MAA OMWATI DEGREE COLLEGE, HASSANPUR (PALWAL)

NOTES

SUBJECT : Phycial Chemistry

CLASS : B.SC 5th Sem

SESSION : 2021-2022

B. Sc. Vth Semester

Paper XVIII (Theory) Physical Chemistry **Marks: 29**

CH-502 **Time: 3 Hrs.**

Note: Examiner will set nine questions and the candidates will be required to attempt five questions in all. Question number one will be compulsory containing five short answer type questions covering the entire syllabus and will be of five marks. Further, examiner will set two questions from each section and the candidates will be required to attempt one question from each section which will be o f s ix marks each

Section-A

Quantum Mechanic s-I

Black-body radiation, Plank's radiation law, photoelectric effect, heat capacity of solids, Compton effect,wave function and its significance of Postulates of quantum mechanics , quantum mechanical operator, commutation relations, Hamiltonial operator, Hermitian operator, average value of square of Hermitian as a positive quantity, Role of operators in quantum mechanics, To show quantum mechanically that position and momentum cannot be predicated simultaneously, Determination of wave function & energy of a partic le in one dimensional box, Pictorial representation and its significance.

Section-B

Physical Properties and Molecular Structure

Optica l activity, polarization – (clausius – Mossotti equation). Orientation of dipoles in an electric field, dipole moment, included dipole moment, measurement of dipole moment-temperature method and refractivity method, dipole moment and structure of molecules, Magnetic permeability, magnetic susceptibility and its determination. Applica tion of magnetic susceptibility, magnetic properties – paramagnetism, diamagnetism and ferromagnetics.

Section-C

Spectroscopy-I

Introduction: Electromagnetic radiation, regions of spectrum, basic features of spectroscopy, statement of Bornoppenheimer approximation, Degrees of freedom.

Rotational Spectrum

Diatomic molecules. Energy levels of rigid rotator (semi-classical principles), selection rules, spectral intensity distribution using population distribution (Maxwell-Boltzmann distribution), determination of bond length, qualitative description of non-rigid rotor, isotope effect.

5th sem

Unit → 3

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Physical chemistry

Electromagnetic radiation and its interaction with matter :-

Electromagnetic radiation :- electromagnetic radiation is a form of energy that is propagated through space at a constant velocity of 3×10^8 ms^{-1}. These radiations contain both an electric and a magnetic field oscillating at right angles to each other and ⊥ to the direction of propagation of the wave. The component E is conventionally taken to be oscillating in xy plane because the interaction of electromagnetic radiation with matter is more commonly through the electric component (E)

some characteristics of electro-magnetic radiations :-

(1) These radiation travel with same velocity ($3 \times 10^8 ms^{-1}$) and do not require any medium for propagation.

(2) These are characterised by their wavelength (λ) and frequency (ν)

(3) These radiation have dual nature exhibiting both wave and particle characteristics.

The E energy associated with em electromagnetic radiation is directly proportional to its frequency i.e.

$E = h\nu$.

The absorption or emission of radiation is quantised and each quantum is called a photon.

WAVE PARAMETERS :-

(1) Wavelength :-

The distance b/w two adjacent crests or troughs in a particular wave is called its wavelength λ. It is expressed in Angstrom (Å), millimicrons (mμ), nanometers (nm) or metres (m).

(2) Wave number :-

It is the reciprocal of the wavelength and represents the no. of waves per unit of length. It is usually represented as the no. of waves that pass through a space of one cm and is expressed as $\bar{\nu}$.

(3) Frequency :- It is defined as the no. of waves passing through a given point per second. It is expressed as ν and is measured in cycles per second or in Hertz (Hz).

$1\ Hz = 1\ cycle\ sec^{-1}$

frequency $\propto \frac{1}{\text{wavelength}}$.

Energy of an electromagnetic radiation :

The energy of an electromagnetic radiation can be calculated using the relation.

$$E = h\nu = hc/\lambda$$

where E = energy of radiation in joules
h = plank's const. (6.626×10^{-34} Js)
ν = frequency of the radiation (Hz)
c = velocity of light ($3 \times 10^8\ ms^{-1}$)
λ = wavelength (m)

Quantity	Relationship	units
wavelength (λ)	$\lambda = \frac{c}{\nu}$	Å, nm, μm, m
wave no. ($\bar{\nu}$)	$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$	cm^{-1}, m^{-1}
frequency (ν)	$\nu = \frac{c}{\lambda} = c\bar{\nu}$	s^{-1} (Hz)
Velocity (c)	$c = \lambda\nu$	ms^{-1}

Electromagnetic Spectrum:-

All electromagnetic radiations have the same speed ($3 \times 10^8 ms^{-1}$).

The arrangement of different types of electromagnetic radiations in the order of increasing wavelength or decreasing frequencies is called electromagnetic spectrum.

The lowest frequency region is marked by radiowaves and the highest frequency regions are marked by cosmic waves.

The increasing frequency regions along with various types of spectra arising in these are given as —

(1) Radiofrequency region:-

It lies in the frequency range $3 \times 10^6 - 3 \times 10^{10}$ Hz. The energy changes in this region involve change in the spin of a nucleus or of an electron. As a result the nuclear magnetic resonance (NMR) and electron spin resonance (ESR) spectra are obtained in this region.

(2) Microwave region:- The frequency range for the microwave region is $3 \times 10^{10} - 3 \times 10^{12}$ Hz. The rotational spectra are observed in this region.

(3) Infra-red region:- This region spreads in the frequency range $3 \times 10^{12} - 3 \times 10^{14}$ Hz. The vibrational spectra are obtained in this region of electromagnetic spectrum.

(4) Visible and ultra violet regions:-

These region lie in the frequency range $3 \times 10^4 - 3 \times 10^{16}$ Hz. and electronic spectra due to excitation of electrons in the valence orbitals of atoms or molecules are obtained in these regions.

(5) X-ray region:- The frequency range of X-ray region is $3 \times 10^{16} - 3 \times 10^{18}$ Hz. This is very high energy region and electronic spectra involving changes in electrons in the inner core of atom or molecules are obtained.

(6) γ-ray and cosmic ray regions:-

The γ-ray region extends in the frequency range $3 \times 10^{18} - 3 \times 10^{20}$ Hz whereas the cosmic ray are the highest energy radiations

present in frequency range 3×10^{20} * 3×10^{22} Hz.

The diff electromagnetic radiations are arranged in the order of increasing wavelength and decreasing frequency.

Cosmic rays > gamma rays > X-rays > ultraviolet radiation > visible radiation > Infrared radiation > microwaves > radiowave.

Absorption and emission of electromagnetic radiation By molecules:-

When a molecule absorbs a particular electromagnetic radiation it can jump from one energy level to another. Consider two energy level labelled E_1 and E_2 as shown in the diagram. The molecule can jump from E_1 to E_2 by absorbing ΔE amount of energy taken up in the form of electromagnetic radiation.

The energy absorbed by a molecule is quantised. so that,

$$\Delta E = E_2 - E_1 = nh\nu \quad \text{---} (1)$$

where n = integer

* The lowest energy state of the molecule is called the ground state.
* The molecule jumps to next higher energy level and is said to be excited state.

* The wavelength of absorbed radiation are measured with the help of spectrometer.

* The study of absorbed radiations from a source that are utilized to raise internal energy of the molecule is called absorption spectroscopy.

After absorbing the energy the molecule returns to the return to the ground state by emitting energy as radiation.

The study of emitted radiation constitutes emission spectroscopy.

As the absorption spectra are easies to interpret than emission spectra so in the present discussion we will ~~unit~~ ~~incident~~ include only absorption spectroscopy.

The molecular energy levels and molecular spectra:-

A molecule can have several types of energies viz. rotational energy, vibrational energy, electronic energy etc. When energy is absorbed by a molecule it can undergo rotational, vibrational or electronic transition depending

on the amount of energy absorbed. At the same time, all these energy of the molecule are quantized i.e. there are only discrete rotational, vibrational or electronic transition energy levels available to the molecule for excitation. These rotational, vibrational and electronic energy levels are also called molecular energy levels and the translation which a molecule undergoes b/w these levels are designated to an absorption of suitable radiation results in a molecular spectra.

* Different types of molecular energies:-

A molecule possess four diff. type of energies.

(i) Translational energy (E_{tr}) → is due to the translational motion of the molecule in space. As a result of this motion the centre of gravity of the molecule changes. Translational energy levels of a molecule have very small energy gap b/w them. So translational energy is not quantised whereas all other types of molecular energies are quantised.

(ii) Rotational energy (E_{rot}) → It is due to rotation of molecule about an axis ⊥ to the internuclear axis and passing through the centre of gravity of the molecule. Rotational energy is quantised.

(iii) Vibrational energy :- (E_{vib}) → it is due to periodic to and fro motion of the nuclei of molecule without any change in the position of the centre of gravity of the molecule.

(iv) Electronic energy (E_{el}) → is due to various electronic interaction in the molecule. This energy is associated with the transition of an electron from the ground state energy level to excited state on absorption of photon of suitable frequency.

physical properties and molecular structure

The physical properties like density, optical activity, dipole moment, refractive index, magnetic susceptibility.

The basic fact that these physical properties are additive, constitutive or both in nature helps us to determine the molecular structure.

① Additive Property :- The physical property the total value of which is equal to the sum of values of corresponding properties of the constituent atoms is called additive property.

Ex:- molecular mass of a compound.

② Constitutive Property :- The physical property which depends upon the constitution of the molecule i.e. the arrangement of atoms and bond st. in a molecule is called constitutive property.

Ex:- optical activity, surface tension, viscosity etc.

(3) Additive and Constitutive property :-

It is defined as an additive property that also depend on the arrangement and bond structure of atom in a molecule.

Ex :- surface tension, viscosity, magnetic susceptibility etc.

OPTICAL ACTIVITY :-

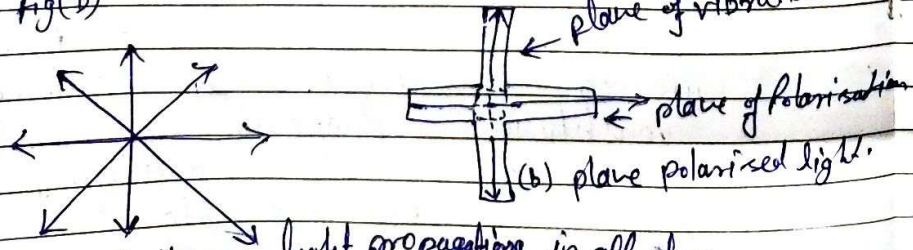
Some Common Terms :-

(1) Plane polarised light :-

A beam of ordinary light consists of electromagnetic waves vibrating in all planes ⊥ to its direction of propagation. fig (a)

When ordinary light is passed throught a nical prism, its vibrations in all directions except the direction of axis of the prism are cut off. The emergent rays come out with their vibration only in one plane.

fig (b)



A beam of light having vibrations only in one plane is said to be plane polarised light.

(2) Optical Activity :-

The substance which rotate the plane of polarised light are called optically active substance.

The property of substance to rotate the plane of polarised light is called optical activity.

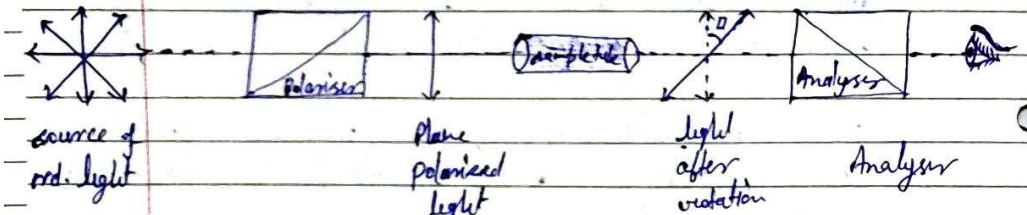
optically activity occurs only in chiral molecule which are non-superimposable on their mirror images. All optically active substance do not rotate the plane of polarised light in the same dirn.

Polarimeter :-

The dirn. of rotation of light and the angle of rotation caused by a substance is measured with the help of an instrument called polarimeter.

polarimeter consist of a light source, two nical prism and a sample tube to hold the substance.

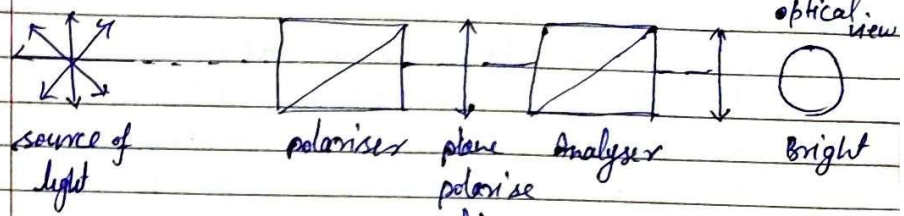
the nicol prism placed near the source of light is called polariser. And other placed near the eye is called analyser.



the polariser, sample tube and analyser are arranged in such a way that the light after passing through polariser sample tube and the analyser can be seen through eye piece.

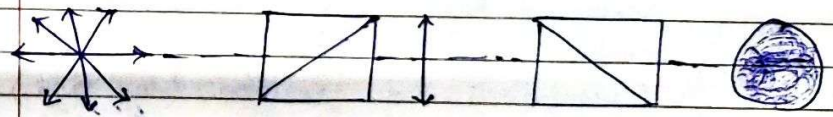
Principle of Polarimeter

(a) If the polariser and Analyser are placed with their polarisation planes parallel to each other, the plane polarised light emerging from first prism passes through the second and bright field is seen through the eye piece



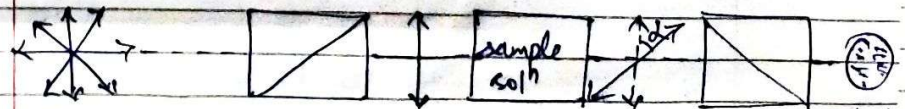
(a) Axis of polariser and analyser parallel.

(b) If the second prism is turned through 90° so that the plane of polarisation of two prism are at right angles then the light rays coming out of first prism are stopped by the second and a dark filed is seen through the eye piece.



(b) Axis of polariser and analyser crossed park.

(c) When an optical active substance is placed b/w the polarisation and analyser kept at dark field position some light starts coming through the analyser and optical view appears some what bright.



(c) Axis of polariser and Analyser crossed and optically active substance placed in b/w.

To obtain dark field when the analyser is turned towards right (clockwise) the optically active substance is said to be dextro-rotatory and when the analyser is turned to left (anticlockwise) the substance is called levo-rotatory.

Factors affecting the angle of rotation

The angle throught which an optically active substance rotates the plane of polarised light depends on following factor:

1. Nature of the substance
2. Nature of solvent
3. Concentration of solution (in g/ml)
4. The temp. of sol^n
5. The length of the tube containing optically active substance.
6. The wavelength of light used.

The angle of rotation α of a substance is related to the path length and concentration of sol^n (in g/ml) as

$$\alpha \propto \frac{l \times m}{V} \quad ---(1)$$

$$\alpha = \text{Constant} \times l \times \frac{m}{V} \quad --- (2)$$

The Const. in eq^n (1) depends upon the nature of the nature of the substance, temp. (t) and wavelength (λ) of the light used and is called the specific rotation of the substance represented as $[\alpha]^t_\lambda$.

eq^n (1) become $\alpha = [\alpha]^t_\lambda \times l \times \frac{m}{V}$ --- (3)

$$[\alpha]^t_\lambda = \frac{V \times \alpha}{l \times m} \quad --- (4)$$

If the sample concentration is 1g/mL
i.e. $m = 1$, $V = 1$mL optical path length = 1

$$[\alpha]^t_\lambda = \alpha$$

Thuse sperific rotation may be defened as the angle of rotation observed when the concentration of the sol^n of optically active substance is 1g/mL and the optical path length is one decimeter ($l = 1$ dm).

for solution, the Concenbation is taken in g/100mL. Then $m = c$ and $V = 100$mL
eq^n (2) becomes,

$$[\alpha]^t_\lambda = \frac{100 \times \alpha}{l \times c}$$

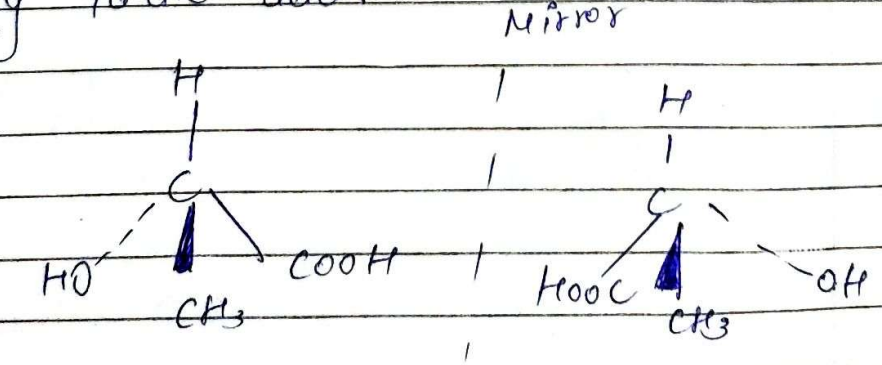
for pure liquids and solids m/V is replaced by density (d) of substance and eq^n (2)

$$[\alpha]^t_\lambda = \frac{\alpha}{l \cdot d} \quad --- (6)$$

OPTICAL ACTIVITY AND MOLECULAR STRUCTURE:-

It is observed the optical activity depends upon the arrangement of atom within the molecule. Thus, optical activity is a constitutive property. Optical property is a property related to a asymmetry of the molecules. If all the atoms or groups attached to a carbon atoms are different, then such a carbon is called asymmetric carbon. The molecule containing asymmetric carbon would lack symmetry is called asymmetric molecules. The asymmetric carbon is indicated by asterisk as C*. A simple example of molecules having asymmetric or chiral carbon is lactic acid.

Lactic acid is exists in two optically five active forms:- one form of lactic acid rotates the plane polarised light towards right and hence is known as dextro-rotatory lactic acid.



d and l enantiomers of lactic acid.

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Dipole Moment

★ polar and non-polar Covalent bonds :-

When a covalent bond is formed b/w two similar atom, the shared pair of electron is equally attracted by both the atoms.

H : H

The Common ex. are H_2, O_2, Cl_2, N_2 etc.

The bond form b/w identical atoms is called non-polar bond.

On the other hand, if the bond is formed b/w atoms diff. atoms the e^- attracting powers of the two atoms are diff.

★ Polar Molecule :- The molecule which have both positive and negative molecul is called polar molecule :- HCl. H has +ve charge and Cl have -ve charge.

★ Polar Covalent bond :- the bond formed b/w two diff. atoms having slightly diff. electronegativity is called polar Covalent bond.

H : Cl : or $H^{\delta+}$ $Cl^{\delta-}$

Dipole moment (A measure of degree of polarity)

It is defined as the product of the magnitude of the charge and the average distance of separation b/w the charge i.e. b/w the two nuclei.

It is denoted by μ.

$\mu = q \times d$ $\quad \mu$ = dipole moment

q = charge, d = distance of separation

Unit of dipole moment :-

In C.G.S. → Debye denoted by D

$1D = (10^{-10}\ e.s.u)(10^{-8}\ cm) = 10^{-18}\ e.s.u\ cm$

In S.I → charged expressed in coulomb C and distance in meters (m)

$1D = 1.602 \times 10^{-19}\ C \times 10^{10}\ m$

$1D = 3.336 \times 10^{-30}\ cm$

Dipole moment is a vector quantity and represented by a tail at positive centre

Ex

the dipole of HCl → $H \xrightarrow{+} Cl$

The shift in e^- density is symbolised by crossed arrow ($\xrightarrow{+}$)

Dipole moment of a polyatomic molecule :-

In Case of the polyatomic molecules, the dipole moment not only depends upon the individual dipole moment of the bonds but also on the spatial arrangement of the various bonds in the molecule.

The Contribution of the individual bond to the dipole moment called the bond moment. The net dipole moment of a polyatomic molecule is the resultant of diff. bond moment.

Tow types of ~~triangular~~ triatomic molecule.

(1) AB_2 type triatomic molecules :-

Consider triatomic molecule AB_2 containing 2 A-B bonds oriented at an angle θ. Let μ be the dipole moment of the molecule

$$\mu = 2\mu_{AB} \cos\frac{\theta}{2}$$

(2) ABC type triatomic molecule :-

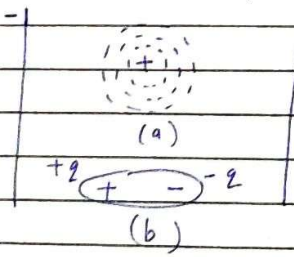
for a triatomic molecule of the type ABC with two bonds AB and AC having bond moment μ_1 and μ_2 and inclined at angle θ the dipole moment of the molecule.

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2\cos\theta}$$

Knowing the value of θ we can be calculate μ_1 and μ_2.

Polarisation of Molecules in an electric field:-

A neutral molecule consists of a positively charged nucleus and negatively charged electron. As a whole the molecule is neutral because the centre of positive charge coincide with the centre of negative charge. When such molecule is placed in an electric field, the positively charged nucleus is displaced towards the negatively charge plate and the -ve charge e⁻ cloud is displaced towards positively charge plate. As a result one end gets of the molecule become +vely charged and other get -vely charged This is termed as polarisation or distortion of molecule and the distrotion of molecule is called electric dipole. This type of polarisation is called induced polarisation and such dipole is called induced dipole.



(a) non polarised molecule

(b) polarised molecule.

If q is the charge produced and d is distance of separation of induced charge q_+ and q_- then the dipole moment is

$$\mu_i = q * d$$

The magnitude of μ_i depends upon the strength of applied field and the nature of molecule.

$$\mu_i \propto X$$

$$\mu_i = \alpha X$$

where X is the strength of applied field and α is a const. called the polarisability of the given molecule.

Types of Induced polarization

The electric field polarizes the molecule in the following three ways.

(1) **Electronic polarisation :-** The applied electric field caused temporary displacement of the electrons relative to the position of the nucleus. This is called electronic polarisation. It is represented as P_e corresponding polarisability is called electronic polarisability α_e.

(2) **Atomic polarisation :-** The nuclei of the atoms are distorted towards the negative end of the electric field. This polarisability is called atomic polarisability α_a. It is represented as P_a.

(iii) **Orientation polarisation :-** The electric field tends to align molecules possessing permanent dipole moment along the direction of the field. The polarisability that arises is called orientation polarisation. inesprented as P_o

Thus, the total polarizability (α) of a polar molecule placed in an electric field is sum of these three polarizability

i.e. $\alpha = \alpha_e + \alpha_a + \alpha_o$

$\alpha = \alpha_d + \alpha_o$ for polar molecule

where $\alpha_d = (\alpha_e + \alpha_a)$ is called disortion polarizability

for non polar molecule there is no orientation polarisibility hence total polarisibility contains only two terms i.e. $\alpha = \alpha_e + \alpha_a$

$\alpha = \alpha_d$

for non-polar molecule. the total polarisation value is

$P = P_e + P_a + P_o$

Clausius Mosotti Equation P_o -

The relationship b/w the distortion polarizability α_d of a molecule and the dielectric constant D of the medium b/w the the charged plates was deduced by clausius and Mosotti is known as clausius mosotti eqn.

consider a uniform electric field produced by two charged plates in vacuum. Let the strength of the uniform field be E_o. Now if any non-polar medium is placed in b/w the plates, the field strength reduce to E. The ratio E_o/E is called the dielectric const. D of the medium. It can be shown by elerostatics that

$$E_o = E + 4\pi I \quad -- \quad (1)$$

where I is called the dielectric polarisation and it is the total induced dipole moment per unit volume of the dielectric

$$I = \mu_i \times n \quad -- \quad (2)$$

volume μ_i = induced dipole moment in one molecule

n = the no. of molecul per unit Volume of the dielectric

dividing both side eqn (1) by E

$$\frac{E_o}{E} = 1 + \frac{4\pi I}{E}$$

put $E_o/E = D$

$$D = 1 + \frac{4\pi I}{E}$$

$$4\pi I = (D-1)E \quad -- \quad (3)$$

The electric field X is made up of following parts.

(1) the field strength of charge on plates = E_o

(iii) The charge induced on the surface of dielectric in contact with the plates $= -4\pi I$

(iii) The charge induced on the surface of spherical cavity $= +\frac{4}{3}\pi I$

the value of X is given by

$$X = E_0 + \frac{4\pi I}{3} - 4\pi I \quad \text{—— (4)}$$

substituting for E_0 from eqn (4)

$$X = [E + 4\pi I) + \frac{4\pi I}{3} - 4\pi I$$

$$= E + \frac{4\pi I}{3} \quad \text{—— (5)}$$

substituting the value of $4\pi I$ from eqn (3) into (5)

$$X = E + \left(\frac{D-1}{3}\right)E = \left(1 + \frac{D-1}{3}\right)E$$

$$\Rightarrow \left[\frac{D+2}{3}\right]E \quad \text{—— (6)}$$

On comparing eqn (3) and (6)

$$E + \frac{4}{3}\pi I = \left[\frac{D+2}{3}\right]E$$

$$\frac{4}{3}\pi I = \left(\frac{D+2}{3}\right)E - E = \left(\frac{D+2}{3} - 1\right)E \quad \text{—— (7)}$$

$$\left(\frac{D-1}{3}\right)E = \frac{4}{3}\pi I$$

We have already defined $I = q_i \times n$

$$= \alpha_d X \times n \quad \text{—— (8)}$$

where is α_d is the distortion polarisability putting the value of X from eqn (6)

$$I = \alpha_d \left(\frac{D-2}{3}\right) E \times n \quad \text{—— (9)}$$

putting the value of I from eqn (9) into (7)

$$\left(\frac{D-1}{3}\right)E = \frac{4}{3}\pi\alpha_d \left(\frac{D+2}{3}\right) E \times n$$

$$\left(\frac{D-1}{D+2}\right) = \frac{4}{3}\pi n \alpha_d \quad \text{—— (10)}$$

If ρ is the density of the substance taken b/w the charged plates, M is the molar mass and molar volume of the sub. $= \frac{M}{\rho}$

If N is the Avogadro's no. then no. of molecule in the unit volume is

$$n = \frac{N\rho}{M} \quad \text{—— (11)}$$

substituting value of n from eqn (11) into (7)

$$\left(\frac{D-1}{D+2}\right) = \frac{4}{3}\pi \frac{N\rho}{M}\alpha_d$$

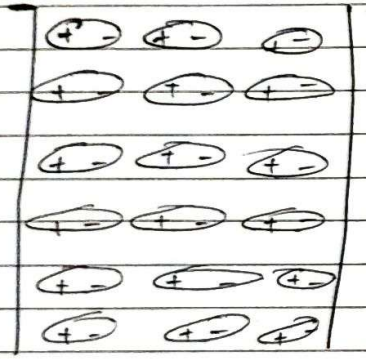
$$\left(\frac{D-1}{D+2}\right)\frac{m}{\rho} = \frac{4}{3}\pi N\alpha_d = P_m \text{ or } P_i \quad \text{—— (12)}$$

$$\left(\frac{D-1}{D+2}\right)V = \frac{4}{3}\pi N\alpha_d = P_m \text{ or } P_i \quad \text{—— (13)}$$

Where P_m or P_i is called the induced molar polarisation eqn (12) is Clausius mosotti eqn.

$$\frac{4}{3}\pi N\alpha_d = \text{Const.}$$

P_m or induced molar polarisation may be defined as the amount of polarisation produced in 1 mole of substance in an electric field of unit strength.



The induced dipole tends to neutralize the applied electric field.

Effect On temperature On Polarisation: The Debye Equation

from clausius Mosotti eqn it is clear that the quantity P_m is constant and does not vary with temp. because N and α_d are const. and do not depend on temp.

It is found that the molar polarisation P_m of the non-polar molecules like O_2, N_2, CO_2, CH_4 etc is independent of temp. However in case of polar molecule like HCl, $CHCl_3$, $C_6H_5NO_2$ etc. the molar polarisation decrease as the temp. is increased. Thus Clausius mosotti eqn is applicable only to non-polar molecule and is not obeyed by polar molecules.

Debye considered the behaviour of polar molecules in the presence of applied electric field.

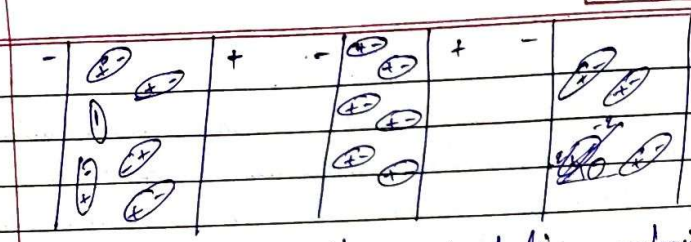
The polar molecule like HCl, $CHCl_3$, Co possess permanent dipole moment.

These molecule undergoes two type of polarisation

(1) Induced polarisation :- Due to distortion of electron cloud and distortion of nuclei towards negative end of electronic field. The polarizability is called distortion polarizability α_d.

(2) Orientation polarisation :-

When a polar molecule are placed in electric field, electric field tends to orient the permanent dipoles in the direction of the applied field. If the molecule were stationary they would orient with the field at an angle of 180° or 90° to the charged plates.



Debye gave the orientation polarizability α_0

$$\alpha_0 = \frac{\mu^2}{3KT} \quad - (1)$$

It is seen that α_0 depends upon permanent dipole moment and the temp.

$$\alpha = \alpha_d + \alpha_0$$

$$P_m = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = \frac{4}{3}\pi N\left(\alpha_d + \frac{\mu^2}{3KT}\right) \quad - (2)$$

$$P_m = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = \frac{4}{3}\pi N\alpha_d + \frac{4}{3}\pi N\frac{\mu^2}{3KT} \quad - (3)$$

eq^n (2) and (3) called Debye eq^n in simple form it can written as

$$P_m = A + \frac{B}{T} \quad - (4)$$

$$A = \frac{4}{3}\pi N\alpha_d$$

Measurement of Dipole Moment :-

(1) Vapour - temperature method :-

This method is used to measure the dipole moment of substances in gas or vapour phase.

molar polarisation as given by debye eq^n is

$$P_m = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = \frac{4}{3}\pi N\alpha_d + \frac{4}{3}\pi N\frac{\mu^2}{3KT} \quad - (1)$$

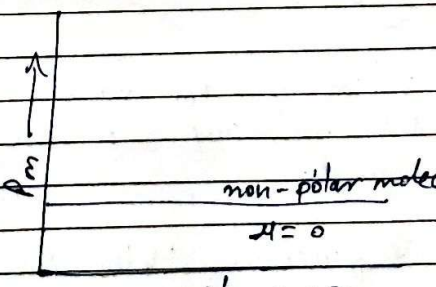
This is the eq^n of straight line and can be written in the form

$$P_m = A + \frac{B}{T} \quad - (2)$$

where A and B are Const.

$$A = \frac{4}{3}\pi N\alpha_d \;,\; B = \frac{4\pi N\mu^2}{9K}$$

a plot of P_m versus $1/T$ will give a straight line will slope equal to B



plots of P_m versus $1/T$ for polar and non-polar molecules

$$\mu = 0.218\sqrt{B} \times 10^{-18} \text{ esu cm}$$

$$\Rightarrow 0.218\sqrt{B} \text{ Debye}$$

Slope B is known from the plot of P_m vs $1/T$ for non polar molecule $\mu = 0$

Thus, the plot of P_m vs $1/T$ will give a straight line with slop equal to zero.

Method of determination of dipole moment:

In this method the dielectric constant D and density of vapour ρ is determined at differencee temp.

$$P_m = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho}$$

where

$$D = \frac{C}{C_0} = \frac{\text{Capacitance of condenser in medium}}{\text{vacuum}}$$

If the values of P_m varies linearly with $1/T$ then the molecule possesses a permanent dipole moment.

Molar Refraction Method :-

The molar polarisation of a non-polar substance is given by Clausius mosotti eqn as

$$P_m = \left(\frac{D-1}{D+2}\right)\frac{M}{\rho} = \frac{4}{3}\pi N\alpha_d.$$

for non-polar molecule having $\mu = 0$, the molar polarisation P_m is independent of temp. Maxwell showed that for the light of long wavelength, the dielectric const. D and the refractive index n_∞ of a non-polar substance are related acc. to eqn

$$D = n_\infty^2$$

substituting value of D from eq^n (2) into eq^n (1)

$$P_m = \left(\frac{n_\infty^2 - 1}{n_\infty^2 + 2}\right)\frac{M}{\rho} = \frac{4}{3}\pi N\alpha_d \quad \text{— (3)}$$

To calculate total molar polarisation we need the value of n_∞. We cannot determine n_∞ by extrapolation of refractive index values obtained with visible light. Because visible light can cause only electronic distortion whereas the nuclei remain unaffected.

For non-polar molecule

$$P_m = P_e + P_a$$

Infrared rays can be used to cause both atomic polarisation and electronic polarisation but it is difficult to measure the refractive index using infrared radiations.

$$P_e = \left(\frac{n^2-1}{n^2+2}\right)\frac{M}{\rho} \quad \text{---} (4)$$

The R.H.S terms of eqn is molar refractivity so the method gets name molar refraction method.

$$P_m = P_e + P_a = P_d \quad \text{--} \{\because P_d = P_e + P_a\}$$

for polar molecules having permanent dipole moment the total molar polarisation is sum of three terms.

$$P_m = P_e + P_a + P_o \quad \text{---} (5)$$

$$\Rightarrow P_d + P_o$$

P_o = orientation polarisation

the value of P_o from debye eq^n is

$$P_o = \frac{4}{3}\pi N\frac{\mu^2}{3KT} = \frac{4}{9}\pi\frac{N\mu^2}{KT}$$

putting the value of P_o in eq^n (5)

1st sem

unit → 1

Quantum Mechanics

physical chemistry - B.Sc 5th sem

Black Body and Black Body Radiation:-

Black Body:- A body which completely absorbs all the radiation falling on it is called black body.

To understand the concept of black body we consider following two situation.

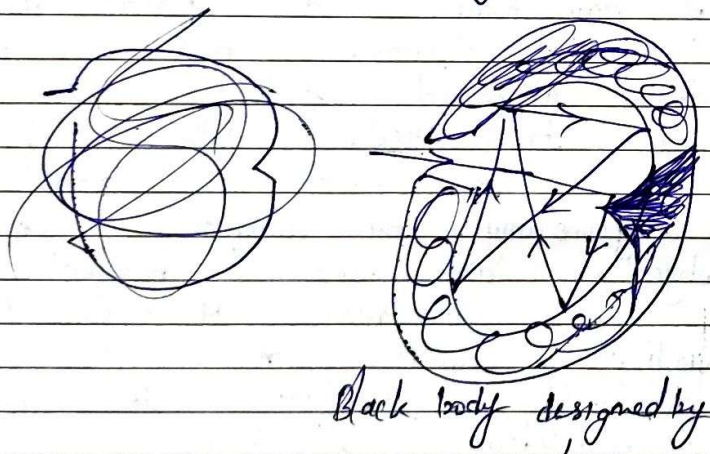
1. Absorption of radiation by a body.
2. Emission of radiation by a body.

When a radiation falls on the surface of a body a part of it is reflected some portion of it it absorbed and the rest of is transmitted. Whole of radiant energy is not absorbed because generally the surface of the object are not perfect absorbers of radiation. However if the radiation falls on a blackened metallic surface it is almost completely absorbed.

Now in the case of emission of radiation by the objects. Radiation is emitted by solid body at any temp. as a result of vibrations of its particles. At low temp. the emitted radiations

are of low frequency. As the temp is raised the emitted radiation goes from a lower frequency to the higher frequency. different solid emit radiation at different rates at same temp. the emittion rate is maximum when amount of the solid is perfectly black.

So A black body is a perfect emitter of radient energy.



Black body designed by feg.

Black body Radiations:- The radiation emitted by a black body at a particular temp. are called black body radiation

Kirchoff's law of thermal Radiations:-

The relationship b/w the energy absorbed and emitted by a body is called kirchoff's law of thermal radiation.

It is given by kirchoff in 1859.

This law states that at any temp. the ratio of emissive power (or emittance) of a body to its absorptive power (or absorptivity) is constant, independent of the nature of the body and is equal to the emissive power of the black body the same temp.

The emissive power of a body is the energy emitted by the surface per unit time per unit area.

The absorptive power is the fraction of incident radiation absorbed by the surface per unit time per unit area.

$$\frac{E_s}{A_s} = E_B$$

E_s = emissive power of surface
A_s = absorptive power of surface
E_B = emissive power of a perfect black body.

Derivation of kirchoff's law:-

Let Q be the amount of radiation incident per unit area per second on a body. If A_s is the absorptive power of the surface, then the amount of radiation absorbed per unit area per second by the body $= A_s \times Q$.

If E_s is the emissive power of the surface, then the amount of radiation emitted per unit area per second by the body $= E_s$

When the body attains thermal equilibrium with the enclosure, then,

the amount of radiation emitted by the surface = Amount of radiation absorbed by the body per unit area per second.

$$E_s = A_s \times Q \quad \text{---} \quad (1)$$

for a perfectly black body

$A_s = A_B = 1$ and E_s may be substituted by E_B

where A_B and E_B are the absorptive power and emissive power of the black body.

$$E_B = Q \quad \text{---} \quad (2)$$

from eq^n (1) and (2)

$$E_s = A_s \times E_B$$

$$\boxed{\frac{E_s}{A_s} = E_B} \quad \text{---} \quad (3)$$

Hence prove.

In eq^n (3) E_B = Const.

Plank's Radiation law:-

Plank assumed that the radiation emitted by a black body was due to oscillations of the electrons in the constituent particles of the body

Acc. to this theory:-

(1) The oscillator can lose or gain energy discontinuously in the form of discrete packets of energy called quantas.

(2) The amount of energy emitted or absorbed depends upon the frequency of the oscillator and is given by the expression $= h\nu$ where h is Plank's constant and ν = frequency of the oscillator.

(3) The total energy emitted or absorbed can be in whole no. multiples of quantum.
i.e. $\varepsilon = nh\nu$, $n = 0, 1, 2 \ldots$

$$E_\lambda = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda KT} - 1}\right) \quad -(1)$$

This is called planck's radiation law.

Case (I) At low values of wavelength.

In a case when value of wavelength (λ) is small the factor $e^{hc/KT\lambda} >> 1$ we may write:-

$$e^{(hc/KT\lambda)} - 1 \simeq e^{hc/KT\lambda}$$

This reduce the expression (1) to

$$E_\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/KT\lambda}$$

which is identical to the wein's law.

Case II At high value of wavelength

If λ is high, then the term $e^{hc/\lambda KT}$ in eqn (3) will be small may be expanded as

$$e^{hc/KT\lambda} \simeq 1 + \frac{hc}{KT\lambda} + \ldots$$

Neglecting the higher powers

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \times \frac{KT\lambda}{hc}$$

$$E_\lambda = \frac{8\pi}{\lambda^4} \cdot KT$$

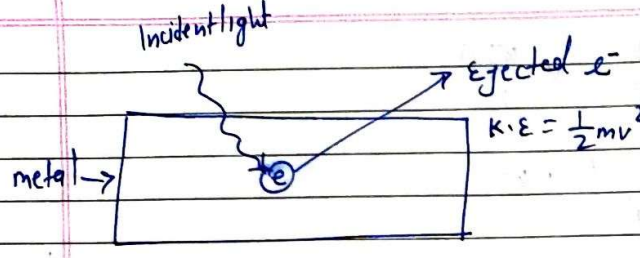
This is expression is identical to the Rayleigh-Jean's law.

Photo electric effect :-

When a beam of radiation of a particular frequency falls on a metal surface the electron are emitted from the surface. This occurs as an effect of absorption of energy by electrons from the incident radiation which happen to overcome the binding energy of parent metal.

(1) The photoelectrons are emitted only with a light of certain minimum frequency (ν) this is also called threshold frequency and it varies from metal to metal.

(2) The kinetic energy of emitting electron increases on increasing the frequency of incident light but remain unaffected on increasing the intensity of light.



Heat Capacity of solids :-

The heat capacity of solids should not change with change in temp. However the experimental observation show that this value of heat capacity is observed only at high temp. The heat capacity descreas as the temp. decrease

∴ energy of one mole of oscillaters

$$E = N_0 \times 3KT = 3RT$$

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V = 3R \quad --(1)$$

It was proposed that vibrational energy of an oscillator is whole no. multiple of $h\nu_0$.

$$\bar{E} = \frac{h\nu_0}{e^{h\nu_0/KT} - 1}$$

The molar energy of the solid will be given as

$$E = N_0 \times 3\bar{E}$$

$$= \frac{3N_0 h\nu_0}{e^{h\nu_0/KT} - 1}$$

$$\therefore \left(\frac{\partial E}{\partial T}\right)_V = C_V = 3N_0 K \left(\frac{h\nu_0}{KT}\right)^2 \frac{e^{h\nu_0/KT}}{\left(e^{h\nu_0/KT} - 1\right)^2} \quad --(2)$$

At low temp

$$\frac{h\nu_0}{KT} >> T$$

$$e^{h\nu_0/KT} >> 1$$

Hence eqn (2) becomes

$$C_V = 3N_0 K \left(\frac{h\nu_0}{KT}\right)^2 e^{-h\nu/KT} \quad --(3)$$

The net effect is that C_V descrease with decrease in temp.

At high temp.

$$C_V = 3R$$

At high temp. $h\nu_0/KT << 1$

eqn (2) can be solved using expension series $e^x = 1 + x + x^2 + \cdots$

$$\boxed{C_V = 3N_0 K = 3K}$$

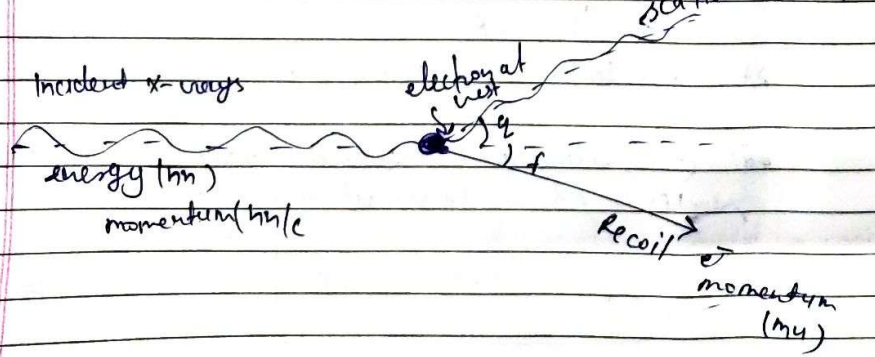
Compton effect :-

Arthur Compton observed that when a monochromatic beam of X-rays is made incident on carbon or some other light element they get scattered. The scattered x-rays have larger wavelength than the incident rays. This increasing in wavelength or decrease in energy of X-rays after scattering from the surface of an object is known as Compton effect.

$$\Delta\lambda = (\lambda' - \lambda) = \frac{2h}{mc} \sin^2\theta/2 \quad \text{— (1)}$$

where $\Delta\lambda$ is the increasing wavelength,
θ = angle b/w incident and scattered
m = rest mass of electron

eqn (1) is known as Compton shift.



Following conclusions can be derived from eqn :-

(i) The Compton shift is independent of the wave length of the incident X-rays

(ii) Compton shift does not depend upon the nature of material used as target.

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

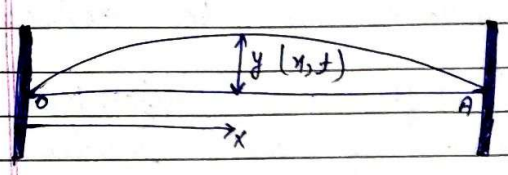
$\theta = 0°$, then $\cos\theta = 1$
$\theta = 90°$, $\cos\theta = 0$
$= 180°$, $\cos\theta = -1$

It is clear from above data that Compton shift depends upon an angle θ.

Schrodinger wave eqn :-

In 1926 schrodinger formulated a general quantum theory and gave a wave eqn to describe the behaviour of e⁻ waves. This wave fn ψ is related to the probability of finding e⁻ around the nucleus.

Let y be the amplitude of this wave at any point of wave moving along x-axis at a time 't' and v be the velocity of the wave.



$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \times \frac{\partial^2 y}{\partial t^2} \quad \text{— (1)}$$

This eqn has two variable x and t y depends upon variables x ~~and~~ & t,

$$y = f(x) \cdot g(t) \quad \text{— (2)}$$

where f and g are function of x-cordinate at time t

$$f(x) = A \sin \frac{2\pi}{\lambda} x \quad \text{[Time independent part]} \quad \text{(3)}$$

$$g(t) = A \sin Kt + B \cos Kt \quad \text{[Time dep. part]} \quad \text{(4)}$$

We are at present concerned only with the time independent part or stationary wave and therefore the time dependent part is neglected or ignored.

$$y = A \sin \frac{2\pi}{\lambda} \cdot x \quad \text{— (5)}$$

In this eqn if y is replaced by $\psi(x)$ and called the wave fn of electron wave

$$\psi(x) = A \sin \frac{2\pi}{\lambda} \cdot x \quad \text{— 6}$$

$\psi(x)$ represents the amplitude of wave moving along x-axis.

& Double diff. of eqn (6)

$$\frac{\partial^2 \psi(x)}{\partial x^2} = -\frac{4\pi^2}{\lambda^2} A \sin \frac{2\pi}{\lambda} \cdot x$$

In three dimensions

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{-4\pi^2}{\lambda^2} \psi \quad \text{— (8)}$$

Incorporating de-Broglie's relation

$$\lambda = h/mv$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{-4\pi^2 m^2 v^2}{h^2} \psi \quad \text{— (9)}$$

The K.E. of the particle is given by $\frac{1}{2}mv^2$

$$\text{K.E.} = \frac{1}{2}mv^2 = E - V \quad \text{or} \quad m^2 = 2(E-V)$$

substituting p^2 in (9)

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

Eqn (10) is schrodinger wave eqn

Some Operaters frequently used in quantum mechanics:-

(1) Laplacian operaters:-

This is the most commonly used operator in quantum mechanics. It is represented by ∇^2

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

The schrodinger wave eqn

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

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

(2) Hamiltonian Operaters:-

The total energy E of a particle

$$\frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + V = E \quad \text{—①}$$

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]\psi = E\psi \quad \text{—②}$$

Ignoring ψ, the Comp. of eqn (1) and (2)

$$\frac{1}{2}(p_x^2 + p_y^2 + p_z^2) = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$p_x^2 = \frac{-h^2}{4\pi^2}\frac{\partial^2}{\partial x^2}, \quad p_y^2 = \frac{-h^2}{4\pi}\frac{\partial^2}{\partial x^2}$$

$$p_z^2 = \frac{-h^2\partial^2}{4\pi^2\,\partial z^2}$$

✱ Postulates of Quantum Mechanics

The schrodinger eqn does not provide a complete explanation of quantum mechanics. Some postulates have been devised which provide mathematical expression to quantum mechanics.

Postulates I: state of a system in terms of ψ:-

Every time independent state of a quantum mechanical system can be described in terms of a function ψ of position coordinates.

called wave function ψ which is continuous, single valued in and finite in a given volume element of space. ψ contains all the information that can be obtained about the system.

Postulate II :- Operators and Mechanical variables :- to every observable, i.e. a quantity that can be experimentally measured (e.g., position, momentum, potential energy etc.) there corresponds a linear hermitian mathematical operator in quantum Mechanics.

Postulate III :- Eigen value postulate :- According to the first postulate the wave function ψ of a system contains all available information about the values of observable quantities of the state. The second postulates provides a mathematical operator for each observable quantity. Whereas, the third and the fourth postulates provides the mathematical procedure for obtaining the available information from the wave function ψ.

Postulate IV :- Expectation value or average value: the expected average or expectation value for the measurement of an observable quantity A is given by the formula.

$$\langle A \rangle = \frac{\oint \psi^* \hat{A} \psi \, d\tau}{\oint \psi^* \psi \, d\tau}$$

If ψ is a normalized wave function then $\oint \psi^* \psi \, d\tau = 1$, therefore expression (1) can be simplified to obtain;

$$\langle A \rangle = \oint \psi^* \hat{A} \psi \, d\tau$$

unit → 4

Physical chemistry

 Sheet ①

* VIBRATIONAL ROTATIONAL SPECTRA :-

1. Energy levels in Vibrational Rotational spectra :-

In a diatomic molecule has the rotational energy levels have seperation of $1 - 10\ cm^{-1}$ whereas the vibrational energy level have much larger seperations. e.g. vibrational energy seperations of HCl are nearly $3000\ cm^{-1}$. Pure vibrational spectra are obtained only in liquids as the molecular interactions hinder the rotational motion. But in gaseous state the molecules are undergoing random motion so both rotational and vibrational motions takes place. the total energy of the molecule is taken to be equal to the sum of rotational and vibrational energies is :,

$$E(v, J) = E_r + E_v$$

In terms of wave no., we can writes

$$\bar{\nu}(v, J) = \bar{\nu}_j + \bar{\nu}_v \quad -①$$

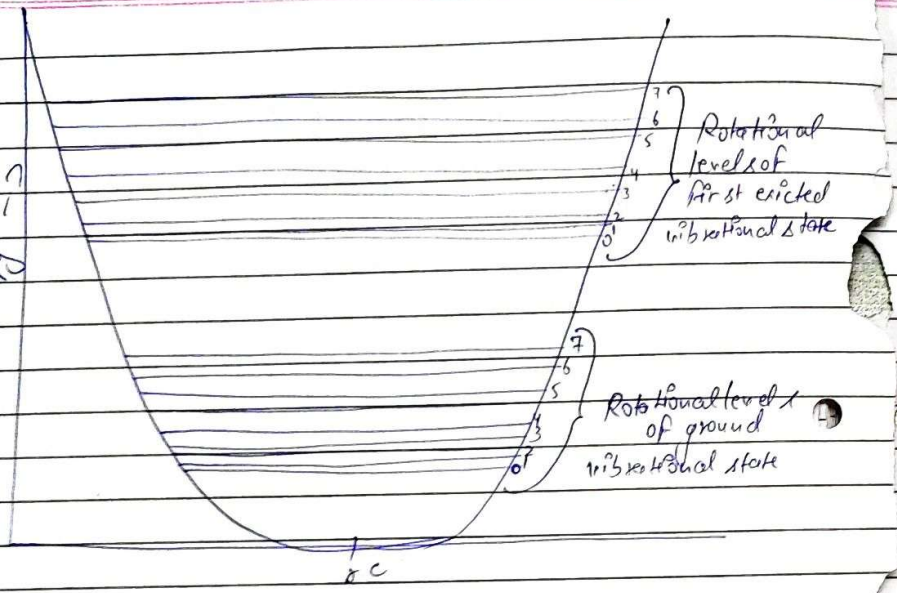
$$\bar{\nu}_j = BJ(J+1)\ cm^{-1}$$

$$\bar{\nu}_{jv} = \left(v + \frac{1}{2}\right)\omega_e - \left(v + \frac{1}{2}\right)^2 x_e\omega_e\ cm^{-1}$$

Substituting the values in eq^n. ①, we get :,

$$\bar{\nu}_{v,J} = BJ(J+1) + \left(v + \frac{1}{2}\right)\omega_e -$$

$$\left(v + \frac{1}{2}\right) x_e\omega_e\ cm^{-1}$$



$$\Delta\bar{\nu} = \left[BJ'(J'+1) + (v'+\tfrac{1}{2})\omega_e - (v'+\tfrac{1}{2})^2\omega_e x_e \right] - \left[BJ(J+1) + (v+\tfrac{1}{2})\omega_e - (v+\tfrac{1}{2})^2\omega_e x_e \right]$$

Now, from $v=0$ to $v=1$,

$$\Delta\bar{\nu} = \left[BJ'(J'+1) + \tfrac{3}{2}\omega_e - \tfrac{9}{4}\omega_e x_e \right] - \left[BJ(J+1) + \tfrac{1}{2}\omega_e - \tfrac{1}{4}\omega_e x_e \right]$$

$$= B\left[J'(J'+1) - J(J+1) \right] + \omega_e - 2\omega_e x_e$$

$$= B\left[J'-J \right]\left[J+J'+1 \right] + \omega_e + [1-2x_e]$$

taking $(1-2\omega_e x_e) = \omega_0$, we get,

$$\Delta\bar{\nu} = \omega_0 + B\,(J'-J)(J+J'+1)$$

(i) For a transition where $\Delta J = +1$

i.e. $J'-J = +1$ or $J' = J+1$ — (2)

$$\Delta\bar{\nu} = \omega_0 + 2B(J+1),\ J = 0, 1, 2 \text{ ---}$$

(ii) For a transition with $\Delta J = -1$,

i.e., $J'-J = -1$ or $J = J'+1$

$$\Delta\bar{\nu} = \omega_0 - 2B(J'+1),\ J' = 0, 1, 2 \text{ ---} \quad (3)$$

Combining equations (2), (3), we gets,

$$\Delta\bar{\nu} = \omega_0 + 2Bm \text{ cm}^{-1};\ m = \pm 1, \pm 2, \pm 3 \quad (4)$$

where $m = J+1$ in eq. (2) we gets,

$m = -(J'+1)$ in eq. (3)

2) P, Q, R Branches of Vibration - Rotation Spectrum:-

The equation (4) represents a combined vibration - rotation spectrum.

(i) Lines with frequency higher than the fundamental frequency are obtained for $\Delta J = -1$. These lines are called P-branch of the spectrum.

(ii) The lines with frequency higher than the fundamental frequency are obtained for $\Delta J = +1$. These lines constituted the R-branch of the spectrum.

(iii) For a transition occuring with $\Delta J = 0$ i.e. when no rotational transition accompanies vibration, the equation (4) becomes,

$$\Delta\bar{\nu} = \omega_0$$

ΔJ =	-1	0	$+1$
Lines obtained	P	Q	R

* NORMAL MODES of VIBRATION of POLYATOMIC MOLECULE :-

A diatomic Molecules has only one mode of vibration i.e. Stretching or compression along the lines of centres. Whereas a polyatomic Molecules has more than one mode of vibration. A Molecules having N atoms has total $3N$ degree of freedom, out of which three are the translational degrees of freedom.

A Normal mode of vibration can be defined as a Molecular motion in which all the atoms of the Molecules vibrate with same frequency and all the atoms simultaneously pass through their equilibrium positions. Normal Modes of vibration includes bending and Stretching Modes. For both linear and Non-linear Molecules, the No. of stretching and bending modes can be calculated. For a Molecules having N atoms there are $(N-1)$ bonds, then,

The No. of vibration stretching modes for both linear and Non-linear Molecules $= N-1$

the stretching Modes Further are symmetric stretch and asymmetric stretch.

No. of bending Modes for a linear Molecule $= 2N-4$

No. of bending Modes for a Non-linear Molecules $= 2N-5$

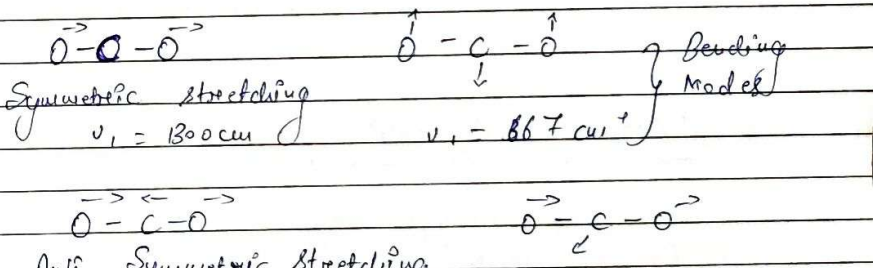
For example, take the case of triatomic linear CO_2 Molecules. the normal Modes of vibration

$= 3N-5 = 3\times3-5 = 4$

Stretching Modes of vibration $= N-1 = 3-1 = 2$

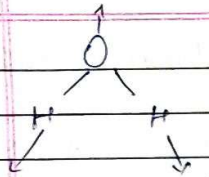
Bending Modes of vibration $= 2N-4 = 2\times3-4 = 2$

these Modes of vibration are shown in fig:-

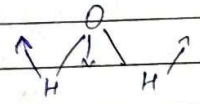


CO_2 Molecules has four Normal Modes of vibration out of which it's two bending modes at $\bar{\nu}_2$ is Not IR - active because it does not produces change in the dipole Moment whereas asymmetric stretch vibration at $\bar{\nu}_3$ is IR- active.

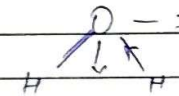
In case of triatomic Non - linear H_2O Molecules, the Normal Modes of vibration are $(3\times3-6) = 3$ these are shown in fig :-



Symmetric stretching
$\nu_1 = 3657\ cm^{-1}$



Symmetric bending
$\nu_2 = 1595\ cm^{-1}$



Anti - Symmetric Stretching
$\nu_3 = 3756\ cm^{-1}$

* RAMAN SPECTRA :-

The spectra studied till now deal with the absorption of light by a Molecules, however Raman spectroscopy deals with scattering of light and not with its absorption.

When a beam of monochromatic light is passed through a substances, a small fraction of light is scattered. Almost the entire scattered radiation has frequency equal to that of incident radiation.

This type of scattering is called Rayleigh scattering. Professor C.V. Raman observed in 1928 that in addition, some scattered light has frequencies above and below that of the incident beam and this is referred to as Raman scattering or Raman effect.

Let ν_i be the frequency of to as Rayleigh scattering and case II and III are called the Raman scattering. whereas the Raman spectra, the lines appearing at lower frequency are called Stoke's lines symmetrically placed about the Rayleigh line.

The difference $\Delta\nu = \nu_i - \nu_s$ is called Raman frequency or Raman shift.

* PURE ROTATIONAL RAMAN SPECTRUM :-

The rotational energy levels of a non-rigid diatomic rotator have given by

$$E_J = BJ(J+1) - DJ^2(J+1)^2\ cm^{-1}$$
$$(J = 0, 1, 2 - - -) \quad -①$$

However, in Raman spectroscopy, we ignore the term involving centrifugal distortion const. D then, eq°. ① becomes,

$$E_J = BJ(J+1)\ cm^{-1} \quad (J = 0, 1, 2, - - -) \quad -②$$

Thus, expression ② represents the energy levels of a non-rigid diatomic rotator, the transition blw these rules for pure rotational Raman spectrum of diatomic Molecules is,

$$\Delta J = 0, \text{ or } +2$$

where $\Delta J = 0$ corresponds to Rayleigh scattering. the operative part of selection rules is $\Delta J = +2$ results in Raman lines while $\Delta J = -2$ is ignored because since we define ΔJ = Upper state − Lower state

is always greater than lower state
Therefore the selection rule $\Delta J = \pm 1$ ignored

for a transition taking place from lower rotational level J to a higher rotational level with quantum no. J'

$$\Delta\bar{\nu} = B_{J'}(J'+1) - B_J(J+1)\ cm^{-1}$$

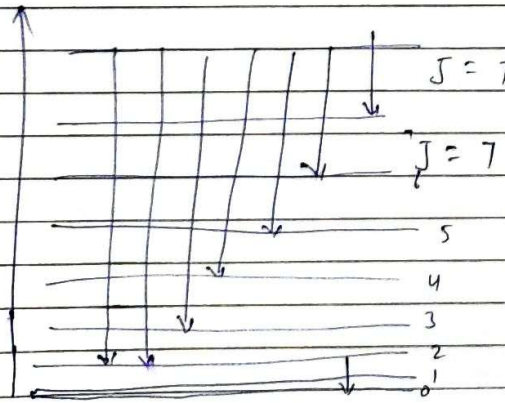
Applying selection rule $\Delta J = +2$ ie.

$$J' - J = 2 \quad \text{or} \quad J' = J+2$$

$$\Delta\bar{\nu} = B(J+2)(J+3) - BJ(J+1)$$

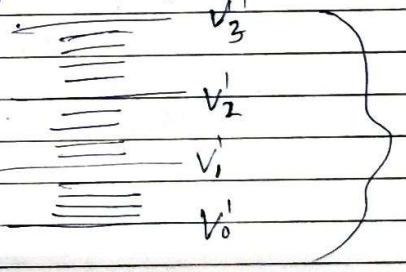
$$\Rightarrow B(4J+6)\ cm^{-1} \quad [J = 0, 1, 2 \cdots]$$

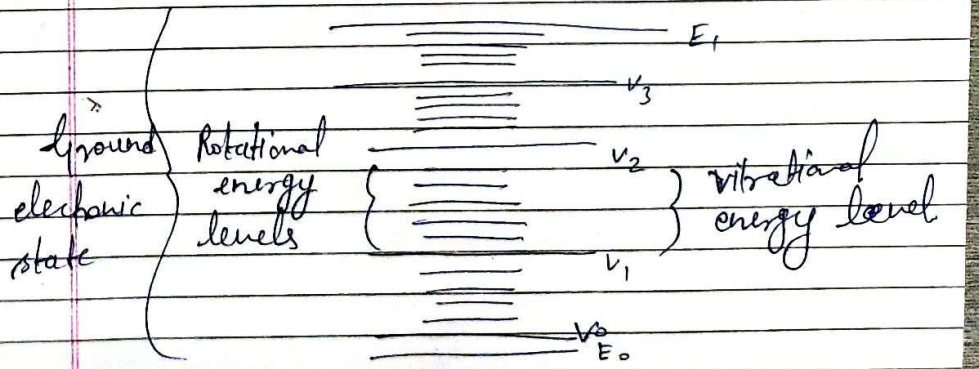
$$\bar{\nu}_S = \bar{\nu}_i \pm B(4J+6)\ cm^{-1}$$



electronic spectrum :-

A molecule can have several type of energies viz. rotational energy, vibrational energy, translation energy. When energy is absorbed by a molecule it can undergo rotational, vibration or electronic energy depending upon the amount of energy absorbed. All these type of molecule are quantised.





molecular energy level.

When the molecule absorbs energy in microwave region the translation in rotational energy levels take place and rotational energy specha is observed. When a molecule absorbed energy in the visible region or ultra violet region, it jumps from one electronic level, so the electronic specha of the molecules are observed in visible and ultraviolet regions of the electromagnetic spectrum.