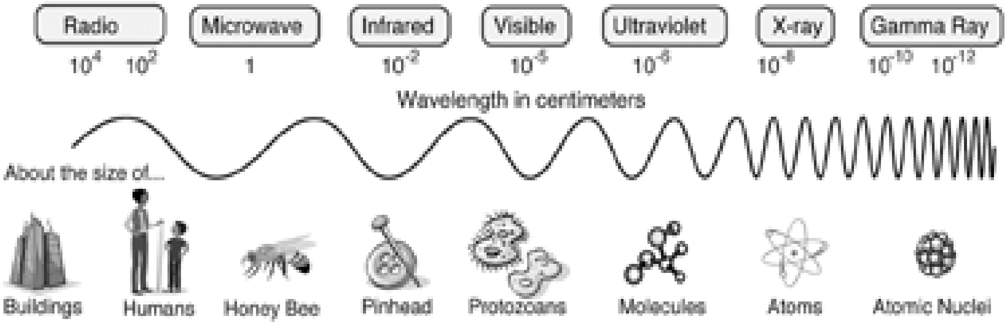


Figure 4: Region of electromagnetic radiation

Table 4: Regions of electromagnetic radiation

Region	Wavelength, λ (m)	Frequency, ν (Hz)	Energy, kJ/mole
Cosmic rays	10^{-14}	10^{22}	
Gamma(γ) rays	10^{-11}	10^{19}	
X-rays	10^{-9}	10^{17}	
Far ultraviolet	10^{-7}	10^{15}	7980-598
Near UV	10^{-7}	10^{15}	598-229
Visible	10^{-6}	10^{14}	229-149
Near infrared	10^{-5}	10^{13}	149-47.7

Vibrational infrared	10^{-5}	10^{13}	47.7-4.8
Far infrared	10^{-4}	10^{12}	4.8-2.4
Microwave	10^{-3}	10^{11}	2.4-2.2 x 10^{-4}
Radar	10^{-2}	10^{10}	
Television	10^{0}	10^{8}	
Nuclear magnetic resonance	10	10^{7}	
Radio	10^{2}	10^{6}	
Alternating current	10^{6}	10^{2}	

From the electromagnetic spectrum, we get the following points (Table 5):

a. **Cosmic rays** - Cosmic rays are high energy charged particles, originating in outer space, that travel at nearly the speed of light and strike the earth from all directions. Most cosmic rays are the nuclei of atoms, ranging from the lightest to the heaviest elements in the periodic table. They also include high energy electrons, positrons, and other subatomic particles. These rays originate outside our galaxy and provide information of distant objects such as quasars. The energy of cosmic rays is usually measured in units of MeV, for mega-electron volts, or GeV, for giga-electron volts.

b. **Gamma rays** - Gamma rays are the most energetic form of electromagnetic radiation, having shortest wavelength and highest frequency of all electromagnetic radiation. They are produced in areas of extremely high temperature, density and magnetic field. Natural sources of gamma rays on earth are gamma decay from naturally occurring radioisotopes such as potassium-40, and also as secondary radiation from various atmospheric interactions with cosmic ray particles. Gamma rays are the highest energy electromagnetic radiation and typically have energies greater than 100 keV, frequencies greater than 10^{19} Hz, and wavelengths less than 10^{-12}m. These rays have characteristics identical to X-rays of the same frequency butdiffer in source. Gamma rays are usually distinguished by their origin, X-rays are emitted by electrons outside the nucleus, while gamma rays are emitted by the nucleus. These rays are ionizing radiation and are thus biologically hazardous. The most biological damaging forms of gamma radiation occur at energies between 3 to 10 MeV.It can be used to kill cancer cells, sterilize medical equipments and in radioactive tracers.

c. **X-rays** - X-rays are electromagnetic radiation of exactly the same nature as light but of much shorter wavelength. Energies of X-ray range from about 100 eV to 10 MeV. They are classified as hard (shorter wavelength) or soft (longer wavelengths). When a high voltage with several tens of kV is applied between two electrodes, the high-speed electrons with sufficient kinetic energy, drawn out from the cathode, collide with the anode (metallic target). The electrons rapidly slow down and lose kinetic energy. Since the slowing down patterns (method of losing kinetic energy) vary with electrons, continuous X-rays with various wavelengths are generated. X-rays are used inX-ray crystallography for determining the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electronswithin the crystal.

Due to their penetrating ability, hard X-rays are used to image the inside of object. So, it is widely used to detect structural deficits or cracks in metal objects and to reveal stress related changes in building materials for bridges and aircrafts. X-rays are extensively used in medical imaging to reveal the architecture of the bone and other soft tissues and to find out any abnormality in the form of fracture, growth of tumor, used in dental imaging, etc. The use of X-rays in airports to examine for the presence of dangerous weapons or bombs is a routine practice.

d. **UV- Visible radiations** – The UV-Visible region extend from 200 nm-800 nm. The frequency of this region lies between 10^{15}-10^{14} Hz. UV-Visible radiation is used in UV-Visible spectroscopy which is primarily used to measure the multiple bonds or aromatic conjugation within molecule. It is also used in analytical chemistry for the quantitative determination of different compounds that absorbs UV radiation, such as transition metal ions, biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied. This is also known as electronic Spectroscopy because it causes the promotion of electrons from the ground state to higher energy state. Ultraviolet wavelengths are extensively used in astronomical observations. Some remote sensing observations of the earth are also related with the measurement of ozone. A tungsten filament lamp is commonly used as the visible light source. The wavelength range for this type of lamp extends across the entire visible range and extends into the ultraviolet (300 nm to 3000 nm). Ultraviolet light is normally supplied with a deuterium arc lamp made from quartz. It produces an intense UV output in the range from about 180 nm to 380 nm.

e. **Infrared radiation** - Infrared (IR) light is electromagnetic radiation with longer wavelengths than those of visible light. This range of wavelengths for IR radiation is 100μm- 1μm and frequency range is approximately 10^{14}. This region includes most of the thermal radiation emitted by objects near room temperature. Infrared light is emitted or absorbed by molecules when they change their rotational-vibrational movements.Scientists divide the IR spectrum into three regions. The wavelengths are specified in microns (symbolized μ, where $1\ \mu = 10^{-6}$meter) or in nanometers (abbreviated nm, where $1\ \text{nm} = 10^{-9}$ meter = 0.001 μ). The near IR bandcontains energy in the range of wavelengths closest to the visible, from approximately 0.8 -2.5μ. The middle IR band consists of wavelength in the range of 2.5μ-15μ. The far IR band extends from 15μ- 100μ. Infrared is used in a variety of wireless communications, monitoring, and control applications. A few of the applications include home-entertainment remote-control boxes, wireless local area networks, links between notebook computers and desktop computers, cordless modems, intrusion detectors, motion detectors, and fire sensors. It is also used for identification of functional groups in organic molecules.

f. Microwave Radiation-Microwaves lies in frequency range of 10^{10}-10^{12} Hz and corresponding wavelength range is between 1cm-100μm. This region of electromagnetic spectrum generally overlaps with the highest frequency radio waves. Microwave sources include artificial devices such as circuits, transmission towers, radar, masers, and microwave oven as well as natural sources such as Sun and the cosmic microwave. Microwaves can also be produced by atoms and molecules. Thermal motion of atom and molecules in any object at a temperature above absolute zero causes them to emit and absorb.

g. Radiofrequency region-The range of frequency and wavelength in radiofrequency region is 10^{6}- 10^{10} and 10m-1cm respectively. Radio waves can be generated by natural sources such as lightning or astronomical phenomena or artificially by broadcast radio towers, cell phones, satellites and radar.

Table 5: Summary of various branches of spectroscopy

E M Branch	**Type of transition**	**Spectra**
γ-rays	Nuclear transition	Mossbauer
X-ray	Electronic transition (core orbitals)	Electronic
UV-Visible	Electronic transition(valence electrons)	Electronic,Absorption,Fluorescence Phosphorescence
Infrared	Molecular rotation and vibration	Rotational and Vibrational
Microwave	Molecular rotation	Electron Spin Resonance
Radiofrequency	Nuclear spin transition	NMR and NQR

2.6 BASIC FEATURE OF DIFFERENT SPECTROMETERS

The spectrometer used in various region of the spectrum differs widely from each other in construction. Here we will discuss the basic features of all common type of spectrometer. For this purpose, we may consider absorption and emission spectrometers separately.

(1) Absorption Spectrometer: Figure 5 shows the block diagram for the components of absorption spectrometer which might be used in the IR, visible and ultraviolet regions. The radiation from the white source is directed by some guiding device (e.g.-mirror) on to the sample, from which it is passed through an analyzer, which selects the frequency reaching the detector at any given time. The modulator is placed between sample and analyzer, its effect is to cause the detector to send an alternating current signal to the recorder, with a fixed frequency rather than direct current signal. Amplification of AC signal is simpler to construct. The amplifier can be tuned to select only that frequency which the modulator impose on the signal, thus it ignores all other signals. Now signal passes through a recorder which is synchronized with analyzer so as to produce a trace of the absorbance as the frequency varies. In microwave and radiofrequency region, monochromatic sources can be constructed. So no analyzer is required in this case, the source being is its own analyzer.

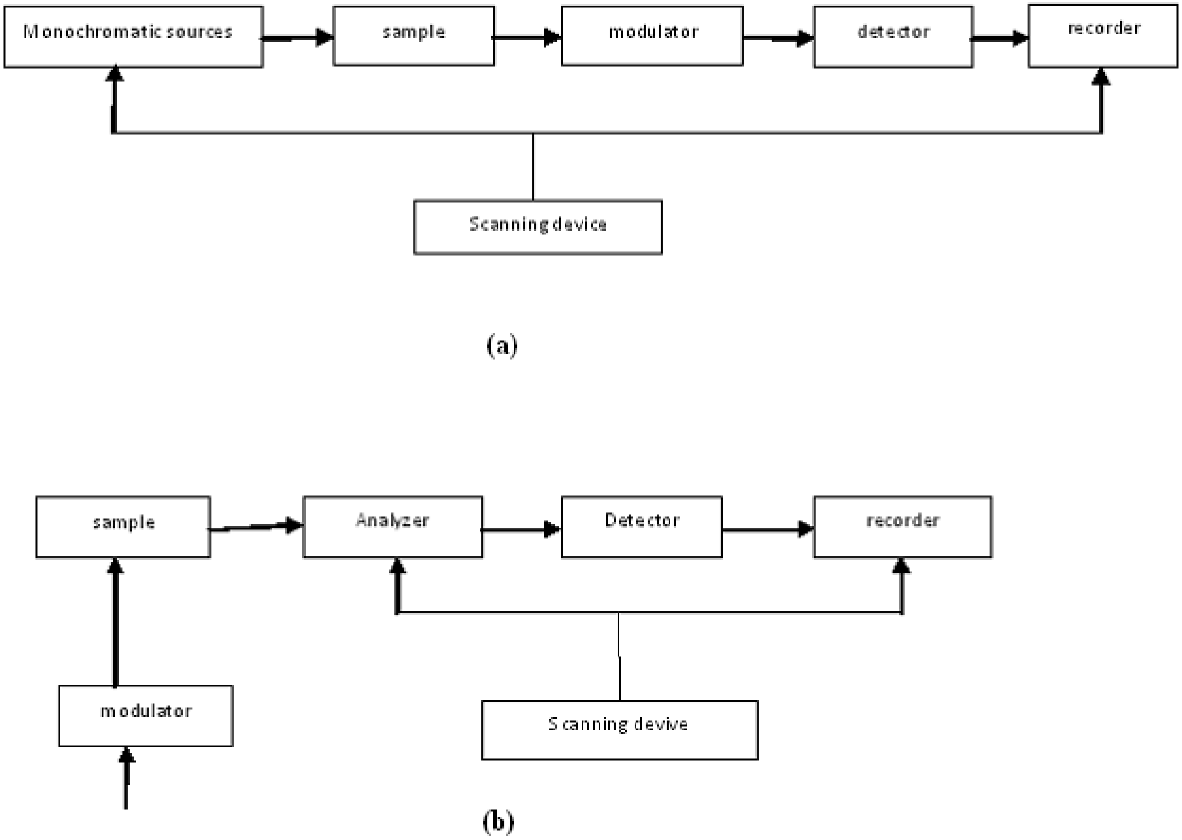


Fig5: Block diagram of a absorption spectrometer (a) the infrared, visible and UV region; (b) the microwave and radiofrequency region

(2) **Emission Spectrometer:** Fig 6 shows schematically, a typical spectrometer. The excitation can be thermal or electrical, but often takes the form of electromagnetic radiation. In this case, it is essential that the detector does not collect radiation directly from the exciting beam, and two are placed right angles as shown. A modulator is placed between the source of excitation and the sample along with tuned detector-amplifier, so that only emission recorded from the sample arises directly from excitation can be recorded, any other spontaneous emission is ignored.

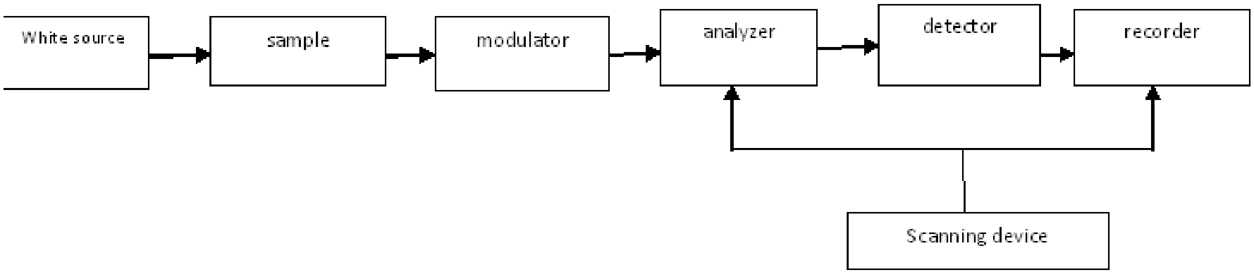


Fig 6: Block diagram of typical emission spectrometer.

2.7 DIFFERENCE BETWEEN ATOMIC AND MOLECULAR SPECTROSCOPY

Spectroscopy is a general term that deals with the interaction of various types of radiation with the matter. We can differentiate spectroscopy into two types.

(1) Absorption Spectroscopy: Atomic spectroscopy deals with the interaction of electromagnetic radiation with atomic species.

Types of Atomic Spectroscopy:

Atomic Absorption Spectroscopy: In this level, the quantities of energy supplied to excited electrons can be measured and studied in terms of the frequency and the intensity of electromagnetic radiation.

Atomic Emission Spectroscopy:In this level quantities of energy emitted by excited electrons as they return to their ground state, can be measured.

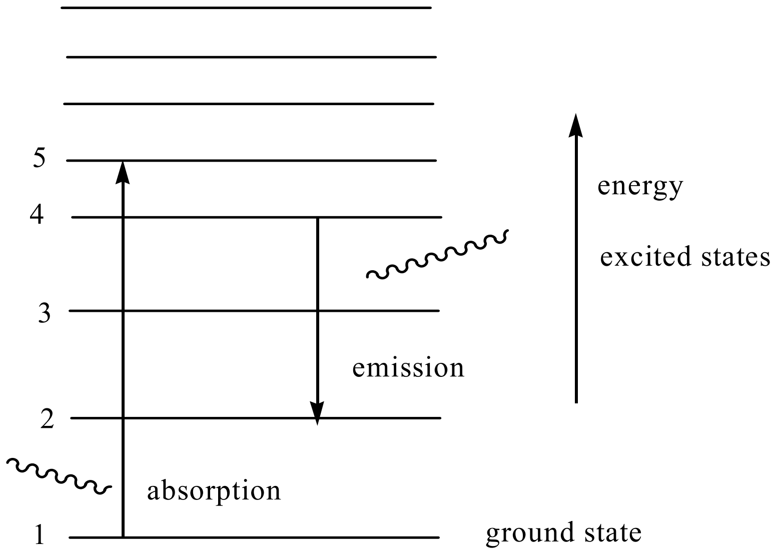
(2) Molecular Spectroscopy: Molecular Spectroscopy deals with the interaction of electromagnetic radiation with molecular species. Molecules have certain energy levels that can be analyzed by detecting the molecule's energy exchange through absorbance or emission.

Examples of molecular spectroscopy: UV- Spectroscopy, Fluorimetry, IR Spectroscopy, Raman Spectroscopy, Raman Spectroscopy, NMR Spectroscopy, Mass Spectrometry

2.8 ABSORPTION AND EMISSION SPECTRA

The electrons surrounding the atomic nucleus are arranged in a series of levels of increasing energy. Each element has a fixed number of electrons in a unique configuration. Therefore each element has its own distinct set of energy levels. When an electron jumps amongst energy levels in an atom, energy is emitted or absorbed in the form of electromagnetic radiation and this radiation produces spectral lines of frequencies or wavelength associated with an atom, called atomic spectra.

The emission and absorption of light take place in a particular manner. All form of electromagnetic radiation interacts with matter in the process of emission and absorption. The radiation propagates in a wave like fashion but in interaction with matter the radiation behaves as a photon having certain amount of energy equal to *hv* moving at the speed of light. Each electron resides usually in its ground state (the lowest energy state). When an atom absorbs a sufficient amount of energy, the electron moves to higher energy state called excited state (Fig 7). Transition between the energy level is only possible when the absorbed energy is equal to the difference between two energy levels.



Energy level diagram for an atom

Fig 7: Energy level diagram of an atom.

The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum. To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it as result of this electrons reaches to excited state. In excited state electron is unstable so, it comes back to ground state by emitting radiation of suitable wavelength or frequency.

An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark space in the bright continuous spectrum.

- Emission spectra- bright lines on a dark background
- Absorption spectra- dark lines on a bright background

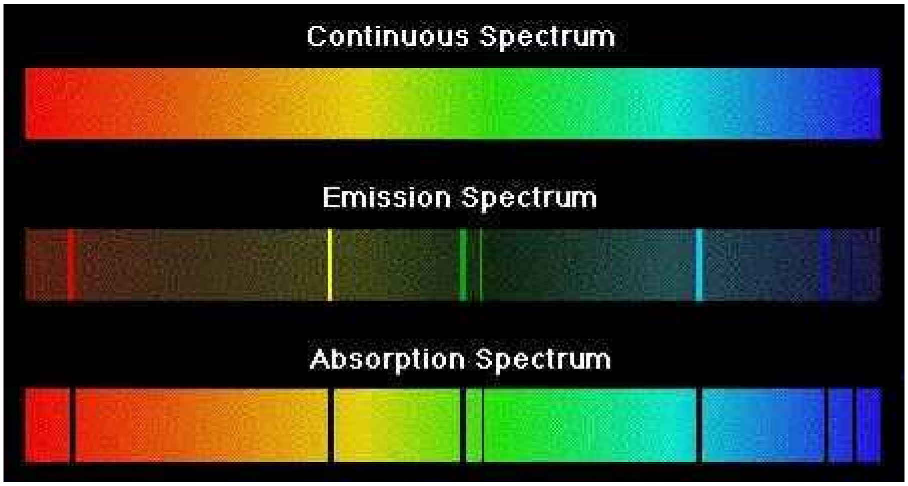


Fig 8: Emission spectra shows bright lines on a dark background and absorption spectra-dark lines on a bright background

2.9 BORN-OPPENHEIMER APPROXIMATION

The Born- Oppenheimer approximation is the assumption that the motion of atomic nuclei and electrons in a molecule can be separated. This approach is named after Max Born and J. Robert Oppenheimer. An isolated molecule in space has various form of energy due to its different kinds of motion and intramolecular interactions. The molecule possessestranslation energy due to the motion of the molecule as a whole. It may possess rotational energy due to bodily rotation about an axis perpendicular to the internuclear axis and passing through it's the centre of gravity. The molecule exhibit vibrational energy due to periodic displacement of its atoms from their equilibrium position. It also possesses electronic energy since the electrons associated with each atom and bonds are in constant motion. Electronic energy is associated with the transition of an electron from the ground state energy level to an excited state energy level of the molecule due to the absorption of a photon of suitable frequency. The molecule exhibits energy due to nuclear and electron spin.

As a first approximation, the total energy of a molecule can be expressed as the sum of translational, rotational, vibrational, electron, spin and nuclear energies.

$E_{\text{total}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} + E_{\text{spin}} + E_{\text{nuclear}}$

It is assumed that the various types of energy associated with different motions of the molecule are independent of one another. A molecule has several levels of these energies. The translational energy is not quantized whereas all the energies are quantized. It means molecule can exist only in certain discrete rotational, vibrational, electronic, spin and nuclear states. The separation between energy level is given as-

$E_{\text{el}} >> E_{\text{vib}} >> E_{\text{rot}} >> E_{\text{trans}}$

Since the translation energy is negligibly small, the Born- Oppenheimer approximation can be written as-

$$E = E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}}$$

2.10 SUMMARY

Spectroscopy deals with the transitions induce in a chemical species by its interaction with the photons of electromagnetic radiation. Spectroscopic techniques are used widely in all technical fields of science and technology. Electromagnetic radiation has electric and magnetic fields that simultaneously oscillate in plane which are mutually perpendicular to each other. Electromagnetic radiation has dual natureas it exhibits wave properties and particulate (photon) properties. Regions of electromagnetic spectrum have specific wavelength/frequencies. Spectrometer used in various region of the spectrum differs widely from each other in constructionbut some features are common in all type of spectrometers. Commonly absorption and emission spectrometers are used.Atomic spectroscopy deals with the interaction of electromagnetic radiation with atomic species and molecular spectroscopy deals with the interaction of electromagnetic radiation with molecular species.The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum. An absorption spectrum is like a photograph negative of an emission spectrum. Emission spectra produce bright lines on a dark background and absorption spectra produce dark lines on a bright background.

2.11 TERMINAL QUESTIONS

(1) A wave that consists of two perpendicular transverse waves with one component of the wave being a vibrating electric field and the other being a corresponding magnetic field is called a
  a) Induction waves
  b) Radiant waves
  c) Sound waves
  d) Electromagnetic waves

(2) The following are the electromagnetic waves except
  a) Infrared
  b) Gamma waves
  c) Sound waves
  d) Radio waves

(3) Find the frequency of the electromagnetic wave with a wavelength 2.75x 10-8 cm
  a) 1.10 Hz
  b) 1.09 x 1015 Hz
  c) 9.17 x 1015 Hz
  d) 9.17x 1016 Hz

(4) Which of the following have the highest wavelength?
  a) Radio waves

b) Infrared
c) Ultraviolet
d) Gamma rays

(5) Electromagnetic waves carry
a) Positive charge
b) Negative charge
c) No charge
d) Both positive and negative

(6) Electromagnetic waves travel
a) Without medium
b) With medium
c) With medium and without medium
d) In a disturbed path

(7) All electromagnetic waves travel through a vacuum at
a) The same speed
b) Speed that is proportional to their frequency
c) Speed that is inversely proportional to their frequency
d) None of the above

(8) Which of the following is correct in order from longest to shortest wavelength
a) γ rays, UV, IR, microwaves
b) microwaves, UV, visible light, γ rays
c) radio waves, IR, γ rays, UV
d) television, IR, visible light, X-rays

(9) Which of the following is true about the frequency and velocity of electromagnetic waves
a) as frequency increases, wavelength decreases
b) as frequency increases, wavelength increases
c) frequency is constant for all wavelength
d) frequency and wavelength are independent of each other

(10) Compared with light waves radio waves
a) have higher energy
b) are higher frequency
c) are not composed of photons
d) have longer wavelength

(11) Which of the following cannot be polarized
a) Sound wave
b) X-rays
c) Microwaves
d) Radio waves

(12) The light which cannot be completely plane polarized by reflection is
a) Red color

b) Green color
c) White color
d) Blue color

(13) The property that distinguishes the transverse waves from the longitudinal wave is

a) Reflection
b) Dispersion
c) Polarization
d) Interference

(14) Sound waves cannot be polarized while light waves can be polarized because

a) Sound travels slower than light
b) Light waves are transverse while sound waves are longitudinal
c) Light waves are longitudinal while sound waves are transverse
d) Sound waves have longer- wavelength than waves.

2.12 ANSWERS

(1) d ,(2) c, (3) , (4) b, (5) c , (6) c, (7)a, (8)d, (9)a, (10)d ,(11)a, (12) c, (13) c ,(14) b

UNIT- 3 ROTATIONAL SPECTRUM

CONTENTS

3.1 OBJECTIVES

(1) Classification of molecules (rotor)
(2) Calculate the energy level of diatomic molecule.
(3) Calculate the bond lengths of diatomic moleculefrom the value of their rotational constant.
(4) Outline the selection rules for rotational spectra and rationalize the role of the molecular dipole moment in the selection rules.

3.2 INTRODUCTION

To obtain the pure rotational transitions for molecules, scientists use microwave rotational spectroscopy. Rotational spectrum is obtained by the interaction of radiation with a rotating molecule as a result transition between rotational energy level occurs. The molecule gives a rotational spectrum only if it has permanent dipole moment. The heteronuclear diatomic molecule such as HCl, CO, NO, H_2O, etc. give rotational spectrum i.e. they are microwave active. The homonuclear diatomic molecules such as H_2, N_2, O_2, Cl_2, etc. and linear polyatomic molecules such as CO_2 do not have permanent dipole moment i.e. they are microwave inactive. Rotational spectroscopy is only practical in gaseous phase where the rotational motion is quantized. In solids or liquids, rotational motion is usually quenched due to collision between their molecules. Rotational (microwave) spectra occur in the spectral range of 1 – 100 cm^{-1}.

3.3 CLASSIFICATION OF MOLECULES

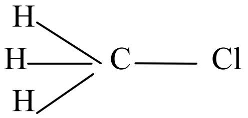
The rotation of rigid body can be described in terms of angular momentum (P) about an axis of rotation. Angular momentum is the product of the angular velocity ω and moment of inertia I. The rotation of a three-dimensional body may be quite complex and it is advantageous to resolve into rotational components about three mutually perpendicular directions through the center of gravity. Thus a body has three principal moments of inertia, one about each axis, usually designated I_A, I_B and I_C. The molecules are classified into groups according to their shapes or relative values of their principal moment of inertia about the three axes.

(1) Linear molecules- In linear molecules, all atoms are arranged in a straight line. For example- HCl, OCS, HCN, C_2H_2, NNO, CO, etc.

Linear molecules have three axes of rotation (i) about the bond axis (ii) end-over-end rotation in the plane of the paper and (iii) end-over-end rotation perpendicular to the plane of paper. The moment of (ii) and (iii) are same i.e. $I_B = I_C$, while about the bond axis of (i) is very small. As an approximation, the moment of inertia about the molecular axis is taken as zero, i.e. $I_A = 0$.

Thus for linear molecule we have: $I_B = I_C$ and $I_A = 0$.

(2) Symmetric tops: Examples of symmetric topes are CH_3F, BCl_3, CH_3I, $CHCl_3$. Consider a molecule such as methyl chloride,



In case of linear molecules $I_B = I_C$, since the end-over-end rotation in, and out of, the plane of the paper is identical. The moment of inertia about the C-Cl bond axis (chosen as the main rotational axis) is not negligible, because it involves the rotation of three comparatively massive hydrogen atoms of this axis.

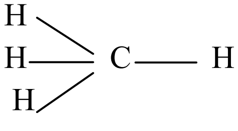
Symmetric topes: $I_B = I_C \neq I_A; I_A \neq 0$

Symmetric topes can be subdivided into two classes

If, $I_B = I_C > I_A$, then the molecule is called a *prolate* symmetric top.

If, $I_B = I_C < I_A$, then the molecule is called an *oblate* symmetric top.

(3) Spherical tops- Spherical top molecules have all three moment of inertia identical. For example CH_4.



Spherical tops: $I_A = I_B = I_C$

These molecules do not produce dipole change and hence no rotational spectrum is observed.

(4) Asymmetric tops: These molecules have all three moment of inertia different:

$I_A \neq I_B \neq I_C$

Majority of substances belongs to this category. For example- H_2O, $CH_2{=}CHCl$

3.4 DIATOMIC MOLECULES

Consider a linear diatomic molecule AB of atomic masses m_1 and m_2 at an internuclear distance *r* (Fig 1),whose length is

$$r = r_1 + r_2 \qquad \text{…..(1)}$$

The molecule rotates about an axis passing through its centre of gravity 'C'. It is defined by the equality of the moments about it, i.e.

$$m_1 r_1 = m_2 r_2 \qquad \text{…..(2)}$$

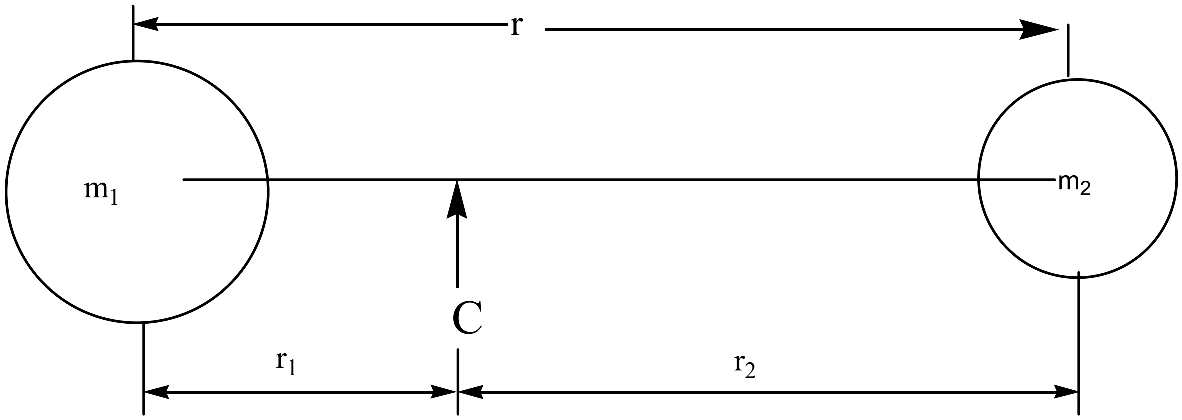


Fig 1: Rotation of a rigid diatomic molecule treated as two masses, m_1 and m_2, with internuclear distance r, about its centre of gravity

The moment of inertia about C is defined by

$$I = \Sigma i m_i r_i^2 \qquad \text{…..(3)}$$

Where r_i is the distance of the ith particle of mass m_i from the centre of gravity, since a diatomic molecule has two atoms, we have

$I = m_1 r_1^2 + m_2 r_2^2$ …..(4)

$= m_2 r_2 r_1 + m_1 r_1 r_2$ …..(5)

$= r_1 r_2 (m_1 + m_2)$ …..(6)

From equation 1

$r = r_1 + r_2$

Thus from eq 1 and 2

$m_1 r_1 = m_2 r_2 = m_2 (r - r_1)$ …..(7)

Hence, $r_1 = \underline{\;m_2 r\;}$ and $r_2 = \underline{\;m_1 r\;}$

$m_1 + m_2 m_1 + m_2$

Substituting the above values of r_1 and r_2 in equation 4, we have

$m_1 m_2^2 m_1^2 m_2$

$I = \rule{4em}{0.4pt}\, r^2 + \rule{4em}{0.4pt}\, r^2$ …..(8)

$(m_1 + m_2)^2 \qquad (m_1 + m_2)^2$

$= m_1m_2\,(m_1+m_2) \qquad m_1m_2$

$r^2 = \overline{\qquad\qquad} r^2 = \mu r^2 \quad \overline{\qquad}$ …..(9)

$(m_1+m_2)^2 m_1 + m_2$

Where $\mu = m_1m_2/(m_1+m_2)$ is called the reduced mass of the molecule. Equation (9) defines the use of Schrödinger equation it may be shown that the rotational energy levels allowed to the rigid diatomic molecule are given by the expression:

h^2

$E_J = \quad \overline{J\,(J}+1)$ joules where $J = 0,1,2,\ldots$ …..(10)

$8\pi^2 I$

In this expression h = Planck's constant, I = moment of inertia. The quantity J, which can take integral values from zero upwards, is called the rotational quantum number. Equation (9) expressed the allowed energies in joules; however, it is customary to express the energy in terms of wavenumber (cm^{-1}). This can be done by dividing energy in joules by hc,

$\varepsilon j = \; E_J \; = \; hJ(J+1)$ cm^{-1} ; $(J = 0,1,2\ldots.)$ …..(11)

$hc \quad \overline{8\pi^2 Ic} \quad \overline{\qquad}$

Equation (11) is usually abbreviated to :

$\varepsilon j = BJ\,(J+1)$ cm^{-1}; $(J = 0,1,2\ldots.)$ …..(12)

Where$B$, the *rotational constant,* is given by

h

$B \; = \; \overline{\qquad}$cm^{-1} …..(13)

$8\pi^2 Ic$

3.5 ENERGY LEVEL OF A RIGID ROTOR (Semi Classical Principles)

From equation (12) we can show the allowed energy level diagrammatically as in the figure 2.

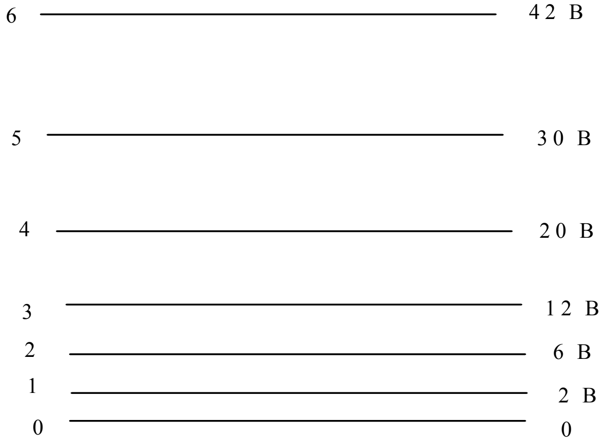


Fig 2: The allowed rotational energies of a rigid diatomic molecule.

For $J = 0$, the value of $\varepsilon_J = 0$, it means molecule is not rotating at all.
For $J = 1$, the rotational energy is $\varepsilon_1 = 2B$ and it is lowest angular momentum of a rotating molecule.
We may continue to calculate ε_J with increasing J values and, in principle, there is no limit to the rotational energy the molecule may have. However, the centrifugal force of a rotating molecule increases with increasing J and a situation may arise when the centrifugal force of a rapidly rotating molecule is greater than the strength of the bond and the bond is broken. However, this situation does not arise at normal temperature. The difference between two rotational levels can be calculated as follows. Suppose, the molecule is in $J = 0$ state (the ground state, in which no rotation occurs) on applying incident radiation molecule jumps into $J = 1$ state.Plainly the energy absorbed will be:

$$\varepsilon_{J=1} - \varepsilon_{J=0} = 2B - 0 = 2B \text{ cm}^{-1}$$

And therefore,

$$\tilde{\upsilon}_{J=0 \rightarrow J=1} = 2B \text{ cm}^{-1} \quad \text{…..(14)}$$

Therefore the absorption line will occur at 2B. If a transition occurs from J= 0 to J= 2 level, then the absorption of energy needed is given by

$$\tilde{\upsilon}_{J=0 \rightarrow J=2} = \varepsilon_{J=2} - \varepsilon_{J=1}$$

$$= 6B - 2B = 4B \text{ cm}^{-1} \quad \text{…..(15)}$$

In general, the frequency of the rotational spectral line arising from rise of molecule from the state J to state $J+1$, we would have:

$$\tilde{\upsilon}_{J \rightarrow J+1} = B(J+1)\ (J+2) - BJ\,(J+1)$$

$$= B\,[J^2 + 3J + 2 - (J^2 + J)]$$

Or

$$\tilde{\upsilon}_{J \rightarrow J+1} = 2\,B(J+1) \text{ cm}^{-1} \quad \text{…..(16)}$$

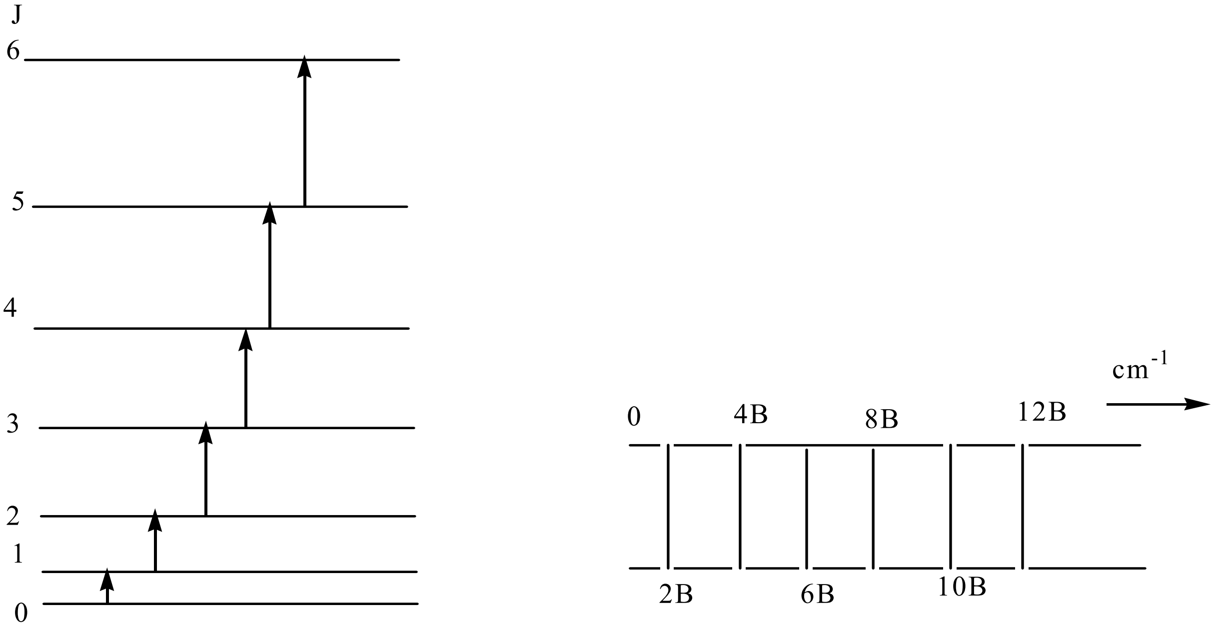


Fig 3: Allowed transition between the energy levels of a rigid diatomic molecule

The allowed energy levels of a rigid diatomic rotor are shown in figure 3. Thus a stepwise raising of the rotational transition results in an absorption spectrum consisting of spectral line with a separation of $2B$, i.e. at $2B$, $4B$, $6B$,….(Fig. 3). These lines are equally spaced by an amount of $2B$ called frequency separation. The lowering of stepwise energy results in identical emission spectrum.

3.6 SELECTION RULE

Selection rule is required to determine the radiative transition between the rotational energy levels. The derivation of the selection rule is a quantum mechanical problem; its details are not required here. In rotational energy levels, transition can occur from a particular level only to its immediate neighbor, either above or below.

$$\Delta J = \pm 1$$

i.e., only those transitions are allowed in which the rotational quantum number changed by unity. The + sign refers to absorption and the – sign to emission of radiation. Microwave spectra are usually observed as absorption spectra so that the operative part of the selection rule is $\Delta J = +1$

3.7 ROTATIONAL SPECTRA OF RIGID DIATOMIC MOLECULE

We know that B = B/hc

Energy levels of a rigid symmetric or linear rotor expressed as wave numbers of the allowed J+1 J= 2B $\longleftarrow$(J+1) = 2B (J+1)

For $J = 0,1,2$…… spectra consist of lines with $v= 2B,4B,6B,$ line separation will be $2B$. Intensities of spectral lines increase with J and pass through a maximum because of the existence of a maximum in the population of rotational levels.

3.8 DETERMINATION OF BOND LENGTH

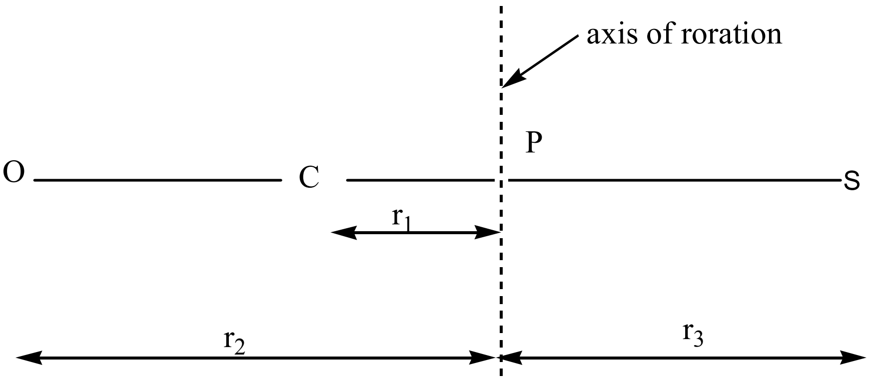


Fig 4:The rotation of $^{16}O=^{12}C=^{32}S$ molecule about an axis of rotation passing through its centre of mass

Consider the gaseous linear triatomic molecule O=C=S. In this molecule, we have to determine O-C and C-S. Bond distance can be determined by isotopic substitution method. Consider first the molecule $^{16}O=^{12}C=^{32}S$(Fig. 4).

Since the centre of mass is at P(from where we measure various distances)

$m_Cr_1 + m_Or_2 = m_Sr_3$ …..17

The moment of inertia is given by

$I= m_Cr_1^2 + m_Or_2^2 + m_Sr_3^2$ …..18

Also, $r_2 = r_{CO}+ r_1$; …..19

$r_3 = r_{CS} – r_1$ (Fig.4)

Wherer_{CO} and r_{CS} are two interatomic distances to be determined. Substituting eq. 19 into eq. 17, we have

$m_Cr_1+ m_O(r_{CO} + r_1) = m_S (r_{CS}-r_1)$ …..20

or, rearranging,

$(m_C + m_O + m_S) r_1 = m_Sr_{CS} – m_Or_{CO}$ …..21

Since $m_C + m_O + m_S$ = M(the mass of the O=C=S molecule), hence,

$Mr_1 = m_Sr_{CS} – m_Or_{CO}$

$r_1 = (m_Sr_{CS} – m_Or_{CO})/M$ …..22

Substituting eq 19 into eq 18, we have

$I = m_Cr_1^2+ m_O(r_{CO} + r_1)^2 + m_S(r_{CS} – r_1)^2$ …..23

Substituting for r_1 from eq 22 into eq 23 and simplifying, we obtain

$I = (m_S r^2_{CS} - m_O r^2_{CO} + 2m_O m_S r_{CO} r_{CS} - m_S r^2_{CS})/M$ …..24

Eq. 24 contains the unknown'sr_{CO} and r_{CS}.

Now we make an important assumption that isotopic substitution does not alter the interatomic distances. Applying this assumption to the $^{16}O{=}^{12}C{=}^{32}S$ molecule, we obtain a similar expression for the moment of inertia I' of the molecule:

$I' = (m_{S'} r^2_{cs} - m_o r^2_{co} + 2m_o m_{S'} r_{co} r_{cs} - m_{S'} r^2_{cs})/M$ …..25

Thus, we can obtain both *I* and *I'* from the microwave spectra of $^{16}O{=}^{12}C{=}^{32}S$ and $^{16}O{=}^{12}C{=}^{34}S$ Molecules and from these moment of inertia, the unknown rco and rcs can be determined.

The interatomic distance in gaseous O=C=S, using several pairs of isotopes are given in table 1.

Table1: Interatomic Distance in O=C=S molecule

Pairs of Isotopic molecules	$r_{C—O}$ (in Å)	$r_{C—S}$ (in Å)
$^{16}O{=}^{12}C{=}^{32}S$ and $^{16}O{=}^{12}C{=}^{34}S$	1.1647	1.5576
$^{16}O{=}^{12}C{=}^{32}S$ and $^{16}O{=}^{13}C{=}^{32}S$	1.1629	1.5591
$^{16}O{=}^{12}C{=}^{34}S$ and $^{16}O{=}^{13}C{=}^{34}S$	1.1625	1.5594
$^{16}O{=}^{12}C{=}^{32}S$ and $^{18}O{=}^{12}C{=}^{32}S$	1.1652	1.5653

There is a small difference in bond lengths caused by changing the isotopes.

3.9 NUMERICAL PROBLEMS

(1) What is the moment of inertia of a diatomic molecule whose internuclear distance is 140 pm and the reduced mass is 1.7 x 10^{-27}.

Solution- Moment of Inertia is given by the relation

$$I = \frac{(m_1 + m_2)}{(m_1 + m_2)^2} r^2$$

Where $m_1 m_2/(m_1+m_2)$ is the reduced mass and r is internuclear distance

In SI units

Reduces mass = 1.7 x 10^{-27} kg

r = 140 pm

= 140 x 10^{-12}m

On putting the values in formula we get,

= 1.7 x 10^{-27} x (140 x 10^{-12}) kgm^2

= 1.7 x 140 x 140 x 10^{-27}x 10^{-24}

= 33320 x 10^{-51}

= 3.375 x 10^{-47} kgm^2

(2) The pure rotational spectrum of gaseous HCl contains a series of equally spaced lines separated by 22.80 cm-1. Calculate the internuclear distance of the molecule. The atomic masses of H and Cl are 1.673 x 10^{-27} kg and 58.06 x 10^{-27} kg respectively.

Solution-

The spacing between the lines ($2B$) = 22. 80 cm^{-1}

$B = 11.40\ cm^{-1}$

$$B = \qquad cm^{-1} \quad \text{or} \quad I = \frac{h}{8\pi^2 Ic} \qquad \frac{h}{8\pi^2 Bc}$$

Substituting the values

$$I = \frac{6.626 \times 10^{-34}\ Js}{(8\ \pi^2)(11.40\ cm^{-1})(3\times 10^{10}\ cm\ s^{-1})}$$

$$= 0.2456 \times 10^{-46}\ kg\ m^2$$

The reduced mass is given by

$$\mu = \frac{(m_1 m_2)}{(m_1 + m_2)}$$

Where m_1 and m_2 are atomic masses of H and Cl, respectively

$$= \frac{(1.673\times10^{-27} kg)\ (58.06\times10^{-27} kg)}{(1.673 + 58.06) \times 10^{-27}\ kg}$$

$$= 1.626 \times 10^{-27}\ kg$$

Since $I = \mu r^2$

$$r^2 = \frac{1.626 \times 10^{-27}}{0.2689 \times 10^{-46}}$$

$r = 1.29 \times 10^{-10}$ m = 129 pm

(3) The internuclear distance of carbon monoxide molecule is 1.13×10^{-10}m. Calculate the energy (in joules) of this molecule in the second excited rotational level. The atomic masses of carbon and oxygen are 1.99×10^{-26} kg and 2.66×10^{-26}kg respectively.

Solution-

The given, internuclear distance of CO molecule $r = 1.13\times 10^{-10}$m

The reduced mass μ of CO is given by the equation

$$\mu = \frac{(m_1 m_2)}{(m_1 + m_2)}$$

$$= \frac{(1.99\times 10^{-26}\ kg)\ (2.66\times10^{-26} kg)}{(1.99\times 10^{-26}\ kg) + (2.66\times10^{-26} kg)}$$

$$= 1.14\times 10^{-26}\ kg$$

Moment of Inertia, $I = \mu r^2$

$$= 1.14 \text{x } 10^{-26} \text{ kg x } (1.13 \text{x } 10^{-10} \text{m})^2$$
$$= 1.46 \text{ x } 10^{-46} \text{ kgm}^2$$

The rotational energy levels of diatomic molecule is given by

$$E_j = \frac{h^2}{8\pi^2 I} J(J+1) \text{ joules}$$

For the second excited rotational level, $J = 2$

$$= \frac{h^2}{8\pi^2 I} 2(2+1) \text{ joules}$$

$$= \frac{(6.626 \text{ x } 10^{-34} \text{ Js})^2}{8\pi^2(1.46 \text{ x } 10^{-46} \text{ kgm}^2)} 2(2+1) \text{ joules}$$

$$= 45.66 \text{ x } 10^{-23} \text{ J}$$

3.10 SUMMARY

In the present unit, we have explored some of the main features of rotational spectroscopy. It is concerned with the measurement of the energies of transition between quantized rotational states of molecules in the gas phase. The spectra of polar molecules can be measured in absorption or emission by microwave spectroscopy. The selection rule $\Delta J = \pm 1$ gives the value of rotational constant B, using which bond length can be calculated.

3.11 TERMINAL QUESTIONS

(1) Among HCl, CO, Cl_2, NO, C_2H_4, the microwave active species are
    (a) CO, Cl_2 (b) HCl, CO, NO (c) Cl_2, C_2H_4 (d) Cl_2, NO
(2) The rotational spectrum of a rigid diatomic rotor consists of equally spaced lines with spacing equal to
    (a) $2B$ (b) B (c) $B/2$ (d) $3B/2$
(3) When $I_A > I_B = I_C$ then the molecule is
    (a) Oblate (b) Prolate (c) Asymmetric top (d) Linear
(4) In case of asymmetric top molecules, the moment of inertia is
    (a) $I_A \neq I_B \neq I_C$ (b) $I_A = I_B = I_C$ (c) $I_B = I_C > I_A$ (d) $I_B = I_C < I_A$
(5) Transition from one rotational state to other in rotational spectra is governed by

(a) Bohr quantum condition
(b) Molecule must have a permanent dipole moment
(c) $\Delta J = \pm 1$
(d) All

(6) Calculate the reduced mass and moment of inertia of DCl^{35}, given that internuclear bond distance is 0.1275 nm.
(7) Calculate the energy in joules per quantum and joules per mole of photons of wavelength of 300 nm.
(8) Show that for a rigid diatomic rotor the moment of inertia is given by $I = \mu r^2$

3.12 ANSWERS

(1) b
(2) a
(3) a
(4) a
(5) d
(6) 3.162×10^{-27}kg, 5.141×10^{-47}kgm^2
(7) 6.62×10^{-19} J, 3.98 x 105J mol^{-1}

UNIT- 4 VIBRATIONAL SPECTRA

CONTENTS

4.1 OBJECTIVES

The skeletal of this unit include the following topics:

- Basic concept of vibrational spectroscopy and its applications.
- Vibrational modes and their symmetries.
- Symmetry-based selection rules and their general consequences.
- Spectroscopic activities and structures of nonlinear molecules.
- Overtones, combinations, and other complications.
- Effect of harmonic motion and isotope on the spectrum.
- Idea of vibrational frequencies of different functional groups

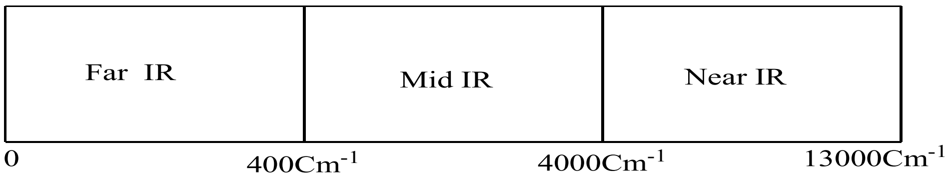
4.2 INTRODUCTION

Infrared spectroscopy (IR) is one of the frequently used spectroscopic techniques among organic and inorganic chemists, dealing with the absorption of radiation in the IR region of the electromagnetic spectrum. IR spectrum gives detailed information about the functional group and can also be used as an analytical tool for structure elucidation or for assessing the purity of compound.

The absorption of IR radiation by molecule cause changes in their vibrational and rotational energy levels and hence this type of spectroscopy is also known as vibrational-rotational spectroscopy. Not like UV-Spectroscopy which has very few peaks in their spectrum, IR spectroscopy provides a spectrum with a large number of absorption bands. Infrared radiation spans a section of the electromagnetic spectrum having wavenumbers from roughly 13,000 to 10 cm^{-1}, or wavelengths from 0.78 to 1000 μm. IR absorption positions are generally presented as either wavenumbers ($\tilde{\nu}$) or wavelengths (λ). Wavenumber defines the number of waves per unit length. Thus, wavenumbers are directly proportional to frequency, as well as the energy of the IR absorption. Wavenumbers and wavelengths can be interconverted using the following equation:

$$\bar{\nu}\ (\text{in cm}^{-1}) = \frac{1}{\lambda\ (\text{in }\mu\text{m})} \times 10^{4}$$

The Infrared spectrum can be divided into three different regions.



This chapter focuses on the most frequently used mid IR region, between 4000 and 400 cm^{-1} (2.5 to 25 μm). The far IR requires the use of specialized optical materials and sources. It is used for analysis of organic, inorganic, and organometallic compounds involving heavy atoms (mass number over 19). It provides useful information to structural studies such as conformation and lattice dynamics of samples. Near IR spectroscopy needs minimal or no sample preparation. It offers high-speed quantitative analysis without consumption or destruction of the sample. Its instruments can often be combined with UV-visible spectrometer and coupled with fiberoptic devices for remote analysis. Near IR spectroscopy has gained increased interest, especially in process control applications.

Functional group region: (1300-4000cm^{-1}):

Most of the functional groups present in organic molecules exhibit absorption bands in the region 1800-4000cm^{-1}, hence this is known as functional group region. In this region each bond gives information about movement of group of atoms or bending and stretching of a particular bond.

Finger Print region (600-1300cm^{-1}):

The region from 1300cm^{-1} to 600cm^{-1} usually contains a very complicated series of absorption. These are mainly due to molecular vibrations, usually bending motions that are characteristic of the entire molecule or large fragments of the molecule expect enantiomers.

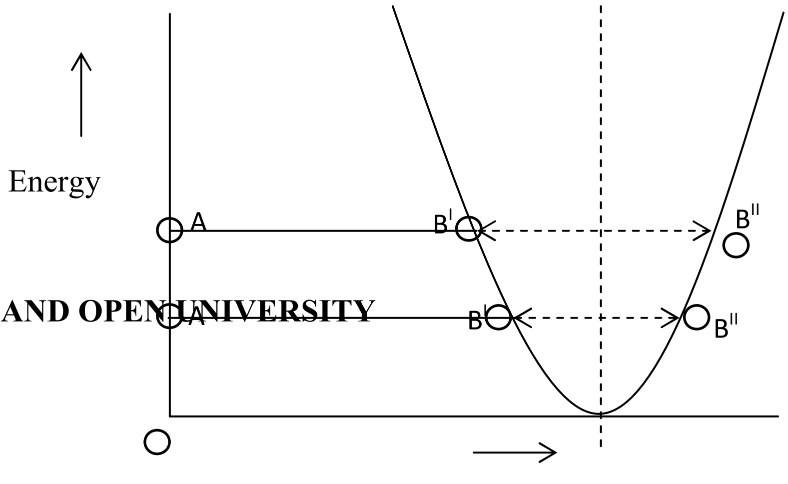
4.3 ORIGIN OF IR SPECTROSCOPY:

IR spectroscopy gives information about molecular vibrational or transitions between vibrational and rotational energy level. The absorption of IR radiation leads to transition between vibrational and rotational levels.When a molecule absorbs IR radiation below 100cm^{-1} transition takes place between rotational energy levels. Since there energy levels are quantised, a rotational spectrum consists of discrete lines. If a molecule absorbs radiation in the range 100-10000cm^{-1}, it causes transition between vibrational energy level. This energy level is also quantised, but vibrational spectra appear as bond rather than discrete lines. Each vibrational energy level is associated with a large number of closely spaced rotational energy levels. Therefore the vibrational spectra appear as vibrational rotational band.

4.4 THE VIBRATIONAL DIATOMIC MOLECULE:

Energy of a diatomic molecule:

When two atoms combine to form a stable covalent molecule line HU, they may be said to do so because of some internal electronic rearrangement. In this mechanism of the bond formation, on one hand, there is repulsion between the positively charged nuclei of both atomic and between the negative electron clouds; on the other hand, there is an attraction between the nucleus of one atom and electrons of the other and vice versa. The two atoms settle at the mean intermolecular assistance such that these forces are just balanced and the energy of the whole system is at a minimum. Further, the atoms more closely together and the repulsive force rapidly attempt to pull them further apart and we are resisted by the attractive force. In either case, an attempt to distant the bond requires an input of energy can be shown by graphical plot of energy against intermolecular distance as in figure 1.



Intermolecular distance

Figure 1: Parabolic cause of energy plotted against the extension or compression of a spring obeying Hook's law.

At the minimum, the internuclear distance is referred as the equilibrium distance (r_{eq}) or bond length. The Compression and extension of a bond is like behaviour of spring and we may extend the analogy by assuming that the bond, like a spring obeys hook's law, as given in the following equation:

$$f = -K(r - r_{eq.}) \rightarrow ①$$

Where f is the restoring force, K is the force constant and r is the internuclear distance. In this case, the energy curve is parabolic and has the below equation form –

$$E = \frac{1}{2} K (r - r_{eq.})^2 \rightarrow ②$$

4.5 SIMPLE HARMONIC OSCILLATOR:

In the figure 1, we have plotted the energy according to equation 2. The zero of curve and equation was found at $r = r_{eq}$ and any energy in excess of this. For example, E arises because of extension or compression of the bond. The figure shows that if one atom (A) is considered to be stationary at the r = o axis, the other will become more vigorous, that is to say, the degree of compression or extension will be greater. But the vibrational frequency will not change. An elastic bond, like spring, has a certain vibration frequency dependent upon the mass of the system and the force constant, but independent of the amount of distortion. Classically it is easy to show that the oscillation frequency is:

$$\text{Wose} = \frac{1}{\pi}\sqrt{\frac{k}{u}}\, H_z \rightarrow ③$$

Where, *u* is the reduced mass of the system.

$$W_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{u}}\ \text{cm}^{-1} \rightarrow ④$$

The vibrational energy, like all other molecular energies, is quantized and the allowed vibrational energies for any particular system may be calculated from the Schrodinger equation. For the simple harmonic oscillator these run out to be:

$$E_v = \left(v + \frac{1}{2}\right) h\omega_{osc}\ \text{Joules}$$

$$(\upsilon = 0, 1, 2, 3\ldots\ldots\ldots\ldots) \rightarrow ⑤$$

Where υ is the vibrational quantum number, converting to the spectroscopic unit cm^{-1}, we have:

$$E_v = \frac{Ev}{hc} = \left(v + \frac{1}{2}\right)\overline{\omega}_{osc}\ \text{cm}^{-1} \rightarrow ⑥$$

In particular, we should notice that the lowest vibrational energy, obtained by putting $\upsilon = 0$ in equation 5 or 6, then

$$E_0 = \frac{1}{2} h\ \omega_{osc}.\ \text{Joules}$$

$$E_0 = \frac{1}{2}\ \omega_{osc}\ \text{cm}^{-1} \rightarrow ⑦$$

So it is clear that the diatomic molecule can never have zero vibrational energy. The atoms can never be completely at rest relative to each other.

The quantity $\frac{1}{2}h\ \omega_{osc}$ joules or $\frac{1}{2}\ \omega_{osc}\ \text{cm}^{-1}$ is known as the zero-point energy, it depends only on the classical vibrational frequency and hence on the strength of the chemical bond and the atomic mass.

Further use of Schrodinger equation leads to the simple selection rule for the harmonic oscillator undergoing vibrational changes.

$$\Delta V = \pm \rightarrow ⑧$$

Applying the selection rule we have:

$$E_{v+1\rightarrow v} = \left(v + 1 + \frac{1}{2}\right)\bar{\omega}\text{ose} - \left(v + \frac{1}{2}\right)\bar{\omega}\text{ose} \rightarrow ⑨$$

$$= \bar{\omega}ose\ cm^{-1}$$

For emission

$$E_{v+1\rightarrow v+1} = \bar{\omega}ose\ cm^{-1} \rightarrow (9.1)$$

For absorption whatever the initiate value of v such a simple result is also represented the following figure 2.

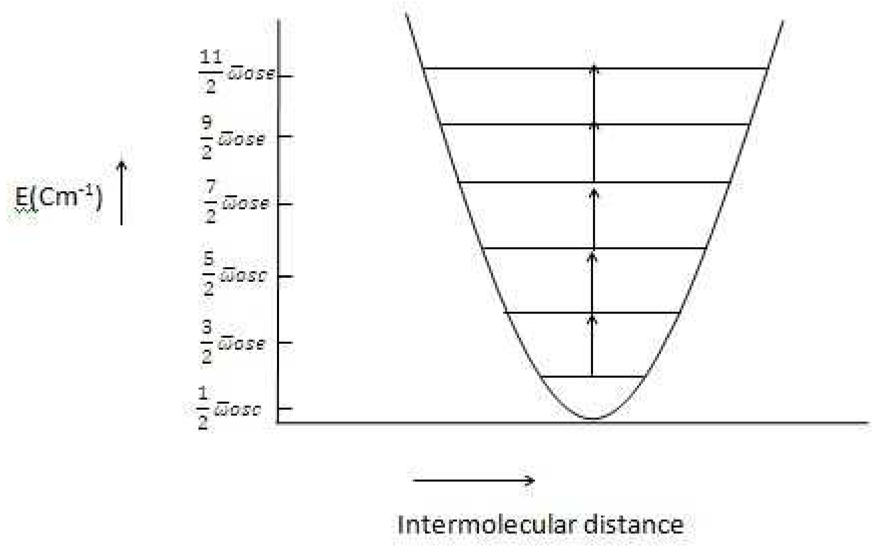


Figure 2: The vibrational energy levels and allowed transition between them for a diatomic molecule undergoing simple harmonic motion.

4.6 HARMONIC OSCILLATOR

Real molecule does not obey exactly the low of simple harmonic motion, real bonds, although elastic are not so homogenous as to obey Hook's law. If the bond between atoms is stretched, for instance, there comes a point at which it will break the molecule dissociate into atoms. Thus for small compression and extension are occurring the bond may be taken as perfectly elastic, for large amplitude. A simple energy curve for a typical diatomic molecule can be diagrammatically represented as in figure 3.

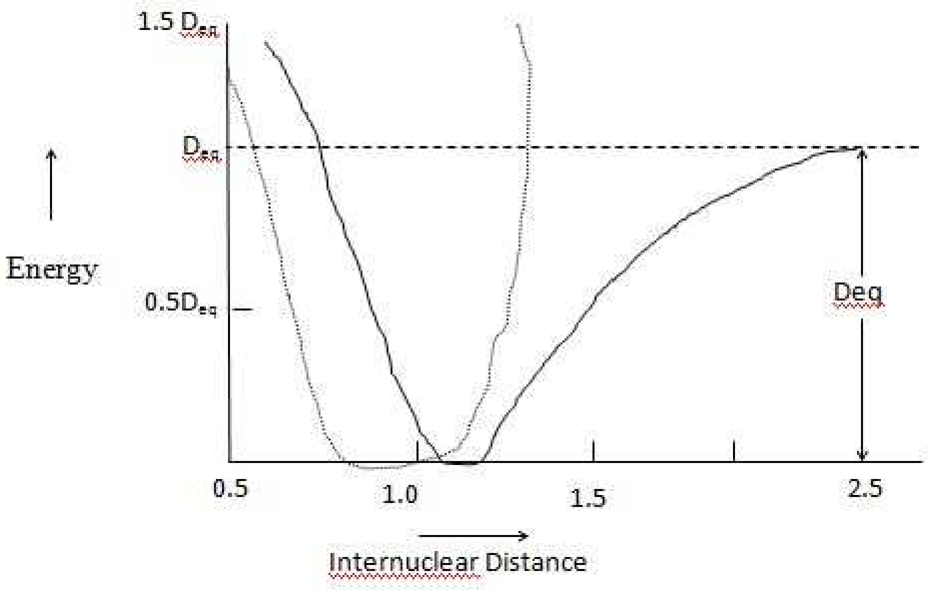


Figure 3: The Morse curve: The energy curve of a diatomic molecule undergoing enharmonic confusion and compression.

4.7 SELECTION RULES:

According to the selection rule for a molecular vibration the electronic dipole moment must change when the atom is displaced. It means they need not have a permanent dipole moment. Thus according to the above selection rule for a vibrational transition is:

$$\boxed{\Delta v = \pm 1}$$

i.e., change is vibrational quantum number should be unity. The transitions for which $\Delta v = \pm 1$ corresponds to absorption and those with $\Delta v = -1$ corresponds to emission.

4.8 VIBRATIONAL SPECTRUM OF SIMPLE HARMONIC OSCILLATOR

Only those transition law takes place between two vibrational levels whose vibrational quantum number differ by unity $(\Delta v = \pm 1)$ when the transition takes place from V_0 to V_1, the energy absorbed by diatomic molecule. This can be written by following expression-

$$\Delta Ev = \left(0 + 1 + \frac{1}{2}\right) hc\omega e - \left(v + \frac{1}{2}\right) he\omega e = hc\omega e$$

$$\frac{\Delta E}{he} = \omega e$$

or

$$\overline{\Delta ve} = \omega e$$

Thus, according to above expression, only those absorption lines will be obtained in the vibrational spectrum whose wave number is equal to equilibrium vibrational frequency of the diatomic molecule. In this regard, the vibrational levels are equally spaced and any transition from V to V+1 give rise to the same energy (Figure 4)

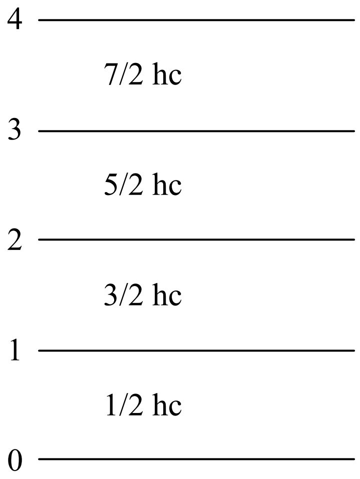


Figure 4: Equally spaced Vibrational energy levels of a harmonic oscillator.

Furthermore, at the room temperature, most of the molecules are in the ground state (V_0) whereas, after absorption, a certain amount of energy molecule gets excited in their higher energy state i.e. from V_0 to (V+1). The frequency thus observed is called the fundamental frequency.

4.9 DETERMINATION OF VIBRATIONAL FREQUENCY AND FORCE CONSTANT FOR ANHARMONIC OSCILLATOR

The Classical Vibrational frequency for a harmonic oscillator is:

$$V_{0sc}=\frac{2}{\pi}\sqrt{\frac{k}{\mu}}$$

Where k is the force constant and μ is the reduced mass. The separation of successive vibration level is constant and equal to w($w=V_{osc}/c$) which is the classical frequency in cm^{-1}.

In case of anharmonic oscillator, the classical frequency as given above holds for very small amplitude only. In fact, it decreases slowly as the amplitude (i.e. v) increases. The real classical expression for the vibrational frequency of the anharmonic oscillator in the state v is given by figure 5.

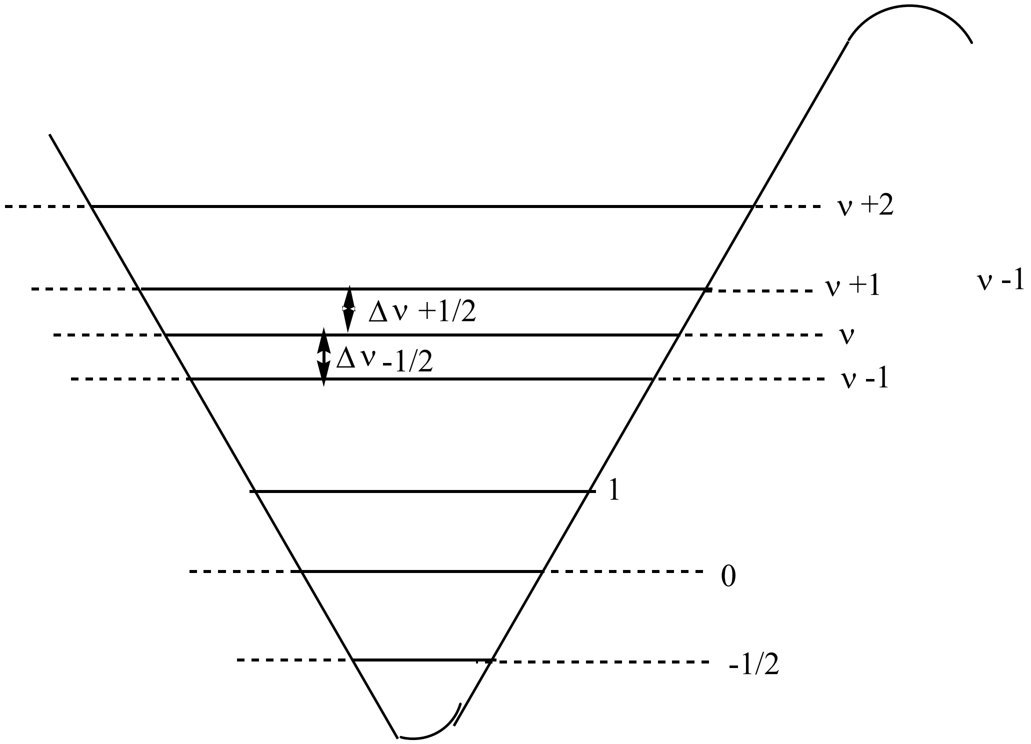


Figure5: Vibrational frequency of the anharmonic oscillator

$$V_{osc} = C \text{ x } \Delta G\upsilon$$

$$= C\,\frac{DG\upsilon+\frac{1}{2}+DG\upsilon-\frac{1}{2}}{2}$$

$$=\frac{1}{2}C[\{G(v+1)-GCv\}]+\{G(v)-G(v-\mathbf{1})\}$$

$$=\frac{1}{2}C[G(v+1)-G(v-1)]$$

$$=\frac{1}{2}C\left[\left\{\omega e\left(v+\frac{3}{2}\right)-wexe(v+\frac{3}{2}^{2}\right\}\left\{we\left(v-\frac{1}{2}\right)-wexe(v-\frac{1}{2}^{2}\right\}\right]$$

$$=\frac{1}{2}C\left[\omega e\left(V+\frac{3}{2}-v+\frac{1}{2}\right)-wexe\left\{\left(v+\frac{3}{2}^{2}\right)-(v-\frac{1}{2}^{2}\right\}\right]$$

$$=\frac{1}{2}C[2\omega e-\omega exe(4\_+2)]$$

$$=\mathrm{c}[\omega e-\omega exe(2v+1)]$$

$$\upsilon_{osc}(\upsilon)=\mathrm{c}\ [C\omega e-\omega exe)-2\omega exe\ v]$$

Thus, as υ increases the classical vibrational frequency decreases.

Let us consider a hypothetical state with υ = -1/2 (υ = 0). The frequency for this state is given by $\upsilon_{0sc}\left(-\frac{1}{2}\right)=c\ we$

Thus we represent the vibrational frequency in cm^{-1} and the anharmonic oscillator at infinitesimal amplitude i.e. in the imaginary state V= $-\frac{1}{2}$ at the very bottom of the potential curve.

4.10 ISOTOPE EFFECT IN VIBRATIONAL LEVELS

Isotope molecules differ only in mass of the substance and the vibrational frequencies. Let us consider the harmonic vibration; the classical vibrational frequency is given by.

$$V_{osc}=\frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

The force constant k is determined by the electronic motion only and is therefore exactly the same for different isotopic molecules. The reduced mass is, however, different for different isotopes.

If w^{i} stands for the heavier isotope, we have

$$\frac{w^i}{w} = \frac{Vosc^i}{Vosc} = \sqrt{\frac{\mu}{\mu^i}} = P$$

The heavier isotopic molecule has a smaller frequency (P<1). The Vibrational terms of two isotopic molecules are given by the following expression.

$$G(\upsilon) = w\left(\upsilon + \frac{1}{2}\right)$$

$$G^i(\upsilon) = w^i\left(\upsilon + \frac{1}{2}\right) = P\left(\upsilon + \frac{1}{2}\right)$$

Therefore, the isotopic shift of a Vibrational level V is-

$$G^i(\upsilon) - G(\upsilon) = (P-1)w\left(\upsilon + \frac{1}{2}\right)$$

Since (P<1), we have

$$G^i(\upsilon) < G(\upsilon)$$

Thus the Vibrational levels of the heavier isotope are lower than the corresponding level of the lighter isotope.

Similarly $G^i(\upsilon) < G(\upsilon)$ is negative, thus the vibrational levels of the heavier isotope are lower than those of the lighter, and the shift between corresponding levels increases with increasing-(V) (Figure 6).

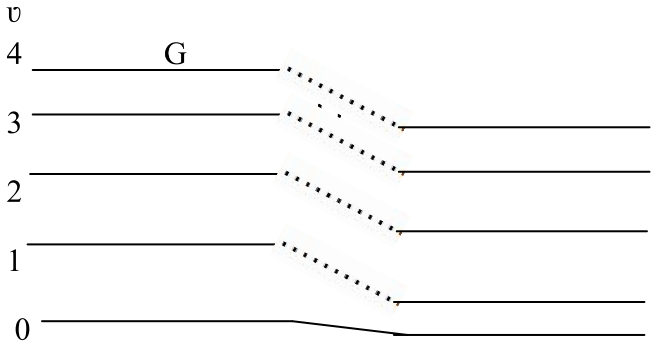


Figure 6: Isotope effect

4.11 INFRARED SPECTRA OF SOME COMMON FUNCTIONAL GROUPS

Hydrocarbons:

Hydrocarbon compounds contain only C-H and C-C bonds, but there is plenty of information to be obtained from the infrared spectra arising from C-H stretching and C-H bending.

In alkanes, which have very few bands, each band in the spectrum can be assigned:

- C–H stretch from 3000–2850 cm^{-1}
- C–H bend or scissoring from 1470-1450 cm^{-1}
- C–H rock, methyl from 1370-1350 cm^{-1}
- C–H rock, methyl, seen only in long-chain alkanes, from 725-720 cm^{-1}

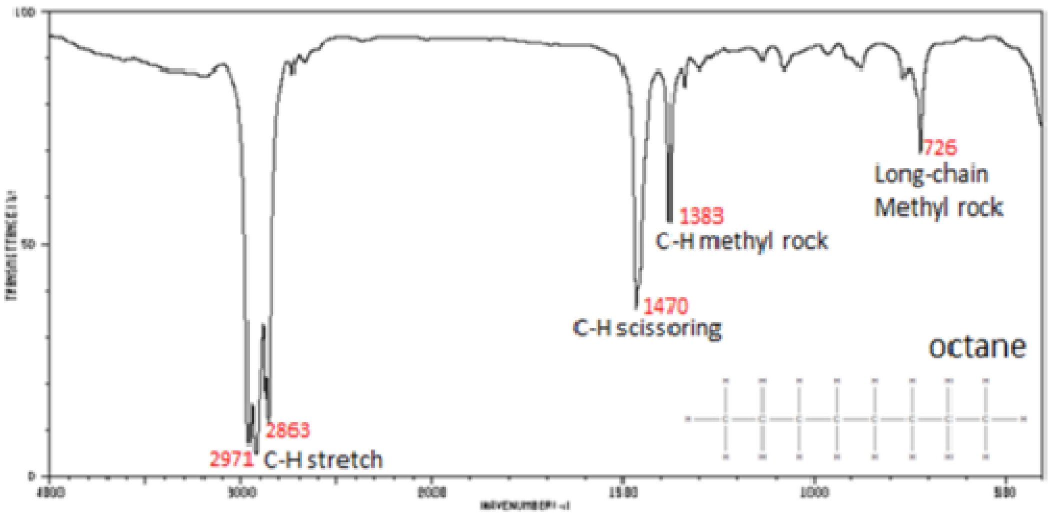


Figure 7: Shows the IR spectrum of octane. Since most organic compounds have these features, these C-H vibrations are usually not noted when interpreting a routine IR spectrum. Note that the change in dipole moment with respect to distance for the C-H stretching is greater than that for others shown, which is why the C-H stretch band is the more intense.

In alkenes compounds, each band in the spectrum can be assigned:

- C=C stretch from 1680-1640 cm^{-1}
- =C–H stretch from 3100-3000 cm^{-1}
- =C–H bend from 1000-650 cm^{-1}

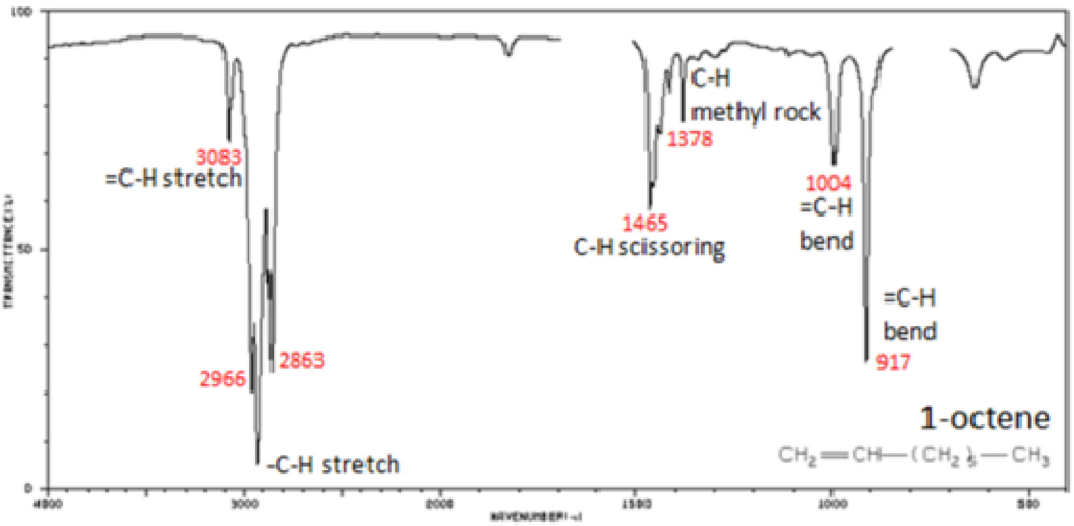


Figure 8: Shows the IR spectrum of 1-octene. As alkanes compounds, these bands are not specific and are generally not noted because they are present in almost all organic molecules.

In alkynes, each band in the spectrum can be assigned:

–C-C– stretch from 2260-2100 cm^{-1}

C–H stretch from 3330-3270 cm^{-1}

C–H bend from 700-610 cm^{-1}

The spectrum of 1-hexyne, a terminal alkyne, is shown below.

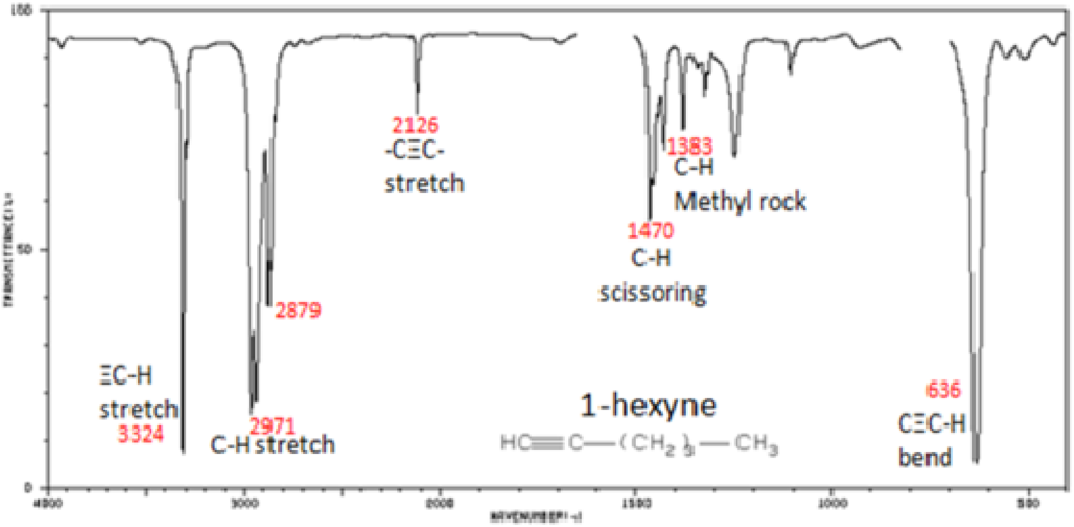


Figure 9: Infrared Spectrum of 1-Hexyne

In aromatic compounds, each band in the spectrum can be assigned:

- C–H stretch from 3100-3000 cm^{-1}
- overtones, weak, from 2000-1665 cm^{-1}
- C–C stretch (in-ring) from 1600-1585 cm^{-1}
- C–C stretch (in-ring) from 1500-1400 cm^{-1}
- C–H "oop" from 900-675 cm^{-1}

Spectrum of toluene:

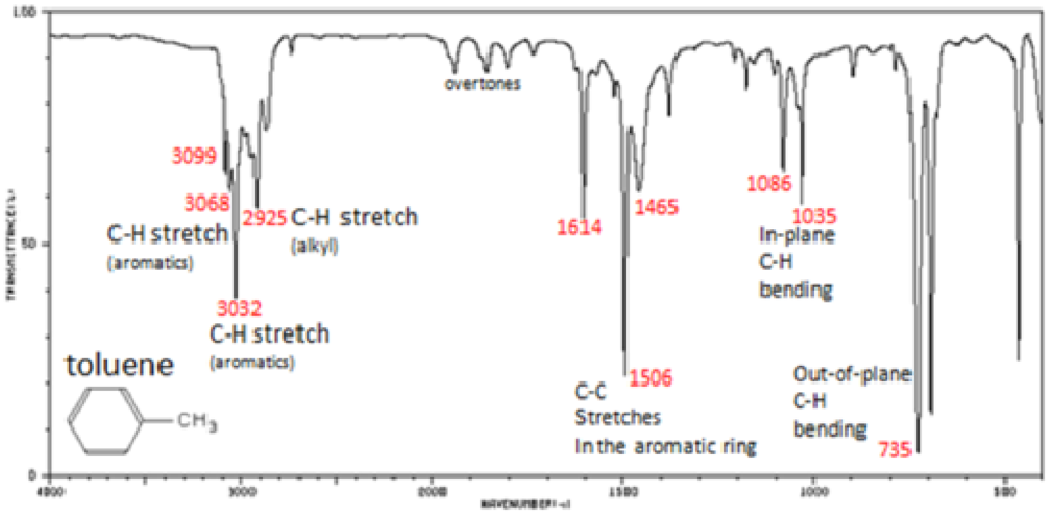


Figure 10: Infrared Spectrum of Toluene

Functional Groups Containing the C-O Bond

Alcohols have IR absorptions associated with both the O-H and the C-O stretching vibrations.

- O–H stretch, hydrogen bonded 3500-3200 cm^{-1}
- C–O stretch 1260-1050 cm^{-1} (s)

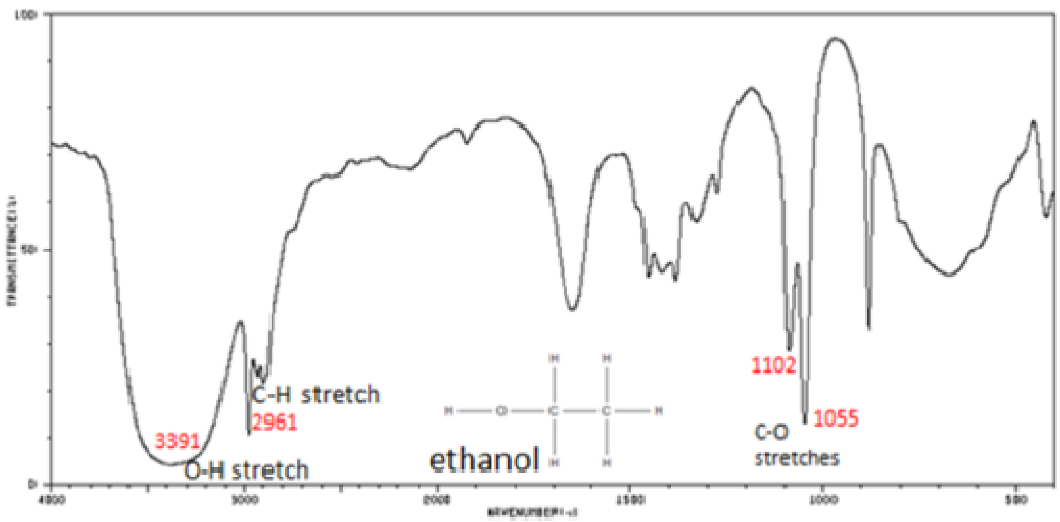


Figure 11: Infrared Spectrum of Ethanol

The carbonyl stretching vibration band C=O of saturated aliphatic ketones appears:

C=O stretch - aliphatic ketones 1715 cm^{-1}

Unsaturated ketones 1685-1666 cm^{-1}

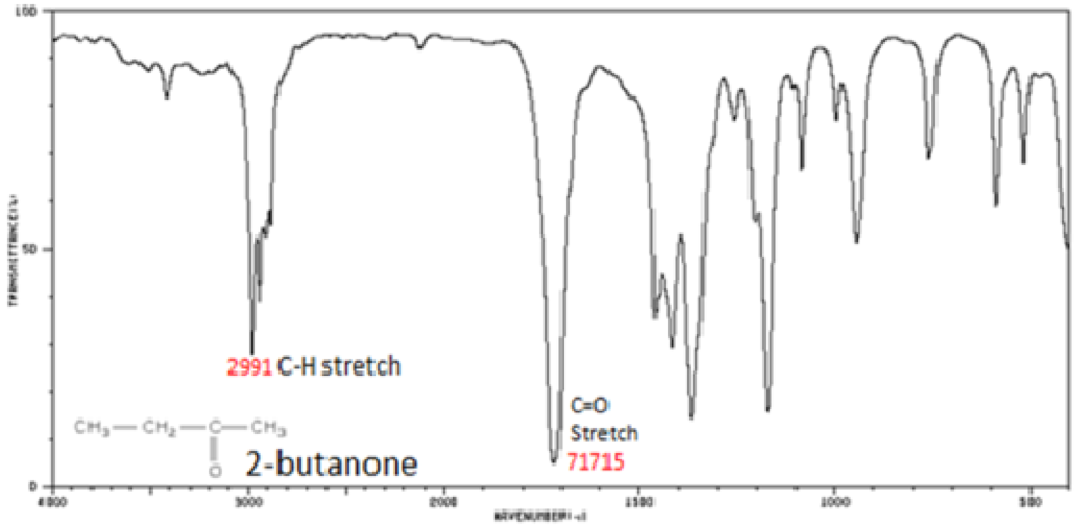


Figure 12: Infrared Spectrum of 2-Butanone

IR Spectrum of Organic Nitrogen Compounds:

N–O asymmetric stretch from 1550-1475 cm^{-1}
N–O symmetric stretch from 1360-1290 cm^{-1}

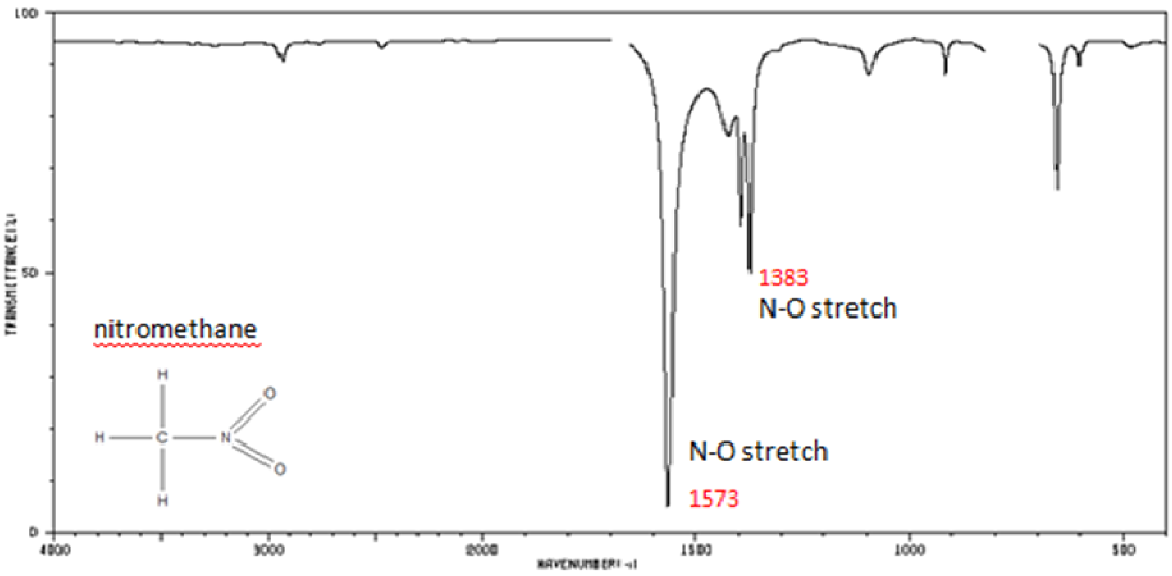


Figure 13: Infrared Spectrum of Nitromethane

IR Spectrum of Organic Compounds Containing Halogens:

Alkyl halides are compounds that have a C–X bond, where X is a halogen: bromine, chlorine, fluorine, or iodine.

- C–H wag ($-CH_2X$) from 1300-1150 cm^{-1}
- C–X stretches (general) from 850-515 cm^{-1}
    - C–Cl stretch 850-550 cm^{-1}
    - C–Br stretch 690-515 cm^{-1}

The spectrum of 1-chloro-2-methylpropane are shown below.

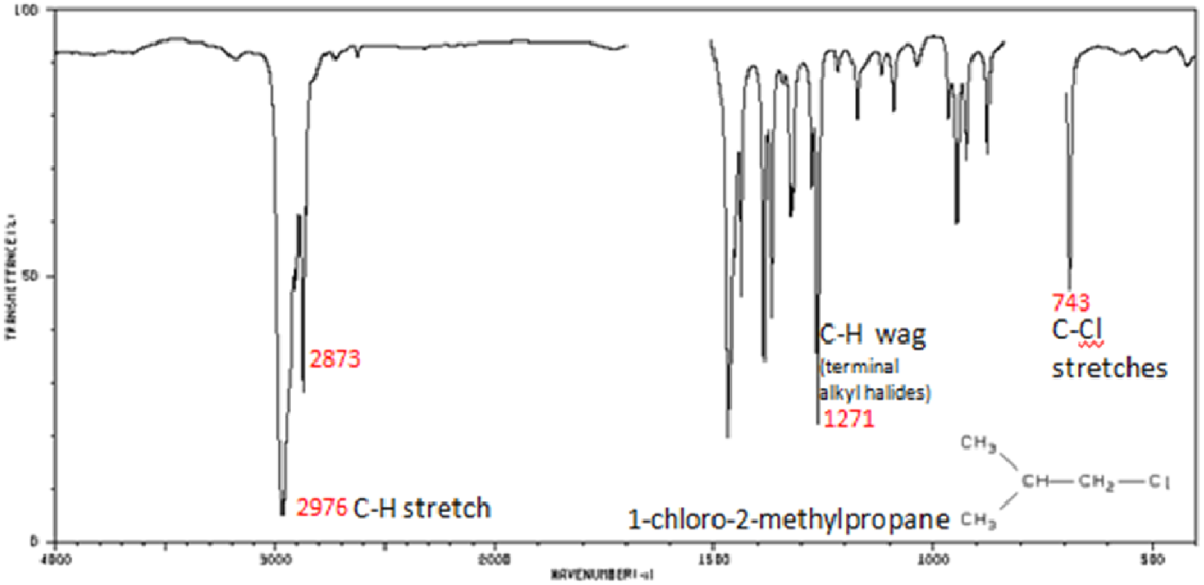


Figure 14: Infrared Spectrum of 1-chloro-2-methylpropane

4.12 SUMMARY

Vibrational rotational molecular spectra arise from transitions between vibrational energy states associated with the same electronic state of the molecule and are observed in the near IR region of the electromagnetic spectrum. Like pure rotational spectra, the vibrational rotational spectra are obtained only for molecules having permanent dipole moments such as heteromolecular diatomic molecules.

4.13 TERMINAL QUESTIONS

1. Discuss the conditions under which the Infrared spectrum of a diatomic molecule can be observed.
2. Give an account of the salient features of near-infrared spectrum of a diatomic molecule like HCl.
3. Find the vibrational energy of a diatomic molecule.
4. Draw a schematic diagram to represent the energy levels of a diatomic molecule regarded as an anharmonic oscillator.
5. Give a theory of a vibrational-rotational spectrum of diatomic molecules.
6. Give a selection rule for vibrational spectrum.

4.14 REFERENCES

1. Atomic and Molecular Spectra by Raj Kumar, published by Kedar Nath Ram Nath, Meerut.

2. Fundamentals of Molecular Spectroscopy by Colin N. Banwell and Elaine M. McCash. Tata McGraw- Hill 40th reprint, 2012.
3. https://chem.libretexts.org/ Bookshelves/Organic Chemistry.

Unit- 5 RAMAN SPECTROSCOPY

CONTENTS:

5.1 OBJECTIVES

After reading this unit, you will be able to:

- Define Raman spectroscopy.
- To know the region of radiation in which molecule shows Raman spectroscopy.
- Explain the selection rule involved during the transition between different energy levels.
- Define polarizability of a molecule.
- Explain pure rotational Raman spectra of a diatomic molecule.
- Explain pure vibrational Raman spectra of a diatomic molecule
- Have knowledge of Raman shift.

5.2 INTRODUCTION

We know that within molecule, there are certain energy levels which are associated with rotation, vibration or electronic level. When radiation of a particular wavelength falls on a molecule, there is absorption of radiation which results in transition between these energy levels. This technique is known as spectroscopy. Nowadays, spectroscopy is a very vast topic in chemistry and constitutes one of the subjects in chemistry. It involves several spectra depending on the type of radiation absorbed. For example, if a molecule absorbs radiations falling in microwave region, there is a transition between rotational energy levels. This spectroscopy is known as pure rotational spectroscopy or microwave spectroscopy. Likewise, when a molecule absorbs radiations falling in infrared region, the spectroscopy is known as vibrational spectroscopy in which there is transition between vibrational energy level of a molecule.

The present unit deals with Raman spectroscopy which was observed by C. V. Raman (Physicist) and for this, he was awarded Nobel Prize. This spectroscopy includes the concept of polarizability that changes on exposure to the radiations. Polarizability is defined as the ability of a non-polar molecule to acquire dipole moment in presence of an electric field. We will discuss about the selection rule on the basis of which we decide whether the transition between energy levels are allowed or forbidden. In order to understand the unit more clearly, we will consider Raman spectra of a diatomic molecule which includes pure rotational and pure vibrational Raman spectra.

Raman spectra are different from all other types of spectra, as all other spectra involve absorption of radiation while in Raman spectra, there is scattering of radiation instead of absorption. This makes this spectroscopy quite different from the other and this is the reason for taking interest in having complete knowledge of Raman spectroscopy.

5.3 CONCEPT OF POLARIZABILITY

As we have discussed earlier that there is scattering of radiation in Raman spectroscopy instead of absorption. We can obtain Raman spectra for solid, liquid and gaseous sample. Homo diatomic molecules or molecules without permanent dipole moment like N_2, O_2, H_2 etc also show Raman spectra whereas for a molecule to be infrared active, molecule must possess permanent dipole moment. In Raman spectroscopy, an intense beam of monochromatic light of visible region is allowed to pass through the molecule and the scattered light which is observed at right angle to the incident beam is observed. It has been seen that some of the scattered light have same frequency as that of the incident light while some scattered light have frequencies different (less or more) from the incident light. This is known as Raman Effect or Raman shift. The scattering in which the scattered light and the incident light possess same frequency is called Rayleigh scattering and the line produced is called Rayleigh line. When the scattered light has more frequency than the incident light, anti-stokes lines are produced whereas when the scattered light has less frequency than the incident light, the lines produced are called stokes lines. In this way, scattering results in the formation of three types of lines: Rayleigh lines, stokes lines and anti-stokes lines.

Raman shift ($\Delta\upsilon$) is the difference in the frequency of the incident light and the scattered light. Therefore:

$$\Delta\upsilon = \upsilon_i - \upsilon_s$$

Where υ_i is the frequency of the incident light, υ_s is the frequency of the scattered light and $\Delta\upsilon$ is Raman shift or Raman Effect. Raman shift lies in the region of near and far infrared radiation. We know that in case of stokes lines, the frequency of the scattered light is less than the frequency of the incident light i.e. $\upsilon_i > \upsilon_s$. Hence Raman shift is positive whereas, in the case of anti-stoke lines, the frequency of the scattered light is more than the frequency of the incident light i.e. $\upsilon_i < \upsilon_s$. Hence Raman shift is negative. It is important to remember that Raman shift ($\Delta\upsilon$) is independent of the frequency of the incident radiation but it depends on the characteristic of the molecule showing Raman effect. This has been explained on the basis of classical theory of Raman effect.

5.3.1 Classical theory of Raman scattering

This theory is also known as theory of polarizability. According to this theory, in the presence of an electric field, the electrons of a molecule (neutral) are attracted to the positive pole while nuclei of a molecule are attracted towards the negative pole. As a result, a dipole moment is induced or produced in the molecule. In this state, a molecule is said to be polarized. In this way, electron cloud gets distorted in the presence of an electric field. This ability of a molecule to gain dipole moment is called polarizability. The induced dipole moment (μ) is related to electric field (E) by an expression:

$$\mu = P\,E$$

Where, P is polarizability of the molecule.

$$E = E_o \text{ Sin } 2\Pi\upsilon t$$

Where υ is the frequency of the incident light, $E_o$is the vibrating electric field's amplitude

$$\mu = PE_o \text{ Sin } 2\Pi\upsilon t$$

This equation shows that oscillating dipole scatters light having same frequency. If the vibration in the molecule does not change the polarizability of the molecule then we will observe Rayleigh lines. There must be a change in polarizability of the molecule to be Raman active (Stokes and anti-stokes lines). Homo-nuclear diatomic molecule such as O_2, N_2, show Raman spectra as there is change in polarizability of the molecule due to vibration.

5.3.2 Quantum theory of Raman scattering

According to the quantum theory, there is a collision between the incident photon and the molecule. Let a photon of frequency (υ) collides with a molecule in an elastic manner then there is conservation of energy i.e. the energy of the incident photon is equal to the energy of the scattered photon whereas if the collision is inelastic, there is no conservation of energy. Therefore the scattered radiations have energy different from the incident radiation. The energy will be higher or lower than the energy of the incident radiation. Form the law of conservation of energy:

$$E + h\upsilon_i = E^l + h\upsilon_s$$

Where $h\upsilon_i$ is the energy of the incident photon, $h\upsilon_s$ is the energy of the scattered photon, E^l is the energy of the molecule after collision and E is the energy of the molecule before collision. Three conditions arise:

Case 1: If $\upsilon_i = \upsilon_s$: $E = E^l$: Rayleigh lines are produced
Case 2: If $\upsilon_i > \upsilon_s$: $E^l > E$: Stokes lines are produced
Case 3: If $\upsilon_i < \upsilon_s$: $E^l < E$: Anti-stokes lines are produced

5.4 PURE ROTATIONAL RAMAN SPECTRA OF A DIATOMIC MOLECULE

The diatomic molecule as we know consist of two atoms. When two atoms are same, the molecule is called homo-nuclear diatomic molecule like H_2, N_2 whereas when two atoms are different, the molecule is called hetero-diatomic molecule like HCl, HCN. When homo-nuclear diatomic molecule undergoes rotation, there is change in the orientation of the molecule with respect to the electric field of rotation. If molecule possess different polarizabilities in different direction or we can say that if the molecule is optically anisotropic then there is variation in the polarization with time. If α is the change in polarizability of a molecule then:

$$P = P_o + \beta \sin 2\Pi (2\upsilon_r) t \qquad (1)$$

Where, υ_r is the rotational frequency. The induced dipole moment (μ) is related to electric field (E) by an expression:

$$\mu = P E$$

Where, P is polarizability of the molecule.

$$E = E_o \text{ Sin } 2\Pi\upsilon t$$

Where υ is the frequency of the incident light, E_o is the vibrating electric field's amplitude

$$\mu = PE_o \text{ Sin } 2\Pi\upsilon t$$

On putting the value of P from equation 1 in the above equation, we obtain:

$$\mu = P_o + \beta \sin 2\Pi (2\upsilon_r) t \, (E_o \text{ Sin } 2\Pi\upsilon t)$$

$$\mu = P_oE_o \text{ Sin } 2\Pi\upsilon t + \beta E_o \text{ Sin } 2\Pi\upsilon t \sin 4\Pi \upsilon_r t$$

$$\mu = P_oE_o \text{ Sin } 2\Pi\upsilon t + \tfrac{1}{2} \beta E_o [\text{Cos } 2\Pi (\upsilon - 2\upsilon_r) t - \text{Cos } 2\Pi (\upsilon + 2\upsilon_r) t]$$

It is clear from the above equation that Raman lines have frequencies $(\upsilon - 2\upsilon_r)$ and $(\upsilon + 2\upsilon_r)$. Raman shift ($\Delta\upsilon$) is therefore equal to twice the frequency of rotation of a molecule.

$$\Delta\upsilon = (\upsilon + 2\upsilon_r) - \upsilon = 2\upsilon_r$$

The pure rotational Raman spectra contain a series of equidistant lines on both side of a Rayleigh line as shown in Figure 1. On the right of the Rayleigh line, anti-stokes lines are present. The separation between Rayleigh line and first anti-stokes line is 6B followed with the separation of 4B between two successive anti-stokes lines. Here B is rotational constant. On the left of the Rayleigh line, stokes lines are present. The separation between Rayleigh line and first stokes line is 6B followed with the separation of 4B between two successive stokes lines. It has been observed that greater is the anisotropy of the molecule, more will be the intensity of the rotational Raman lines.

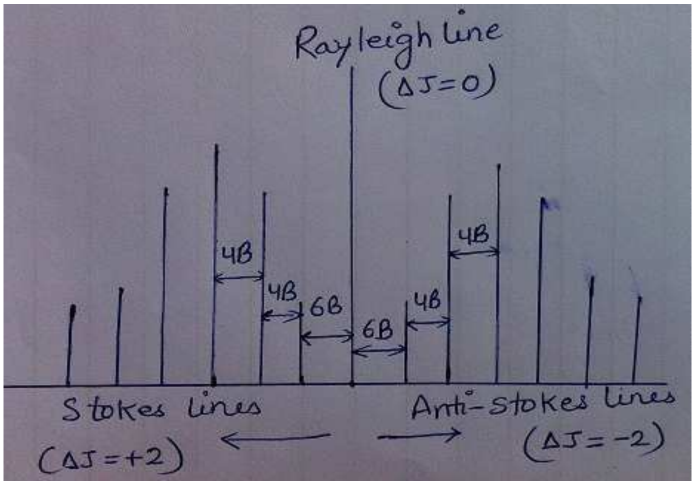


Figure 1Pure rotational Raman spectra

5.4.1 Selection rule

There are certain rules on the basis of which we decide whether the transition between energy level is allowed or forbidden. For rotational Raman spectra, the selection rule is:

$$\Delta J = 0, \pm 2$$

Where, J is rotational quantum number.

Case 1: If $\Delta J = 0$

This shows that there is no change in the rotational quantum number. In this case, the frequency of the incident and scattered radiation is same i.e. the scattering is Rayleigh scattering.

Case 2: $\Delta J = -2$

This corresponds to anti-stokes Raman lines. Here the scattered radiations have more frequency than the incident radiation.

Case 3: $\Delta J = +2$

This corresponds to stokes Raman lines. Here the scattered radiations have less frequency than the incident radiation.

5.5 PURE VIBRATIONAL RAMAN SPECTRA OF A DIATOMIC MOLECULE

This type of Raman spectra results from the change in polarizability of a molecule that results when a photon strikes a molecule. As we have studied that in case of rotational Raman spectra, more is the anisotropy, more is the intensity of Raman line. Similarly, in case of pure vibrational Raman spectra, more is the change in polarizability of the molecule; more is the intensity of vibrational Raman line produced. Examples of molecules that show pure vibrational Raman spectra are CO_2, NO_2. Let us consider a diatomic molecule, when light falls on a molecule, there is vibration in the molecule that results in the change in polarizability of the molecule. If d represents the change in the displacement due to vibration, the change in polarizability of a molecule (P) is given by expression:

$$P = P^o + \beta\, d/A$$

Where P^o represents the polarizability when there is no vibration or P^o represent equilibrium polarizability, A is the amplitude while β is the rate of vibration of the polarizability with displacement. Assuming that molecule undergoes simple harmonic motion, then the displacement (d) is written as:

$$d = A \text{ Sin } 2\Pi \upsilon_v t$$

Where, υ_v is the frequency of vibration of a molecule. We know that:

$$\mu = PE_o \text{ Sin } 2\Pi \upsilon t$$

$$\mu = (P^o + \beta\, d/A)\, E_o \text{ Sin } 2\Pi \upsilon t$$

$$\mu = P^o E_o \text{ Sin } 2\Pi \upsilon t + \beta\, E_o \text{ Sin } 2\Pi \upsilon t \text{ Sin } 2\Pi \upsilon_v t$$

$$\mu = P^o E_o \text{ Sin } 2\Pi \upsilon t + 1/2\beta\, E_o[\text{Cos } 2\Pi\,(\upsilon - \upsilon_v)t - \text{Cos } 2\Pi\,(\upsilon + \upsilon_v)t]$$

In the above equation, $(\upsilon - \upsilon_v)$ and $(\upsilon + \upsilon_v)$ terms are present, which indicates that there are certain lines in the vibrational Raman spectra that have frequency more than that of the frequency of the incident radiation while other have frequency less than that of the frequency of the incident radiation. Thus Raman shift ($\Delta\upsilon$) is given by expression:

$$\Delta\upsilon = (\upsilon - \upsilon_v) - \upsilon = \upsilon_v$$

It is therefore concluded that Raman shift in case of pure vibrational Raman spectra of a diatomic molecule is equal to the frequency of vibration.

5.5.1 Selection rule

Whether the transition is allowed or not, there is selection rule. For pure vibrational Raman spectra, selection rules are:

$$\Delta v = \pm 1$$

Where, v is vibrational quantum number. Two cases arise:

Case 1: $\Delta v = +1$

This corresponds to stokes Raman lines when there is transition from v to v + 1.

Case 2: $\Delta v = -1$

This corresponds to anti-stokes Raman lines when there is transition from v + 1 to v.

5.6 ROTATIONAL-VIBRATIONALRAMAN SPECTRA OF A DIATOMIC MOLECULE

This type of Raman spectra involves both rotation and vibration of a diatomic molecule when a monochromatic light falls on the molecule. Therefore there is change both in the vibrational and rotational quantum number. The selection rule for rotational-vibrational Raman spectra is:

$$\Delta J = 0, \pm 2; \Delta v = \pm 1$$

For rotational-vibrational Raman spectra, three branches are observed named as O branch, Q branch and S branch. The O branch refers to $\Delta J = -2$; Q branch refers to $\Delta J = 0$ while S branch refers to $\Delta J = +2$.

5.7 EXPERIMENTAL SETUP FOR RAMAN SPECTROSCOPY

The experimental setup consists of a cell into which a sample is taken. One end of a cell is horn like while the other end is provided with optically glass plate. A beam of monochromatic radiation is allowed to fall on the cell containing the sample. Sample must be colorless, pure and clean solid, liquid or gas molecule. Concentrated samples are taken so that the Raman lines produced possess high intensity. The source of monochromatic radiation is helium tube which was used in previous time but nowadays mercury arc is used. This mercury arc is placed close to the cell so that the cell receives radiations of high intensity. The scattered radiations emerge through the optically plane glass plate. There is a lens that directs the scattered radiations on the spectrograph. Spectrograph possesses short focus camera, prism having high resolving power and large light gathering power. The complete experimental setup for Raman spectra is shown in Figure 2.

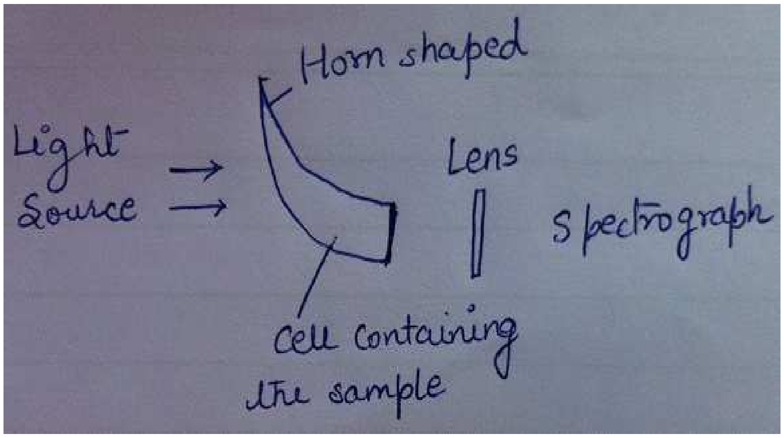


Figure 2: Experimental setup for Raman spectroscopy

5.8 INTENSITY OF RAMAN LINES

It is to be noted here that the intensity of Raman lines depends on the frequency of the incident radiation and concentration of the sample used. Intensity is directly proportional to the frequency of the incident light raise to the power four. Rayleigh line possess more intensity than stokes lines whereas stokes lines possess more intensity than the anti-stokes lines.

5.9 MUTUAL EXCLUSION PRINCIPLES

According to mutual exclusion principle, those molecules which possess center of symmetry i.e. they are centrosymmetric, the vibrations that are active in infrared spectroscopy are inactive in Raman spectroscopy. For example, CO_2 symmetric stretching vibrations are inactive in infrared but are active in Raman spectra. Similarly, H_2, O_2 (homonuclear diatomic molecule) are infrared inactive but are Raman active. This principle provides information about the structure of a molecule whether it contains center of symmetry or not.

5.10 APPLICATION OF RAMAN SPECTROSCOPY

There are several applications of Raman spectroscopy. These are:

1. Identification of unknown compound: It is one of the most important applications of Raman spectroscopy. This can be done by comparing the spectra of unknown compound with the spectra of the known compound. Each compound possesses a unique spectrum as there is a fingerprint region which is the characteristic of a particular molecule or a compound.
2. By using Raman spectra, we can determine whether a substance possess crystalline form or an amorphous form. Raman spectra of the crystalline form of a substance consist of fine lines whereas Raman spectra of an amorphous form of a substance consist of broad and closely packed lines.
3. Using Raman spectra, we can determine whether the dissociation of an electrolyte is partial, incomplete or complete. We can obtain Raman spectra of pure substance (electrolyte) as well as Raman spectra of ions into which an electrolyte dissociates. By comparing the intensity and position of Raman lines, we can detect the number of ions produced.
4. Raman spectra are also used in order to produce whether the compound is covalent or ionic. It has been found that Raman lines in case of covalent compounds possess high intensity whereas ionic compounds which are also known as electrovalent compounds possess low intensity Raman lines. For example, NaCl does not show Raman lines as it is ionic whereas on the other hand $HgCl_2$ which is a covalent in nature show sharp Raman lines.
5. By using Raman spectra, we can determine whether a given organic compound is aliphatic or aromatic.

5.11 SUMMARY

In this unit, we have discussed Raman spectroscopy which includes polarizability concept, theories of Raman scattering, selection rules, pure rotational Raman spectra of diatomic molecules, pure vibrational Raman spectra of diatomic molecules and mutual exclusion principle. By using mutual exclusion principle, one can predict whether a molecule contains center of symmetry or not. In addition to this, we have also discussed about the intensity of Raman line along with the application of Raman spectroscopy as applied for the identification of the unknown compounds.

5.12 GLOSSARY

- **Polarizability**: Ability of a non-polar molecule or atom to acquire dipole moment in presence of an electric field.
- **Selection rule**: Rules that decides whether the transition between energy levels are allowed or not.
- **Homo-nuclear diatomic molecule:** Molecule in which both atoms possess same nuclei like O_2, N_2.
- **Hetero-nuclear diatomic molecule**: Molecule in which atom possess different nuclei like HCl, NO_2.

- **Stokes lines**: Raman lines that possess frequency less than the frequency of the incident radiations.
- **Anti-stokes lines**: Raman lines that possess frequency more than the frequency of the incident radiations.

5.13 TERMINAL QUESTIONS

Q.1 Fill in the blanks:

1. Raman spectra involve ………. of radiations.

2. In Raman spectra, there is ………. in polarizability.

3. In Raman spectra, when the scattered radiation has frequency same as the incident radiation, ………. line is produced.

4. In Raman spectroscopy, when the scattered radiation has frequency less than the frequency of the incident radiation, the line produced is called ………. line.

5. In Raman spectroscopy, when the scattered radiation has frequency more than the frequency of the incident radiation, the line produced is called ………. line.

6. The sample taken for Raman spectra may be ………., ………. and ………..

7. Homo-nuclear diatomic molecule can even undergo ………. effect.

8. Ionic compounds possess Raman spectra that are ………. in intensity.

9. The selection rule for pure vibrational Raman effect of a diatomic molecule is ……….

10. The selection rule for pure rotational Raman effect of a diatomic molecule is given by ……….

11. Law of mutual exclusion principle is applied to those molecules that possess …………

12. The radiation used for studying Raman effect is ……….

13. The selection rule for rotational- vibrational Raman spectra of a diatomic molecule is ……….

14. The sample used for Raman scattering should be ………. and ……….

Q.2 True and False

1. We can observe Raman effect only for solid samples.

2. According to mutual exclusion principle, Raman active vibrations are infra-red inactive while infra-red active vibrations are Raman inactive in case of molecules that contains center of symmetry.

3. We can determine the structure of a molecule by using Raman spectroscopy.

4. Covalent compounds possess Raman lines of higher intensity than the ionic compounds.

5. The selection rule for pure rotational Raman spectra is $\Delta v = \pm 1$.
6. Selection rule predicts whether the transition within the energy level is allowed or not.
7. Molecules must possess center of symmetry in order to obey law of mutual exclusion principle.
8. Intensity of Raman line is directly proportional to the fourth power of the frequency of the incident radiation.
9. The frequency of Raman lines or Raman shift depends on the frequency of the incident radiation.
10. The polarizability of a molecule remains unchanged in Raman spectroscopy.

Q.3 Multiple Choice Questions:

1. Raman spectroscopy occurs in
   a. Infrared region
   b. Microwave region
   c. Visible region
   d. Ultraviolet region
2. In Raman spectroscopy, which condition of frequency is satisfied for anti-stokes lines provided that $\upsilon_i$is the frequency of the incident light, $\upsilon_s$is the frequency of the scattered light.
   a. $\upsilon_i=\upsilon_s$
   b. $\upsilon_i>\upsilon_s$
   c. $\upsilon_i<\upsilon_s$
   d. No relation between $\upsilon_i$and υ_s
3. In Raman spectroscopy, which condition is satisfied for stokes lines provided that $\upsilon_i$is the frequency of the incident light, $\upsilon_s$is the frequency of the scattered light.
   a. $\upsilon_i=\upsilon_s$
   b. $\upsilon_i>\upsilon_s$
   c. $\upsilon_i<\upsilon_s$
   d. No relation between υ_i and υ_s
4. For pure vibrational Raman spectra of diatomic molecule, selection rule is
   a. $\Delta v = 0$
   b. $\Delta v = \pm 1$
   c. $\Delta v = \pm 2$
   d. $\Delta v = \pm 3$
5. For pure rotational Raman spectra of diatomic molecule, selection rule is
   a. $\Delta J = 0, +1$
   b. $\Delta J = 0, \pm 1$
   c. $\Delta J = 0, \pm 2$

d. $\Delta J = \pm 1$

6. Raman shift ($\Delta \upsilon$) is zero for which of the following scattered line:
   a. Stokes line
   b. Anti-stokes line
   c. Rayleigh line
   d. None of the above
7. By using Raman spectroscopy, we can determine whether a substance possess crystalline form or amorphous form. Which of the following statement is correct?
   a. Crystalline form shows Raman spectra with fine lines.
   b. Amorphous form shows Raman spectra with fine lines.
   c. Crystalline form and amorphous form do not show Raman spectra.
   d. All of the above statements are false.
8. Raman spectra can be obtained for
   a. Solids only
   b. Liquids only
   c. Gases only
   d. All of the above
9. Which is the correct statement?
   a. Covalent compounds possess less intensity than the ionic compounds.
   b. Covalent compounds possess more intensity than the ionic compounds.
   c. Both covalent compounds, as well as ionic compounds, possess same intensity.
   d. Covalent compounds do not show Raman spectra.
10. Raman shift ($\Delta \upsilon$) is positive for
   a. Stokes lines
   b. Rayleigh lines
   c. Anti-stokes lines
   d. None of the above
11. For rotational- vibrational Raman spectra of diatomic molecule, selection rule is
   a. $\Delta J = 0, \pm 2$
   b. $\Delta v = \pm 1$
   c. Both a and b
   d. None of the above
12. In Raman spectroscopy, the spectrograph must possess
   a. High light gathering power
   b. High resolving power
   c. Short focus camera
   d. All of the above

Q.4 Explain Raman scattering in detail with respect to pure vibrational and pure rotational Raman spectra of a diatomic molecule.

Q.5 Explain the applications of Raman spectroscopy.

Q.6 Explain the classical and quantum theory of Raman scattering.
Q.7 Describe the concept of polarizability in Raman scattering.
Q.8 Discuss the experimental setup of Raman spectra along with the diagram.

5.14 ANSWERS

Q.1 Fill in the blanks:
1. Scattering; 2. Change; 3. Rayleigh; 4. Stokes; 5. Anti- stokes; 6. Solid, liquid and gas; 7. Raman effect; 8. Low; 9. $\Delta v = \pm 1$; 10. $\Delta J = 0, \pm 2$; 11. Centre of symmetry; 12. Visible radiation; 13. $\Delta J = 0, \pm 2$;$\Delta v = \pm 1$; 14. Pure and colorless

Q.2 True and False
1. False; 2. True; 3. True; 4. True; 5. False; 6. True; 7. True; 8. True; 9. False; 10. False

Q.3 Multiple choice Questions:
1. c. Visible region; 2. c. $\upsilon_i<\upsilon_s$; 3.b. $\upsilon_i>\upsilon_s$ 4. b. $\Delta v = \pm 1$; 5.c. $\Delta J = 0, \pm 2$; 6. c. Rayleigh line; 7. a. Crystalline form show Raman spectra with fine lines; 8. d. All of the above; 9. b. Covalent compounds possess more intensity than the ionic compounds; 10. a. Stokes lines; 11. c. Both a and b; 12. d. All of the above

References:

1. Sharma, B. K. (2006), Spectroscopy, Goel Publishing House, Meerut.
2. Raj, G. (2017), Advanced Physical Chemistry, Goel Publishing House, Meerut.
3. Puri, B. R., Sharma, L. R. and Pathania, M. S. (2012), Principles of Physical Chemistry, Vishal Publishing Co., Delhi.

UNIT 6: ELECTRONIC SPECTRUM

6.1 INTRODUCTION

In the previous classes, we have already learned about various types of properties of a substance such as chemical properties and physical properties. The chemical properties deal with the ability of one substance to change into another substance or we can say that how one substance undergoes chemical change or simply the properties that allow the substance to react with another substance. While on the other hand, physical properties deal with the ability of a substance not to change or we can say that identity of a substance do not change or simply these properties are related to the internal structure of the molecules, for example, density, viscosity, dipole moment, optical activity, magnetic susceptibility. All these physical properties are related to intermolecular forces (forces that exist among molecules in a substance) that includes ion-ion interaction, metal-ion interaction, ion-dipole interaction, dipole-dipole interaction, dipole-induced dipole interaction, London forces and hydrogen bond.

The present unit deals with physical properties of a substance in detail with reference to properties like optical activity, dipole moment and magnetic property for which the concept of magnetic susceptibility has been undertaken. Along with these properties, the method to measure these properties will be studied like for the measurement of dipole moment there is a method known as temperature change method and for the measurement of magnetic susceptibility; Gouy's method has been undertaken.

Further this unit will also include the applications of these physical properties. While going through the unit, we will come across how physical properties play an important role in structure elucidation.

6.2 OBJECTIVES

After reading this unit, you will be able to

- Define optical activity.
- Define specific rotation of a compound.
- Know the concept of plane polarized light.
- Define molar rotation of a compound.
- Measure the optical activity of a substance.
- Define dipole moment.
- Know the concept of polar and non-polar covalent bonds.
- Find the dipole moment of diatomic and polyatomic molecules.
- Define polarization of a molecule.
- Measure dipole moment by temperature change method.
- Know the concept of magnetic susceptibility and its measurement by Gouy's method.
- Know the applications of optical activity, dipole moment and magnetic susceptibility in determining the structure of a molecule.

6.3 OPTICAL ACTIVITY

Optical activity is an effect of an optical isomer's interaction with plane-polarized light. It was first observed by the French physicist Jean-Baptiste Biot. He concluded that the change in direction of plane-polarized light when it passed through certain substances was actually a rotation of light, and that it had a molecular basis. His work was supported by the experimentation of Louis Pasteur. Pasteur observed the existence of two crystals that were mirror images in tartaric acid, an acid found in wine. Through meticulous experimentation, he found that one set of molecules rotated polarized light clockwise while the other rotated light counterclockwise to the same extent. He also observed that a mixture of both, a *racemic mixture* (or *racemic modification*), did not rotate light because the optical activity of one molecule canceled the effects of the other molecule. Pasteur was the first to show the existence of chiral molecules. In order to understand the concept of optical activity, we have to discuss about plane polarized light.

6.3.1 Plane polarized light

As we know light possess wave nature which was confirmed by method like diffraction and interference. A light that possesses only one plane of vibration is said to be plane polarized light. Here we must have to know the difference between plane polarized light and light. Light ray travels in all direction or we can say that it possesses vibrations of wave in all directions. The picture of light and plane polarized light is given in Figure 1.

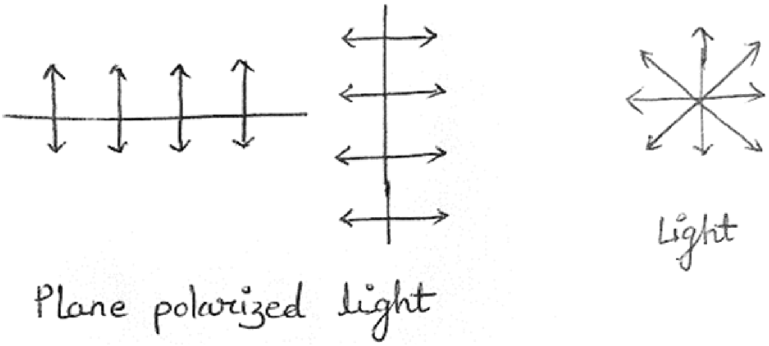


Figure 1. The vibration of wave of plane polarized light and light.

Now the question arises from where the plane polarized light emerges. If light (having wave vibration in all directions) is passed through crystal (Nicol prism), the emerging light possess vibrations only in one plane which is said to be plane polarized light. The crystal that causes light to travel only in one plane is known as polarizer. William Nicol introduced the Nicol prism and the operation is detailed in Figure 2.

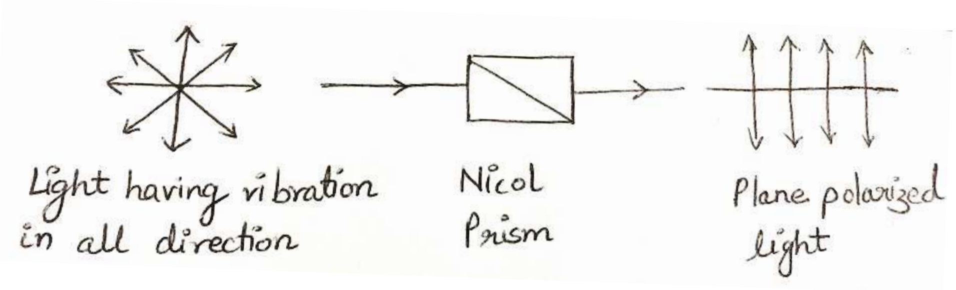


Figure 2. Figure showing Nicol prism's operation.

Another example of polarizer is polaroid. This polaroid consist of certain dichroic derivatives of quinine which are embedded in transparent plastic. The concept of polaroid was given by E. H. Land who was an American.

Now after discussing the concept of plane polarized light we can now move forward to the optical activity. It has been found that when plane polarized light passes through certain substances (organic substances like sugar, quartz, sodium chlorate) there is change in the direction of motion or simply we can say that the plane of the polarized light after passing through certain substances gets rotated either to the right or to the left. This property of rotation of the plane of the polarized light by some substances is known as optical activity and the substances which rotate the plane of polarized light are called optically active substances. Optical activity occurs only in chiral materials, those lacking microscopic mirror symmetry, fluids, gases or solutions of chiral molecules such as sugars, molecules with helical secondary structure such as some proteins, and also chiral liquid crystals. The phenomenon of optical activity is shown in Figure 3. These substances are classified as dextro-rotatory (d) and levo-rotatory (l). The levo-rotatory substances are those substances that rotate the plane of polarized light left or anticlockwise whereas dextro-rotatory substances are those substances that rotate the plane of polarized light towards right or clockwise.

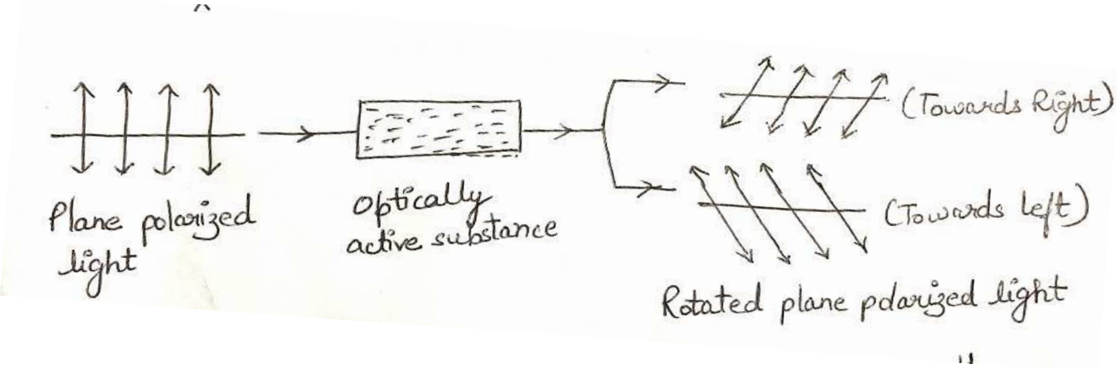


Figure 3. The phenomenon of optical activity.

Optical activity is a property which is related to the arrangement of atoms in a molecule thus it is a constitutive property. It has been found that optically active organic compound include at least one carbon atom having four different groups attached to it. Such a carbon atom that bears four different groups in its four valencies is said to be an asymmetric carbon, for example, in lactic acid, carbon is asymmetric carbon and rotate the plane of the polarized light towards right or left. The form of lactic acid that rotate the plane of polarized light towards right or clockwise is called d-form or (+) form and the form that rotate the plane of polarized light towards left or anticlockwise is called l-form or (−) form. These two forms of lactic acid are given in Figure 4. If equal amount of d-form and l-form are mixed, the product thus formed is optically inactive and a mixture is said to be racemate or racemic mixture. It is denoted by (±) as prefix or by writing dl- as a prefix. There are several factors on which the rotation (angle or degree) of the plane of the polarized light depends. These factors include wavelength of the light used, temperature of the system or solution, nature of the substance, length of the tube containing optically active substance and on the concentration of the solution in g/ml of optically active substance. The different types of rotation are discussed in the following section.

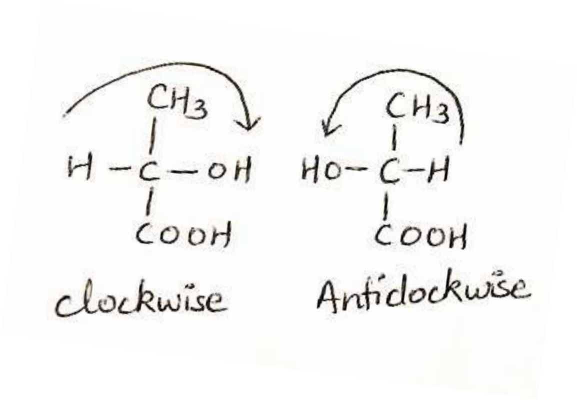


Figure 4. The d-form and l-form of lactic acid

6.3.2 Specific rotation

It is found that angle of rotation in degree (α) is directly proportional to the concentration of the solution (c) in g/ml of optically active substance and length of the tube (l) in decimeter through which light passes. Mathematically:

$$\alpha = [\alpha\,]_{\lambda}^{T}\ c \times l \qquad \text{Eq.a}$$

Where $[\alpha\,]_{\lambda}^{T}$ is constant which is known as specific rotation of the substance. Here T represents temperature of the solution and λ is the wavelength of the light used. If sodium light is used having D-line and temperature of the solution is 25°C. Then specific rotation is represented by $[\alpha\,]_{D}^{25}$. It is already known that concentration of the solution is equal to the amount of the substance (optically active) in grams (say m) dissolved in a definite volume of the solution say V ml i.e.,

$$c = m/V \qquad \text{Eq.b}$$

On substituting Eq.b in Eq.a we get,

$$\alpha = [\alpha\,]_{\lambda}^{T} \times m/V \times l$$

$$[\alpha\,]_{\lambda}^{T} = \alpha \times V/\ m \times l$$

Now in order to define specific rotation, let m = 1gram, V = 1ml, l = 1dm, then resulting value of $[\alpha\,]_{\lambda}^{T}$ equals α. Therefore, specific rotation of a substance is defined as the angle of rotation produced when concentration of the solution is 1 g/ml or when one gram of the substance is dissolved in 1ml of the solution and the path length of 1 dm through which light passes at temperature T.

The concentration term exists only in case of solution but it is clear from above discussion that optically active substance can be in form of solid or liquid also. In this case, concentration term is replaced by density (ρ) of the substance (solid or liquid). Therefore, specific rotation is given by:

$$[\alpha]_{\lambda}^{T} = \alpha / \rho \times l$$

6.3.3 Molecular rotation

Molecular rotation is also known as molar rotation. Molecular rotation is obtained by multiplying the specific rotation $[\alpha]_{\lambda}^{T}$ of the substance with the molecular mass of the substance, the result of the product thus obtained is divided by 100. It is represented by $[M]_{\lambda}^{T}$ and is given by the expression:

$$[M]_{\lambda}^{T} = M \times [\alpha]_{\lambda}^{T} / 100$$

Where, M is the molecular mass of the substance.

6.3.4 Measurement of optical activity

The polarimeter is used for the measurement of angle of rotation of the plane of the polarized light or simply we can say for the measurement of optical activity. This instrument is composed of two prisms, one prism is known as polarizer and another prism is known as analyzer. These two prisms are placed on the same metal tube but opposite to each other. In between these two prisms, solution (optically active substance) is kept which is under study in a glass tube which is about 20 cm in length. One thing to be noted here is that polarizer is fixed while analyzer can be rotated about the axis of the metal tube. There is an eye piece after the analyzer and a circular scale for reading.

First of all light (monochromatic) from sodium vapour lamp or from any other source is allowed to fall on the polarimeter when glass tube is empty or there is no solution under study. The light moves from polarizer to glass tube and then to analyzer. The conditions are set for complete darkness by slowly rotating the analyzer which can be observed by eye-piece and the reading is noted from circular scale. Up to now, the glass tube was empty. Now onwards, the glass tube is filled with a solution of known concentration of optical substance. By seeing through eye-piece, we will observe that the condition is not completely dark. Now analyzer is rotated to bring the condition of complete darkness and again by using scale, we can take the reading. The difference between initial (done when glass tube is empty) and final reading (done when glass tube is filled with solution) gives the value of angle of rotation. Now question arises whether solution of optically active substance is dextro-rotatory or levo-rotatory. If the difference between two readings comes out to be positive, the substance under study is dextro-rotatory whereas if this difference is negative, the substance under study is levo-rotatory. The diagrammatic representation of measurement of optical activity is shown in Figure 5.

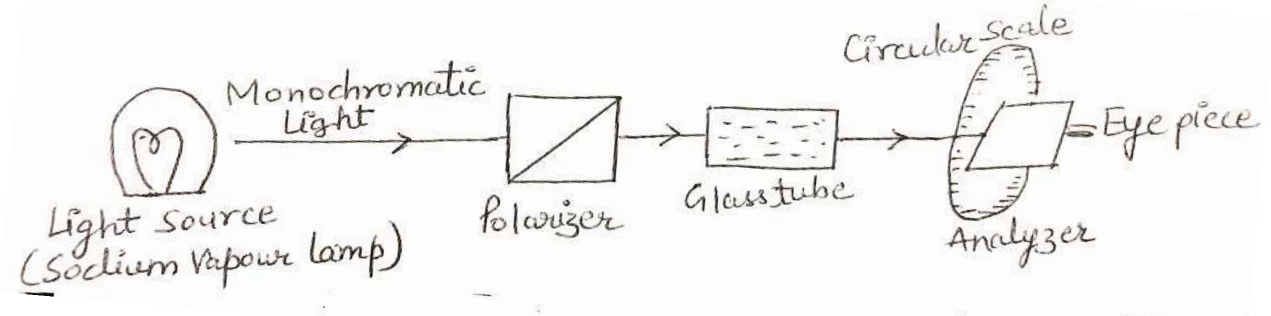


Figure 5. Schematic showing working principle of Polarimeter.

6.4 DIPOLE MOMENT

In order to understand the concept of dipole moment, let us have some look on covalent bond. We know that covalent bonds are formed by sharing of electrons between two atoms. For example, hydrogen molecule is formed when two hydrogen atom shares one electron. Now if both the sharing atoms are same as in hydrogen, the shared electron pair (two electrons) remains exactly in the middle of two atoms. As a result, a non-polar covalent bond is formed because there is no difference in the electronegativity of two sharing atoms. Now if atoms involved in a covalent bond possess electronegativity difference, then the shared electron pair will no longer remain in the middle. In this case, it will shift to a more electronegative atom like in HCl. Chlorine is more electronegative than hydrogen, here the shared electron pair will move towards chlorine which results in separation of charge. As a result, one atom acquires partial positive charge while the other atom (electronegative) acquires a partial negative charge. This leads to the formation of polar covalent bond $H^{\delta+}Cl^{\delta-}$. This charge must be equal and opposite. The concept of dipole arises from polar covalent bonds. As polar covalent bond give rise to charge separation, this makes one end positive and another end negative. This is known as dipole (di means two; pole means one end positive and another negative). In simple words, we can say that dipole is a molecule that consists of atoms having an electronegativity difference. A dipole is represented by $X^{\delta+}Y^{\delta-}$. One point to be noted is that there is a partial polarity which is produced on two poles (atoms). For homo-nuclear diatomic molecules, like H_2, N_2, I_2, CH_4, C_2H_6, dipole moment is zero and for hetero-nuclear diatomic molecules like HI, HCl, HBr, there is some value of dipole moment.

Dipole moment measures the extent of polarity of a molecule and polarity is a property of a molecule to become polar (dipole). The dipole moment is defined as the product of the magnitude of charge (equal and opposite) and the distance between the centre of their nuclei shown in Figure 6.

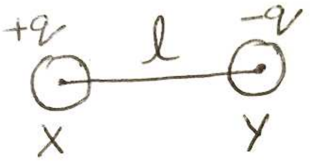


Figure 6. Representation of dipole moment

Let us consider a dipole XY having equal and opposite charge q and their separation of centre of nuclei is l. The dipole moment which is represented by μ is given by the product of q and l. The dipole moment is a vector quantity (depends on direction) and always points from the positive end to the negative end of the molecule. For example, in case of BF_3 and NH_3, the net dipole moment of BF_3 is zero while the net dipole moment of NH_3 is 1.47D which is shown in Figure 7.

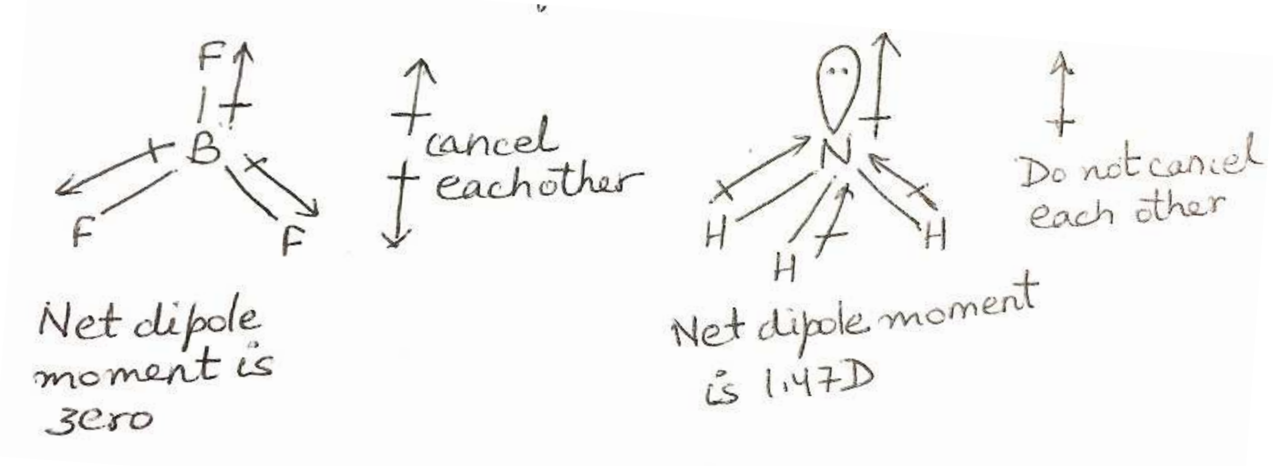


Figure 7. Structure of BF_3 and NH_3

Now coming to the unit of dipole moment, we know that it is a product of charge and distance between the centre of nuclei, therefore, unit of dipole moment is e.s.u. cm. As the magnitude of electric charge is of the order of 10^{-10}e.s.u. and the distance between the charges is of the order of 10^{-8} cm therefore, dipole moment is of the order of 10^{-18}e.s.u. cm. This quantity is known as Debye. Thus dipole moment can also be expressed in Debye (D). The word Debye comes from the name of Peter Debye who contributed a lot in understanding the concept of polar molecules. For non-polar molecules, the dipole moment is zero. For polyatomic molecule (molecule containing more than two atoms), dipole moment exists between each bond and in this case, it is known as bond moment. Let us consider a polyatomic molecule with all three different atoms say XYZ. In this molecule there are two bonds, one is X-Y bond and other is X-Z bond having bond moment μ_1 and μ_2 respectively making an angle θ. For this molecule XYZ, dipole moment (μ) is measured experimentally and the value of θ is calculated by using an expression:

$$\mu = (\mu_1^2 + \mu_2^2 + 2\,\mu_1\mu_2\cos\theta)^{1/2}$$

By knowing the value of θ, we can decide the structure of the molecule i.e. angle between X-Y bond and X-Z, thereby predicting the shape of the molecule. The value of dipole moment of some common molecules is listed below in Table 1.

Table 1. The value of dipole moment of some common molecules

Molecule	H_2, I_2, Br_2, Cl_2, CH_4, CH_2=CH_2, CCl_4	HCl	H_2O	NH_3	HBr
Dipole moment (D)	0	1.02	1.83	1.47	0.78

Certain groups like $-NO_2$, $-CH_3$ possess dipole moment and in this case it refers to the group moment. Group moments possess negative as well as positive values. The positive value of group moment shows that the particular group is less electronegative while the negative value of group moment shows that the attached group is more electronegative. The value of group moment depends on whether the given group is attached to an aliphatic chain or an aromatic chain. For example, if $-NO_2$ is attached to the aliphatic chain, its group moment value is −3.05 D whereas if $-NO_2$ is attached to the aromatic chain, its group moment value is −3.93 D. Here group moment values are negative which shows that group attached is more electronegative or electron-withdrawing. In this way by knowing the sign of group moment, we can predict the mechanism of a particular reaction. Therefore we can say that by using the concept of dipole moment, we can predict the shape of molecules including the reaction mechanism. This is the reason that dipole moment plays an important role in the field of chemistry.

There is a term induced dipole, in order to understand the concept of induced dipole let us move forward. We know that a molecule is electrically neutral as it is made up of a positively charged nucleus and negatively charged electrons. When this neutral molecule is placed in an electric field, the nuclei attract towards negative plate while the electrons are attracted towards positive plate. This brings positive charge to one side and negative charge to another side. In this way, neutral molecule becomes charged under the influence of an electric field. This process is known as polarization of the molecule which is shown in Figure 8. The molecule now becomes charged and is said to be induced dipole as it becomes dipole by applying electric field.

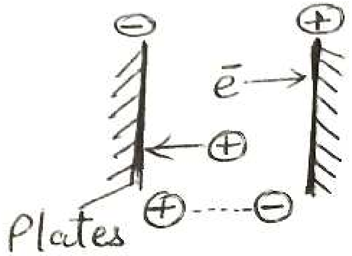


Figure 8. Polarization of a molecule

One point to be noted is that only in presence of electric field, molecule remains charged and as the electric field is removed, it becomes neutral. Thus we can say that the dipole thus formed have temporary existence. The value of induced dipole moment depends upon the strength of the applied electric field. If μ_i indicates induced dipole moment and E represent electric field, then μ_i is directly proportional to E.

$$\text{Thus: } \mu_i = \alpha E$$

Here α is the polarizability of the given molecule, defined as the strength of an electric field to make the molecule polar. Polarizability of a molecule is related to the dielectric constant of the medium which is present between the plates. Dielectric constant of a medium (solvent) is defined as the capacity of a medium to weaken the force of attraction between electrical charges immersed in that medium and as a result, electrical charges get separated. The dielectric constant is represented by D. For vacuum, the value of D is unity and for other medium, it possesses value more than unity. Clausius and Mosotti had given relation between polarizability of a molecule and dielectric constant of a medium which is known as Clausius-Mosotti equation. This equation is given below:

$$(D - 1)M/ (D + 2)\rho = 4\Pi N \alpha/ 3$$

Where M represents molecular mass of the molecule, ρ represent density of the molecule while N represents Avogadro's number.

6.4.1 Measurement of dipole moment

There are different methods for measuring dipole moment like temperature change method, refraction method and dilute solution method. The only method that we have to study is temperature change method. Let us discuss this method.

6.4.1.1 Temperature change method

This method is the most accurate method for measuring dipole moment of a molecule. The method is applicable only to those molecules which are in gaseous or vapour phase as here the molecules are far apart from each other. In this method the temperature range that is required is large. We know that Clausius- Mosotti equation is given as:

$$(D - 1)M/ (D + 2)\rho = 4\Pi N \alpha/ 3 \qquad (1)$$

On right hand side, all the quantities are constant, i.e. it does not depend on temperature. Thus left hand side must also be constant (do not depend on temperature) for a particular substance or a molecule. Thus equation 1 can be written as:

$$P_i = 4\Pi N \alpha/ 3 \qquad (2)$$

Where P_i is equal to $(D - 1)M/(D + 2)\rho$, also known as induced molar polarization. When one mole of a substance is placed between the plates of an electric field of unit strength, the amount of polarization produced refers to induced molar polarization. For molecules having permanent dipole moment, total polarization (P_t) is equal to the sum of induced molar polarization (P_i) and orientation molar polarization (P_o). Therefore:

$$P_t = P_i + P_o$$

From equation 2,

$$P_t = 4\Pi N \alpha/ 3 + P_o$$

Orientation molar polarization (P_o) is given by

$$P_o = 4\Pi N \mu^2/ 9 k T$$

Here μ is permanent dipole moment of a molecule, k is Boltzmann constant and T is temperature.

$$P_t = 4\Pi N \alpha/ 3 + 4\Pi N \mu^2/ 9 k T \qquad (3)$$

Equation 3 is Debye equation which can be written as:

$$P_t = X + Y/ T \qquad (4)$$

Here $X = 4\Pi N \alpha/ 3$ and $Y = 4\Pi N \mu^2/ 9 k$. These X and Y are constant for a particular substance. From Debye equation, it is clear that if a graph is plotted between P_t and 1/T, a straight line will be obtained with slope equal to Y and intercept equal to X (Figure 9). As slope is equal to Y whose value is $4\Pi N \mu^2/ 9k$. From this expression, we can calculate μ, permanent dipole moment of the molecule.

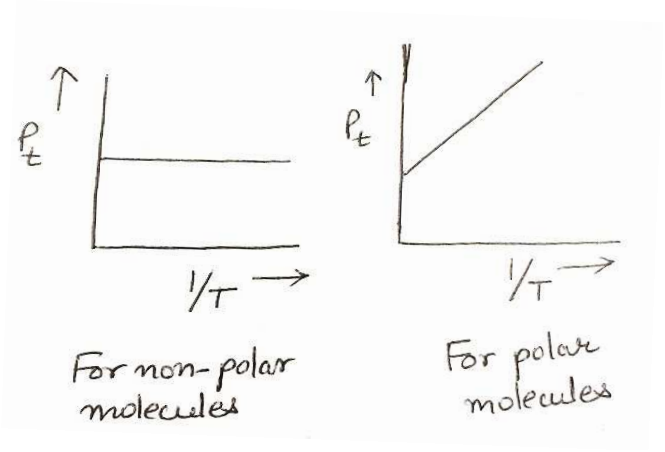


Figure 9. The plot between P_t and 1/T.

Let us consider the temperature change say from T_1 to T_2 having total polarization P_1 and P_2 respectively. Thus: $P_1 = X + Y / T_1$

$$P_2 = X + Y / T_2$$

$$P_1 - P_2 = (X + Y / T_1) - (X + Y / T_2)$$

$$P_1 - P_2 = X + Y / T_1 - X - Y / T_2$$

$$P_1 - P_2 = Y / T_1 - Y / T_2$$

$$P_1 - P_2 = Y (1/ T_1 - 1 / T_2)$$

$$P_1 - P_2 = Y (T_2 - T_1 / T_1 T_2)$$

$$Y = (P_1 - P_2) T_1 T_2 / (T_2 - T_1)$$

From here the calculated value of Y can be used to calculate dipole moment by changing the temperature. Thus the method is known as temperature change method.

6.5 MAGNETIC PROPERTY

The magnetic property of a substance is not very important as electric properties as there are some substances that possess permanent magnetic dipole moment. Magnetic moment represents orientation and magnetic strength of a substance that produces a magnetic field. Based on the behavior of the substance in a magnetic field, substances are classified into different types:

1. Diamagnetic Substances: Those substances which are repelled by magnets are called diamagnetic substances or simply when these substances are placed in magnetic field, these are pushed out as shown in Figure 10. These substances must possess electrons that are paired and produces magnetic fields which are in direction opposite to the external magnetic field or magnet. Some examples are copper, water, alcohol, bismuth.

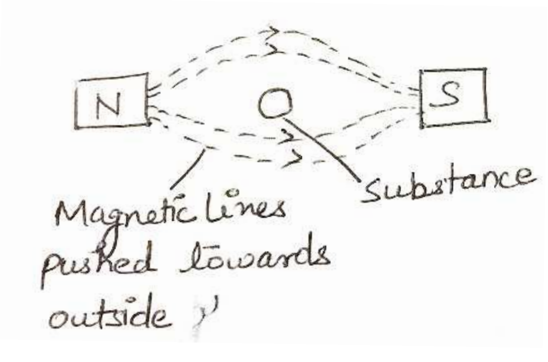


Figure 10. Diamagnetic substances pushing magnetic lines towards outside.

2. Paramagnetic substances: Those substances which are attracted by magnets are called paramagnetic substances. When these substances are placed in a magnetic field, these are pulled in as shown in Figure 11. These substances must have at least one unpaired electron and produces magnetic fields which are in the direction of the external magnetic field or magnet. Some examples are oxygen, aluminum. Paramagnetic behavior of a substance is stronger than the diamagnetic behavior.

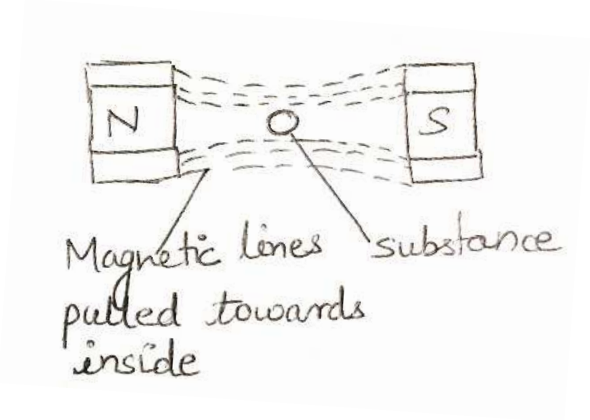


Figure 11. Paramagnetic substances pulling magnetic lines towards inside

3. Ferromagnetic substances: There are some substances which retain their magnetic property even after they are removed from the magnetic field (Figure 12). These substances are known as ferromagnetic substances. Some examples are iron, nickel, cobalt. These substances show all properties of paramagnetic substances but to a higher degree. Like paramagnetic substances, this substance produces magnetic field which are in the direction of the external magnetic field. These substances become permanently magnetized and are strongly attracted by magnets.

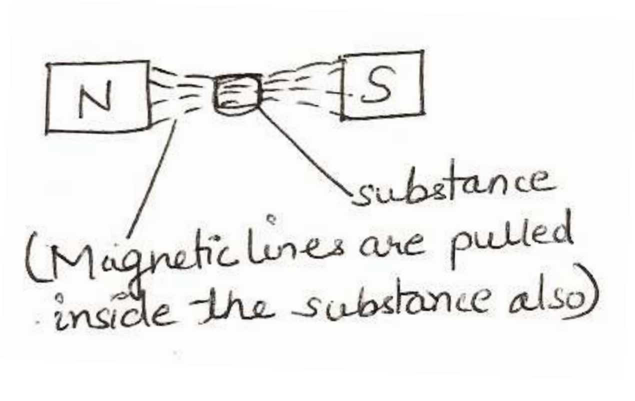


Figure 12. Ferromagnetic substance pulling magnetic line inside the substance

In ferromagnetic substances, the electron spin is in an ordered arrangement which is shown in Figure 13.

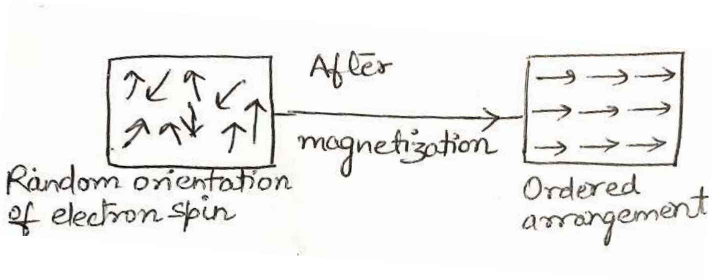


Figure 13. The ordered arrangement of electron spin in ferromagnetic substances

4. Antiferromagnetic substances: These substances, constituent particles possessing spin of electrons that align in a regular pattern with neighboring spins directed in opposite direction as shown in Figure 14. Some example are transition metal compounds, hematite, nickel oxide.

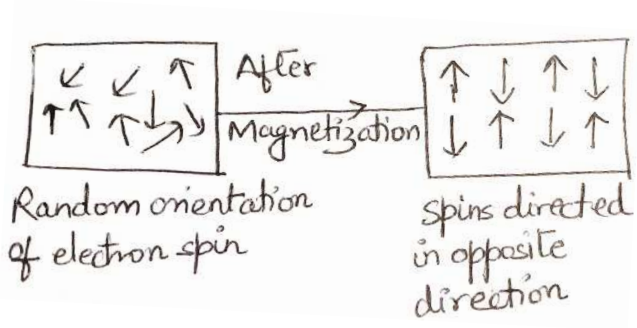


Figure 14. Opposite electron spin arrangement in antiferromagnetic substances

5. Ferrimagnetic substances: In these substances, the arrangement of constituent particles (atoms or molecules) is same as in antiferromagnetic substances but opposing moments are unequal and a spontaneous magnetization remains, for example, ferrite (Fe_3O_4).

Beside these substances, there are certain terms that are to be discussed inside magnetic property. The first term is magnetic permeability. Let us consider two magnetic dipoles having strength s_1 and s_2 respectively. Let r be the distance between these two dipoles and F is the force acting between them. Therefore $F = s_1 s_2 / \mu r^2$

Here μ is magnetic permeability of the medium and is a characteristic for a medium. Magnetic permeability of a medium represents the tendency of magnetic lines of force to pass through the medium relative to the tendency of the same magnetic lines of force to pass through the air or vacuum. By using the value of magnetic permeability, we can classify the substances like for μ values less than one, the substance is said to be diamagnetic, for μ values greater than one, the substance is said to be paramagnetic and for μ values of the order of 10^3 is said to be ferromagnetic. For vacuum, μ value is taken as one.

Another term is magnetic susceptibility. If a substance is placed in a magnetic field, the strength of the magnetic field thus present in the material is called magnetic induction, represented by B. Let the strength of the applied magnetic field is S then, magnetic induction is given by:

$$B = S + 4 \Pi I.$$

Here I, the intensity of magnetization is defined as magnetic moment per unit volume and possesses positive or negative value. The intensity of magnetization (I) induced at a point in a substance is related to the strength of magnetic field (S) by I = K S. Here K is magnetic susceptibility of the medium and is measured experimentally.

There is another term, mass susceptibility which is defined as magnetic susceptibility per gram of the substance. Mass susceptibility is also known as specific susceptibility. It is represented by χ and is given by:

$$\chi = K / \rho$$

Here ρ is the density of the substance. χ possess different value for different substances like for diamagnetic substances, mass susceptibility is negative, for paramagnetic substances, the value of mass susceptibility is positive whereas for ferromagnetic substances the value of mass susceptibility is very high that ranges from 200 to 10^5. The diamagnetic, paramagnetic and ferromagnetic substances can be differentiated by using the aforementioned terms (Table2).

Table2: Differentiation between diamagnetic, paramagnetic and ferromagnetic substances.

Property	**Diamagnetic**	**Paramagnetic**	**Ferromagnetic**
Magnetic susceptibility	Small & negative	Large & positive	Very large & positive
Magnetic field intensity	Independent	Independent	Dependent
Temperature	Independent	Dependent	Dependent

In order to show the relation between magnetic property and temperature, a French Physicist Pierre Curie discovered a temperature or a point known as Curie point or Curie temperature. At this point, some magnetic substances undergo a sharp change in their magnetic properties. Curie point for nickel is 400 ^{o}C. There is another point or temperature known as Neel temperature. It is a temperature above which antiferromagnetic substances become paramagnetic.

There is another term molar susceptibility which is defined as the susceptibility per gram mole of the substance. It is represented by χ_M and is given by expression:

$$\chi_M = \chi . M$$

Here M is the molecular weight of the substance and χ is mass susceptibility. χ_M is an additive and constitutive property.

6.5.1 Measurement of magnetic property

Under this heading, we will discuss about measurement of the magnetic susceptibility by Gouy's method given by French Scientist Gouy in 1889. The method is simple and requires a very small quantity of sample (0.5 gram to 1 gram). Gouy's apparatus consists of a long cylindrical tube in which sample is taken which can be either solid or liquid. This cylinder containing sample is then suspended in a balance. The arrangement of balance is in the way that the lower end of the balance containing cylinder remains in a strong magnetic field (5×10^3 to 15×10^3oersteds) while the upper end of the balance is in the region where no or negligible magnetic field occurs. One thing to be noted is that strong magnetic field is applied at the right angle to the axis of cylinder as shown in Figure 15. The other end of the balance (upper end) is counterbalanced by keeping weight on the balance pan.

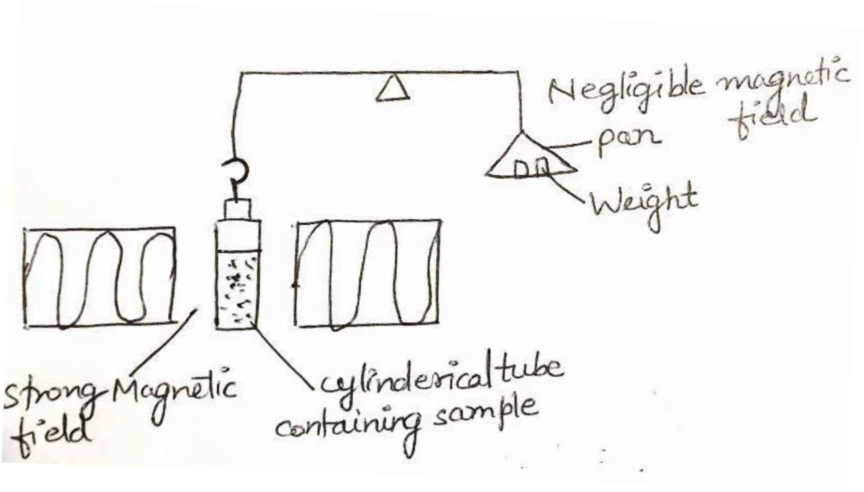


Figure 15. Schematic of Gouy's apparatus

In order to show whether a substance is paramagnetic or diamagnetic, a current is now switched on and the movement of cylindrical tube is observed. If cylindrical tube is pushed towards upper side, the substance will be diamagnetic and weights are removed from the pan in order to maintain the balance. If the cylindrical tube is pulled towards down then the substance will be paramagnetic and some more weights are to be added into the pan in order to maintain the balance. The magnetic force that acts on a substance is equal to the change in the weight. Therefore if Δ mg represents change in weight then:

$$\Delta \text{ mg} = \frac{1}{2} (\chi - \chi_a) aH^2$$

Here χ is the volume susceptibility of a substance, χ_a represents volume susceptibility of the air, a represents area of cross-section and H represents field strength. As the value of χ_a is fixed i.e. 0.03×10^{-6}, then by using the above equation, we can calculate χ which is the magnetic susceptibility of a substance. In this way, we can determine the value of magnetic susceptibility of a substance or a sample under study. By Gouy's method, we can measure the magnetic susceptibility of metals or alloys. Though the method is accurate but by this method, the magnetic susceptibility of gaseous sample thus obtained is not accurate and at higher temperature from 400 to 500 ^{o}C, this method does not give accurate results.

6.6 APPLICATIONS OF OPTICAL ACTIVITY

As we know that optical activity is a constitutive property which is related to the asymmetry of the molecule. Therefore, a molecule shows the phenomenon of optical activity only when it contains asymmetric carbon atom or nitrogen or silicon like in case of lactic acid. We have discussed earlier that asymmetric carbon atom contains four different groups at its four valencies. Along with carbon, nitrogen and silicon atoms containing molecules show the phenomenon of optical activity. If it shows the phenomenon of optical activity, the molecule can rotate the plane of polarized light towards right or left, the detail of which is given in section 6.3.

The four different groups attached to carbon atom do not exist in the same plane but are arranged at four corners of a regular tetrahedron. Therefore we can say that the molecule showing the phenomenon of optical activity must possess asymmetric carbon atom which finds its applications in predicting the structure of the molecule.

6.7 DETERMINATION OF STRUCTURE OF MOLECULE

We have discussed certain physical properties of a substance like optical activity, dipole moment and magnetic susceptibility. All these physical property plays an important role in determining the structure of a molecule. The application of optical activity is aforementioned; now let us consider the dipole moment and magnetic susceptibility in determining the structure of the molecule.

6.7.1 Dipole moment

We know that dipole moment is a vector quantity which is constant for a particular bond. For example, let us discuss the applications of dipole moment for triatomic molecules (molecules having three atoms). In case of carbon dioxide (CO_2), as dipole moment directs from positive end to the negative end, the resultant dipole moment is zero, therefore the molecule is linear in nature as the bond moment is equal and opposite of each other. Similar is the case with carbon disulphide (CS_2). Thus by knowing that dipole moment having zero value shows that the structure of molecule is linear. Now let us discuss the condition for water, here the value of dipole moment is 1.84 D. This shows that the structure of water is not linear as it possesses some value of dipole moment. Thus the structure of water is bent or V- shape with bond angle 104^{o}. This is the condition for triatomic molecules. The structure of CO_2 and H_2O is shown below in Figure 16.

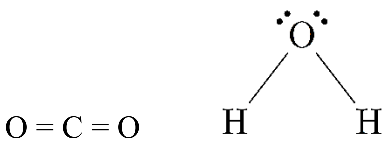


Figure 16. Structure of CO_2 and H_2O

For tetratomic molecules like BF_3 and NH_3, the dipole moment of BF_3 is zero which shows that all three fluorides (F^-) and one boron (B) are in the same plane, making the shape trigonal planar. For NH_3 there is a definite value of dipole moment which shows that all atoms do no lies in the same plane. Here one atom lies out of the plane making the shape pyramidal. The shape of BF_3 and NH_3 is given in Figure 17.

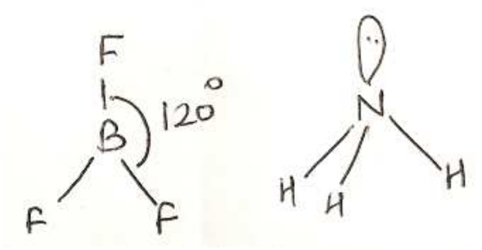


Figure 17. Structure of BF_3 and NH_3

For polyatomic molecules containing five atoms, the dipole moment of some molecules like CH_4, CCl_4 is found to be zero. This shows that the molecule is symmetrical as different bond moment cancel out each other.

By using the concept of dipole moment we can predict whether the geometrical isomer is cis- or trans–. If dipole moment is zero then the geometrical isomer that exists is trans- as the bond moment cancel each other. If the dipole moment possesses some definite value then the geometrical isomer that exists is cis- as the bond moment do not cancel each other. Both cis and trans – are shown in Figure 18.

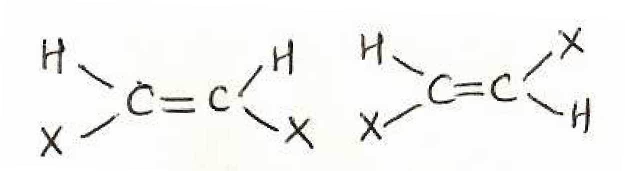


Figure 18. Cis- and trans-form

In case of cyclic structure, the dipole moment of para-isomer is zero as the same group are attached to different carbon are opposite and equal. For ortho-isomer and meta- isomer, the dipole moment is not equal to zero, therefore it possesses some definite value of bond moment. The dipole moment of meta- isomer is less than ortho-isomer. These three isomers are shown in Figure 19.

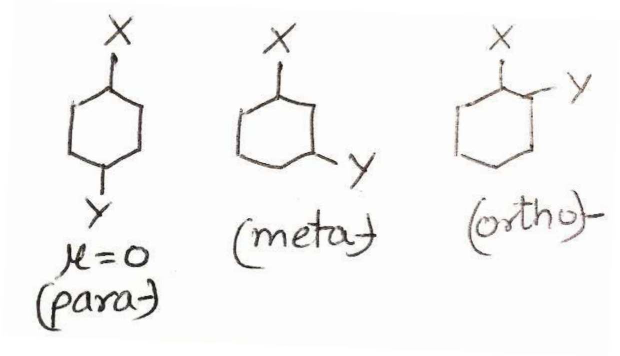


Figure 19. Three isomer ortho-, meta- and para-

6.7.2 Magnetic property

Magnetic property that we have discussed here is magnetic susceptibility. From earlier studies in section 6.5, it is clear that magnetic susceptibility (χ) is constitutive as well as additive property of a molecule. By using Gouy's method, the value of magnetic susceptibility of different atoms and structural parameters like carbon-carbon double bond, nitrogen-nitrogen double bond, carbon-carbon triple bond, carbon-nitrogen triple bond can be determined. The standard value of magnetic susceptibility is available. By calculating the magnetic susceptibility of a molecule and comparing with standard values or experimental values, one can predict the type of atom and the nature of the bond between the atoms useful in determining the structure of a molecule.

6.8 SELF- ASSESSMENT QUESTIONS (SAQ)

- Fill in the blanks

1. The plane polarized light possesses vibration in ………. plane.
2. The crystal causing the light to travel only in one plane is ……….
3. Some substances possess property to rotate the plane of the polarized light, this property refers to ……….
4. Those substances that rotate the plane of polarized light towards left are known as ……….
5. Those substances that rotate the plane of polarized light towards right are known as ……….
6. Optical activity is a ………. property.
7. The specific rotation of a substance is represented by ……….
8. The amount of substance dissolved in a definite volume of a solution is known as ……….of that solution.

9. Lactic acid is an example of ………. substance.
10. Molecular rotation is given by the product of ………. and ………. of the substance.
11. The instrument used for measuring the angle of rotation is known as ……….
12. Polarimeter consists of two prisms, ………. and ………. at two ends of the metal rod opposite to each other.
13. While measuring the optical activity, a condition of complete ………. is to be maintained.
14. The dipole moment of a molecule is a product of ………. and ………. between the nuclei of two atoms of a molecule.
15. The unit of dipole moment is ……….
16. Dipole moment always direct from ………. end to a ………. end of a molecule.
17. Dipole moment of a non-polar molecule is ……….
18. Dipole moment of Boron trifluoride is ……….
19. The induced dipole thus produced as a result of polarization of a molecule have ………. existence.
20. Dipole moment is used for determining the ………. of a molecule.
21. Polarizability of a molecule refers to the ………. of an electric field to charge the molecule.
22. The most accurate method for the determination of dipole moment is ………. method.

6.9 SUMMARY

In this unit, we have discussed about the physical properties of a molecule with reference to optical activity, dipole moment and magnetic susceptibility. We have also discussed how these properties are helpful in determining the structure or shape of a molecule or a compound along with the method of their measurement which plays an important role in elucidating the structure of a molecule.

6.10 GLOSSARY

- **Plane polarized light**- Light having only one plane of vibration.
- **Optical activity**- Property of rotation of plane polarized light by some substances.
- **Specific rotation** - Angle of rotation produced when concentration of the solution is 1g/ml.

- **Molecular rotation-** Specific rotation of a substance multiplied by molecular mass of the substance.
- **Dipole moment** - Product of magnitude of charge which is equal and opposite and distance between the centre of their nuclei.
- **Diamagnetic substance** - Substances that are repelled by magnets.
- **Paramagnetic substances** - Substances that are attracted by magnets.
- **Ferromagnetic substance -** Substances that retain their magnetic property even after the removal of magnetic field.

6.11 POSSIBLE ANSWERS TO SAQ

- Fill in the blanks

1. One; 2. Polarizer; 3. Optical activity; 4. Levo-rotatory; 5. Dextro-rotatory; 6. Constitutive; 7. $[\alpha\ ]_{\lambda}^{T}$; 8. Concentration; 9. Optically active; 10. Specific rotation and molecular mass; 11. Polarimeter; 12. Polarizer and analyzer; 13. Darkness; 14. Charge and distance; 15. Debye; 16. Positive, negative; 17. Zero; 18. Zero; 19. Temporary; 20. Shape; 21. Strength; 22. Temperature change

6.12 REFERENCES

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6.13 TERMINAL QUESTIONS

1. Explain different physical properties of a molecule in detail.

2. Explain different method of measurement of optical activity, dipole moment and magnetic susceptibility with suitable diagram.

UNIT- 7 PHOTOCHEMISTRY

CONTENTS:

7.1 OBJECTIVES

At the end of this chapter, we will be able to understand the fundamental principles of photochemistry, the process and condition of photoreactions, the process of the photosensitization, and kinetics of the photochemistry.

7.2 INTRODUCTION

The study of interaction of photon with matter and change in the chemical behaviour of matter is called photochemistry. The related photon (*the smallest amount of light carrying energy*) with sufficient energy raises the molecule or the atom from ground electronic state into an electronically excited state. Which can undergo a number of different primary processes involving promotion of an electron from bonding molecular orbital (BMO) to an anti-bonding molecular orbital (ABMO). In other words, the study of chemical reactions, in which the excited species dissociates, isomerizes, rearranges, or reacts with another molecule that may occur under the influence of electromagnetic radiation or photons. It also concerns with absorption, excitation and emission of photon by constituents (atoms, atomic ions, molecules, molecular ions, etc.). If we compare chemical bond energies (ranging from 100–1000 kJ/mol) with light (electromagnetic radiation) energies viz. Ultraviolet region (ranging from 302-604 kJ/mol) and visible region (ranging from 151-302 kJ/mol) and study the range, vacuum ultraviolet, ultraviolet and Visible region is expected to induce chemical reactions chiefly involved in such reactions.

Photochemistry has great importance in life by using natural radiations. Natural complexes such as proteins and nucleic acid occur through photochemical reactions. Some chemical reactions take place in the earth's stratosphere initiated by radiation and modified by suspended particles. For example, formation of ozone from oxygen, formation of vitamin D, and formation of smog and skin cancer inducing reactions takes place through photochemical reactions. They are very peculiar in supporting life on earth.

Some examples of industrially viable photochemical synthesis may be:(i) synthesis of vitamin **D,** from ergosterol isolated from certain(ii) synthesis of cubanes which are antiviral agents, (iii) industrialsynthesis of caprolactam, the monomer for Nylon **6,** (iv) manufacture ofcleaning solvents, insecticides and halogenated aromatics (used as syntheticintermediates) by photochlorination, and (v) synthesis of antioxidantsby photochemistry.

7.3 INTERACTION OF RADIATION WITH MATTER

A particular molecule when interact with electromagnetic radiation it absorbs radiation of certain wavelength or frequency (Fig 1). The frequency (ν) of the radiation absorbed by a molecule is given by Bohr's frequency rule:

$$\nu = \frac{E_2 - E_1}{h}$$

Where, $E_2$and $E_1$are energies of the final and the initial states respectively. The energy absorbed is expressed in terms of 'Einstein'.

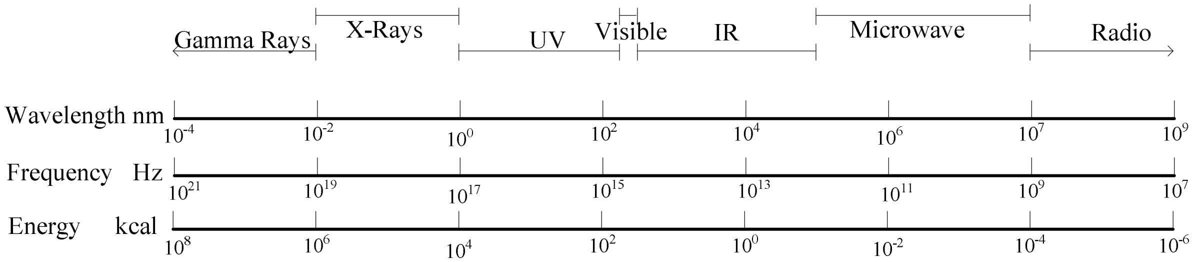


Fig1:The electromagnetic spectrum

Energy of photons can be explained with the help of the following law proposed by Albert Einstein.

$$E = h\nu = h\frac{c}{\lambda}$$

Where, h= Planck's constant (6.6 X 10^{-34} Js); c = speed of light (3 X 10^{8} ms^{-1});λ= wavelength; υ= frequency.

According to Einstein's equivalence principle, one particle of a chemical substance can absorb only one photon from electromagnetic radiation beam i.e.

$$E = h\nu$$

But for one mole of chemical substances the law changes as;

$$E = Nh\nu$$

Where, N = Avogadro's number (6.023 X 10^{23})

$$One\, Einstein = \frac{Nhc}{\lambda}$$

$$= \frac{(6.626 \times 10^{-34} Js \times 3 \times 10^{8} m\, s^{-1} \times 6.02 \times 10^{23})}{\lambda \times 10^{-9} m}$$

$$= \frac{119666}{\lambda} \text{Jmol}^{-1}$$

Where,λ is expressed in nm.

When any X molecule absorbs radiation or photon excitation is takes place as follows:

$$X_2 \xrightarrow{h\nu} X_2^*$$

A bonding electron is lifted to a higher energy level (higher orbital) of anti-bonding molecular orbital. The mechanism of excitation is as follows.

a) $X_2^* \longrightarrow X_2 + M^*$ (excess energy transferred to the surrounding)

b) $X_2^* \longrightarrow X_2 + h\nu$ (fluorescence or phosphorescence)

c) $X_2^* + Y \longrightarrow chemical\ reaction$ (excess energy supplies the activation energy of the reaction)

7.4 DIFFERENCE BETWEEN THERMAL AND PHOTOCHEMICAL PROCESSES

The difference between thermal and photochemical processes lies in the distribution of the energy in the ground and excited electronic states of a molecule, which can lead to major alteration of chemical behaviour. On the basis of electronic state we can differentiate both the processes as follows:

S. No.	Thermal Processes	Photochemical Processes
1.	They are initiated by the absorption of heat energy, by an increase in the temperature of the reaction medium.	Photochemical reactions take place on the absorption of radiations (photons) by molecules.
2.	The activation energy results from the random intermolecular collision between the reactive species with itself or with other reactants or even with vessel containing the reaction	In photochemical reaction molecules can be excited electronically, using monochromatic light of a particular wavelength in the visible and ultraviolet region. The concentration of the

	mixture. There is no way of controlling the energies of the colliding molecules and thermal energy may be distributed among all the modes of excitation in the species.	molecules produced in the excited state depends upon a number of factors, e.g. intensity of the radiation source and rate of decrease of excited molecules by many competing processes.
3.	Thermal excitation increases in random manner mainly in the rotationally-vibrationally excited states while remaining in the ground electronic state to almost the same extent.	Energy can be located in any one particular quantum state and hence a particular bond can be broken in a molecule if it absorbs mono-chromatic radiation of an appropriate frequency.
4.	Dissociated complex molecules result into large number of free radicals. At high temperatures, free radicals are highly reactive, short lived and have a very low concentration.	Selective bond dissociation can be achieved with monochromatic wavelength even at low temperature with large concentrations.

7.5 LAWS OF PHOTOCHEMISTRY

Beers and Lambert’s Law governs the absorption of light in visible and ultraviolet regions by a solution (Fig 2). The intensity of incident radiation plays pivotal role for identification of photochemical change.

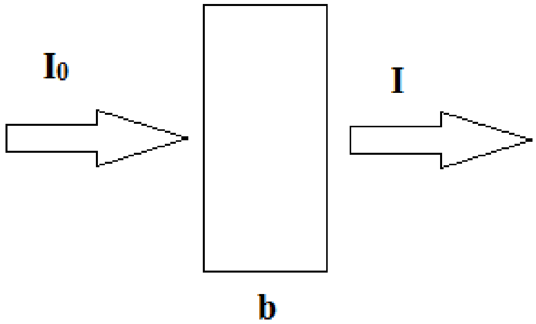


Fig2:Beer’s and Lambert law illustration

The Lamberts Law: This law states that decrease in the intensity of monochromatic radiation (one wavelength radiation) of suitable frequency with the thickness (concentration) of the absorbing medium is proportional to the intensity of incident light.

$$-\frac{dI}{dx}\alpha I \text{ Or } -\frac{dI}{dx}=KI$$

Where, k= absorption coefficient. The negative sign is introduced because there is reduction in intensity.

The Beer's Law states that decrease in the intensity of monochromatic light with the thickness of the solution is not only proportional to the intensity of the incident light but also to the concentration 'c' of the solution.

Mathematically,

$$-\frac{dI}{dx}\,\alpha\, IC \text{ or} -\frac{dI}{dx}=KIC$$

On combining both laws it was found that the probability of absorption of the photon of a beam of intensity I by the sample is directly proportional to the concentration and the thickness of the absorbing solution. Mathematically, we express it by,

$$\frac{dI}{I}=-KCdx$$

Where dI is the change in intensity produced by absorption of radiation on passing through a thickness dx of the solution of concentration C and K is the proportionality constant.

On integration between the limit $I=I_0$ at x=0 and I=I at x=b gives

$$\int_{I_o}^{I}\frac{dI}{I}=-KC\int_{0}^{b}dx$$

$$\text{or}\ln\left(I/I_0\right)=2.303\,log\left(I/I_0\right)=-KbC$$

$$or\, I=I_0e^{-KbC}$$

This is **Beer-Lambert law**, which says that the intensity of a beam of monochromatic radiation decreases exponentially with increase in the thickness x and the concentration C of the absorbing medium.

Defining $log\left(I_0/I\right)$ as absorbance, A, and putting k/2.303= •, of the solution, we get

$$A=log\left(I_0/I\right)=\varepsilon bC$$

Where, •is the absorption coefficient or extinction coefficient of the absorbing medium. If concentration is expressed in mol dm^{-3} and the path b in cm, then • expressed as dm^3mol^{-1} cm^{-1}, is referred to molar absorption coefficient.

The transmittance T is defined as $T=I/I_0$

Hence evidently, transmittance 'T' and Concentration 'C' are related as

$A=-\log T$

$T=10^{-A}=10^{-\varepsilon bC}$

We can understand more conveniently the relation with the help of the following data as in table 1. Which can be plotted comfortably, as can be seen, the plot of %T versus path length and absorption versus path length is a straight line passing through the origin (Fig 3).

Table 1: Data showing relationship between transmittance, concentration and path length.

Path length / cm	0	0.2	0.4	0.6	0.8	1.0
T	100	50	25	12.5	6.25	3.125
Absorbance	0	0.3	0.6	0.9	1.2	1.5

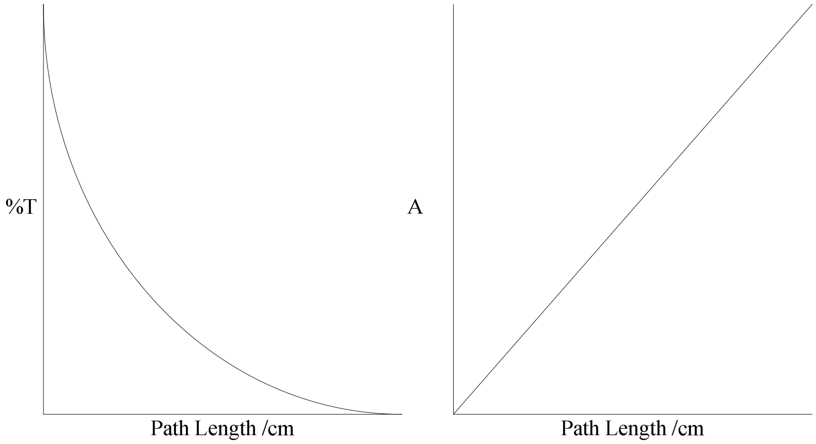


Fig3: The plot of %T versus path length and absorption versus path length

Lambert-Beer law also works for mixtures for given wavelength and frequency. Mathematically,

$$A_{net} = A_1 + A_2 + A_3 + ...$$
$$A_{net} = \varepsilon_1 bC_1 + \varepsilon_2 bC_2 + \varepsilon_3 bC_3 + ...$$

Limits to Lambert-Beer Law

1. Chemical Deviations are observed because after interaction with radiation molecules undergo association, dissociation or reaction with the solvent.
2. High concentration of solutions limits the law because particles are too close. Average distance between ions and molecules are diminished to the point. It affects the charge distribution and extent of absorption, causing deviations from linear relationship.
3. Chemical interactions,monomer-dimer equilibria, metal complexation equilibria, acid/base equilibria and solvent-analyte association equilibria also contribute to deviation from law.
4. The extent of such departure can be predicted from molar absorptivity and equilibrium constant.
5. The Beer-Lambert law is not obeyed if instrumental deviations like non-monochromatic radiation and stray light are observed.

6. High temperature of solution causes bathochromic effects, i.e. shorter wavelength bands shifts towards longer wavelength, so the temperature of the system should not be allowed to higher extent.

Example 1: 0.25 mg of compound A with molecular weight 140 g mol^{-1} was dissolved in 50 mL of the solvent. If the absorbance of this solution at wavelength 310 nm is 0.35, calculate the molecular extinction coefficient at 310 nm.

Solution: Molarity of compound A $= (0.25\times10^{-3}\ g/140\ g\ mol^{-1})\ (1000\ mL\ L^{-1} / 50\ mL)$

$= 3.57\times10^{-4}\ mol\ L^{-1}$

$\varepsilon = A/Cb$

$= \{0.35/ (1\ cm)(3.57\times10^{-4}\ mol\ L^{-1})\}$

$= 980\ L\ mol^{-1}\ cm^{-1}$

Example 2: The percentage radiation transmitted by a solution containing 2- aminonicotinic acid at pH 3.6 and 298 K at 320 nm is 72.4% for a solution $2\times10^{-5}\ mol\ L^{-1}$ in a one cm cell. Calculate: **(a)** the absorbance at 320 nm, **(b)** the molecular extinction coefficient, **(c)** radiation transmitted if the cell length is 5 cm.

Solution:(a) $A = \log (I_0/I) = \log (100/72.4) = 0.14$

(b) $\varepsilon = A/Cb = 0.14/(2\times10^{-5}\ mol\ L^{-1})\ (1\ cm) = 7\times10^{3}\ L\ mol^{-1}\ cm^{-1}$

(c) $\log (I_0/I) = \varepsilon Cb = (7\times10^{3}\ L\ mol^{-1}\ cm^{-1})\ (2\times10^{-5}\ mol\ L^{-1})\ (5\ cm) = 0.7$ $I_0/I = 5$ and thus $I/I_0 = 20\%$

Example 3: In an absorption cell, the transmittance of 0.1 M solution of a substance X is 80% and that of 0.1 M solution of another substance Y is 60% at a given wavelength. What is the transmittance of a solution that is simultaneously 0.1 M in X and 0.1 M in Y?

Solution: Since absorbance are additive, hence

$$A = A_1 + A_2 = \log\left({}^{I_0}\!/_{I} \right)_1 + \log\left({}^{I_0}\!/_{I} \right)_2$$

$$= \log\left({}^{100}\!/_{80} \right) + \log\left({}^{100}\!/_{60} \right) = 0.0969 + 0.2219 = 0.3188$$

$$A = \log\left({}^{I_0}\!/_{I} \right) = 0.3188$$

$$\therefore I_0/I = 2.084$$

$$T = I/I_0 = 1/2.084 = 0.48, i.e., 48\%$$

7.6 GROTTHUSS-DRAPPER LAW

This law was proposed by two scientists Theodor von Grotthuss (1785-1822) and John W. Draper (1811-1882) in the 19th century. They found that light must be absorbed by a compound in order for a photochemical reaction to take place. According to Grotthus-Draper law (also called the Principle of activation),*only the light which is absorbed by a molecule can be effective in producing photochemical changes in the molecule*.

Materials such as dyes and phosphors must be able to absorb "light" at optical frequencies. This law provides a basis for fluorescence and phosphorescence. This is considered to be one of the two basic laws of photochemistry.

7.7 STARK-EINSTEIN'S LAW (SECOND LAW OF PHOTOCHEMISTRY):

This law (also known as photo-equivalence law) was enunciated by Johannes Stark (1874-1957) and Albert Einstein (1879-1955). They applied the concept of energy quantum to photochemical reaction. It states that *for each photon of light absorbed by a chemical system, only one molecule is activated for a photochemical reaction*. The energy absorbed by one mole of the reacting molecules is given by $E = N_A h\nu$. This energy is called one Einstein.

The simplest photochemical process is seen with the absorption and subsequent emission of a photon by a gas phase atom such as sodium. When the sodium atom absorbs a photon it is said to be excited. After a short period of time, the excited state sodium atom emits a photon of 589 nm light and falls back to the ground state (Fig 4).

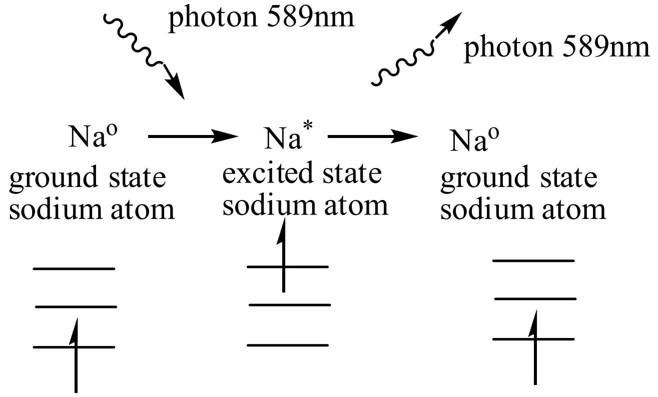


Fig4:Absorption and emission of radiation by sodium atom

Numerical value of Einstein

In CGS Units

$E=2.86/\lambda$ (cm) cal mol^{-1}

Or $2.86 \times 10^5 / \lambda$ (A^0) K cal mol^{-1}

In SI units

E=0.1197/λ (m) J mol^{-1}

Or 11.97X10^{-5}/λ(m) KJmol^{-1}

Types of photochemical reactions:

a) **Photodissociation:** In photodissociation, also called photolysis, the absorption of light raises the molecule into an excited state in which one of the chemical bonds no longer exists. Thus, absorption of light causes cleavage of a chemical bond and the release of two fragments called radicals because they each have enough electrons to form half of a chemical bond and are generally quite reactive. After absorption of radiation energy of the photon, X molecule get dissociated as follows.

$$X_2 \xrightarrow{h\nu} X + X$$

For example,

Photolysis of hydrogen bromide

$$HBr \xrightarrow{h\nu} H + Br \text{ (Photochemical } reaction\text{)}$$

$$\text{H} + \text{HBr} \longrightarrow H_2 + Br \text{ (dark reaction)}$$

$$\text{Br} + Br \longrightarrow Br_2$$

$$overall\ reaction$$

$$2HBr \xrightarrow{h\nu} H_2 + Br_2$$

Ozone formation in the atmosphere (at about 25 km altitude)

$$O_2 \xrightarrow{h\nu} O + O \quad (\lambda < 240 nm)$$

$$2\text{O}_2 + 2O \longrightarrow 2O_3$$

Ozone formed in the reaction absorbs UV light as well

$$O_3 \xrightarrow{h\nu} O_2 + O \quad (\lambda < 340 nm)$$

$$\text{O} + O_3 \longrightarrow 2O_2$$

Ozone shield protects the earth surface from high energy UV radiation (of the Sun). Air pollution (freons: fully halogenated hydrocarbons; nitrogen oxides emitted by aeroplanes etc.) may accelerate the decomposition of ozone ⇨ ozone hole.

b) **Photosynthesis:** When a larger molecule is formed from simple ones known as photosynthesis. e.g.

The photosynthesis of hydrogen chloride

$$H_2 + Cl_2 \longrightarrow 2HCl$$

Mechanism:

$$Cl_2 \xrightarrow{hv} 2Cl\,(< 500nm)$$

$$\mathrm{Cl} + \mathrm{H}_2 \longrightarrow HCl + H \qquad Dark\,\mathrm{Re}action$$

$$H + Cl_2 \longrightarrow HCl + Cl \qquad Chain\,\mathrm{Re}action$$

$$\vdots$$

$$\vdots$$

$$\left.\begin{array}{l} H + H + M \longrightarrow H_2 + M^* \\ Cl + Cl + M \longrightarrow Cl_2 + M^* \end{array}\right\}\text{Recombination reactions chain is terminated}$$

Photosynthesis in plants

Overall reaction:

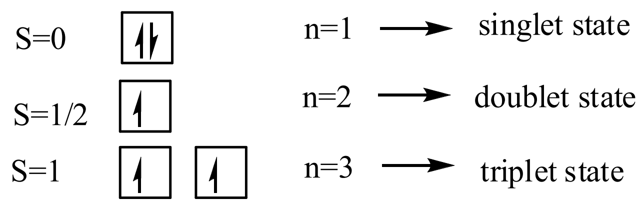
$$6CO_2 + 6H_2O \xrightarrow{\text{hv; Chlorophyll}} C_6H_{12}O_6 + 6O_2$$

Chlorophyll acts as a catalyst absorbing and transferring the photon energy for reduction of carbon dioxide to carbohydrate. This reaction maintains the life on the Earth.

c) **Photosensitized reactions:** When an excited molecule supplies activation energy for the reactants known as photosensitized reaction.

7.8 JABLONSKI DIAGRAM QUALITATIVE DESCRIPTION OF FLUORESCENCE

In order to understand Jablonski diagram we need to understand selection rule. This rule helps us to decide which transitions are possible and which are not. They depend on knowing the value of certain quantum numbers. Only certain changes in these quantum numbers are allowed for certain transitions. The most useful selection rule in photochemistry has to do with spin quantum number. This measured the number of unpaired electrons in the molecule resultingin a new term known as spin multiplicity. Spin multiplicity is the quantification of the amount of unpaired electron spin. The spin quantum number S for a molecule is the sum of the value of the entire electron spins. Usually, all the electrons are paired one up and one down. Then the spin quantum number is zero. If a species in a particular electronic state has one unpaired electron, the spin quantum number is ½. If the species has two unpaired electrons whose spins are aligned parallel the spin quantum number in 2x1/2 = 1. The spin multiplicity is just 2S+1 i.e. n = 2S+1. The number of possible quantum states (n) of a system based on the spin quantum number S (S is the angular spin momentum). If a molecule has S=0, or 1, we say it is in singlet state. If a molecule has S=1, or 3, we say it is in triplet state. Doublet (S=1/2) and quartet states (S=3/2) are also commonly observed. This is illustrated below:



Absorption and emission of the photons in different energy levels can be explained and shown in fig.5.

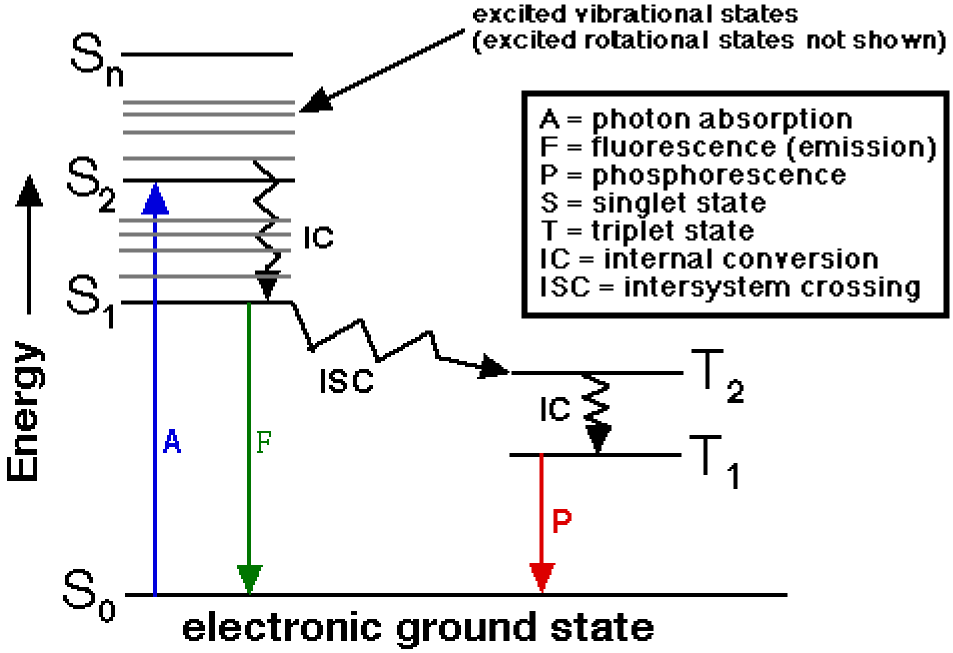


Fig5: Energy Levels and transition between levels.

Certain substances when exposed to light or certain other radiations absorb the energy and then immediately start re-emitting the energy. Such substances are called fluorescent substances. The first step is the transition from higher excited singlet states to the lowest excited singlet state S_1.This is called internal conversion (IC).It is a non-radiative process and occurs in less than 10^{-11} second .Now from S_1 the molecule return to ground state by any of the following paths.

- Path I: The molecule may lose rest of the energy also in the form of heat so that the complete path is non-radiative.
- Path II: Molecule releases energy in the form of light or uv radiation.This is called Fluorescence
- Path III: Some energy may be lost in transfer from S_1 to T_1 in the form of heat. It is called intersystem crossing (ISC). This path is non-radiative.

- Path IV: After ISC,the molecule may lose energy in the form of light in going from the excited triplet state to the ground state.This is called phosphorescence.

7.9 PHOSPHORESCENCE

There are certain substances that continue to glow for some time even after the external light is cut off. This process is known as phosphorescence. Thus, phosphorescence is a slow fluorescence (Fig 6). It is a type of photo-luminescence whose time-scale is approximately 10^{-3}–10^{-1}s indicating singlet-triplet-singlet transition. This phenomenon is best explained with the help of Jablonski diagram shown in fig 7.

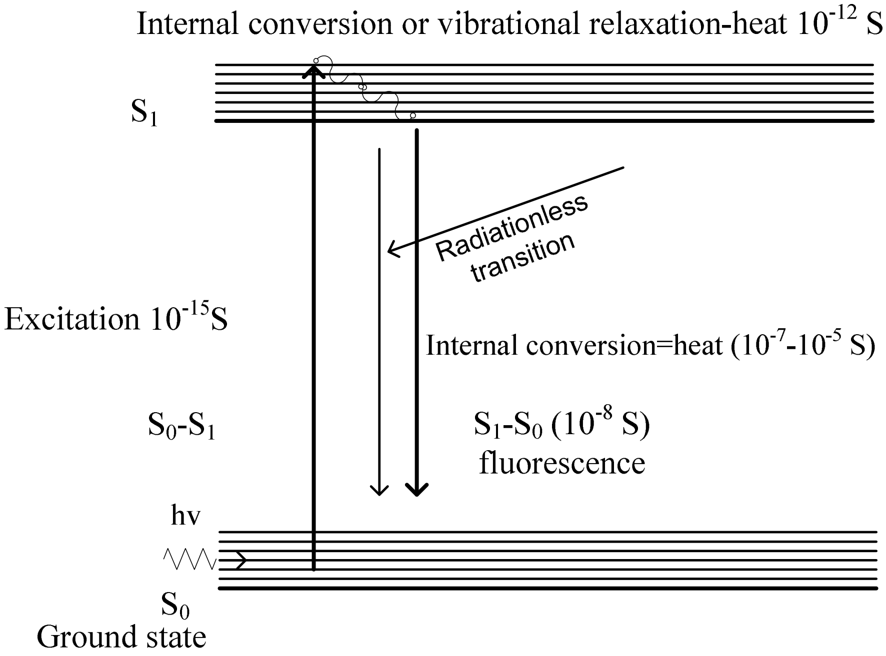


Fig6:Jablonski diagram for description of fluorescence

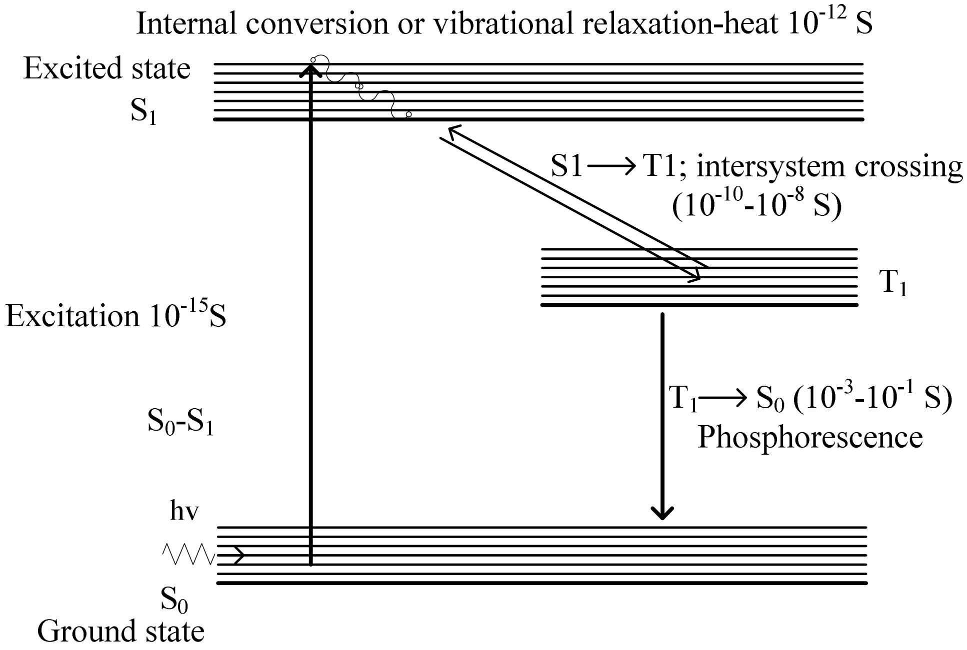


Fig7:Jablonski Diagram for phosphorescence

Luminescence

The glow produced in the body by methods other than action of heat i.e. the production of cold light is called Luminescence. It is of following types:

1. **Chemiluminescence:** The emission of light in chemical reaction at ordinary temperature is called Chemiluminescence e.g. the light emitted by glow-worms.
2. **Pyroluminescence:** The emission when a sample is heated e.g. NO_2.
3. **Electroluminescence:** The emission in the presence of an electric field e.g. solid ZnS
4. **Cathodoluminescence:** The emission by electron impact on solid phosphors e.g. in TV tubes
5. **Tirboluminescence:** The emission when crushing crystals e.g. ice and uranyl nitrate.
6. **Crystalloluminescence:** The emission on rapid crystallization from solution e.g. strontium bromine.

7.10 NON-RADIATIVE PROCESSES (INTERNAL CONVERSION, INTERSYSTEM CROSSING)

Internal conversion (IC): Where the electron relaxes to the ground state with no radiation termed as internal conversion. The molecule transfers to a high vibrational level of the ground state and then loses the vibrational energy through non-radiative decay via collisions with solvent. It can easily be understood with the help of fig.6.

Intersystem crossing (ISC): Where the molecules transfer to a triplet state by flipping an electron spin termed as intersystem crossing. The triplet state then undergoes non-radiative decay and ultimately phosphorescence. It can easily be understood with the help of fig.7.

7.11 QUANTUM EFFICIENCY

The efficiency of a reaction initiated by absorption of energy is expressed in terms of Quantum yield. It is a measure of efficiency of the photochemical process. This is expressed as:

$$\text{Quantum Efficiency } (\Phi) = \frac{\text{No. of molecules reacting in a given time}}{\text{No. of quantas of light absorbed in the same time}}$$

Experimentally,

$$\Phi = \frac{\text{Rate of chemical reaction}}{\text{Quanta absorbed per second}}$$

Quantum Yield

Suppose we have a reaction

$$\text{A} + \text{h}\nu \longrightarrow \text{products}$$

The overall rate of removal of A is,

$$-\frac{d[A]}{dt} = \frac{number\ of\ reacted\ molecules\ of\ A}{Time \times volume}$$

The intensity of light absorbed per unit volume to cause the above reaction is

$$I_{abs} = \frac{number\ of\ photons\ absorbed}{time \times volume}$$

Since one photon removes one molecule of A, I_{abs} is also equal to the rate of removal of A due to absorption in the primary step.
The overall quantum yield is

$$\Phi = \frac{\text{change in [A] per second}}{\text{I}_{\text{abs}}\alpha\text{A}} = -\frac{d[A]/dt}{I_{abs}\alpha[A]}$$

$$\therefore \quad -\frac{d[A]}{dt} = \Phi I_{abs}\alpha[A]$$

This is the photochemical rate law. This equation evidently indicates that the photochemical decomposition of A is first order in A. To measure quantum yields we need to measure both number of photon and number of product molecules. For transient species, steady state approximation (s. s. a.) is used to derive rate laws for a number of photochemical reactions.

Example: A sample of gaseous HI was irradiated by light of wavelength 253.7 nm when 307 J of energy was found to decompose 1.30x10^{-3} mole of HI. Calculate the quantum yield for the dissociation of HI.

Solution: the energy of quantum of radiation of wavelength 253.7 nm,

$$E = \frac{hc}{\lambda} = \frac{\left(6.626\times10^{-34}Js\right)\left(3\times10^{8}ms^{-1}\right)}{253.7\times10^{-9}m} = 7.835\times10^{-19}J$$

Number of quanta of radiation absorbed by $HI = \frac{307J}{7.835\times10^{-19}J} = 3.92\times10^{20}$

Number of molecules of HI decomposed $= 1.30\times10^{-3}mol\times6.022\times10^{23}mol^{-1} = 7.83\times10^{20}$

$$\Phi = \frac{\text{Number of molecules that react}}{\text{Number of quanta of radiation absorbed}} = \frac{7.83\times10^{20}}{3.92\times10^{20}}$$
$$= 1.997 = 2.00$$

Kinetics of photochemical reaction

Photochemical reaction involves two types of process: primary and secondary processes. In primary process the radiation is observed by the light absorbing substance, quantum efficiency of this process is always equal to one.

According to quantum efficiency, the number of molecules of light absorbing substances removed or reacted per unit time is equal to intensity of light, as in the case of following reaction.

$$Br_2 \xrightarrow{I_{abs}} 2Br \qquad I_{abs} = Intensity\ absorbed$$

$$\phi = \frac{Amount\ of\ Br_2\ reacted}{No.of\ \ photon\ absorbed} = 1$$

$$\Rightarrow -\frac{d[\mathrm{Br}_2]/dt}{I_{abs}} = 1 \Rightarrow \frac{d[Br_2]}{dt} = I_{abs}$$

Secondary process represents the subsequent reactions that are not photochemical reaction i.e. the reaction between the primary product and other substances. The only difference that appears in writing the difference rate law in photochemical reaction is that it depends on intensity of light.

Kinetics of Hydrogen-Bromide reaction:

$$H_2 + Br_2 \xrightarrow{h\nu} 2HBr$$

The following mechanism has been suggested for this reaction

Primary Process

$$Br_2 \xrightarrow{h\nu} 2Br$$

Secondary Process

$$Br + H_2 \xrightarrow{k_2} HBr + H$$

$$H + Br_2 \xrightarrow{k_3} HBr + Br$$

$$Br + Br \xrightarrow{k_4} Br_2$$

The rate of formation of HBr is given by

$$\frac{d[\mathrm{HBr}]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] \qquad ....1$$

$$\frac{d[Br]}{dt} = 2I_{abs} - k_2[Br][H_2] + k_3[H][Br_2] - 2\,\mathrm{k}_4[Br]^2 \qquad ....2$$

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k_3[H][Br_2] = 0 \qquad ....3$$

$$by\ adding\ eq.2\ and\ eq.3, we\ get$$

$$2I_{abs} - 2\,\mathrm{k}_4[Br]^2 = 0$$

$$[Br]^2 = \frac{I_{abs}}{\mathrm{k}_4}$$

$$[Br] = \frac{I_{abs}^{1/2}}{\mathrm{k}_4^{1/2}}$$

By putting the value of Br in eq.3

$$k_2 \frac{I_{abs}^{1/2}}{\mathrm{k}_4^{1/2}}[H_2] = k_3[H][Br_2]$$

$$[H] = \frac{k_2}{k_3}\frac{I_{abs}^{1/2}}{\mathrm{k}_4^{1/2}}\frac{[H_2]}{[Br_2]}$$

$$\therefore \frac{d[\mathrm{HBr}]}{dt} = k_2 \frac{I_{abs}^{1/2}}{\mathrm{k}_4^{1/2}}[H_2] + k_3 \frac{k_2}{k_3}\frac{I_{abs}^{1/2}}{\mathrm{k}_4^{1/2}}\frac{[H_2]}{[Br_2]}[Br_2]$$

$$= 2k_2 \frac{I_{abs}^{1/2}}{\mathrm{k}_4^{1/2}}[H_2]$$

The rate depends upon the square root of the intensity I_{abs} of the absorbed radiation. The quantum yield for this reaction is 0.01.

Kinetics of photolysis of acetaldehyde

The following mechanism has been suggested for the photochemical decomposition of acetaldehyde.

$$CH_3CHO \xrightarrow{I_{abs}} CH_3 + CHO$$
$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_2CHO$$
$$CH_2CHO \xrightarrow{k_3} CH_3 + CO$$
$$CH_3 + CH_3 \xrightarrow{k_4} C_2H_6$$

Rate law for the CO is

$$\frac{d[CO]}{dt} = k_3[CH_2CHO]$$

$$\frac{d[\mathrm{CH_2}\,CHO]}{dt} = -k_3[CH_2CHO] + \mathrm{k_2}[\mathrm{CH_3}][CH_2CHO] = 0\,(\text{using}\,ssa)$$

$$\Rightarrow k_3[CH_2CHO] = \mathrm{k_2}[\mathrm{CH_3}][CH_2CHO] \quad ....1$$

$$\therefore \frac{d[CO]}{dt} = \mathrm{k_2}[\mathrm{CH_3}][CH_3CHO] \qquad ....2$$

$$\frac{d[CH_3]}{dt} = I_{abs} - \mathrm{k_2}[\mathrm{CH_3}][CH_3CHO] - k_3[CH_2CHO] - 2k_4[CH_3]^2 = 0\,(\text{using}\,ssa)......3$$

by putting the value of $\mathrm{k_3[CH_2CHO]}$ in eq.3

$$\Rightarrow I_{abs} - \mathrm{k_2}[\mathrm{CH_3}][CH_3CHO] - \mathrm{k_2}[\mathrm{CH_3}][CH_2CHO] - 2k_4[CH_3]^2 = 0$$

$$\therefore [CH_3]^2 = \frac{I_{abs}}{2k_4} \Rightarrow [\mathrm{CH_3}] = \left(\frac{I_{abs}}{2k_4}\right)^{1/2}$$

Now eq.2 becomes

$$\frac{d[CO]}{dt} = \mathrm{k_2}\left(\frac{I_{abs}}{2k_4}\right)^{1/2}[CH_3CHO]$$

Kinetics of decomposition of HI

The following mechanism has been suggested for the photochemical decomposition of HI

$$HI + h\nu \xrightarrow{k_1} H + I$$
$$H + HI \xrightarrow{k_2} H_2 + I$$
$$I + I \xrightarrow{k_3} I_2$$

The rate law for the decomposition of HI is given by

$$-\frac{d[HI]}{dt} = k_1 I_a + k_2[H][\mathrm{HI}]$$

Applying ssa to [H], we have

$$\frac{d[H]}{dt} = k_1 I_a - k_2[H][\mathrm{HI}] = 0$$

$$\therefore \qquad k_2[H][\mathrm{HI}] = k_1 I_a$$

$$-\frac{d[H]}{dt} = 2k_1 I_a$$

The quantum yield of the reaction is given by

$$\phi = \frac{\text{Rate of disappearance of HI}}{\text{Rate of absorption of light}} = \frac{-d[HI]/dt}{k_1 I_a} = \frac{2k_1 I_a}{k_1 I_a} = 2$$

In this case, the value ofø decreases as the reaction proceeds. This is due to the accumulation of I_2, thermal reaction becomes significant.

$$H + I_2 \xrightarrow{k_4} HI + I$$

If this reaction is also included in the mechanism, then SSA for [H] gives

$$\frac{d[H]}{dt} = k_1 I_a - k_2[H][\mathrm{HI}] - k_4[H][\mathrm{I_2}] = 0$$

$$\therefore \quad [H] = \frac{k_1 I_a}{k_2[\mathrm{HI}] + k_4[\mathrm{I_2}]}$$

Substituting [H] value $\frac{d[H]}{dt}$ becomes

$$-\frac{d[H]}{dt} = k_1 I_a + k_2[\mathrm{HI}]\frac{k_1 I_a}{k_2[\mathrm{HI}] + k_4[\mathrm{I_2}]}$$

$$= k_1 I_a \left(1 + \frac{1}{1 + \{k_4[I_2]/k_2[HI]\}}\right)$$

$$\therefore -\frac{d[HI]/dt}{I_a} = k_1 + \frac{k_1}{1 + \{k_4[I_2]/k_2[HI]\}}$$

As the reaction proceeds, $[I_2]$ increases and hence the quantum yield decreases.

In the **photolysis of Cl_2 and H_2**, Φ_{HCl} can be as high as 1 million.

$$Cl_2 + h\nu \longrightarrow 2Cl$$
$$Cl + H_2 \longrightarrow HCl + H \ (exothermic)$$
$$H + Cl_2 \longrightarrow HCl + H$$

7.12 PHOTOSENSITIZED REACTIONS

Photosensitized phenomenon involves reactions of molecules with light that is mediated by a light-absorbing molecule, which is not the ultimate product. The reactions are significant in living cells and tissue (photobiology) and also provide valuable insights into photo-physical processes.

Photosensitization is the indirect method of excitation of the molecule using another molecule which absorbs energy. A suitable molecule is excited by exposing it to the radiation which can transfer its energy to the sample molecule by a number of energy transfer method. The molecule which is used for absorption of the radiation and transfer of energy to the sample molecule is called ‘sensitizer’ and the process is called ‘photosensitization’. The sensitizer molecule does not undergo chemical change itself but only transfer’s energy to the substrate molecule which undergoes photochemical reaction. The method allows photophysical and photochemical changes in the energy acceptor molecule by the electronically excited energy donor molecule. The photosensitized reaction by the electronic energy transfer mechanism has become one of the most useful processes in photochemistry. Photosensitized reaction is one of the important techniques for the decomposition of organic molecules. This type of reaction allows sample molecules to accept energy which is called the acceptor molecule by the electronically excited sensitizer molecule which donates energy to the receptor molecule and returns to the ground state.

$D + h\upsilon \rightarrow D^*$

$D^* + A \rightarrow D + A^*$

$A^* \rightarrow$ Products

The direct light absorption forms electronically excited donor (D^*) molecule. It can transfer the electronic energy to suitable acceptor molecule (A), present in the solution resulting in the de-excitation of D^* to D and electronic excitation of A to A^*. The energy transfer occurs before D^* loses energy by radiative process.

The acceptor molecule thus excited indirectly, can undergo various photophysical and photochemical processes. The characteristic feature of the photosensitized reaction is that light absorbing species remains unchanged while acceptor molecule undergoes chemical changes. Among the photosensitizers in common use are the atomic sensitizers such as mercury, cadmium and zinc and the molecular photosensitizers such as benzophenone and sulphur dioxide. Important photosensitized chemical reactions are the photosynthesis by plants, in which the green chlorophyll molecules of leaves are light absorbing molecules and $CO_2$and H_2O are acceptor molecules.

The important factors for photosensitization are:

(a) Absorption spectrum of the donor (sensitizer) and acceptor (substrate) molecules

(b) The singlet and the triplet energies of the donor (sensitizer) and acceptor (substrate) molecules

(c) The quantum yield of the triplet formation of the sensitizer

7.13 SUMMARY

A reaction in which chemical change is caused by the absorption of light radiations (photon) is termed as photochemical reaction and such study of chemical reaction is photochemistry. Energy of photons can be explained with the help of the following law of Albert Einstein.

$$E = h\nu = h\frac{c}{\lambda}$$

The principle of photochemical activation of chemical reaction was proposed by Grotthus-Draper. The absorption of light may cause photochemical change and cause decrease in intensity of incident radiation which is governed by Beers-Lambert law.

$$A = log\left(\frac{I_0}{I}\right) = \varepsilon bC$$

After absorption, emission and re-emission of radiation depending upon internal conversion (IC) and inter system crossing (ISC) occur simultaneously resulting in fluorescence and phosphorescence. The phenomenon is best explained with the help of the Jablonski diagram. Spin orientation on the absorption of light for transition governed by selection rule (spin multiplicity) for different photo-physical processes. The quantum efficiency of a photochemical process is used to find out the number of molecules that react with respect to number of quanta's of radiation absorbed.

$$\text{Quantum Efficiency } (\Phi) = \frac{\text{No. of molecules reacting in a given time}}{\text{No. of quantas of light absorbed in the same time}}$$

Experimentally,

$$\Phi = \frac{\text{Rate of chemical reaction}}{\text{Quanta absorbed per second}}$$

In order to find out quantum yield, the determinations of number of moles of light-absorbing substances and number of Einstein's of light of required wavelength are needed. This can be experimentally determined.

7.14 TERMINAL QUESTIONS

Q1. The molar extinction coefficient of phenanthroline complex of iron (II) is 12,00.0 $dm^3mol^{-1}cm^{-1}$ and the minimum detectable absorbance is 0.01. Calculate the minimum concentration of the complex that can be detected in a Lambert-Beer law cell of path length 1.00 cm.

Q2. A substance when dissolved in water at 10^{-3} M concentration it absorbs 10 percent of incident radiation in a path of 1 cm length. What should be the concentration of the solution in order to absorb 90 percent of the same radiation?

Q3. A system absorbs $2.0 x 10^{16}$ quanta of radiation per second. When it is irradiated for 15 minutes it is found that $3.0 x 10^{-4}$ mole of the reaction has reacted. What is the quantum yield of the reaction?

Q4. For the photochemical formation of ethylene from di-n-propylketone using a radiation of wavelength 313 nm, the quantum yield is 0.21. Calculate the number of moles of ethylene formed when the sample is irradiated with 50 watts of this radiation assuming that all the radiation is absorbed by the sample.

Q5. Calculate the number of moles of HCl(g) produced by the absorption of one joule of radiant energy of wavelength 480 nm in the reaction $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ if the quantum yield of the photochemical reaction is 1.0x10^6.

7.15 ANSWERS

Ans1. 8.33x10^{-6} M

Ans2. 0.0218 mol dm^{-3}

Ans3. 10.03

Ans4. 2.74x10^{-5} mol

Ans5. 4.0

UNIT- 8 DILUTE SOLUTION AND COLLIGATIVE PROPERTIES

CONTENTS:

8.1 OBJECTIVES

At the end of the chapter, we will be able to understand

1. The classification of solutions into ideal and non-ideal behavior
2. Expression of solution concentration like normality, molarity, molality etc
3. Activity and activity coefficient
4. Colligative properties of solution
5. Molecular weight determination by using colligative properties

8.2 INTRODUCTION

A homogenous mixture of two or more compounds (chemical species) is known as solution. Homogenous solution whose composition and properties are uniform throughout the mixture are furthersubdivided into real (non-ideal) solutions (particle size: < 1 nm) and colloids (particle size: 1-500 nm). The solutions are of different type but in this chapter, we will discuss only solutions in which solid getsdissolved in liquid. The solid is referred to as the soluteand the liquid as the solvent**.** Generally, the component that is present in the largest quantity is known as solvent. Solvent determines the physical state in which solution exists. One or more components present in the solution other than solvent are called solutes. Solutions form in part because of intermolecular forces. The particles of the solute interact with the particles of the solvent through intermolecular forces like London dispersion force, dipole-dipole interaction, H-bonding and ion-dipole interaction.

For the solvent and solute to mix, we must overcome all of the solute–solute attractive forces or some of the solvent–solvent attractive forces. These processes are endothermic, for example when some compounds, such as NaOH, dissolve in water, a lot of heat is released making container hot. In cases where some of the energy to do this comes from making new solute–solvent attractions, which is exothermic, for example when compounds, such as NH_4NO_3, dissolve in water, heat is absorbed from the surroundings resulting cold container. When the solute-to-solvent attractions are weaker than the sum of the solute-to-solute and solvent-to-solvent attractions, the solution will form whereas the energy difference seems small enough to be overcome by the increase in entropy from mixing.A solute will dissolve in a solvent if it has a similar structure to the solvent i.e. *like dissolve like*. Polar molecules and ionic compounds will be more soluble in polar solvents. Nonpolar molecules will be more soluble in nonpolar solvents.

8.3 IDEAL AND NON-IDEAL SOLUTION

An ideal solution is that which is formed by dissolving such a small amount of the non-volatile solute in the solvent that there is no absorption or evolution of heat. In ideal solutions, the solute–solvent interactions are equal to the sum of the broken solute–solute and solvent–solvent interactions. Any solvent that obeys Raoult’s law and solute that obeys Henry’s law is called an ideal solution (Fig 1).

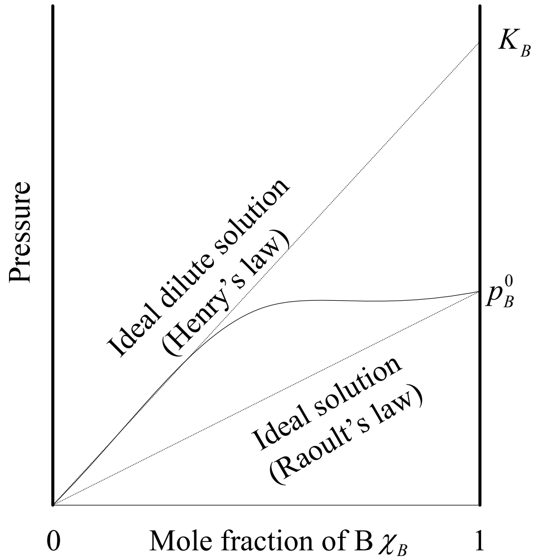


Fig 1: Behavior of an ideal solution.

Ideal solutions includespecies of the non-interacting components and very dilute solutions having no electrolyte/ions, e.g. mixtures of similar compounds (benzene + toluene). In other words, there are no energetic interactions between molecules of different species. At constant temperature and pressure, there is ideal entropy of mixingthat contributes to the total entropy, due to the presence of different components. Ideal solutions are valid in the very dilute limit, where there is one major component and the concentrations of all other species are very small. Ideal solution does not form azeotropic mixture (Azeotropes are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature, for example ethanol-water mixture). For ideal solutions, there is no change in volume on mixing and no change in enthalpy, resultingin no internal energy change.

$$\Delta_{mix}V = 0; \Delta_{mix}H = 0$$

$$\Delta_{mix}U = \Delta_{mix}H - P\Delta_{mix}V = 0$$

If the solute–solvent interactions are stronger or weaker than the broken interactions of solute-solute and solvent-solvent, such solution is said to benon-ideal. Any solvent that does not obeys Raoult's law and solute that does not obey Henry's law is called a non-ideal solution. For non-ideal solution, the volume of solution will change after mixing and there is enthalpy change, resulting in internal energy change.

$$\Delta_{mix}V \neq 0; \Delta_{mix}H \neq 0$$

$$\Delta_{mix}U \neq \Delta_{mix}H - P\Delta_{mix}V \neq 0$$

8.4 METHODS OF EXPRESSING CONCENTRATIONS OF SOLUTIONS

Composition of a solution can be described by expressing its concentration. The solution can be expressed either qualitatively or quantitatively. For example, qualitatively low amount of solute is dissolved in a solvent is known as dilute solution. Concentrated solutions are such solutions in which high amount of solute is dissolved in a solvent. These terms will not tell us whether a solution is saturated, unsaturated, or supersaturated. The concentration of solutions may be expressed in the following common sets of units.

1. **Molarity:**The molarity of a solution is the number of moles of solute present in one litre of the solution. It is expressed by 'M'.

$$\text{Molarity}=\frac{\text{Number of moles of solute}}{\text{Volume of solution in litre}}$$

2. **Molality:** The molality is defined as the number of moles of the solute present in one kg of solvent. It is denoted by 'm'. It does not depend on temperature.

$$\text{Molality}=\frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg}}$$

3. **Normality:** The normality is the number of equivalents of solute present in one litre of solution. It is expressed by 'N'.

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

4. **Mole fraction:** The ratio of the number of moles of the component (solute or solvent) to the total number of moles of the solution is known as mole fraction of the component. It is represented by 'x'. It is unit less quantity and does not depend on temperature.

$$\text{Mole fraction of component}\left(solute\ or\ solvent\right)=\frac{\text{Number of moles of component}}{\text{Total number of moles of component}}$$

If x_1 and x_2 represent the mole fraction of the solute and solvent respectively, we have,

$$x_1=\frac{n_1}{n_1+n_2}\ and\ x_2=\frac{n_2}{n_1+n_2}$$

It can be given that

$$x_1+x_2=1$$

Where, n_1 and n_2 are the number of moles of the solute and the solvent respectively.

5. **Mole percentage:** Itis the percentage of moles of one component in the total moles of all the components of the solution. It does not depend on temperature.

$$\text{Mole \%}=\text{mole fraction}\times 100\%$$

6. **Parts per million:** When solute is present in trace amount than concentration is expressed in parts per million (ppm).

$$\text{Parts per million}=\frac{\text{number of parts of the component}}{\text{Total number of parts of the all component of solution}}\times 10^6$$

8.5 ACTIVITY AND ACTIVITY COEFFICIENT

Strong interionic electrostatic attraction of ionic concentrations in solution is experimentally observed less than they actually are. The term 'activity' is the apparent value of concentration and effective concentration of ion in solution that can be written as follows,

$$a = \gamma c$$

Where"a" is the activity of the ion and γ is the activity coefficient.

Activities of pure solids/liquids can also be derived by chemical potential. Chemical potential, a partial molar quantity, diffuses from high to low potential.For any non-ideal solution, the chemical potential for the solute (or solvent) is given by

$$\text{Chemical Potential} \equiv \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j}$$

$$\mu_i = \mu^o + RT\ln a_i$$

For multi-components:

$$G = f(P,T,n_i)$$

n_i is sum of moles of components

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_j} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{P,S,n_j} = \left(\frac{\partial U}{\partial n_i}\right)_{V,S,n_j}$$

Chemical potential for pure solids and pure liquids

$$0 = RT\ln a_i$$

or $a_i = 1$

The chemical potential of a real gas is written in terms of its fugacity as follows,

$$\mu_J = \mu^o + RT\ln f_i$$

Activity Coefficient

The activity coefficient (γ) relates the activity to the concentration terms of interest. It can be defined as the ratio between effective and actual concentration of the ion in solution. Thus,

$$\gamma = \frac{\text{effective concentration}}{\text{actual concentration}} = \frac{a}{c}$$

The activity coefficient 'γ' is always less than one and it approaches one at infinite dilution.

8.7 COLLIGATIVE PROPERTIES

Colligative properties(Greek *colligatus* = Collected together) are properties whose value depends only on the number of solute particles (invariably taken as non-volatile) contained in a known volume of a given solvent, and do not depend on the identity or nature (i.e. chemical composition or constitution) of the solute. Value of these properties depends on the concentration of the solution. This means that when considering the impact of solute on a colligative property, 1 mole of sugar≡ 1 mole Na^+ ≡ 1 mole O_2^- ≡ 1 mole urea does exactly the same thing. The difference in the value of the property between the solution and the pure substance generally related to the different attractive forces and solute particles occupying solvent molecules positions. The various colligative properties are:

1. Lowering of Vapour Pressure
2. Osmotic Pressure
3. Elevation of Boiling Point
4. Depression of Freezing Point

They are properties of only dilute solutions which are supposed to behave ideal solutions.

8.8 RAOULT'S LAW

Henry's Law: At constant temperature, solubility of a gas in a liquid is directly proportional to the partial pressure of gas present above the solution, OR

At constant temperature, the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.

Mathematically,

$$p \propto x \; ; \; p = K_H x.$$

Where K_H is Henry's law constant and depends on the nature of the gas. This law is used when solution turns into vapour phase.

Raoult's Law: F. Raoult a French chemist proposed a study of vapour pressures of binary solutions of volatile liquids at a constant temperature and gave a law, which is known as Raoult's Law.

The partial vapour pressure of a volatile solvent above a solution at any temperature is equal to its normal vapour pressure, P°, multiplied by its mole fraction in the solution.

$$P_{\text{solvent in solution}} = \chi_{\text{solvent}} \cdot P^\circ$$

Because the mole fraction is always less than one, the vapour pressure of the solvent in solution will always be less than the vapour pressure of the pure solvent.

Suppose a binary solution contain n_A mole of volatile liquid A and n_B moles of a volatile liquid B, if p_A and p_B are partial pressure of two liquids, then, according to Raoult's law,

$$p_A = \chi_A p_A^0 \qquad and \qquad p_B = \chi_B p_B^0$$

In other terms Raoult's law can be expressed as*the vapour pressure of a liquid in a solution is directly proportional to the mole fraction of that liquid in the solution.*

$$P \propto \chi$$

The law is obeyed perfectly by an *ideal solution*. An ideal solution is a solution of A and B in which the intermolecular forces between A and A molecules, B and B molecules, and A and B molecules are all the same, then, according to Dalton's law of partial pressure, the total vapour pressure P is given by (Fig 2)

$$P_{total} = p_A + p_B = p^\circ_A \chi_A + p^\circ_B \chi_B$$

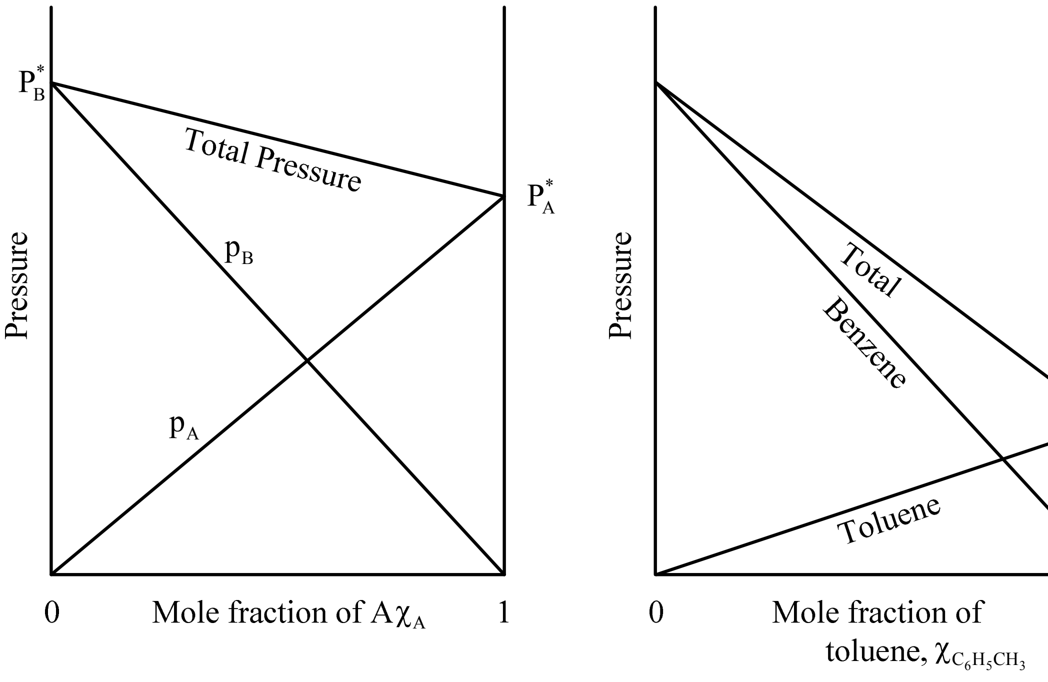


Fig2: Raoult's law interpretation

The total vapour pressure and partial vapour pressure of an ideal binary mixture depends on the vapour pressure on mole fractions of the components. For example, benzene and toluene behave almost ideally which follow Raoult's law over the entire composition range.

Systems that deviate from Raoult's law

(A) Positive deviation

A system in which mixing is energetically not favorable in liquid phase, so vapour pressure will be higher than expected by Raoult's Law. It can be shown by such system that forms a minimum boiling point azeotrope,i.e. the azeotropic mixture has a boiling point lower than either of the two pure components. Total vapour pressure is greater for an ideal solution. Change in enthalpy and volume of solution after mixing A and B will be higher than before i. e. ΔHmixing > 0 and ΔVmixing > 0. Solute-solvent (A-B) intermolecular forces are weaker than solute-solute (A-A) and solvent-solvent (A-B) interaction e.g. CS_2-acetone (Fig 3).

(B) Negative deviation

A system in which mixing is energetically favorable in liquid phase, so vapour pressure will be lower than expected by Raoults. It can be shown by such system that forms a maximum boiling point azeotropei.e. the azeotropic mixture has a boiling point higher than either of the two pure components. Total vapour pressure is smaller than for an ideal solution. Change in enthalpy and volume of solution after mixing A and B will be lower than before i. e. ΔHmixing < 0 and

ΔVmixing < 0. Solute-solvent (A-B) intermolecular forces are stronger than solute-solute (A-A) and solvent-solvent (A-B) interaction e.g. $CHCl_3$-acetone and ethanol-water (Fig 3).

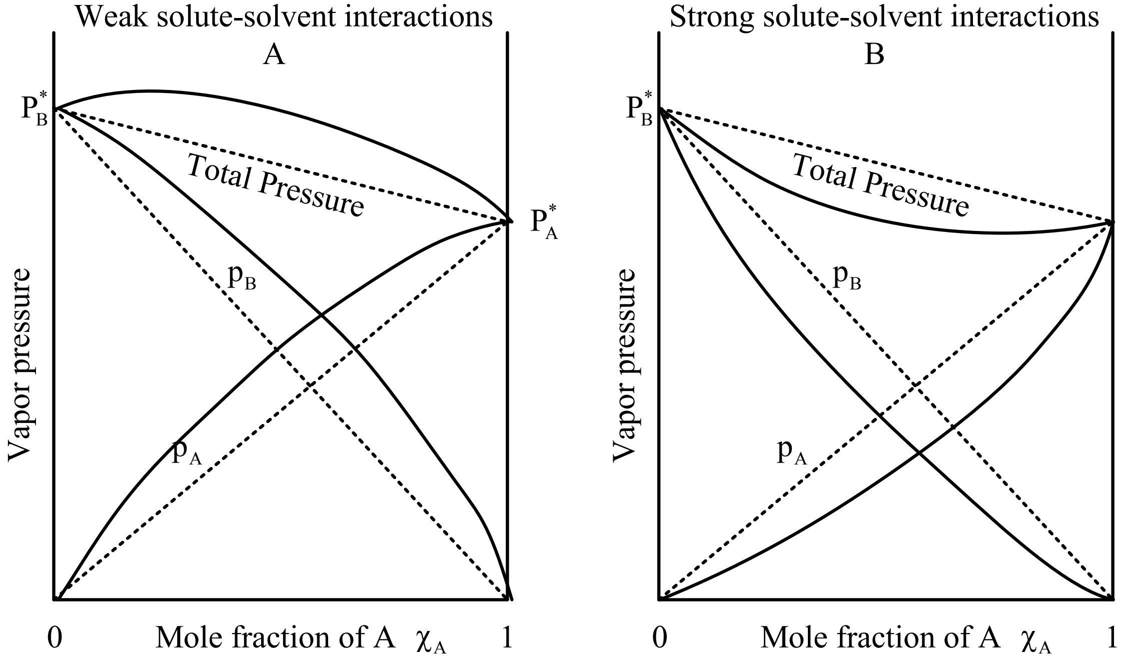


Fig3: Deviations from Raoult's Law (A) Positive deviation (B) Negative deviation

8.9 RELATIVE LOWERING OF VAPOUR PRESSURE MOLECULAR WEIGHT DETERMINATION

Vapour pressure is the pressure exerted by a vapour that is in dynamic equilibrium with solid or liquid at a given temperaturein a closed system. The vapour pressure of a solvent above a solution is lower than the vapour pressure of the pure solvent. In solution, the solute particles replace some of the solvent molecules at the surface and the pure solvent establishes liquid vapour equilibrium. Addition of a non-volatile solute into the solution reduces the rate of vapourization, decreasing the amount of vapour.Since a molecular non-volatile solute has zero vapour pressure than volatile solute. From Raoult's law, the total vapour pressure of the solution is,

$$P_{solution} = P^{\circ}_{solvent}\chi_{solvent} = \left(1 - \chi_{solute}\right)P^{\circ}_{solvent}$$

Since $\chi_{solvent} + \chi_{solute} = 1$

$$\Delta P = P^\circ_{solvent} - P_{solution} = \chi_{solute} P^\circ_{solvent} = \left(\frac{n_{solute}}{n_{solvent} + n_{solute}} \right) P^\circ_{solvent}$$

$$\frac{\Delta P}{P^\circ_{solvent}} = \frac{n_{solute}}{n_{solvent} + n_{solute}}$$

If we consider dilute solutions then $\frac{\Delta P}{P^\circ_{solvent}} \cong \frac{n_{solute}}{n_{solvent}}$

Therefore, the lowering of the vapour pressure in a *dilute solution of a non-volatile solute is directly proportional to the amount of the solute dissolved in a definite amount of solvent.*

The difference between the vapour pressure of the pure solvent and the vapour pressure of the solvent in solution is called the vapour pressure lowering.

$$\text{Lowering of vapor pressure } (\Delta P) = P^\circ_{solvent} - P_{solution} = \chi_{solute} . P^\circ_{solvent}$$

This lowering of vapour pressure relative to the vapour pressure of the pure solvent is termed as the **Relative lowering of Vapour pressure.** Thus,

$$\text{Lowering of vapor pressure} \left(\frac{\Delta P}{P^\circ_{solvent}} \right) = \frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = \chi_{solute} = \frac{n_{solute}}{n_{solute} + N_{solvent}}$$

Determination of Molecular Weight

The molecular mass of a non-volatile solute can be determined by measuring the lowering of vapour pressure $P^\circ_{solvent} - P_{solution}$ produced by dissolving a known weight of it in a known weight of the solvent.

If in a determination *w* grams of solute are dissolved in *W* grams of the solvent, *m* and *M* are molecular masses of the solute and solvent respectively, we have:

No. of Moles of solute (n) = $\frac{w}{m}$

No. of Moles of solvent (N) = $\frac{W}{M}$

Substituting these values in Raoult's law Equation,

$$\frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = \frac{n_{solute}}{n_{solute} + N_{solvent}} = \frac{w/m}{w/m + W/M}$$

For very dilute solution, the number of moles (molecules) of solute (w/m), is very small, it can be neglected in the denominator. The equation can now be written as,

$$\frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = \frac{n_{solute}}{n_{solute} + N_{solvent}} = \frac{wM}{mW}$$

Knowing the experimental value of $\frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}}$, and the molecular mass of the solvent (*M*), the molecular weight of solute (*m*) can be calculated.

Example: The vapour pressure of pure benzene at a certain temperature is 640 mmHg. A non-volatile non-electrolyte solid weighing 2.175 g is added to 39 g of benzene. The vapour pressure of the solution is 600 mmHg. What is the molecular weight of the solid substance?

Solution: As we know,

$$\frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = \frac{n_{solute}}{n_{solute} + N_{solvent}}$$

Given that: $P^O_{\text{solvent}} = 640$ mmHg, $P^O_{\text{solution}} = 600$ mmHg

$$n_{solute} = \frac{2.175}{M_{solute}}; N_{solvent} = \frac{39}{78} = 0.5 \left(\text{No. of moles} = \frac{\text{Wt. in gram}}{\text{Molecular weight}} \right)$$

$$\left(\text{M}_{\text{solute}} \text{ is the mol. wt. of the solute} \right)$$

$$\therefore \frac{640 - 600}{640} = \frac{2.175/M}{2.175/M + 0.5}; M = 65.25$$

Example: 1.20 g of a non-volatile organic substance was dissolved in 100 g of acetone at 20℃. The vapour pressure of the solution was found to be 182.5 torr. Calculate the molar mass of the substance (vapour pressure of acetone at 20℃ is 185.0 torr).

Solution: We know that

$$\frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = \frac{wM}{mW}$$

Substituting values, we have

$$\frac{(185.0\text{-}182.5)\,\text{torr}}{185.0\,\text{torr}} = \frac{(1.20\text{g})(58\,\text{g mol}^{-1})}{(\text{m})(100\text{g})}$$

$$\text{m} = 51.51\,\text{g mol}^{-1}$$

8.10 OSMOSIS, LAW OF OSMOTIC PRESSURE, AND ITS MEASUREMENT

The process of spontaneous movement of a solvent from low solute concentration to high solute concentration across a semipermeable membrane is called **osmosis**. The semipermeable membrane permits passage of some components of a solution. Because solvent can freely move from one side to another, the solvent chemical potential on the left must equal that on the right. There is movement in both directions across the membrane, the fluid levels in the arms becomes uneven. Eventually, the pressure difference between the arms stops osmosis.

Osmotic pressure is the pressure required to stop osmosis. Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity (Fig 4). For dilute solutions, it has been found experimentally that osmotic pressure is proportional to the molarity, C of the solution at a given temperature T, thus,

Osmotic Pressure $\propto$ molar concentration at a given temperature T

Or $\Pi = C\,R\,T$

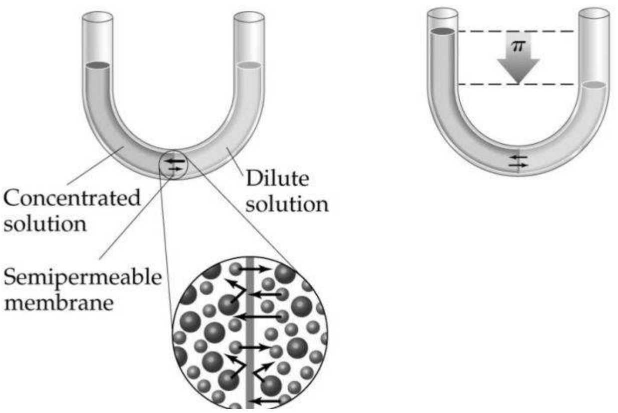


Fig 4: Osmosis and osmotic pressure

Here Π is osmotic pressure and R is gas constant.

Isotonic solutions: Two solutions, with the same osmotic pressure separated by a semipermeable membrane at a given temperature, are known to be **isotonic solutions**. Isotonic solutions have same molar concentrations.

Hypertonic and Hypotonic Solutions: When such solutions are separated by semipermeable membrane where no osmosis occurs between them. Solution of lower osmotic pressure is termed as a **hypotonic solution** and higher osmotic pressure is termed as **hypertonic solutions**.

8.11 DETERMINATION OF MOLECULAR WEIGHT FROM OSMOTIC PRESSUREAND ITS MEASUREMENT

The osmotic pressure of the solution can bewritten as follows,

$$\Pi = (n/V)\,R\,T$$

Here V is volume of a solution in litres containing n moles of solute. If w grams of solute, of molar mass M is present in the solution, then n=w / M and we can write,

$$\Pi V = \frac{wRT}{M}$$

$$or\, M = \frac{wRT}{\Pi V}$$

Thus, knowing the quantities w, T, Π and V we can calculate the molar mass of the solute.

Determination of Osmotic Pressure:

Following methods are used for the measurement of osmotic pressure,

1. Pfeffer's method: Pfeffer gave a direct method to measure osmotic pressure of solution. Here a porous pot (A) containing membrane of copper ferrocyanide in its wallis cemented to a glass tube (B) containing solution and attached to manometer (M). The

porous pot is kept in pure solvent. The osmotic pressure exerted by the solution is given by the manometer (Fig 5). The method is of historical interest only and has been given off.

There are few disadvantages of this method:

a. The osmotic pressure developed in dilute solution is very great and bursts the semipermeable membrane used.
b. It takes a long time to register the final osmotic pressure.

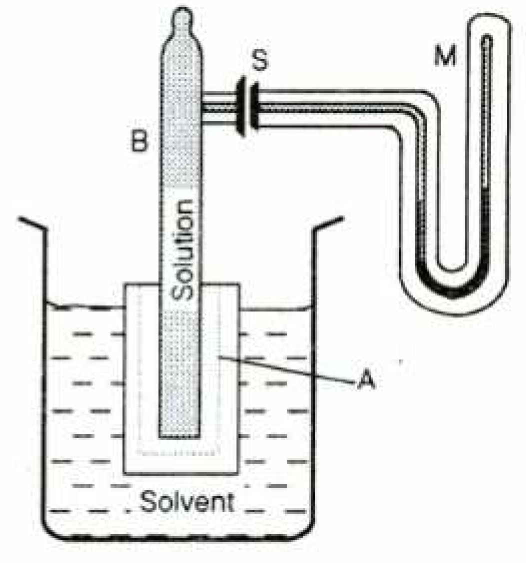


Fig 5: Pfeffer's method

2. Morse and Frazer's method: An improvement was made by H.N. Morse and J.C.W. frazer along with their collaborators. They prepared sophisticated semipermeable membranes of copper ferrocyanide by using an electric current. This made the membranes tougher and they were capable of withstanding high pressures without leakage. The apparatus as shown in Fig 6, has two chambers. Chamber 1 has semipermeable membrane deposited on its wall is filled with water. Tube 2 is also filled with water. Chamber 3 is filled with solution. When osmosis begins, solvent flows from 1 to 3 increasing the hydrostatic pressure in vessel 3. This hydrostatic pressure developed is equal to osmotic pressure, which is measured by a manometer attached to 4.

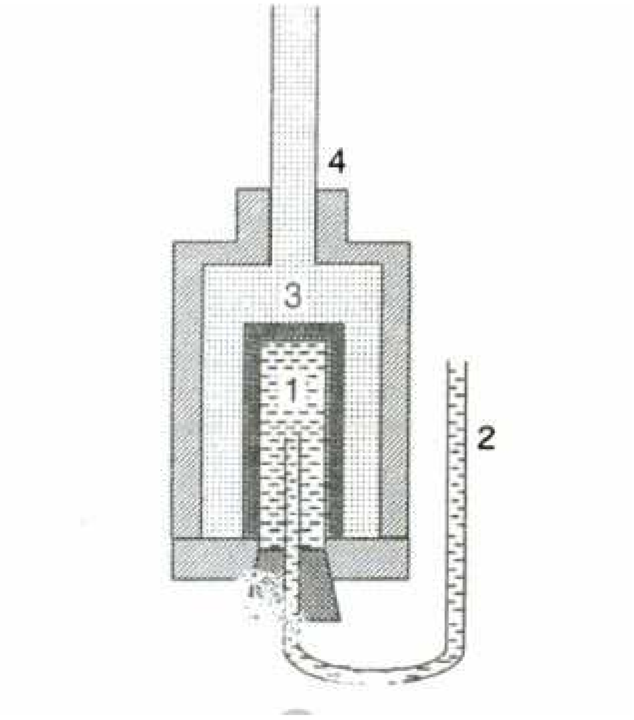


Fig 6: Frazer's Osmotic pressure apparatus.

3. Berkeley and Hartley's method: Berkeley and Hartley (1904-1909) employed the technique of applying external pressure on the solution just enough to prevent osmosis. The osmometer used by them is illustrated in Fig 7. A porcelain tube with copper ferrocyanide membrane deposited in its walls is enclosed in a metallic jacket. The tube is fitted with a reservoir of pure solvent (water) at one end and a capillary tube at the other. Mechanical pressure can be applied on the solution with a piston connected to a pressure gauge.

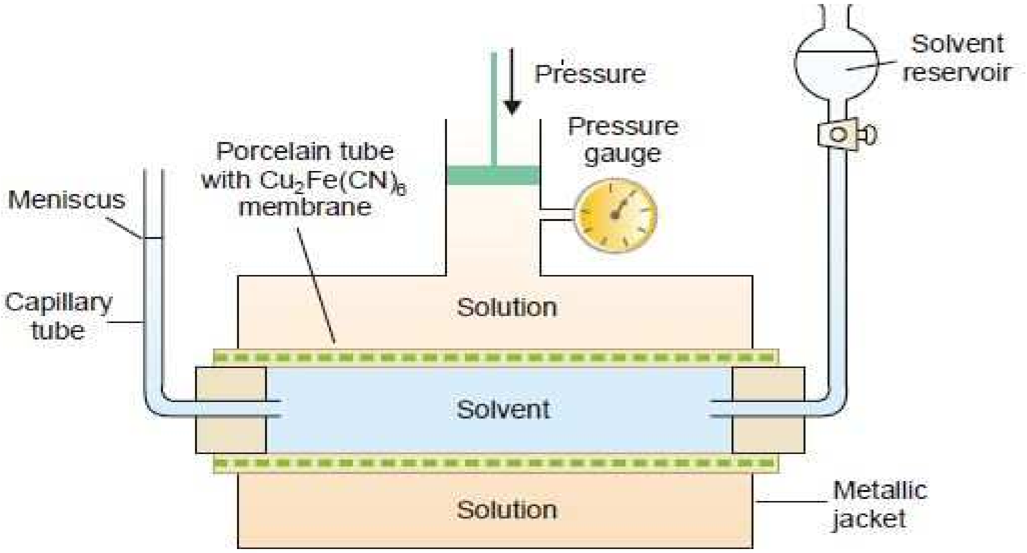


Fig 7: Berkeley's and Hartley's Osmometer

The inner porcelain tube is filled with pure solvent and the jacket with the solutionwhose osmotic pressure is to be determined. The level of the solvent meniscus in the capillary tubewill tend to move down as solvent flows into the solution across the membrane. Pressure is thenapplied through the piston so that the meniscus becomes stationary. It indicates that osmosis hasbeen stopped and now the pressure recorded by the pressure gauge gives the osmotic pressure ofthe solution.

Example: What is the molar mass of a protein if 5.87 mg per 10 mL gives an osmotic pressure of 2.45 torr at 25 °C?

Solution: Given that**:** 5.87 mg protein; 10.0 mL solution; $\Pi = 2.45$ torr; $T = 25$ °C
Need to find:molar mass of protein (g/mol) we know that,
$\Pi = CRT$, $T(\mathrm{K}) = T(°\mathrm{C}) + 273.15$, $R = 0.08206\,\mathrm{atm{\cdot}L/mol{\cdot}K}$
M = mol/L, 1 mL = 0.001 L, MM=g/mol, 1atm =760 torr
$T(\mathrm{K}) = 25 + 273.15 = 298$ K

$$C = \Pi / RT$$

$$C = \frac{2.45\,torr \Big/ 760\,torr/atom}{(0.08206\,\frac{atm\,L}{mol\,K})(298\,K)}$$

$$C = 1.318 \times 10^{-4} M$$

$$10mL \times \frac{1L}{0.001mL} \times \frac{1.318 \times 10^{-4} M\ protein}{1L} = 1.318 \times 10^{-6}\,mol\ protein$$

$$molar\ mass = \frac{5.87 \times 10^{-3} g}{1.318 \times 10^{-6} mol} = 4.45 \times 10^{3}\ g/mol$$

Example: Calculate the osmotic pressure of a decinormal solution of cane sugar at 0 ^{0}C.

Solution:

$$\frac{n}{V} = \text{molar concentration} = 0.1M$$

$$R = 0.082\,\text{lit.atom/K/mole}; T = 273K$$

$$\text{we have, } p = \frac{n}{V} RT$$

$$p = 0.1 \times 0.082 \times 273$$

$$= 2.24\,atm.$$

Example: A solution of 1.73 g of 'A' in 100 cc of water is found to be isotonic with a 3.42 % (wt./vol.) solution of sucrose ($C_{12}H_{22}O_{11}$). Calculate the molecular weight of A. ($C_{12}H_{22}O_{11}$=342)

Solution: We have known that the isotonic solutions have the same molar concentration (i.e. moles/lit.)

Let the molecular weight of A be M.

$$\text{Moles of A} = \frac{1.73}{M}$$

$$\therefore \text{molar conc. of A (moles/litre)} = \frac{1.73}{M} \times \frac{1000}{100} = \frac{17.3}{M}$$

$$\text{Molar conc. of sucrose} = \frac{3.42}{342} \times \frac{1000}{100} = 0.1$$

$$\therefore \qquad \frac{17.3}{M} = 0.1; M = 173$$

Example: Calculate the molecular weight of cellulose acetate if its 0.2 (wt./vol.) solution in acetone (sp. Gr. 0.8) shows an osmotic rise of 23.1 mm against pure acetone at 27 ^{0}C.

Solution: 0.2 % solution means 0.2 g of cellulose acetate dissolved in 100 ml of solution.
Osmotic pressure=2.31 cm acetone

$$\text{p} = 2.31 \times \frac{0.80}{13.6} \text{cm of Hg} = 0.136 \text{ cm of Hg}$$

$$\text{p} = \frac{0.136}{76} atom \,(1 \text{atom} = 76 \text{cm of } Hg)$$

Suppose M is the molecular weight of cellulose acetate.

$$n = \frac{0.2}{M}, V = 100\,mL = 0.1\,lit.atom / K / mole \; and \; T = 273 + 27 = 300\,K$$

$$Now, \qquad p = \frac{n}{V} RT$$

$$\therefore \qquad \frac{0.136}{76} = \frac{0.2/M}{0.1} \times 0.082 \times 300$$

$$\text{M} = 27{,}500$$

8.12 ELEVATION OF BOILING POINT AND DEPRESSION OF FREEZING POINT

Freezing-Point Depression

When a substance freezes, the particles of the solid take on an orderly pattern. The presence of a solute in water disrupts the formation of this pattern. As a result, more kinetic energy must be withdrawn from a solution than from the pure solvent to cause the solution to solidify. The freezing point of a solution is lower than the freezing point of the pure solvent. Therefore, the melting point of the solid solution is lower.The difference in temperature between the freezing point of a solution and the freezing point of the pure solvent is called the **freezing-point depression**(Fig 8).The magnitude of the freezing-point depression is proportional to the number of solute particles dissolved in the solvent and does not depend upon their identity.

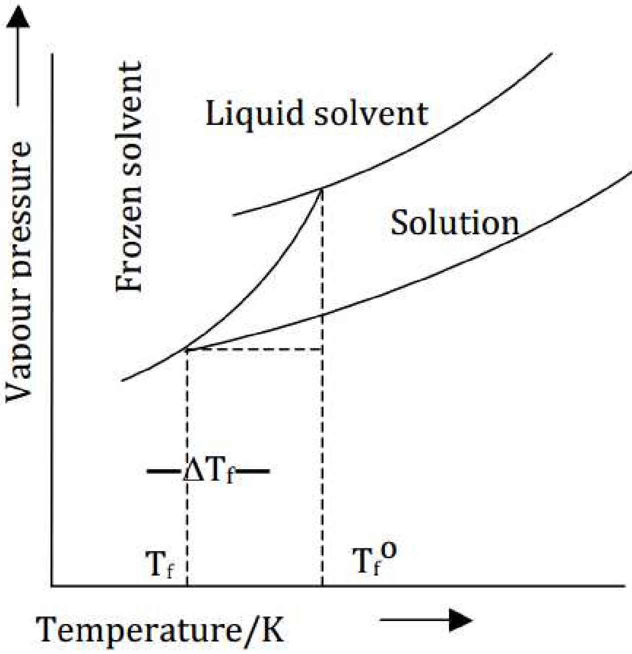


Fig8:Relation between temperature and vapour pressure

Freezing-Point Depression (ΔT_f):

It is directly proportional to the molal concentration of solute particles.

Depression in freezing point $\propto$ molal concentration (m)

$T^\circ_f - T_f = \Delta T_f \propto$ m or $\Delta T_f = K_f .m$

Where T°_f is the freezing point of the pure solvent and T_f is the freezing point of the solution. The proportionality constant, K_f is called the freezing point depression constant. The value of K_f (unit = °C/m) depends on the solvent. K_f is the molal freezing-point depression constant or cryoscopic constant of the solvent, which is defined as the depression in freezing point produced when 1 mol of the solute is dissolved in 1000 g of the solvent.

K_f may also be calculated from the following equation

$$K_f = \frac{RT^2}{1000 l_f}$$

Where T is the freezing point of the solvent and l_f is the latent heat of fusion per gram of solvent. The value of $K_f$for some substances can be seen from table 1.

Boiling-Point Elevation

The boiling point of a substance is the temperature at which the vapour pressure of the liquid phase equals the atmospheric pressure. After adding a non-volatile solute, to a liquid solvent decreases the vapour pressure of the solvent. Because of the decrease in vapour pressure, additional kinetic energy must be added to raise the vapour pressure of the liquid phase of the solution to atmospheric pressure and initiate boiling. The boiling of water increase by 0.512 ^{0}C for every mole of particles that the solute forms when dissolved in 1000 g of water.The boiling point of a solution is higher than the boiling point of the pure solvent for a non-volatile solute.The difference in temperature between the boiling point of a solution and the boiling point of the pure solvent is the **boiling-point elevation**(Fig 9).

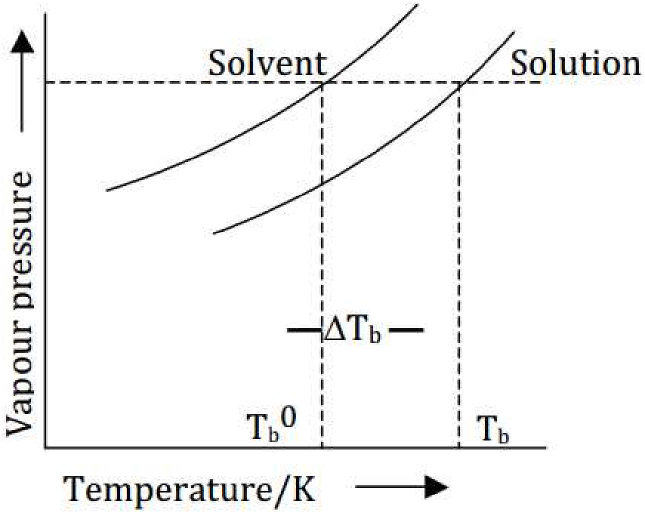


Fig9:Relation between temperature and vapour pressure

Boiling-Point Elevation (ΔT_b):

The difference between the boiling point of the solution and boiling point of the pure solvent is directly proportional to the molal concentration of solute particles.

Elevation in b.p $\propto$ molal concentration (m)

$$\Delta T_b \propto m$$

Or $$T_b - T^\circ_b = \Delta T_b = K_b .m$$

Where T_b is the boiling point of the solution and T°_b is the boiling point of the pure solvent. The proportionality constant, K_b is called the molal boiling point elevation constant or ebullioscopic constant of the solvent. The value of K_b (unit= °C/m) depends on the solvent. K_b may be calculated from the equation,

$$K_b = \frac{RT^2}{1000 l_v}$$

Where T is boiling point of the solvent and l_v is the latent heat of vapourization per gram of the solvent. The value of $K_b$for some substances can be seen from table 1.

Example: How many grams of ethylene glycol, $C_2H_6O_2$, must be added to 1.0 kg H_2O to give a solution that boils at 105 °C?

Solution:

Given that: 1.0 kg H_2O, T_b = 105 °C

We need to find out mass $C_2H_6O_2$ in g

$\Delta T_b = m \bullet K_b$, K_b H_2O = 0.512 °C/m, BP_{H2O} = 100.0 °C

Molar mass, $C_2H_6O_2$ = 62.07 g/mol, 1 kg = 1000 g

$$(105.0 - 100.0\,^oC) = (m)(0.512\,{}^oC/_m)$$

$$m = 9.77\,m$$

$$1.0\,kg\,H_2O \times \frac{9.77\,mol\,C_2H_6O_2}{1.0\,kg\,H_2O} \times \frac{62.07\,g\,C_2H_6O_2}{1\,mol\,C_2H_6O_2} = 6.1 \times 10^2\,g\,C_2H_6O_2$$

Example: Benzyl acetate is one of the active components of oil of jasmine. If 0.125 g of the compound is added to 25.0 g of chloroform ($CHCl_3$), the boiling point of the solution is 61.82 °C. What is the molar mass of benzyl acetate?

Solution:

$$\Delta T_f = K_f \times m_{solute}$$

$$m_{solute} = \frac{\Delta T_f}{K_f}$$

$$\Delta T_{bp} = 61.82\ °C - 61.70\ °C = 0.12\ °C$$

$$m_{\text{benzyl acetate}} = \frac{\Delta T_{bp}}{K_{bp}} = \frac{0.12\ °C}{\frac{3.63\ °C}{m}} = 0.033\ m$$

$$\frac{0.033\ \text{mol benzyl acetate}}{1\ \text{kg}\ CHCl_3} \times 25.0\ \text{g}\ CHCl_3 \times \frac{1\ \text{kg}}{10^3\,\text{g}} = 8.3 \times 10^{-4}\ \text{mol}$$

$$\frac{0.125\ \text{g benzyl acetate}}{8.3 \times 10^{-4}\ \text{mol benzyl acetate}} = 150\ \text{g/mol}$$

Table 1: Molal Boiling-Point-Elevation constants (K_b) and Molal Freezing-point-Depression Constants (K_f) for some common substances

Substance	**K_b [(^{o}C.kg)/mol]**	**K_f [(^{o}C.kg)/mol]**
Benzene (C_6H_6)	2.53	5.12
Camphor ($C_{10}H_{16}O$)	5.95	37.7
Chloroform ($CHCl_3$)	3.63	4.70
Diethyl ether ($C_4H_{10}O$)	2.02	1.79
Ethyl alcohol (C_2H_5OH)	1.22	1.99
Water (H_2O)	0.51	1.86

8.13 ABNORMAL MOLAR MASS

We have already discussed solute of ideal solution which neither undergoes association and dissociation during formation of solutions. Ionic compounds produce multiple (dissociation) solute particles like cation and anion for each formula unit, the experimentally determined molar mass is always lower than the true value. However, in low dielectric constant solvents, molecules of acetic acid dimerize in benzene due to hydrogen bonding. In this case, the number of particles is reduced due to dimerization (association). The molar mass calculated, on the basis of this behavior abnormal results are obtained. Such a molar mass that is either lower or higher than the expected or normal value is called as abnormal molar mass.

In order to account for such abnormal results, in 1880 van't Hoff introduced the theoretical van't Hoff factor, i is the ratio of moles of solute particles to moles of formula units dissolved. This factor 'i' is defined as;

$$\text{i} = \frac{\text{observed magnitude of any colligative property}}{\text{noraml magnitude of the same colligative property}}$$

$$= \frac{\text{normal molecular weight}}{\text{observed mol. weight}} \quad \begin{Bmatrix} \text{as colligative properties and mol.wt.} \\ \text{are inversely related} \end{Bmatrix}$$

'i' can also be calculated as

$$\text{i} = \frac{\text{moles of solute particles after dissociation/association}}{\text{moles of solute particle originally taken}}$$

$$= \frac{\text{observed molality}}{\text{calculated molality}}$$

The measured van't Hoff factors are generally less than the theoretical due to abnormal behavior of ion in solution. Therefore, the measured van't Hoff factors often cause colligative properties to be lower than we expect.

The equation of colligative properties of electrolyte solutions modifies after inclusion of van't Hoff factors.

$$\text{Lowering of vapor pressure} = \frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = i.\frac{n_{solute}}{n_{solute} + N_{solvent}}$$

Osmotic pressure: $\Pi = i\,C\,R\,T$

Boiling-Point Elevation (ΔT_b): $\Delta T_b = \text{i}.\ K_b\ .m$

Freezing-Point Depression (ΔT_f): $\Delta T_f = \text{i}.\ K_f\ .m$

8.14 DEGREE OF DISSOCIATION AND ASSOCIATION OF SOLUTE

The value of van't Hoff factor 'i' depends upon degree of dissociation. For non-electrolytes the value of i is one, for weak electrolytes, it ranges as n >*i* > 1 and *i* = n for strong electrolytes. As a solution is made more dilute, the value of "*i*" for strong electrolytes approaches "n" (the whole number expected on the basis of complete dissociation).

The **degree of dissociation** is the fraction of an electrolyte which is dissociated into ions in aqueous solution. The degree of dissociation is represented by α. Suppose 1 mole of an electrolyte is capable of forming "n" ions on complete dissociation. If the degree of dissociation be α, the total number of particles in solution is:

$$\begin{array}{ll} A_n \longrightarrow & nA \\ 1\,mole & 0 \\ 1-\alpha & \alpha n \end{array}$$

Number of un-dissociated molecule: $=1-\alpha$

Number of ion produces $=\alpha$ n

$\therefore$ Total number of particle $= 1-\alpha+\alpha$ n

Hence, weak electrolytes do not dissociate completely and therefore their degree of dissociation can be expressed according to the following equation:

$$i = \frac{\text{Actual number of particles}}{\text{Number of particle for undissociation}}$$

$$i = \frac{1-\alpha+\alpha n}{1}$$

$$i-1 = \alpha(\text{n}-1)$$

$$\alpha = \frac{i-1}{n-1}$$

$$\%\,\text{dissociation} = \frac{i-1}{n-1}\times 100$$

Where "i" is the van't Hoff factor and "n" is the number of ions per formula unit of the electrolyte.

The **degree of association** is the fraction of an electrolyte, which is associated in aqueous solution. Suppose one mole of an electrolyte is capable of associating "n" ions on complete association. If the degree of association be α, the total number of particles in solution are:

$$\begin{array}{ll} nA \longrightarrow & A_n \\ 1\,mole & 0 \\ 1-\alpha & \alpha/n \end{array}$$

Number of un-associated molecule = $1-\alpha$

Number of ion produces = α/n

$\therefore$ Total number of particle = $1-\alpha+\alpha$/n

The degree of association can be expressed according to the following equation:

$$i = \frac{\text{Actual number of particles}}{\text{Number of particle for unassociation}}$$

$$i = \frac{1-\alpha+\alpha/n}{1}$$

$$i-1 = \alpha(1/n - 1)$$

$$\alpha = n\left(\frac{i-1}{1-n}\right)$$

$$\%\,\text{association} = n\left(\frac{i-1}{1-n}\right)\times 100$$

Example: 20.27 g of benzene containing 0.2965 g of benzoic acid (mol. wt. = 122) freezes at 0.317^0 below the freezing point of pure benzene. If benzoic acid exists as dimer in benzene, find its degree of association. K_f for benzene is 5.12^0C m^{-1}.

Solution:

$$\mathit{Molality}\,(\text{calculated}) = \frac{0.2965/122}{20.27}\times 1000$$

$$= 0.12\,mole/1000g.$$

$$\mathit{Molality}\,(\mathit{obseved})\,\frac{\Delta \mathrm{T}_f}{K_f} = \frac{0.317}{5.12} = 0.0619\,mole/1000g$$

$$\therefore \qquad i = \frac{\mathit{Molality}\,(\mathit{obseved})}{\mathit{Molality}\,(\text{calculated})} = \frac{0.0691}{5.12} = 0.5158$$

Since benzoic acid exists as dimer in benzene, we have

$$\begin{array}{lcc} \text{moles before association} & 1\,mole & 0 \\ & 2C_6H_5COOH \longrightarrow & (C_6H_5COOH)_2 \\ \text{moles after association} & 1-\alpha & \frac{\alpha}{2}\,(\alpha = \text{degree of association}) \end{array}$$

$$\therefore \qquad i = \frac{1-\alpha+\frac{\alpha}{2}}{1} = 0.5158$$

$$\alpha = 0.9684\,or\,96.84\%$$

Example: A 0.01 m aqueous solution of $K_3[Fe(CN)_6]$ freezes at -0.062 ^{0}C. What is the apparent percentage of dissociation? (K_f for water = 1.86)

Solution: we have,

$$\Delta T_f = m \times K_f$$
$$= 0.01 \times 1.86$$

$$i.e.\ (\Delta T_f)_{\text{normal}} = 0.0186^0$$
$$and\ (\Delta T_f)_{\text{observed}} = 0.062^0 \text{(given)}$$

$$\therefore \qquad i = \frac{\text{observed colligative property}}{\text{normal colligative property}}$$
$$= \frac{0.062}{0.0186}$$

Now suppose α is the degree of dissociation of $K_3[Fe(CN)_6]$

Thus,

$$\begin{array}{lcccc} \text{moles before dissociation} & 1\,mole & 0 & 0 & \\ & K_3[Fe(\text{CN})_6] \longrightarrow & 3K^+ & +[Fe(\text{CN})_6]^{3-} & \\ \text{moles after dissociation} & 1-\alpha & 3\alpha & \alpha & (\alpha = \text{degree of dissociation})\,\mathbf{E} \end{array}$$

$$\therefore \qquad i = \frac{1-\alpha+3\alpha+\alpha}{1} = \frac{0.062}{0.0186}$$
$$\alpha = 0.78\ or\ 78\%$$

xample: A decimolar solution of potassium ferrocyanide is 50% dissociated at 300 K. Calculate the osmotic pressure of the solution. (R=8.314 $JK^{-1}mol^{-1}$)

Solution:

$$\begin{array}{lcccc} \text{moles before dissociation} & 1\,mole & 0 & 0 & \\ & K_4[Fe(\text{CN})_6] \longrightarrow & 4K^+ & +[Fe(\text{CN})_6]^{4-} & \\ \text{moles after dissociation} & 1-\alpha & 4\alpha & \alpha & (\alpha = \text{degree of dissociation}) \end{array}$$

$$\therefore \qquad i = \frac{1-\alpha+4\alpha+\alpha}{1} = 1+4\alpha = 1+4\times 0.5 = 3$$

$$\text{Observed osmotic pressure} = icRT$$
$$= 3 \times (0.1 \times 10^3) \times 8.314 \times 300$$
$$= 7.4826 \times 10^5\ pascal\,(\text{N/m}^2)$$

8.15 SUMMARY

Formation of solution takes place when some interactive forces like all of the solute–solute attractive forces or some of the solvent–solvent attractive forces overcome. Based on interactions, solutions are categorized into two ways ideal and non-ideal (real) solutions. An ideal solution is that mixture of solute and solvent where there is no absorption or evolution of heat.For non-ideal solution, there is change in volume on mixing and there is enthalpy change, resulting in internal energy change. These solutions obey and disobey Raoult's and Henry law respectively.

Raoult's law: $P_{solvent\ in\ solution} = \chi_{solvent} \cdot P^\circ$

The colligative properties of solution whose value depends only on the number of non-volatile solute particles contained in a known volume of a given solvent. They do not depend on the chemical composition or constitution of the solute. They are Lowering of Vapour Pressure, Osmotic Pressure, Elevation of Boiling Point and depression of Freezing Point.

$$\text{Lowering of vapor pressure} = \frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = \frac{n_{solute}}{n_{solute} + N_{solvent}}$$

Osmotic pressure: $\Pi = C\,R\,T$

Boiling-Point Elevation (ΔT_b): $\Delta T_b = K_b\,.m$

Freezing-Point Depression (ΔT_f): $\Delta T_f = K_f\,.m$

Molecular weight of solute, non-electrolyte can easily be calculated with the help of mathematical formulas of these properties. Dissociation/association constant plays a very important role for association and dissociation of molecules in solution, which show abnormal molar mass. The measured van't Hoff factors often cause colligative properties to be lower than we expect.

The equation of colligative properties of electrolyte solutions modifies after inclusion of van't Hoff factors.

$$\text{Lowering of vapor pressure} = \frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = i.\frac{n_{solute}}{n_{solute} + N_{solvent}}$$

Osmotic pressure: $\Pi = i\,C\,R\,T$

Boiling-Point Elevation (ΔT_b): $\Delta T_b = \text{i}.\ K_b\,.m$

Freezing-Point Depression (ΔT_f): $\Delta T_f = \text{i}.\ K_f\,.m$

8.16 TERMINAL QUESTIONS

Q1. Calculate the molarity of water.

Q2. An aqueous solution of urea has freezing point of -0.52℃. Predict the osmotic pressure of the same solution at 37℃. Assume that the molar concentration and the molality are numerically equal. (K_f=1.86)

Q3. A solution of urea has a boiling point of 100.18℃. Calculate the freezing point of the same solution. Molal constants for water K_f and K_b are 1.86 and 0.512 respectively.

Q4. Calculate the molecular weight of a substance. 10 g of which in 1 litre of solution exerts an osmotic pressure of 81 mmHg at 27 K.

Q5. A solution containing 2.56 g sulphur in 100 g CS_2 gave a freezing point lowering of 0.383 K. Calculate the molar mass of sulphur molecules. Given K_f of CS_2 = 3.83 K Kg mol^{-1}.

Q6.100 g of water has 3g of urea dissolved in it. Calculate the freezing point of the solution. K_f for water = 1.86 K kg mol^{-1}, molar mass of urea = 60 g mol^{-1}, freezing point of water = 273.15 K (0°C).

Q7. Human blood has osmotic pressure of 7.2 atm at body temperature of 37°C. Calculate the molar concentration of solute particles in blood.

Q8. Vapour pressure of benzene is 200 mm of Hg. 2g of a non-volatile solute in 78 g benzene has vapour pressure of 195 mm of Hg. Calculate the molar mass of the solute. Molar mass of benzene = 78 g mol^{-1}.

Q9. 500 g of water containing 27 g of a non-volatile solute will boil at 100.156°C. Calculate the molar mass of the solute. Given boiling point of water = 100°C, K_b = 0.52 K kg mol^{-1}.

Q10. The vapour pressure of ether (mol. mass = 74) is 442 mmHg at 293 K. If 3g of a compound A are dissolved in 50 g of ether at this temperature, the vapour pressure falls to 426mm Hg. Calculate the molecular mass of A. Assume that the solution of A in ether is very dilute.

Q11. 18.2 g of urea is dissolved in 100 g of water at 50°C. The lowering of vapour pressure produced is 5 mm Hg. Calculate the molecular mass of urea. The vapour pressure of water at 50°C is 92 mm Hg.

Q12. A current of dry air was passed through a solution of 2.64 g of benzoic acid in 30.0 g of ether ($C_2H_5OC_2H_5$) and then through pure ether. The loss in weight of the solution was 0.645 g and the ether 0.0345 g. What is the molecular mass of benzoic acid?

Q13. A stream of dry air was passed through a bulb containing a solution of 7.50 g of an aromatic compound in 75.0 g of water and through another globe containing pure water. The loss in mass in the first globe was 2.810 g and in the second globe, it was 0.054 g. calculate the molecular mass of the aromatic compound. (mol. mass of water = 18)

Q14. In an experiment, air was drawn successively through a solution of sugar (38.89 g per 100 g water) and distilled water, and then through anhydrous calcium chloride. It was found that the water lost was 0.0921 g and calcium chloride tubes gained 5.163 g. Find the molecular mass of the sugar. (Mol mass of H_2O = 18)

Q15. The boiling point of a solution containing 0.20 g of a substance X in 20.00 g of ether is 0.17 K higher than that of pure ether. Calculate the molecular mass of X. Boiling point constant of ether per 1 Kg is 2.16 K.

Q16. Acetone boils at 56.38°C and a solution of 1.41 grams of an organic solid in 20 grams of acetone boils at 56.88°C. If *K* for acetone per 100 g is 16.7, calculate the mass of one mole of the organic solid.

Q17. In a Cottrell determination, 22 g of benzene was used as solvent. The readings on the differential thermometer before and after adding 0.586 g of naphthalene (mol mass= 128), were 1.262 and 1.799 respectively. In a separate experiment, using the same amount of benzene but this time adding 0.627 g of an organic compound *X*, the temperature readings were 1.269 and 1.963. Calculate the molecular mass of *X*.

Q18. 0.440 g of a substance dissolved in 22.2 g of benzene lowered the freezing point of benzene by 0.567°C. Calculate the molecular mass of the substance. (K_f= 5.12°C mol^{-1})

Q19. 1.250 g of naphthalene was dissolved in 60 cm^3 of benzene and freezing point of the solution was found to be 277.515 K, while that of benzene 278.495 K. Density of benzene =0.880 g cm–3, K_f=5.1 K per 1000 g benzene. Calculate the molecular mass of naphthalene.

Q20. A solution of 0.124 g of a substance, *X*, in 25.0 *l* of ethanoic acid (acetic acid) has a freezing point 0.324°C below that of the pure acid 16.6°C. Calculate the molecular mass (relative molecular mass) of *X*, given that the specific latent heat of fusion of ethanoic acid is 180.75 J g^{-1}

Q21. A sample of camphor used in the Rast method of determining molecular masses had a melting point of 176.5°C. The melting point of a solution containing 0.522 g camphor and 0.0386 g of an unknown substance was 158.8°C. Find the molecular mass of the substance. $K_f$of camphor per kg is 37.7.

Q22. A solution containing 1.5 g of barium nitrate in 0.1 kg of water freezes at 272.720 K. Calculate the apparent degree of dissociation of the salt. *Kb*= 1.86 Molecular mass of $Ba(NO_3)_2$ = 261

Q23. Find the degree of ionization for HF (hydrofluoric acid) in 0.100 m aqueous solution, if the freezing point of the solution is – 0.197°C. ($K_f$for water = 1.86°C).

Q24. Phenol (C_6H_5OH) associates in water to double molecules. When 0.6677 g of phenol is dissolved in 35.5 g of water; it depresses the freezing point by 0.215°C. Calculate the van't Hoff factor and the degree of association of phenol. Molal depression constant of water =1.85°C $mole^{-1}$.

8.17 ANSWERS

Ans 1: 55.55 M

Ans 2: 7.1 atm

Ans 3: 0.654^0

Ans 4: 207.99

Ans 5: 256 g mol^{-1}

Ans 6: 272.22 or -0.93°C

Ans 7: 0.2828 M

Ans 8: 80 g mol^{-1}

Ans 9: 180 g mol^{-1}

Ans 10: 123

Ans 11: 57.05

Ans 12: 122

Ans 13: 93.6

Ans 14: 385

Ans 15: 127.81

Ans16: 235 *g*

Ans 17: 106

Ans 18: 178.9

Ans 19: 123

Ans 20: 59.09

Ans 21: 157

Ans 22: 81 or 81%

Ans 23: 0.06 or 6%

Ans 24: 0.838 or 83.8%

UNIT- 9 THERMODYNAMICS III

CONTENTS

9.1 OBJECTIVES

At the end of the chapter, we will be able to understand basic concept of evolution of third law of thermodynamics, Planck, Einstein and Nernst formulation to understand entropy behavior when temperature approaches to absolute zero. Nernst heat theorem and residual entropy are also covered in this section. Calculation of absolute entropy with the help of third law of thermodynamics is also a part of this chapter.

9.2 INTRODUCTION

Thermodynamics introduces new concepts of energy of content and entropy. The second law, the third law and the rest of thermodynamics can also be introduced on the basis of the adiabatic accessibility principle. The third law represents a statement which physically is related to the second law but logically is independent of the second law. Though it does not contain new concept, but it is limited to certain extinct on the value of the entropy of crystalline solids.

The third law of thermodynamics has evolved from the Nernst theorem – the analysis of an entropy change in a reacting system at temperatures approaching absolute zero. The existing statements tend to be derived from the ideas expressed by Planck, Nernst or Einstein and can be classified accordingly.The most common formulation of the third law of thermodynamics belongs to Max Planck stated below;

Planck formulation: When temperature falls to absolute zero, the entropy of any pure crystalline substance tends to a universal constant (which can be taken to be zero).

$S \rightarrow 0$ as $T \rightarrow 0$

Entropy selected according to $S = 0$ at $T = 0$ is called absolute. This is not consistent with understanding the laws of thermodynamics as being the most fundamental and universally applicable principles of nature. This formulation does not comment on entropy of other substances at $T = 0$ and thus is not universally applicable.The Planck formulation necessitates validity of two statements of unequal universality: the Einstein statement and the Nernst theorem.

Einstein statement: As the temperature falls to absolute zero, the entropy of any substance remains finite.

$S(T) \to S(0)$, as $T \to 0$

The limiting value S may depend on parameter, which is presumed to remain finite at $T \to 0$. Considering expression for the entropy change in a constant volume heating process

$$S = \int_0^T \frac{C_V}{T} dT$$

Vanishing heat capacity

$C_V \to 0$ at $T \to 0$

The statement is attributed to Einstein, who was first to investigate entropy of quantum systems at low temperatures and to find that the heat capacities should vanish at absolute zero; this implies that S is finite at $T \to 0$.

Nernst-heat theorem: The entropy change of a system in any reversible isothermal process tends to zero as the temperature of the process tends to absolute zero.

$\Delta S \to 0$ as $T \to 0$

The Nernst theorem implies that

$$\left(\frac{\partial S}{\partial x}\right)_T \to 0 \; as\, T \; \to 0$$

The x is presumed to remain finite at $T \to 0$. The significance of this equation is that the entropy change of a reaction tends to approach zero and that the difference between the heat capacities of products and reactants also tends to approach zero as the temperature is towards the absolute zero.

9.3 STATEMENT AND CONCEPT OF RESIDUAL ENTROPY

Ludwig Boltzmann in 1877, proposed a formula $S = k \ln W$ *(entropy is a logarithmic function of W).* Where S is entropy, $W$is the number of ways of arranging the components of a system having equivalent energy, and $k$is the Boltzmann constant = R/N_A (R = universal gas constant, N_A = Avogadro's number) = 1.38 x 10^{-23} J/K. According to the Boltzmann formula, the entropy is zero if there is only one accessible microstate (W= 1). In most cases, W= 1 at T= 0K because there is only one way of achieving the lowest total energy: put all the molecules into the same, lowest state. Therefore, S= 0 at T= 0K, in accord with the third law of thermodynamics. In certain cases, though, W may differ from 1 at T= 0K. A system with relatively few equivalent ways to arrange its components (smaller *W*) has relatively less disorder and low entropy. A system with many equivalent ways to arrange its components (larger *W*) has relatively more disorder and high entropy. This is the case if there is no energy advantage in adopting a particular orientation even at absolute zero. For instance, for a diatomic molecule AB there may be almost no energy difference between the arrangements...AB AB AB...and...BA AB BA..., so W> 1 even at T= 0K. If S> 0 at T= 0K we say that the substance has a **residual entropy**. Ice has residual entropy of 3.4 J K^{-1} mol^{-1}. It seems from the arrangement of the H bonds between neighboring water molecules: a given O atom has two short O—H bonds and two long O···H bonds to its neighbors, but there is a degree of randomness in which two bonds are short and which two are long. We, thus, conclude that entropies of substance like H_2, D_2, CO, NO, H_2O etc. are not zero at absolute temperature. These entropies are called residual entropies.

Example: In the solid state at 0 K, nitric oxide is capable of existing in two orientations, viz., NONO and NOON, which have practically equal probabilities. Calculate the molar entropy of NO at 0 K.

Solution: At 0 K, the probability of orientation of one molecule of NO is, 2. Thus, W=2. Hence, from the Boltzmann equation, for one mole, i.e., for Avogadro's number of molecules,

$$S = k \ln W, \text{with } W = 2^{N_A}, \text{We find that}$$

$$S = k \ln 2^{N_A} = N_A k \ln 2 = R \ln 2$$

$$= (8.314\, JK^{-1} mol^{-1})(2.303)(0.3010) \qquad (\because \log_{10} 2 = 0.3010)$$

$$= 5.74\, JK^{-1} mol^{-1}$$

9.4 THIRD LAW OF THERMODYNAMICS

It is interesting that the Nernst principle and the Einstein statement can be combined to produce the following formulation of the third law:

Nernst (Nernst-Einstein) formulation: A thermodynamic state with zero absolute temperature cannot be reached from any thermodynamic state with a positive absolute temperature through a finite isentropic process limited in time and space, although the entropy change between these states is finite.This statement implies that

$0 < \Delta S < \infty$ when $0 < T < \infty$

Or, possibly in some cases, $S(T) = S(0)$ but the isentropic process connecting these states need an infinite time for its completion.

For substances in internal equilibrium, undergoing an isothermal process, the entropy change goes to zero as T (in K) goes to zero. This is third law of thermodynamics. Mathematically,

$$\lim_{T \to 0} \Delta S = 0$$

The law is valid for pure substances and mixtures. This is the third law of thermodynamics. The entropy of any perfect crystal is 0 J/ (K mole) at 0 K (absolute zero). Due to the third law, we are able to calculate absolute entropy values. This value equals the entropy increase in a substance upon raising its temperature from 0 K to the specified temperature.

Standard Molar Entropies (S^o)

Standard states: 1 atm for gases; 1 *M* for solutions; pure substance in its most stable form for solids and liquids. **Units:** J/mol/K at 25 °C.

Predicting relative S^o values of a system

S^o increases with increase in temperature of the system and also increases as more ordered phase changes to a less ordered phase. S^o of a dissolved solid or liquid is usually greater than S^o of the pure solute. However, the extent depends on the nature of the solute and solvent. A gas becomes more ordered when it dissolves in a liquid or solid. In similar substances, increase in mass relate directly to entropy. In allotropic substances, increase in complexity (e.g., bond flexibility) relate directly to entropy.

9.5 UNATTAINABILITY OF ABSOLUTE ZERO

Nernst-unattainability principle:

According to Nernst unattainability principle, "any thermodynamic process cannot reach the temperature of absolute zero by a finite number of steps and within a finite time".

The Nernst principle implies that an isentropic process cannot start at any small positive *T* and finish at absolute zero when volume and other extensive parameters remain limited, i.e.

$\Delta S > 0$ when $T > 0$

Close to zero Kelvin, the molecular motions have to be treated using quantum mechanics still it is found that quantum ideal gases obey the third law.

A perfect crystal has zero entropy at a temperature of *absolute zero.* The third law leads to absolute values for the entropies of substances. Absolute zero is a temperature that an object can get arbitrarily close to, but never attain. Temperatures as low as 2.0×10^{-8} K have been achieved in the laboratory, but absolute zero will remain ever elusive.

9.6 NERNST HEAT THEOREM

Walther Nernst (Nobel Prize in Chemistry 1920) had investigated heat capacities and heats of reaction at progressively lower temperatures. Nernst theorem holds good only in the case of pure solids. Considering thermodynamic potential, from the Gibbs-Helmholtz relation we have

$$\Delta G = \Delta H - T\Delta S \text{ …………1}$$

According to reciprocal relations

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_P \left(\text{from second law of thermodynamics}\right)$$

Putting the value in eq. 1

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

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

Where ΔG and ΔH are the change in free energy and change in enthalpy for any chemical reaction.

Experimentally, it was found that the value of $\partial(\Delta G)/\partial T$ decreases with decreasing temperature (Fig 1). Nernst had noticed that, at progressively lower temperatures, the change in enthalpy and the change in the Gibbs function during a chemical reaction become more and more equal. And the rate of change of the Gibbs function with temperature becomes less and less as the temperature is lowered. He suggested that the value of $\partial(\Delta G)/\partial T$ become equal to zero when temperature reaches absolute zero. This implies that chemical reactions at a temperature of absolute zero take place with no change of entropy. This is known as **Nernst heat theorem**.

At the absolute temperature (T=0),

$$\lim_{T\to 0}\Delta G = \lim_{T\to 0}\Delta H$$

$$\lim_{T\to 0}\left(\frac{\partial \Delta G}{\partial T}\right)_P = \lim_{T\to 0}\left(\frac{\partial \Delta H}{\partial T}\right)_P = 0$$

Where $\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$ (from second law of thermodynamics) and $\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P$ (Kirchhoff's law)

ΔS and ΔC_P are the entropy change of the reaction and difference in the heat capacities of the products and the reactants.

From above equations, we can conclude that,

$$\lim_{T\to 0}\Delta S = 0$$

and

$$\lim_{T\to 0}\Delta C_P = 0$$

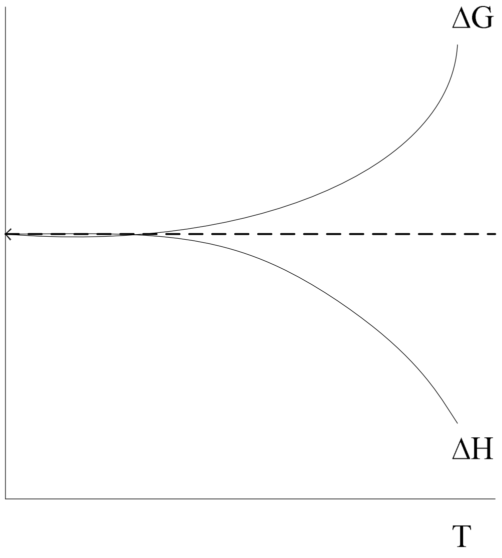


Figure 1 variation of ΔG and ΔH with change in temperature

These equations predict that the change in entropy and the difference between the heat capacities of products and reactants tends to approach zero as the temperature is lowered to absolute zero. This also indicates that the heat capacities of products and reactants in solid state are same.

The Nernst formulation of the Third Law:

"All reactions in a liquid or solid in thermal equilibrium take place with no change of entropy in the neighborhood of absolute zero."

9.7 EVALUATION OF ABSOLUTE ENTROPY FROM HEAT CAPACITY DATA

Third Law Entropy Calculations

The entropy of a perfect gas increases when it expands isothermally. The change in entropy of a substance accompanying a change of state at its transition temperature is calculated from its enthalpy of transition. The increase in entropy when a substance is heated is expressed in terms of its heat capacity. The entropy of a substance at a given temperature is determined from measurements of its heat capacity from T=0 upto the temperature of interest, allowing for phase transitions in that range, especially upto 15°C. It is difficult to measure heat capacities near T=0 K. Theoretically assume that the heat capacity is proportional to T^3 when T is low which is known as Debye extrapolation. $C_p$is measured down to as low a temperature as possible. That fit determines the value of a, and the expression $C_{p,m} = aT^3$ is assumed valid down to T= 0 K.

The Debye 'T-cubed' law says that the heat capacity at constant volume for metals is $C_V = aT^3 + bT$ and for nonmetals heat capacity changes to $C_V = aT^3$. This equation is valid to ≈ 15 K, Above 15 K, the heat capacity data are usually available.

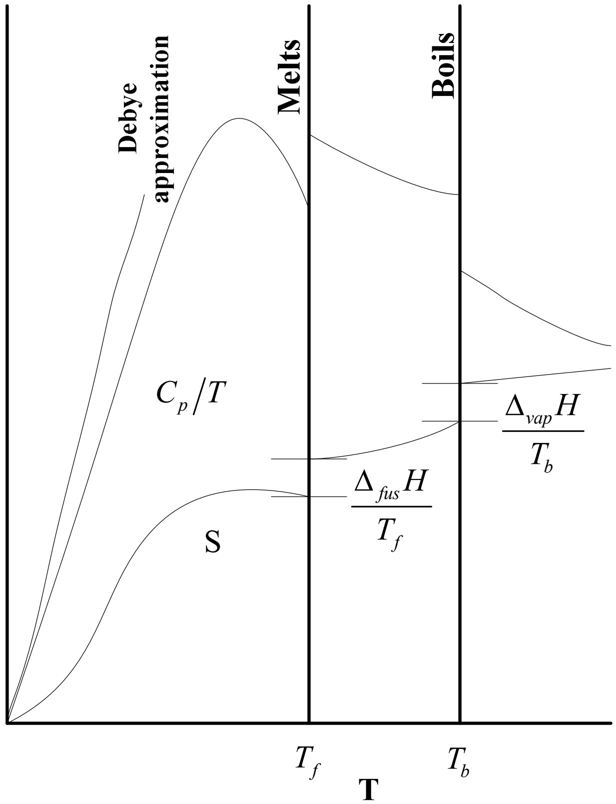


Figure 2 The variation of Cp /T with Temperature

Entropy change of phase transition

For a phase change or transition between 0 – T_1, we add in the appropriate entropy change.Consider a system and its surroundings at the normal transition temperature, T_{trs}, the temperature at which two phases are in equilibrium at one atm pressure.

Entropy of phase transition

$$\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$$

A comparable change in volume occurs (with an accompanying change in the number of accessible microstates) when any liquid evaporates and becomes a gas. Hence, all liquids can be expected to have similar standard entropies of vapourization, known as Trouton's rule.

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T_b}$$

Entropy change on heating

For any system (constant pressure heating), we can write the following for the entropy change between two temperatures 0 and T_1. Entropy variation with constant pressure (when C_p is independent of T in the temperature range of interest):

$$\Delta S = \int_0^{T_1} \frac{C_p}{T} dT$$

The calculation of change in entropy between two temperature T_1 and T_2

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT = C_p \int_{T_1}^{T_2} \frac{dT}{T} = C_p \ln \frac{T_2}{T_1}$$

Heat Capacities at Low Temperatures

The variation of *Cp*/*T* with the temperature for a sample is used to evaluate the entropy, which is equal to the area beneath the upper curve up to the corresponding temperature, plus the entropy of each phase transition passed (Fig 2).

The absolute entropy of metal at certain temperature $S_m(T)$, is equal to the sum of all entropy change during above calculated way.

$$S_m(T) = S_m(0) + \int_0^{T_f} \frac{C_{p,m}(s,T)}{T} dT + \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,m}(l,T)}{T} dT + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T} \frac{C_{p,m}(g,T)}{T} dT$$

Where $C_{p,m}(s, T)$, $C_{p,m}(l, T)$ and $C_{p,m}(g, T)$ are the heat capacities of metal at certain temperature at constant pressure when system is solid, liquid and gas respectively, $\Delta_{fus}H$ and $\Delta_{vap}H$ are change of enthalpy of system that undergoes phase transition and vapourization to attain gaseous state respectively. Thereactions involving only solids and liquids depend on the entropy values of the substances. Entropy values are absolute; the elements have non-zero entropy values, e.g., for H_2 (g), $\Delta_f H^\circ = 0$ kJ/mole, $S^\circ = 130.58$ J/(K mole). Table 1 gives the absolute entropy of nitrogen gas at 25 ℃ determined by the procedure outlined above.

Table 1 Determination of Absolute Entropy of N_2 at 25 ℃

S. No.	Calculation	$S_m^o/(JK^{-1}mol^{-1})$
1.	Debye extrapolation	1.92
2.	Integration from 10K to 35.61K	25.25
3.	Phase transition at 35.61 K	6.43
4.	Integration from 35.61K to 63.14K	23.38
5.	Fusion at 63.14K	11.42

6.	Integration from 63.14K to 77.32K	11.41
7.	Vapourization at 77.32K	72.13
8.	Integration from 77.32K to 298.15K	39.20
9.	Correction for gas imperfection	0.92
Total		**192.06**

S_m^o (298.15K) = S_m^o (0K)+192.1 $JK^{-1}mol^{-1}$

Absolute entropies of some of the elements and compounds in their standard states at 25°C, calculated from third law of thermodynamics, are given in table 2.

Table 2 Standard absolute entropies of elements and compound at 25°C

Substance	**S_m^o ($JK^{-1}mol^{-1}$)**	**Substance**	**S_m^o ($JK^{-1}mol^{-1}$)**
Graphite, C(s)	5.70	Diamond, C(s)	2.40
Sucrose, $C_{12}H_{22}O_{11}$(s)	360.20	Iodine, I_2 (s)	116.10
Benzene, C_6H_6 (l)	173.30	Water, H_2O (l)	69.90
Mercury, Hg (l)	76.00	Bromine, Br_2 (l)	153.97
Methane, CH_4 (g)	186.30	Carbon dioxide CO_2 (g)	213.70
Hydrogen, H_2 (g)	130.70	Helium, He	126.20
Ammonia, NH_3 (g)	192.40	Water, H_2O (g)	188.74

Example: A certain solid at 4.2 K: $C_{p,m} = 0.43\ J\ K^{-1}\ mol^{-1}$. What is its S_m at that Temperature?

Solution: We know that

$$S_m(T) = S_m(0) + \int_0^T \frac{C_{p,m}(\mathrm{s},T)}{T}dT = S_m(0) + \int_0^T \frac{aT^3}{T}dT$$

$$= S_m(0) + a\int_0^T T^2 dT = S_m(0) + \frac{1}{3}aT^3 = S_m(0) + \frac{1}{3}C_{p,m}(T)$$

$$S_m(T) = S_m(0) + 0.14JK^{-1}mol^{-1}$$

9.8 SUMMARY

Nernst heat theorem has relevance to understand the third law of thermodynamics. According to Nernst heat theorem when temperature is lowered to absolute zero, the value of ΔG and ΔH closely approaches to each other and become equal. At progressively lower temperatures, the change in enthalpy and the change in the Gibbs function during a chemical reaction become more and more equal. He suggested that the value of $\partial(\Delta G)/\partial T$ become equal to zero when temperature reaches absolute zero. This implies that chemical reactions at a temperature of absolute zero take place with no change of entropy. This is known as Nernst heat theorem. Now we can conclude that, $\lim_{T\to 0}\Delta S = 0$ and $\lim_{T\to 0}\Delta C_P = 0$. *For substances in internal equilibrium, undergoing an isothermal process, the entropy change goes to zero as T (in K) goes to zero. This is third law of thermodynamics.* Mathematically,

$$\lim_{T\to 0}\Delta S = 0$$

According to the Boltzmann formula, S = k lnW, the entropy is zero if there is only one accessible microstate (W= 1). A system with relatively few equivalent ways to arrange its components (smaller *W*) has relatively less disorder and low entropy. A system with many equivalent ways to arrange its components (larger *W*) has relatively more disorder and high entropy.

It was found that entropies of substance like H_2, D_2, CO, NO, H_2O etc. are not zero at absolute temperature. These entropies are called residual entropies.The absolute entropy of metal at certain temperature, $S_m(T)$, is equal to the sum of all entropy changes during above calculated way.

$$S_m(T) = S_m(0) + \int_0^{T_f}\frac{C_{p,m}(s,T)}{T}dT + \frac{\Delta_{fus}H}{T_f} + \int_{T_f}^{T_b}\frac{C_{p,m}(1,T)}{T}dT + \frac{\Delta_{vap}H}{T_b} + \int_{T_b}^{T}\frac{C_{p,m}(g,T)}{T}dT$$

Where $C_{p,m}(s, T)$, $C_{p,m}(l, T)$ and $C_{p,m}(g, T)$ are the heat capacity of metal at certain temperature at constant pressure when system is solid, liquid and gas respectively, $\Delta_{fus}H$ and $\Delta_{vap}H$ are change of enthalpy of system that undergoes phase transition and vapourization to attain gaseous state respectively. For reactions involving only solids and liquids depends on the entropy values of the substances.

9.8 TERMINAL QUESTIONS

Q1. C_V for uranium metal is 3.04 $JK^{-1}mol^{-1}$at 20 K. Calculate the absolute entropy of the metal in $JK^{-1}mol^{-1}$ at 20 K.

Q2. The heat capacity, C_P (in $JK^{-1}mol^{-1}$) of a substance is given by the following equations:

$$C_P(\mathrm{s}) = 16.74 \times 10^{-5} T^3 \left(0 < T < 50K\right)$$
$$C_P(\mathrm{s}) = 20.92\left(50 < T < 150K\right)$$
$$C_P(\mathrm{l}) = 25.10\left(150 < T < 400K\right)$$

At the melting point (150 K), $\Delta H_f = 1255.2\, J\, mol^{-1}$. Calculate the absolute entropy of the substance in the liquid state at 300 K.

Q3. Show that the entropy of any substance at very low temperature (0<T<20K), where Debye's relation for heat capacities is valid and one-third of the molar heat capacity.

9.9 ANSWERS

Ans1. 1.01 $JK^{-1}mol^{-1}$

Ans2. 55.73 $JK^{-1}mol^{-1}$