

Biyani's Think Tank

Concept based notes

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B.Sc. Part-III

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Preface

I am glad to present this book, especially designed to serve the needs of the students. The book has been written keeping in mind the general weakness in understanding the fundamental concepts of the topics. The book is self-explanatory and adopts the “Teach Yourself” style. It is based on question-answer pattern. The language of book is quite easy and understandable based on scientific approach.

Any further improvement in the contents of the book by making corrections, omission and inclusion is keen to be achieved based on suggestions from the readers for which the author shall be obliged.

I acknowledge special thanks to Mr. Rajeev Biyani, *Chairman* & Dr. Sanjay Biyani, *Director (Acad.)* Biyani Group of Colleges, who are the backbones and main concept provider and also have been constant source of motivation throughout this Endeavour. They played an active role in coordinating the various stages of this Endeavour and spearheaded the publishing work.

I look forward to receiving valuable suggestions from professors of various educational institutions, other faculty members and students for improvement of the quality of the book. The reader may feel free to send in their comments and suggestions to the under mentioned address.

Author

Syllabus

B.Sc. Part-III : Paper-III

Physical Chemistry

Unit-I

Elementary Quantum Mechanics

Black-body, radiation, Planck's radiation law, photoelectric effect, heat capacity of solids, Bohr's model of hydrogen atom (no derivation) and its defects. Compton effect.

De Broglie hypothesis, the Heisenberg's uncertainty principles, sinusoidal wave equation, Hamiltonian operator, Schrodinger wave equation and its importance, physical interpretation of the wave function, postulates of quantum mechanics, particle in a one dimensional box.

Schrodinger wave equation for H-atom, separation into three equations (without derivation), quantum numbers and their importance, hydrogen like wave functions, radial wave functions, angular wave functions.

Unit-II

Molecular orbital theory, basic ideas—criteria for forming M.O. from A.O., construction of M.O.'s by LCAO- H_2^+ ion, calculation of energy levels from wave functions, physical picture of bonding and antibonding wave functions, concept of σ , σ^* , π , π^* orbitals and their characteristics. Hybrid orbitals— sp , sp^2 , sp^3 , calculation of co-efficients of A.O.'s used in these hybrid orbitals.

Introduction to valence bond model of H_2 , comparison of M.O.

Unit-III

Spectroscopy : Introduction : Electromagnetic radiation of the spectrum, basic features of different spectrometers, statement of the Born-Oppenheim approximation, degrees of freedom.

Rotational Spectrum : Diatomic molecules, Energy levels of a rigid rotor (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.

Vibrational spectrum : Infrared spectrum : Energy levels of simple harmonic oscillator, selection rules, pure vibrational spectrum, intensity, determination of force constant and qualitative relation of force constant and bond energies, effect of anharmonic motion and isotope on the spectrum, idea of vibrational frequencies of different functional groups.

Raman Spectrum concept of polarizability, pure rotational and pure vibrational Raman spectra of diatomic molecules, selection rules.

Electronic Spectrum : Concept of potential energy curves for bonding and antibonding molecular orbitals, qualitative description of selection rules and Frank-Condon principle.

Qualitative description of σ , π and n M.O. their energy levels and the respective transitions.

Unit-IV

Photochemistry : Interaction of radiation with matter, difference between thermal and photochemical processes. Laws of photochemistry : Grothus-Draper law, Stark-Einstein law, Jablonski diagram depicting various processes occurring in the excited state, qualitative description of fluorescence, phosphorescence, non-radiative processes (internal conversion, intersystem crossing), quantum yield, photosensitized reactions-energy transfer processes (simple examples).

Physical Properties and Molecular Structure : Optical activity, polarization – (Clausius-Mossotti equation), orientation of dipoles in an electric field, dipole moment, measurement of dipole moment refractivity method, dipole moment and structure of molecules, gentic properties-paramagnetism, diamagnetism and magnetism.

Unit-V

Solutions, Dilute Solutions and Colligative Properties : Ideal and non-ideal solutions, methods of expressing concentrations of solutions, activity and activity coefficient.

Dilute solution, colligative properties, Raoult's law, relative lowering of vapour pressure, molecular weight determination. Osmosis, law of osmotic pressure and its measurement, determination of molecular weight from osmotic pressure, elevation of boiling point and depression of freezing in boiling point. Thermodynamic derivation of relation between molecular weight and elevation of boiling point and depression in freezing point. Experimental methods for determining various colligative properties. Abnormal molar mass, degree of dissociation and association of solutes.

Content

S. No.	Name of Topic	Page No.
1.	Elementary Quantum Mechanics	7
2.	Molecular Orbital Theory	15
3.	Spectroscopy	22
4.	Photochemistry and physical properties and Molecular Structure	31
5.	Solutions, Dilute Solutions and Colligative properties	47
6.	Unsolved Papers 2011-2009	60

Chapter 1

Elementary Quantum Mechanics

Q.1. Write a note on photoelectric effect and its application.

Ans. When light of certain frequency incidents on the surface of a metal, electrons are ejected from the metal. This phenomenon is known as “photoelectric effect” such ejected electrons are known as “Photo electrons”. This effect is shown under the action of visible light and more energetic U.V. light.

Uses of Photoelectric effect:

- (i) The principle of photoelectric effect is used in the construction of photoelectric cells.
- (ii) These are used as photo-tubes in televisions for producing pictures.
- (iii) These are also used in automatic door-openers, raising of burglar’s alarm etc.

Q.2. What is meant by a black body? Explain Stefan’s law in connection with black-body radiations?

Ans. A black body is one which would absorb radiations of all frequencies that are falling on it. Such an ideal substance is called as black-body. According to Stefan-Boltzmann law, “the intensity of the total radiation E is proportional to the fourth power of the absolute temperature T ”.

Or

Emitted energy from the unit area of black body is proportional to the fourth power of the absolute temperature T.

$$E \propto T^4$$

$$E = \sigma T^4$$

Where σ is constant known as Stefan's constant

E = Total emitted energy

T = absolute temperature

If 'A' is the surface area of black body and 't' is the time of emission then emitted energy.

$$E = At \sigma T^4$$

Q.3. What is de-Broglie's equation? Derive it and state what is its significance in relation to atomic structure.

Ans. Any particle having mass 'm' and velocity 'v' has momentum P as follows

$$P(mv) = \frac{h}{\lambda}$$

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

Where h = Plank's constant

m = Mass of Particle

v = Velocity of Particle

λ = Debroglie's wavelength

this equation is known as "Debroglie equations".

Derivation: According to debroglie Hypothesis both light and matter have dual character as wave and as particle.

When electron is taken as wave, it must be associated with wavelength, frequency etc. If ' ν ' is the frequency of this wave and ' E ' is its energy then according to plank's equation

$$E = h\nu \quad \text{where } \nu = \text{frequency of wave}$$

If electron is taken as particle, then its energy E is given by Einstein equation

$$E = mc^2$$

M = Mass of particle

C = Velocity of light

Therefore,

$$h\nu = mc^2$$

$$\frac{h\nu}{c} = mC$$

$$\therefore \frac{\nu}{C} = \frac{1}{\lambda}$$

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

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

$$\therefore P = mc$$

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

Where P = Monentum

λ = wavelength

h = Plank constant

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

This is de Broglie's equation

Significance in connection with atomic structure : When a beam of electrons is allowed to impinge on a crystalline substance, the beam is scattered in a definite pattern. Such a scattering pattern of the beam is characteristic of the atomic structure of the crystalline substance.

Q.4. Write a note on Schrodinger wave equation.

Ans. Schrodinger derived a wave equation for a moving particle, which is known as Schrodinger's fundamental wave equation or Time independent equation.

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

Where x , y and z are the three space co-ordinates

m = Mass of the electron

h = Planck's constant

E = Total energy of the electron

V = Potential energy of the electron

ψ = amplitude of the electron wave

$\frac{\partial^2 \psi}{\partial x^2}$ = second derivative of ψ with respect to x only and so on.

The solutions of Schrodinger wave equation are known as wave function.

Q.5. If \hat{A} and \hat{B} are two operators such that $[\hat{A}, \hat{B}] = 1$. Find the value of the operator $[\hat{A}, \hat{B}^2]$.

Ans. $[\hat{A}, \hat{B}] = (\hat{A}\hat{B} - \hat{B}\hat{A}) = 1$ is given

$$\begin{aligned} [\hat{A}\hat{B}^2] &= \hat{A}\hat{B}^2 - \hat{B}^2\hat{A} + \hat{B}\hat{A} - \hat{B}\hat{A} \\ &= (\hat{A}\hat{B}^2 - \hat{B}\hat{A}\hat{B}) + (\hat{B}\hat{A}\hat{B} - \hat{B}^2\hat{A}) \\ &= (\hat{A}\hat{B} - \hat{B}\hat{A})\hat{B} + \hat{B}(\hat{A}\hat{B} - \hat{B}\hat{A}) \\ &= (1)\hat{B} + \hat{B}(1) \end{aligned}$$

$$[\hat{A}\hat{B}^2] = 2\hat{B}$$

Q.6. What are operators? Find the expression for $\left(\frac{d}{dx} + x\right)^2$.

Ans. An operator is a mathematical instruction or procedure to be carried out on a function.

Operator is written as follows:

$$\boxed{(\text{Operator}) \times (\text{Function}) = (\text{Another Function})}$$

The function on which operator is applied is called operand.

Expression for the operator:

Let $\psi(x)$ is a operand so

$$\left(\frac{d}{dx} + x\right)^2 \psi(x) = \left(\frac{d}{dx} + x\right) \left(\frac{d}{dx} + x\right) \psi(x)$$

OR

$$\left(\frac{d}{dx} + x\right)^2 \psi(x) = \left(\frac{d}{dx} + x\right) \left(\frac{d\psi}{dx} + x\psi\right)$$

OR

$$\left(\frac{d}{dx} + x\right)^2 \psi(x) = \frac{d^2\psi}{dx^2} + 2x\frac{d\psi}{dx} + x^2\psi + \psi$$

$$\left(\frac{d}{dx} + x\right)^2 \psi(x) = \left(\frac{d^2}{dx^2} + 2x\frac{d}{dx} + x^2 + 1\right)\psi$$

On removing ψ from both the sides

$$\boxed{\left(\frac{d}{dx} + x\right)^2 = \frac{d^2}{dx^2} + 2x\frac{d}{dx} + x^2 + 1}$$

Q.7. What is Heisenberg's uncertainty principle? Calculate the uncertainty in position and momentum of a particle.

Ans. Electrons possess particle nature as well as wave nature. Since wave is not located at a particular point, it extends in space so no one can determine its position precisely. Werner Heisenberg, the German physicist put forward this limitation in the form of uncertainty principle.

According to this principle: it is not possible to determine simultaneously the position and momentum of a small moving particle, such as electron, with entire certainty.

Mathematically

$$\boxed{\Delta x \times \Delta P \geq \frac{h}{4\pi}}$$

Where Δx = uncertainty in position

ΔP = uncertainty in momentum

h = plank's constant

Thus it is clear that the more precisely one can define the position of small particle, the less certainly one is able to define its velocity or momentum and vice-versa.

Q.8. Prove that wavelength of a charged particle is inversely proportional to square root of accelerating Potential.

Ans. Let there is an electron of charge e which is accelerated by a potential V . then its kinetic energy is equal to eV . The K.E. of electron is also

given by $\frac{1}{2} MV^2$ where V is the velocity of electron.

Thus

$$\frac{1}{2} MV^2 = eV \quad \dots(1)$$

According to de Broglie equation

$$\lambda = \frac{h}{MV} \quad \text{Or} \quad V = \frac{h}{m\lambda} \quad \dots(2)$$

therefore from eqn (1) and (2)

$$\frac{1}{2}M \left(\frac{h}{M\lambda} \right)^2 = eV$$

$$\frac{Mh^2}{2M^2\lambda^2} = eV$$

$$\therefore \lambda^2 = \frac{h^2}{2MeV}$$

$$\lambda = \frac{h}{\sqrt{2MeV}}$$

$$\lambda = \frac{h}{\sqrt{2eM}} \cdot \frac{1}{\sqrt{V}}$$

This expression is showing that wavelength of a charged particle is inversely proportional to square root of accelerating Potential.

Q.9. Prove that $\left[x, \frac{d}{dx} \right] = -1$.

Ans. $\left(x, \frac{d}{dx} \right) = x \frac{d}{dx} - \frac{d(x)}{dx}$

Let ' ψ ' be a function then

$$\left(x \frac{d}{dx} - \frac{d(x)}{dx} \right) \psi = x \frac{d\psi}{dx} - \frac{d}{dx} (x \cdot \psi)$$

OR

$$\left(x \frac{d}{dx} - \frac{d(x)}{dx} \right) \psi = x \frac{d\psi}{dx} - \psi \frac{dx}{dx} - x \frac{d\psi}{dx}$$

OR

$$\left(x \frac{d}{dx} - \frac{d}{dx} (x) \right) \psi = -\psi$$

$$x \frac{d}{dx} - \frac{d}{dx} (x) = -1$$

$$\boxed{x, \frac{d}{dx} = -1}$$

Q.10. What is Compton effect. Give the formula for Compton shift.

Ans. If monochromatic X-rays (i.e. X-rays having one particular wavelength) are allowed to fall on carbon or some other light element, the scattered X-rays have wavelengths larger than the incident rays or the scattered X-rays have lower frequency, i.e. lower energy than the incident x-rays. Thus this decrease in energy or increase in wavelength of x-rays after scattering from the surface of an object is known as the "Compton effect".

The Compton equation may be written as follows-

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

$\Delta\lambda$ is called Compton shift.

Wave length λ' of scattered x-rays is always greater than the wavelength λ of incident x-rays. Compton shift is always positive it depends neither upon the nature of matter, nor upon the wavelength of incident radiation. It depends only upon the angle of scattering θ .

Chapter 2

Molecular Orbital Theory

Q.1. Using the LCAO for the wave function for H_2^+ , obtain the Normalized wave function for the BMO and ABMO.

Ans. Using the LACO-MO approximation, the wave function for H_2^+ is written as-

$$\psi_{MO} = C_1\psi_a + C_2\psi_b \quad \dots(1)$$

Where C_1 and C_2 are mixing coefficients

ψ_a = wave function at Nucleus 'a'

ψ_b = wave function at Nucleus 'b'

To determine the value of C_1 and C_2 , on applying Normalization condition,

$$\begin{aligned} \int \psi_{MO}^2 d\lambda &= \int (C_1\psi_a + C_2\psi_b)^2 d\lambda = 1 \\ &= C_1^2 \int \psi_a^2 d\lambda + C_2^2 \int \psi_b^2 d\lambda + 2C_1C_2 \int \psi_a\psi_b d\lambda = 1 \end{aligned}$$

where $\int \psi_a\psi_b d\lambda = S_{ab}$

$$\int \psi_a^2 d\lambda = 1$$

$$\int \psi_b^2 d\lambda = 1$$

$$\int \psi_{MO}^2 d\lambda = C_1^2 + C_2^2 + 2C_1C_2S_{ab} = 1 \quad \dots(2)$$

if $C_1 = C_2$ then

$$C_1^2 + C_1^2 + 2C_1 \cdot C_1 Sab = 1$$

or

$$C_1^2 + C_1^2 + 2C_1^2 Sab = 1$$

or

$$C_1^2 (1 + 1 + 2Sab) = 1$$

or

$$C_1^2 = \frac{1}{2 + 2Sab}$$

or

$$\boxed{C_1 = \frac{1}{\sqrt{2(1 + Sab)}}} \quad \dots(3)$$

Then $\psi_s = \psi_1 = C_1(\psi_a + \psi_b)$

$$\boxed{\psi_s = \psi_1 = \frac{1(\psi_a + \psi_b)}{\sqrt{2(1 + Sab)}}} \quad \dots(4)$$

ψ_3 or ψ_1 is known as symmetrical wave function or Bonding molecular orbital wave function.

if $C_1 = -C_2$

then eq. (2) becomes

$$(-C_2)^2 + C_2^2 + 2(-C_2) \cdot (C_2) Sab = 1$$

or

$$C_2^2 + C_2^2 - 2C_2^2 Sab = 1$$

or

$$C_2^2 (1+1 - 2 Sab) = 1$$

or

$$C_2^2 = \frac{1}{(2 - 2Sab)}$$

or

$$C_2 = \frac{1}{\sqrt{2(1-Sab)}} \quad \dots(5)$$

Now $\psi_A = \psi_2 = C_2(\psi_a - \psi_b)$

$$\psi_A = \psi_2 = \frac{1}{\sqrt{2(1-Sab)}} (\psi_a - \psi_b) \quad \dots(6)$$

ψ_A is known as asymmetrical wave function or Antibonding Molecular Orbital wave function.

Q.2. Write down the molecular Orbital wave function for H_2^- Molecule anion.

Ans. H_2^- molecule anion contains three electron which may be labeled as 1, 2 and 3. It contains two Nuclei which may be designated as A and B. Wave function for molecular orbital is as follows :

$$\psi_{MO} = \psi_1 \psi_2 \psi_3$$

where $\psi_1 = C_1 \phi_A(1) + C_2 \phi_B(1)$

$$\psi_2 = C_3 \phi_A(2) + C_4 \phi_B(2)$$

$$\psi_3 = C_5 \phi_A(3) + C_6 \phi_B(3)$$

ψ = molecular orbital wave function

ϕ = Atomic orbital wave function

Q.3. Construct a molecular orbital wave function for the bond between H and Cl in HCl assuming that the bond is formed from the 1s electron of H-atom and a, 3P electron of Cl atom.

Ans. Let H atom be designated by A and Cl atom by B. Let the 1s electron of H-atom be labeled as electron 1 and 3P electron of Cl atom be labeled as electron 2.

ψ is a wave function for molecular orbital and ϕ for atomic orbital.

Molecular orbital may be written as follows :

$$\Psi_{MO} = \Psi_1 \Psi_2$$

Where $\Psi_1 = C_1\phi_A(1) + C_2\phi_B(1)$

$$\Psi_2 = C_3\phi_A(2) + C_4\phi_B(2)$$

Therefore $\Psi_{MO} = [C_1\phi_A(1) + C_2\phi_B(1)] [C_1\phi_A(2) + C_1\phi_B(2)]$
 $= C_1^2[\phi_A(1)\phi_A(2)] + C_1C_2[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)]$
 $+ C_2^2[\phi_B(1)\phi_B(2)]$

Here first and last terms are ionic whereas the middle terms are covalent.

Q.4. Write down the differences between Molecular Orbital theory and Valence bond theory.

Ans. Molecular Orbital theory and valence bond theory has following differences:

- (1) According to VBT, the atoms involved in the formation of molecule retains, a large number of their individual character whereas according to MoT, atomic orbitals lose their individual character.
- (2) In VBT, atomic orbitals are Mono-centric whereas in MoT molecular Orbitals are poly centric.
- (3) The electrons are treated in pairs in VB Model whereas in molecular orbital model electrons are imagined to be fed one by one into the molecule.
- (4) For molecule much larger than hydrogen, valence bond model has not been as successful as molecular orbital model for making exact calculations of molecular properties.

Q.5. What are hybrid Orbitals? Calculate the wave function for two SP hybrid Orbital.

Ans. The redistribution of energy by mixing different orbitals of an atom to give new orbitals of equivalent energy is called Hybridization. The New Orbitals thus formed are called hybrid Orbitals.

Wave function for SP - hybrid Orbitals:

In Be X_2 , Be atom is in SP hybridized. In Be ($1s^2, 2s^1, 2p_x^1$) 2s and $2p_x$ orbitals form two sp hybrid orbitals due to LCAO. These two sp hybrid orbitals are linear and have 180° bond angle. Wave function for these two hybrid orbitals are:-

$$\boxed{\psi_1 = a_1\psi_s + b_1\psi_p} \quad \dots(1)$$

$$\boxed{\psi_2 = a_2\psi_s + b_2\psi_p} \quad \dots(2)$$

Where ψ_1 and ψ_2 are two wave function of sp hybrid orbitals and a_1, a_2, b_1 and b_2 are mixing coefficients.

Calculate of Mixing Coefficients:

- (i) Since the electron density of S-orbital is equally divided amongst the two hybrid orbitals, so

$$a_1^2 = a_2^2 = \frac{1}{2}$$

$$\boxed{a_1 = a_2 = \frac{1}{\sqrt{2}}} \quad (3)$$

- (ii) Since ψ_1 is Normalized so

$$\begin{aligned} \int \psi_1^2 d\lambda &= \int (a_1\psi_s + b_1\psi_p)^2 d\lambda = 1 \\ &= a_1^2 \int \psi_s^2 d\lambda + b_1^2 \int \psi_p^2 d\lambda + 2a_1b_1 \int \psi_s\psi_p d\lambda = 1 \end{aligned}$$

Since atomic orbitals are orthogonal, so above expression may be written as follows-

$$a_1^2 + b_1^2 = 1$$

on placing the value of a_1^2

$$\frac{1}{2} + b_1^2 = 1$$

or

$$b_1^2 = \frac{1}{2}$$

or

$$\boxed{b_1 = \frac{1}{\sqrt{2}}}$$

...(4)

(iii) Since ψ_1 and ψ_2 are orthogonal so $a_1 a_2 + b_1 b_2 = 0$

On placing the value of a_1, a_2, b_1

$$\left(\frac{1}{\sqrt{2}}\right) \left(\frac{1}{\sqrt{2}}\right) + \left(\frac{1}{\sqrt{2}}\right) b_2 = 0$$

or

$$\frac{1}{2} + \frac{1}{\sqrt{2}} b_2 = 0$$

or

$$\frac{1}{\sqrt{2}} b_2 = -\frac{1}{2}$$

$$b_2 = \frac{-1}{2} \times \frac{\sqrt{2}}{1}$$

On multiplying and dividing with $\sqrt{2}$

$$b_2 = \frac{-1}{2} \frac{\sqrt{2}}{1} \times \frac{\sqrt{2}}{\sqrt{2}}$$

or

$$b_2 = -\frac{2}{2\sqrt{2}}$$

or

$$b_2 = \frac{1}{\sqrt{2}} \quad \dots(5)$$

On placing the values of mixing coefficients wave functions will be as follows-

$$\psi_1 = \frac{1}{\sqrt{2}} (\psi_s + \psi_p) \quad \dots(6)$$

$$\psi_2 = \frac{1}{\sqrt{2}} (\psi_s - \psi_p) \quad \dots(7)$$

Q.6. A bonding molecular orbital cannot be formed by the overlapping of S-orbital and perpendicular of P-orbital on molecular axis? Why?

Ans. Generally Z-axis is taken as molecular axis so only P_z atomic orbitals participate in overlapping with s orbital to form molecular orbitals. P_x and P_y orbitals will not overlap since they are perpendicular to Z-axis.

Q.7. Explain the difference between σ and π Molecular Orbitals.

- Ans.**
- (1) σ Molecular Orbitals are present at the molecular axis while π Molecular orbitals are present at perpendicular to the molecular axis.
 - (2) σ Molecular Orbitals has maximum value of ψ and ψ^2 at molecular axis while π molecular orbitals has zero value of ψ and ψ^2 at molecular axis.
 - (3) σ Molecular Orbitals are symmetric about nuclear axis while π molecular orbitals are not symmetric about internuclear axis.

Chapter 3

Spectroscopy

Q.1. What do you understand by Emission and Absorption Spectra. Describe their classification.

Ans. Emission Spectra: When a substance is heated upto incandescence or a gas electrically discharged then radiations are emitted. When these radiation are studied through a spectroscope, then obtained spectrum is called as "Emission Spectra"

Absorption Spectra: When radiations coming from the source are absorbed by a medium (solid, liquid, gas) then on analysing transmitted radiations through spectroscope, the obtained spectrum is known as "Absorption spectrum".

In such spectra dark lines or bands are obtained on the bright background. These bands or dark lines show that certain part of radiations have been absorbed by the medium.

On the basis of their structure emission and absorption spectra are classified as follows:-

- (A) Discontinuous spectrum
- (B) Continuous spectrum

(A) Continuous Spectrum: When spectrum is made up of diffused bands which can not be distinguished separately. Such type of spectrum is known as continuous emission spectrum.

(B) Discontinuous spectrum: Discontinuous spectrum is classified into two types

(i) Line spectrum

(ii) Band spectrum

(i) Line discontinuous spectrum:

That discontinuous spectrum in which diffused bright lines are observed in a series. Such type of spectra are also called as atomic spectra.

For example in the spectrum obtained from the sodium vapours have two bright lines at 5890\AA and 5890\AA wavelength. Since two elements doesn't give identical lines, therefore line spectra are the characteristic properties of atoms, it helps in detection of elements.

(ii) Band or Molecular spectrum:

That discontinuous spectrum in which group of lines are present. Band spectra are produce by molecules only. That's why these spectra are also known as Molecular Spectra.

Q.2. Write a short Note on Frank and Condon Principle.

Ans. It is a principle which gives information about the size and intensity of the absorption bands. According to this principle, an electronic transition in the molecule takes place so rapidly in a short time (10^{-15} Sec) that nucleus does not move i.e. position of the nucleus is still remain same. It's internuclear distance appreciably doesn't change during the transition.

Q.3. Explain Selection rule.

Ans. Electrons can move from the ground state energy level of a molecule to a higher energy level since the energy levels of a molecule are quantized, the amount of energy required to raise an electron in a given molecule from one level to a higher one is a fixed quantity. Only light

with exactly the frequency corresponding to the amount of energy will cause the electron to move to the higher level.

Promotion or transition of a given electron in a molecule between energy levels are governed by selection rules which state that certain transitions are "allowed" and certain are "forbidden" for e.g. Selection rule for rotational spectra is $\Delta J = \pm 1$ i.e. difference between two energy levels should be +1 or -1. (+) ve sign shows absorption of radiation (upward transition) where as (-ve) sign shows emission of radiation (downward transition).

Q.4. What is Raman Effect. Explain.

Ans. When a beam of monochromatic light passes through some organic liquid like benzene, toluene etc. the scattered light contain radiations with different frequencies than that of incident light. This is known as "Roman Effect". It was discovered by Indian Scientist Sir C.V. Raman in 1928.

Lines obtained due to Raman effect are known as Raman Lines. The Lines whose wavelengths are more than that of incident wavelength are called Stokes lines and those having shorter wavelength than that of incident wavelength are called Anti Stoke lines. These lines are generated because of exchange of energy between photons and molecules.

Q.5. Prove that rotational frequency for a diatomic molecule is

Ans. $\bar{E}_J = BJ(J+1)cm^{-1}$

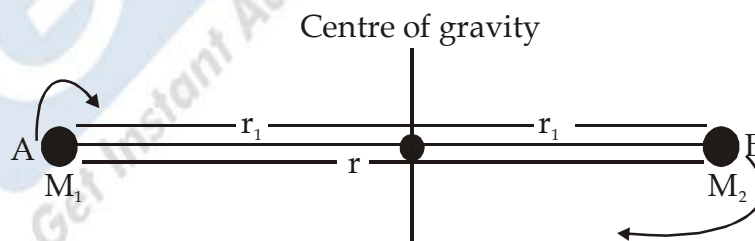


Fig. : Rotating diatomic molecule

Let us consider a diatomic molecule AB which has two atoms A and B of mass M_1 and M_2 respectively and 'r' is a distance between two atoms. r_1 and r_2 is the distance of atoms A and B from centre of gravity of the molecule AB about which the molecule rotates end over end.

The moment of inertia I

$$I = M_1 r_1^2 + M_2 r_2^2 \quad \dots(1)$$

or

$$I = M_1 r_1 \cdot r_1 + M_2 r_2 \cdot r_2 \quad \dots(2)$$

According to equilibrium of gravity

$$M_1 r_1 = m_2 r_2 \quad \dots(3)$$

On putting the value of $M_1 r_1$ and $M_2 r_2$ from equ (3) in eqn (2) we get

$$I = m_2 r_2 \cdot r_1 + m_1 r_1 \cdot r_2 \quad \dots(4)$$

or

$$I = r_1 r_2 (M_1 + M_2) \quad \dots(5)$$

Since $r = r_1 + r_2$

so $r_2 = r - r_1 \quad \dots(6)$

On placing the value of r_2 from eq. (6) in eq. (3) we get-

$$M_1 r_1 = M_2 (r - r_1)$$

or

$$M_1 r_1 = M_2 r - M_2 r_1$$

or

$$M_1 r_1 + M_2 r_1 = M_2 r$$

or

$$(M_1 + M_2)r_1 = M_2r$$

$$r_1 = \frac{M_2r}{M_1 + M_2} \quad \dots(7)$$

Similarly

$$r_1 = r - r_2$$

On placing this value of r_1 in eq. (3) We get-

$$M_1(r - r_2) = M_2r_2$$

or

$$M_1r - M_1r_2 = M_2r_2$$

or

$$M_2r_2 + M_1r_2 = M_1r$$

or

$$r_2(M_2 + M_1) = M_1r$$

or

$$r_2 = \frac{M_1r}{M_2 + M_1} \quad \dots(8)$$

Put the value of r_1 and r_2 from eq. (7) and (8) in eq. (5) we get

$$I = \frac{M_2r}{(M_1 + M_2)} \times \frac{M_1r}{(M_1 + M_2)} (M_1 + M_2)$$

or

$$I = \frac{M_1 \cdot M_2}{M_1 + M_2} r^2$$

Since $\mu = \frac{M_1 \cdot M_2}{M_1 + M_2}$ μ = reduced mass

so $I = \mu r^2$... (9)

Since $E_{\text{rot}} = \frac{1}{2} I \omega^2$... (10)

On dividing and multiplying it with I

$$E_{\text{rot}} = \frac{1}{2I} (I\omega)^2 \quad \dots(11)$$

where ω = Angular Velocity

I = Moment of inertia

Since $L = I\omega$

where L = Angular moment

So eq. (11) becomes -

$$E_{\text{rot}} = \frac{1}{2I} L^2 \quad \dots(12)$$

Since $L = \sqrt{J(J+1)} \frac{h}{2\pi}$

and $L^2 = J(J+1) \frac{h^2}{(2\pi)^2}$

where J = rotational quantum Number

So eq. (12) becomes -

$$E_{\text{rot}} = \frac{1}{2I} J(J+1) \frac{h^2}{4\pi^2} \quad \dots(13)$$

or

$$E_{\text{rot}} = \frac{h^2}{8\pi^2 I} J(J+1) \text{ Joule} \quad \dots(14)$$

$$\frac{E_{\text{rot}}}{hC} = \frac{h^2}{8\pi^2 I hC} J(J+1) \text{ CM}^{-1} \quad (15)$$

or

$$\bar{E}_{\text{rot}} = \frac{h}{8\pi^2 IC} J(J+1) \quad \dots(16)$$

Since $B = \frac{h}{8\pi^2 IC}$

where B = Rotational Constant

So $\bar{E}_{\text{rot}} = BJ(J+1) \text{ CM}^{-1}$

Thus eqn (17) is showing that rotational frequency is equal to the BJ (J+1) CM^{-1} .

Q.6. What do you understand by Degrees of freedom ?

Ans. Minimum Number of independent quantities or co-ordinates required to specify the position of a particle (or body) in space is called "degree of freedom". For e.g. - one particle require three co-ordinates to locate its position in space if one molecule of gas has N atoms then total degree of freedom will be 3N. When any diatomic or polyatomic linear molecule has two degrees of freedom for rotational motion and three degrees of freedom for translational motion then remaining (3N-5) are the degrees of freedom for vibrational motion.

Similarly A non-linear molecule which has three degrees of freedom for rotational motion and three degrees of freedom for translational motion then remaining (3N - 6) are the degree of freedom for vibrational motion.

Q.7. Why H_2 , N_2 and O_2 gases doesn't show IR spectrum ?

Ans. For molecule to show IR spectra, there should be a net change in its dipole moment due to absorption of radiation. Since H_2 , O_2 and N_2 molecules don't (change their dipole moment during vibration) have permanent dipole moment so they don't show IR spectra.

Q.8. Write down Born-oppenheimer approximation.

Ans. Nuclei are much heavier than electrons so nuclei move much more slowly than electrons therefore motion of nuclei are consider independently from the motion of the electrons. This statement is called the "BORN OPPENHEIMER APPROXIMATION".

According to Born-oppenheimer approximation, the total energy of molecule is given by following relation-

$$E_{\text{total}} = E_{\text{Tr}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}}$$

Where E_{Tr} = Translational energy

E_{rot} = Rotational energy

E_{vib} = Vibrational energy

E_{el} = electronic energy

$$E_{\text{total}} = E_{\text{Tr}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}}$$

This relation is showing that translation energy is very small so it total energy may be written as follows-

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

Q.9. Write a short note on Isotopic Effect.

Ans. When in a molecule a particular atom is replaced by its isotope then resulting molecule will be same in every aspect with original one except its atomic mass. Thus on isotopic substitution, total mass changes. Due to which moment of inertia (I) and rotational constant (B) value also changes.

$$B = \frac{h}{8\pi^2 IC}$$

or

$$B = \frac{h}{8\pi^2 \mu r^2 C}$$

or

$$B \propto \frac{1}{I} \propto \frac{1}{\mu}$$

From this relation, it is clear that as the value of rotational constant (B) decreases, value of reduced mass (μ) increases therefore separation between spectral lines is smaller for heavy isotopes.

For e.g.

For ^{12}CO

$$\bar{\nu} = 3.842 \text{ and } B = 1.921 \text{ cm}^{-1}$$

For ^{13}CO

$$\bar{\nu} = 3.673 \text{ and } B = 1.836 \text{ cm}^{-1}$$

Q.10. What do you understand by Hot Bands.

Ans. Those bands which are obtained due to transition from $V = 1$ to $V = 2, 3, 4, 5, \dots$ etc. at high temperature.

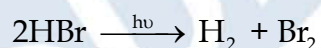
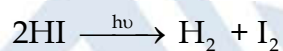
Since at room temperature, maximum molecules (or atoms) are present at zero vibrational level ($V = 0$) but when temperature increases, molecules shifted from zero vibrational level ($V = 0$) to first vibrational level ($V = 1$) Now transition starts from this higher energy state in place of $V = 0$. The lines (bands) obtained by this transition are called "HOT BANDS" and their intensity increases with temperature.

Chapter 4

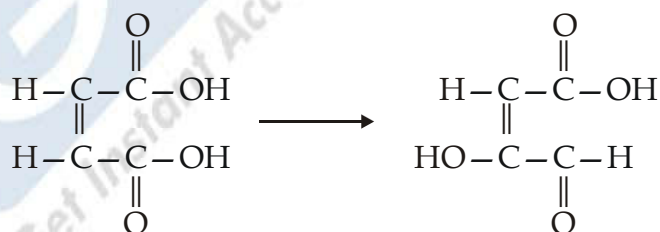
Photochemistry and Physical Properties

Q.1. What are thermal and Photochemical Reactions? Differentiate between thermal and Photochemical reactions.

Ans. Photochemical reactions are those reactions which are induced by the absorption of photons of suitable energy, the photon energies lie mostly in the visible and ultraviolet regions. For e.g.-Decomposition of Hydrogen Halides



and Isomerization of maleic acid to Fumaric acid



Maleic acid
(cis isomer)

Fumaric acid
(trans isomer)

But there are certain other type of reactions which can occur in the absence of light are known as thermal Reactions or Dark Reactions.

Difference between thermal and Photochemical Reactions:

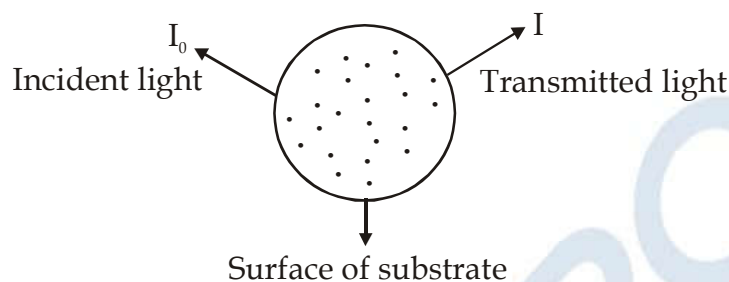
Thermal Reactions	Photochemical Reactions
(i) These reactions are accompanied by absorption or evolution of energy (heat).	These are initiated the absorption of photons in visible or ultraviolet region.
(ii) Light is not required for these reactions so these are called as Dark Reactions also.	These reactions takes place only in the presence of light.
(iii) In these reactions, Reactants get activation energy by collisions.	In these reaction reactants get required energy, through the absorption of light.
(iv) These reactions are accompanied by a decrease in free energy (ΔG) thermal reactions are spontaneous.	These reactions are accompanied by gain in free energy as some of the light energy is converted into free chemical energy of products. i.e. these are non-spontaneous.
(v) The rate of thermal reactions depend upon the temperature so temperature coefficient is high.	The rate of Photochemical reactions is independent of temperature so temperature coefficient is low.
(vi) These reactions may be accelerated by catalysts.	These reactions may be accelerated by photosensitizers which do not act as catalyst.
(vii) These reactions are simple in nature.	These reactions are not simple in nature.

Q.2. Explain Grothuss Draper's law and Stark Einstein Law (Law of Photochemical Equivalence).

Ans. There are two laws of photochemistry which decide the effect of radiation on chemical reactions which are as follows:

Grothuss Draper's Law: This law was enunciated by the two scientists T.V. Grothus and J.W. Draper. They found that all the light which incident

on a sample was not effective in bringing about a chemical change in reactant. According to the Grothus-Draper law (also called the Principle of Photochemical activation), only that light which is absorbed by a system can bring about a photochemical change.



$$E_A = S(I_0 - I)$$

Where E_A = Instein Absorption

S = Surface of Substrate

I_0 = incident light

I = Transmitted light

Q.3. Explain Stark-Einstein law (Law of Photochemical Equivalence).

Ans. The Stark-Einstein law of Photochemical equivalence:

This law (also called the Principle of quantum activation) was enunciated by Stark in 1908 and Einstein by 1912. The two scientists applied the concept of energy quantum to photochemical reactions. According to this law, one molecule is activated by the absorption of one quantum of radiation in primary (or first) step of a photochemical reaction.

Suppose ν is the frequency of the radiation absorbed. Then the corresponding quantum of energy absorbed per molecule will be $h\nu$. The energy E absorbed per mole of the reacting substance is therefore, given by

$$\therefore E = h\nu$$

$$\therefore E = N_A h\nu$$

$$\therefore \nu = \frac{C}{\lambda}$$

$$\therefore \boxed{E = N_A h \frac{C}{\lambda}}$$

Where C = Velocity of light

λ = wave length of light

The quantity E, i.e. the energy absorbed per mole of the reacting substance is called one Einstein. It is evident from the formula that its numerical value changes inversely as the value length of the light absorbed the shorter the wavelength, the greater the energy absorbed.

Q.4. Write Short Note on the following:-

- (i) Quantum Efficiency or yield
- (ii) Causes of High and Low quantum yield
- (iii) Photosensitization
- (iv) Fluorescence
- (v) Phosphorescence

Ans. (i) Quantum Efficiency: The quantum efficiency or yield is the fraction of absorbed light that goes to produce a particular result it is represented by ϕ . The quantum yield (ϕ) for a product P that is formed from a photoreaction of an initially excited molecule A can be expressed as

$$\phi = \frac{\text{Number of molecules of P formed}}{\text{Number of quanta absorbed by A}}$$

(ii) Causes of High and Low Quantum Yield: According to Einstein law, generally one photon activate only one molecule then quantum efficiency is given as follows:

$$\boxed{\phi = \frac{\text{No. of molecules reacting in a given time}}{\text{No. of photon absorbed in the same time}}}$$

So $\phi = 1$

But if one photon activates more than one molecule then $\phi > 1$ i.e. Quantum yield will be high.

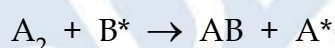
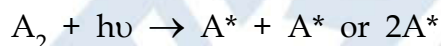
If one photon activates less than one molecule then $\phi < 1$ i.e. Quantum yield is low.

(A) Reasons for High Quantum yield

- (i) One molecule absorbs one photon and becomes excited molecule. Now this excited molecule excites other particles. As a result large number of reacting molecules forms, that's why quantum yield becomes high.



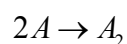
- (ii) Those reactions in which free radicals (highly reactive species) form for e.g. chain reactions in which a single photon, excites a molecule which converts into highly active free radicals which further activates other molecules.



- (iii) Sometimes, intermediate product acts as a catalyst and increases the rate of reaction due to which Quantum yield increases.
- (iv) Those reactions in which heat is involved can activate other molecules. Now these active molecules take part in a reaction without absorbing any radiation (Photon).

(B) Reasons for low Quantum yield: When ratio of the Number of molecules and absorbed photons is less than one then such reactions are known as Reactions of Low Quantum yield. There are various reasons for low quantum yield which are as follows:-

- (i) In some reactions, active molecules convert into deactivate molecules before formation of products.
- (ii) Sometimes as excited molecules collide with non-excited molecules, it loses its energy and is not able to form product.
- (iii) Sometimes, the energy of active molecules is not sufficient that's why they don't convert into products.
- (iv) If the primary photochemical process is reversed, it decreases the quantum yield of reaction.



if dissociated species recombine then quantum yield decreases.

(iii) Photo Sensitization: Photo Sensitization was discovered by Frank and Cario in 1922.

In some chemical reactions, reactant doesn't absorb the light radiation directly so third substance absorbs the light radiation and transfers to the reactant the third substance which itself doesn't undergo any change is called as the Photosensitization and the process is called as photosensitization.

Among the photosensitizer in common use are the atomic sensitizer such as Hg (Mercury), Cd (Cadmium), Zn (Zinc) and the molecular photosensitizer such as Benzophenone and sulphur dioxide (SO₂).

(iv) Fluorescence: A molecule in the S₁ state can drop to some low vibrational levels of the S₀ state all at once by giving off the energy in the form of light. This process, which generally happens within 10⁻⁹ sec, is called Fluorescence. The fluorescing molecules are drop from the lowest vibrational level of the S₁ state to the various vibrational levels of S₀.

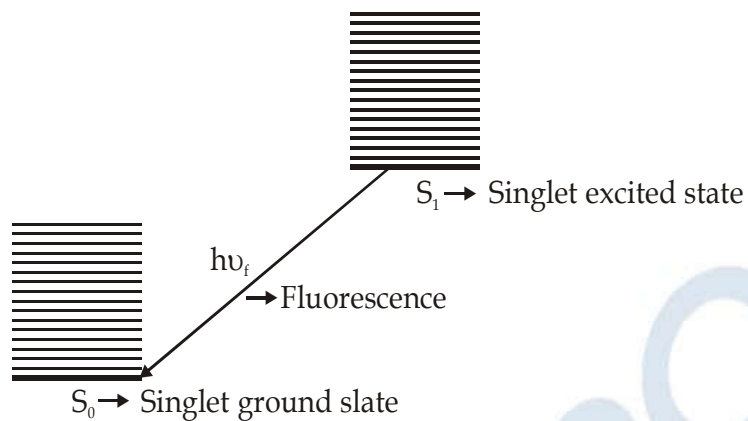


Fig. : Fluorescence

(v) Phosphorescence: A molecule in the T_1 state may return to the so state by giving up heat (intersystem crossing) or light (this is called phosphorescence).

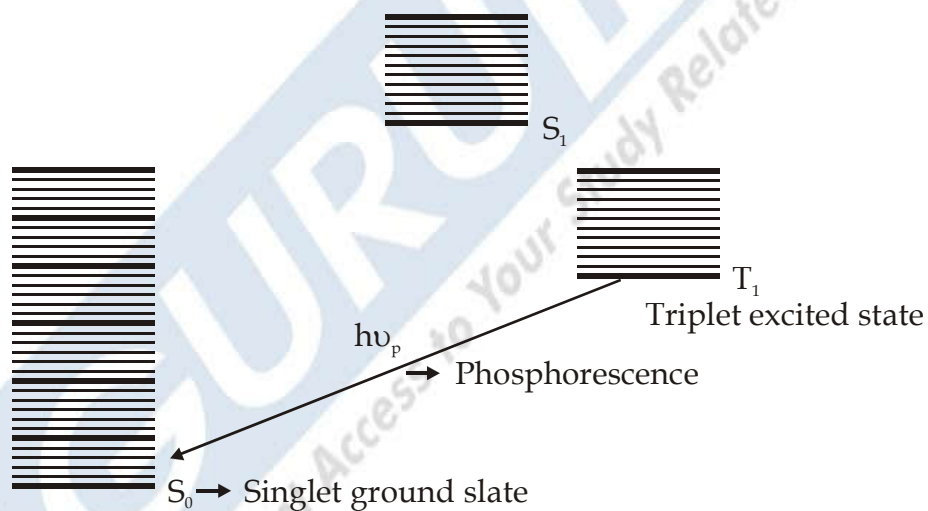


Fig. : Phosphorescence

Q.5. Write a Note on Jablonski diagram.

Ans. The Phenomena of fluorescece and phosphorescence are best explained with the help of the Jablonski diagram. It is not essential that the light

which is absorbed must bring about a photochemical change. The absorption of light may result in a number of other phenomena like Internal Conversion (IC), fluorescence, Intersystem crossing (ISC), phosphorescence. These pathways are shown in the following diagram:

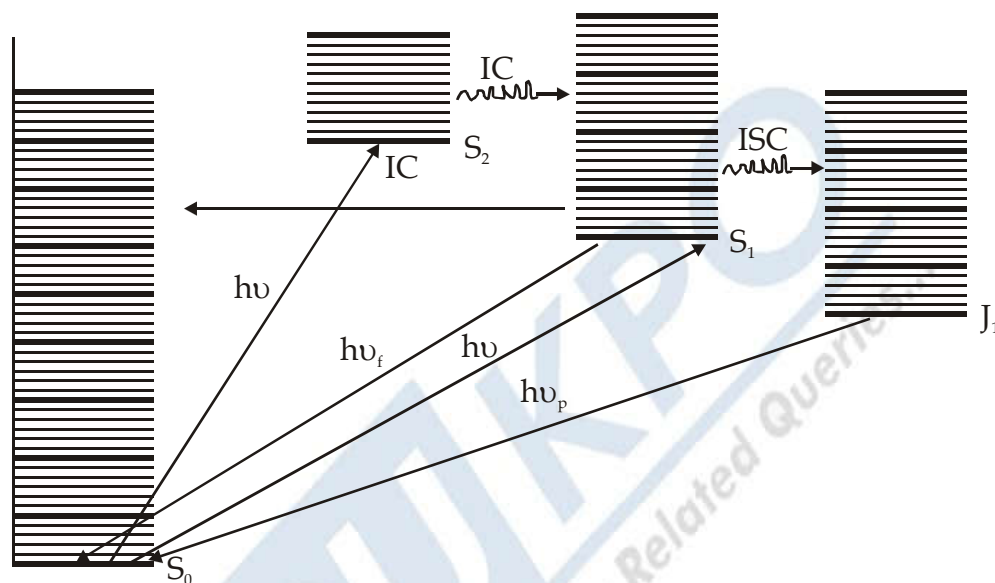


Fig. : Jablonski diagram showing transitions between excited states and the ground state. Radiative Process are shown by straight lines, Radiationless process by wavy lines

IC = Internal conversion

ISC = Intercrossing system

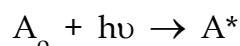
$h\nu_f$ = fluorescence

$h\nu_p$ = Phosphorescence

There are many electrons in the molecule spin of these electrons may be parallel or anti parallel if electrons are anti parallel [] then total spin $S = 0$ and spin multiplicity $2S + 1 = 1$ i.e. electrons are in singlet excited state. If electrons are parallel then total spin $S = 1$ and spin multiplicity $2S + 1 = 3$ i.e. electrons are in triplet excited state.

On absorption of light photon, the electron of the absorbing molecule

may jump from S_0 to S_1, S_2, S_3 singlet excited state depending upon the energy of the light photon absorbed, for each singlet excited state (S_1, S_2, S_3 , etc) there is a corresponding triplet excited state (T_1, T_2, T_3 etc) the molecule, whether in singlet or triplet excited state, is said to be activated thus,



where A_0 is the molecule in the ground state and A^* is the molecule in the excited state. The activated molecule returns to the ground state by dissipating its energy through the following types of processes.

(1) Non-radiative Transitions: Internal-conversion (IC) and ISC (inter-system crossing) processes are called non-radiative or radiation less transitions because these transitions doesn't involve the emission of any radiation, the energy of the activated molecule is dissipated in the form of heat through molecular collisions.

When transition of activated molecule takes place from higher excited states (S_3, S_2 or T_2, T_3) to the first excited state (S_1 or T_1) are said to be IC (internal conversion) while transitions takes place between different multiplicity states for example from S_2 to T_2 or S_1 to T_1 are said to be Inter-system crossing.

(2) Radiative Transitions: In these transitions activated molecule return from singlet excited state S_1 and triplet excited state T_1 to the ground state S_0 . Emission of radiation takes place in these transitions so such type of transitions are called as "Radiative Transitions".

In fluorescence process, transition takes place from the singlet excited state S_1 to the ground state (S_0) while in phosphorescence process, transition takes place from triplet, excited state T_1 to the ground state (S_0).

Q.6. What do you understand by Polarizability of Molecules? Derive Clausius-Mosotti equation.

Ans. When a molecule is placed in an electric field, a distortion occurs in the molecule which is due to the disturbance in the equilibrium state of the Nuclei and electrons of the atoms present in the molecule. Thus electric

field induces a dipole moment in the molecule. The induced dipole moment, μ_{ind} , is directly proportional to the strength (intensity) of the applied electric field, F i.e.

$$\mu_{\text{ind}} \propto F$$

$$\boxed{\mu_{\text{ind}} = \alpha_d F} \quad \dots(1)$$

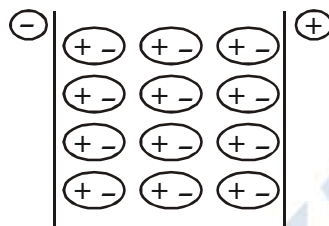


Fig. : Orientation of polar molecule in electric field

Where ' α ' is a proportionality constant known as "Polarizability of the molecule".

When medium between two charged plates is vacuum then molecules will be non-polar and strength of the electric field is E_0 . But when medium is polar (di-electric) then field strength produced by two charged plates is reduced to E because the dipole induced in the molecules acts opposite to the applied field.

Electrostatically, it may be written as follows-

$$E_0 = E + 4\pi I \quad \dots(2)$$

Where E_0 = electric strength in vacuum

E = electric strength in polar medium

I = di-electric polarization

On dividing both side with E

then
$$\boxed{\frac{E_0}{E} = \frac{E}{E} + 4\pi \frac{I}{E}}$$

or

$$\boxed{\frac{E_0}{E} = 1 + 4\pi \left(\frac{I}{E} \right)}$$

Since $\frac{E_0}{E} = \varepsilon$

ε = dielectric constant or relative permittivity

$$\boxed{\varepsilon = 1 + 4\pi \left(\frac{I}{E} \right)}$$

or

$$\boxed{E(\varepsilon - 1) = 4\pi I} \quad \dots(3)$$

where

I = di-electric polarization which is actually induced dipole-moment per unit volume of the di-electric (Polar Medium)

Since di -electric polarization (I) means induced polarization is equal to the product of induced dipole moment (μ_i) and No. of molecules (n)

$$\boxed{I = \mu_i \cdot n} \quad \dots(4)$$

On placing the value of μ_i from eq. (1) in eq. (4) we get-

$$\boxed{I = n\alpha_d \cdot F} \quad \dots(5)$$

In the derivation of clausius-Mosotti equation, it was assumed that each molecule occupies a small sphere and the charges in this spherical molecules are so uniformly distributed that before the application of the external field, the permanent dipole moment in the molecule is zero i.e. molecule is non-polar.

The intensity of electric field F is as follows-

$$\boxed{F = E_0 + \frac{4}{3}\pi I + (-4\pi I)}$$

or

$$F = E_0 + \frac{4}{3}\pi I - 4\pi I \quad \dots(6)$$

Where

 E_0 = stationary field between plates of condenser $\frac{4}{3}\pi I$ = induced charge on the surface of spherical cavity (molecule) $-4\pi I$ = Force produced due to di-electric in contact with plates which is opposite to applied first.

On placing the value from eq. (2) in eq. (6) we get

$$F = E + 4\pi I + \frac{4}{3}\pi I - 4\pi I$$

or

$$F = E + \frac{4}{3}\pi I \quad \dots(7)$$

On placing the value of $4\pi I$ from eq. (3) in eq. (7)

$$F = E + \frac{E(\epsilon - 1)}{3} \quad \dots(8)$$

or

$$F = E + \frac{E\epsilon}{3} - \frac{E}{3}$$

On rearranging

$$F = \left(\frac{E}{1} - \frac{E}{3} \right) + \frac{E\epsilon}{3}$$

or

$$F = \frac{3F - E}{3} + \frac{E\varepsilon}{3}$$

or

$$F = \frac{2F}{3} + \frac{F\varepsilon}{3}$$

On taking $\frac{E}{3}$ common

$$F = \frac{E}{3} (2 + \varepsilon) \quad \dots(9)$$

On placing the value of F from eq. (9) in eq. (5) we get

$$I = n \alpha d \cdot \frac{E}{3} (2 + \varepsilon) \quad \dots(10)$$

On placing the value of I from eqn (10) in eqn (3) we get

$$E(\varepsilon - 1) = 4\pi \cdot n \alpha d \frac{E}{3} (2 + \varepsilon)$$

or

$$\frac{(\varepsilon - 1)}{(2 + \varepsilon)} = \frac{4\pi}{3} n \alpha d \quad \dots(11)$$

Since $n = \frac{N_A e}{M}$

So eq. (11) becomes

$$\frac{\varepsilon - 1}{2 + \varepsilon} = \frac{4}{3} \pi \frac{N_A e}{M} \alpha d$$

or

$$\boxed{\left(\frac{\varepsilon-1}{2+\varepsilon}\right) \frac{M}{e} = \frac{4}{3} \pi \alpha_d N_A} \quad \dots(12)$$

Since $\frac{\varepsilon-1}{2+\varepsilon} \frac{M}{e} = P_m$

So eq. (12) becomes

$$\boxed{P_M = \frac{4}{3} \pi \alpha_d N_A} \quad \dots(13)$$

Where $P_M =$ Molar polarization

This eq. (13) is known as Clausius-Mosotti Equation".

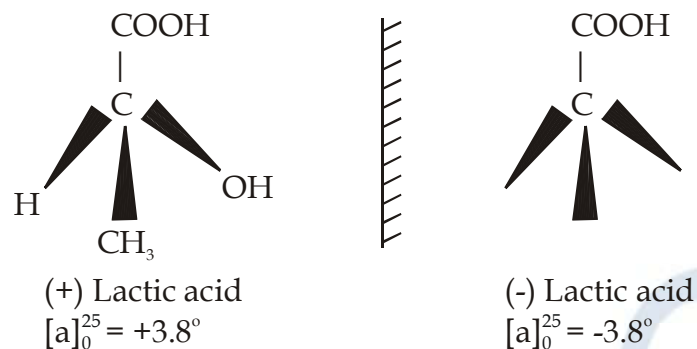
Q.7. Write a detailed essay on optical Activity.

Ans. Certain compounds rotate the plane of polarized light in a characteristic way when it is passed through their solutions. These compounds are referred to as **optically active compounds**. This activity is called as **optical activity**.

The angle of rotation by which the plane-polarized light is rotated, can be measured by using an instrument called **Polarimeter**.

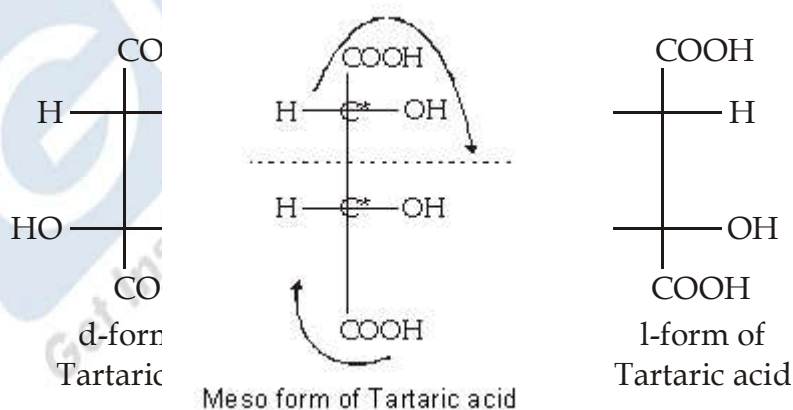
If the optically active substance rotates plane-polarized light to the right i.e. in clockwise direction, it is called **dextro rotatory** (Greek for right rotating) or d-form and it is indicated by placing a positive (+) sign before the degrees of rotation.

If it is rotated towards left, i.e. in anticlockwise direction, the substance is said to be laevo rotatory (Greek for left rotating) or l- form and (-) ve sign is placed before the degrees of rotation for e.g. lactic acid.



When both these enantiomers (Non-super imposable, are mixed in equal quantity then a mixture is form called as Racemic Mixture or r-Mixture it is represented by dl-form or (\pm) form. Racemic mixture is optically inactive because two form d and l have equal and opposite rotation which cancel each other.

When molecule has more than one chiral carbon atom (all the four substituent attached to it are different) then optical activity depends upon the arrangement of atoms or groups attached to the chiral carbon atom. For e.g. if molecule has two chiral carbon-atoms and both rotates the plane polarized light in same direction then optical activity increases if both rotates the plane polarized light in opposite direction then optical activity decreases if chiral carbon atom has identical groups then optical activity will be zero due to Internal Compensation of the rotation this form is known as "Meso form" and cannot be resolved into optically active forms thus, in tartaric acid, we have d, l, meso and racemic.



Q.8. Write down the applications of dipole moment.

Ans. Dipole moment has following advantages:

(i) It helps in distinction between polar and non-polar molecules.

If $\mu = 0$ then molecule will be non-polar like H_2 , N_2 , O_2 , Cl_2 , Co_2 , BF_3 , CH_4 etc. if $\mu \neq 0$ then molecule will be polar for example - HF , HCl , NH_3 , H_2O , NF_3 , etc.

(ii) It determines the ionic character in a molecule. In general, larger the value of dipole moment, more will be the ionic character.

$$\% \text{ ionic character} = \frac{\mu_{(\text{obs})}}{\mu_{(\text{cal.})}} \times 100$$

Chapter 5

Solutions, Dilute Solutions and Colligative Properties

Q.1. Define the following:

- (i) Mole fraction
- (ii) Cryoscopic Constant
- (iii) Isotonic solutions
- (iv) Osmotic Pressure

Ans. (i) Mole Fraction: The mole fraction of a substance in solution is the ratio between number of moles of the substance to the total number of moles of all the substances present in the solution.

If a solution contains n_A moles of substance A and n_B moles of substances B, then the mole fractions of these substances in the solution of A and B are as follows :

$$\text{Mole fraction of A } (X_A) = \frac{n_A}{n_A + n_B}$$

$$\text{Mole fraction of B } (X_B) = \frac{n_B}{n_A + n_B}$$

(ii) Cryoscopic Constant: Cryoscopic Constant is a depression of freezing point when 1 mole of solute is dissolved in 1 kg (1000 gm) of solvent.

It is represented by 'Kf'. It is also known as "Molar depression constant or molal freezing point.

$$\Delta T_f = K \left(\frac{\omega}{M} \right) \cdot \frac{1}{W}$$

Where ω = gms. Of solute

W = gms of solvent

M = Molecular weight of solute

Since $\frac{K}{1000} = K_f$

So $K = K_f \times 1000$

Therefore

$$\Delta T_f = K_f \cdot 1000 \left(\frac{\omega}{M} \right) \cdot \frac{1}{W}$$

or

$$\Delta T_f = K_f \cdot \text{Molality}$$

(iii) Isotonic Solution: When two solution have same osmotic pressure then they are said to be "Isotonic solutions".

(iv) Osmotic Pressure: Osmotic pressure is that pressure which causes movement of solvent particles through semi permeable membrane from lower concentration to higher concentration.

Q.2. What is difference between molarity and molality?

Ans. The Number of Moles (or gram molecules) of a solute dissolved in one litre of the solution is called as Molarity of the solution, while Number of moles of solute dissolved in 1000 gm of the solvent is called as Molality of the solution.

Q.3. What do you understand by Van't Hoff factor?

Ans. Van't Hoff factor (i) is a ratio of observed colligative properties and theoretical colligative properties.

$$i = \frac{\text{Observed value of colligative properties}}{\text{Theoretical value of colligative properties}}$$

Since all the Colligative properties of the solution depends upon Number of solute molecules in the solution. If the solute molecules in the dissolved state does not exist as single molecule then number of molecules will be change. Therefore the observed value of colligative properties like osmotic pressure, the lowering of vapour pressure, the elevation in boiling point and the depression in freezing point will also be change. This condition is known as deviation of colligative properties of the solution. To understand these deviations, van't Hoff introduced a factor i , called van't Hoff's factor.

Q.4. With reference to dilute solution explain relative lowering of vapour pressure and Mole fraction of solute. How are they related?

Ans. Vapour pressure is that pressure which is exerted by the vapour of the liquid on its surface at the equilibrium state. But when non-volatile and non-electrolyte solute is mixed with the pure solvent then vapour pressure of this solution gets lower than the pure solvent. This is known as "lowering in Vapour pressure".

If P is the vapour pressure of solvent and P_s is the vapour pressure of solution then $P - P_s$ is known as lowering in vapour pressure.

When this lowering in vapour pressure is divided by vapour pressure of pure solvent then it is called as "Relative lowering in Vapour pressure".

$\frac{P - P_s}{P}$ is a Relative lowering in vapour pressure.

According to Raoult's law, relative lowering in vapour pressure is equal to the mole fraction of the solute.

If "n" is number of moles of solute and "N" is Number of moles of solvent then

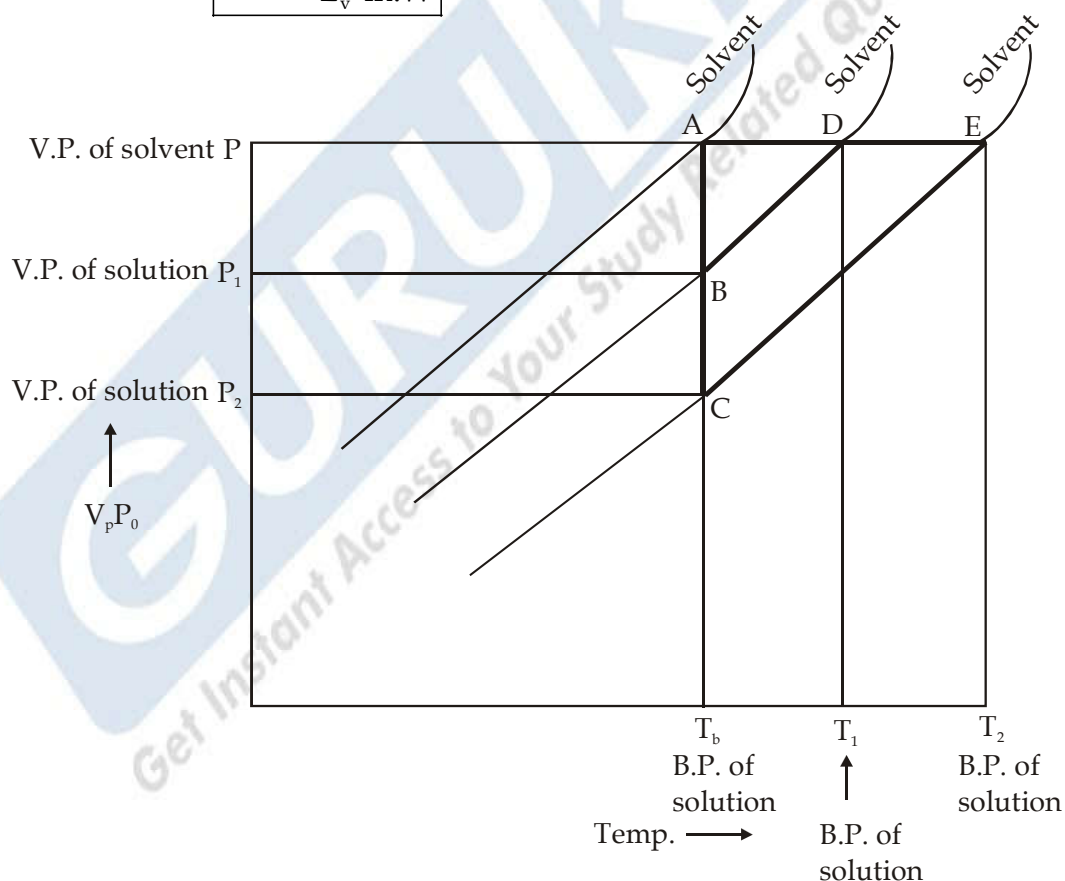
$$\frac{P - P_s}{P} = \frac{n}{n + N}$$

For very dilute solution, 'n' can be neglect in comparison to solvent therefore

$$\frac{P - P_s}{P} = \frac{n}{N}$$

Q.5. Derive the relationship between elevation in boiling point of solvent and molecular mass of a solute. Define molar elevation of constant.

Ans. Derivation of $\Delta T_b = \frac{RT_b^2 \omega}{L_v m.W}$



According to this figure, points B and D are making vapour pressure curve of the solution at T_b and T_1 temp. Since we know the vapour pressure at two temperatures, we can calculate Molar heat of vaporization (ΔH_v) of liquids from Clausius-Clapeyron equation as follows:

$$\ln \frac{P}{P_1} = \frac{\Delta H_v}{R} \left(\frac{1}{T_b} - \frac{1}{T_1} \right) = \frac{\Delta H_v}{R} \frac{(T_1 - T_b)}{(T_1 T_b)} \quad \dots(1)$$

Where

P = V.P. of solvent

P_1 = Vapour pressure of solution

T_b = Boiling point of solvent

T_1 = Boiling point of solution

Since $T_1 - T_b = \Delta T_b$ therefore

$$\ln \frac{P}{P_1} = \frac{\Delta H_v}{R} \frac{\Delta T_b}{T_1 T_b} \quad \dots(2)$$

Where

ΔT_b = elevation of Boiling point

For very dilute solution T_1 and T_b are not very much different so

$$T_1 \cdot T_b \approx T_b^2 \text{ So}$$

$$\ln \frac{P}{P_1} = \frac{\Delta H_v \cdot \Delta T_b}{RT_b^2} \quad \dots(3)$$

or

$$-\ln \frac{P_1}{P} = \frac{\Delta H_v \cdot \Delta T_b}{RT_b^2} \quad \dots(4)$$

or

$$\boxed{-\ln \frac{P - P + P_1}{P} = \frac{\Delta H_v \cdot \Delta T_b}{RT_b^2}} \quad \dots(5)$$

or

$$\boxed{-\ln \left(1 - \frac{P - P_1}{P} \right) = \frac{\Delta H_v \cdot \Delta T_b}{RT_b^2}} \quad \dots(6)$$

Since $\ln(1-x) = -x$ therefore

$$\boxed{-\left(-\frac{P - P_1}{P} \right) = \frac{\Delta H_v \cdot \Delta T_b}{RT_b^2}} \quad \dots(7)$$

or

$$\boxed{\frac{P - P_1}{P} = \frac{\Delta H_v \cdot \Delta T_b}{RT_b^2}} \quad \dots(8)$$

From Raoult's law for dilute solution

$$\frac{P - P_1}{P} = \frac{n}{N}$$

So eq. (8) becomes-

$$\boxed{\frac{n}{N} = \frac{H_v \cdot \Delta T_b}{RT_b^2}} \quad \dots(9)$$

or

$$\boxed{\Delta T_b = \frac{RT_b^2 \cdot n}{\Delta H_v \cdot N}} \quad \dots(10)$$

Where

n = Number of moles of solute molecule

N = Number of moles of solvent molecules.

$$\text{Since } n = \frac{\omega}{M} \quad \varepsilon N = \frac{W}{M}$$

$$\text{therefore } \boxed{\Delta T_b = \frac{RT_b^2}{\Delta H_v} \cdot \frac{\omega}{M} \times \frac{M}{W}} \quad \dots(11)$$

$$\text{Since } \frac{\Delta H_v}{M} = L_v \quad \text{or} \quad \frac{M}{\Delta H_v} = \frac{1}{L_v}$$

$$\text{So } \boxed{\Delta T_b = \frac{RT_b^2}{L_v} \cdot \frac{\omega}{M.W}} \quad \dots(12)$$

This expression (12) is showing the relationship between boiling point of solvent and molecular mass of a solute.

Q.6. What do you mean by Depression of Freezing point (Cryo-scopy):

Ans. On dissolving solid solute in the liquid solvent, its freezing point decreases. Freezing point of the liquid is that temperature at which vapour pressure of both the phase is equal i.e. both the phase (Solid, liquid) are in equilibrium in the solution. Freezing point of pure solvent, decreases on addition of solute viz vapour pressure of solution is less than that of the solvent therefore there is a difference between freezing point of solvent and solution.

$$\boxed{\text{Depression of freezing point} = \text{Freezing point of solvent} - \text{Freezing point of solution}}$$

This difference of freezing point is known as "depression of freezing Point" it is denoted by " T_F ".

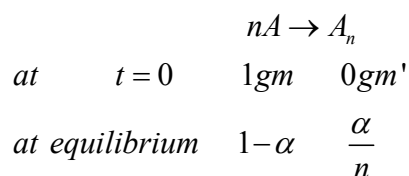
Q.7. Write a short Note on Association of Solute Molecules.

Ans. Many organic solutes like acetic acid in water, benzoic acid in benzene, phenol in benzene associates due to which number of solute particles decreases from the original number of particles. Apart from this, molecular

weight of associated particles increases from normal weight of single particle.

Let

'n' Number of A particles are associated and are forming A_n molecules



Where α = degree of Association

$$\frac{\alpha}{n} = \text{number of produced ions}$$

After association,

Total Number of particle = Number of undissociated particle + Number of produced ion

$$= \left[(1 - \alpha) + \frac{\alpha}{n} \right] \text{mole}$$

So

$$i = \frac{\text{Observed value of particle}}{\text{Theoretical value of particle}}$$

OR

$$i = \frac{\left[(1 - \alpha) + \frac{\alpha}{n} \right]}{1}$$

OR

$$i = \frac{1 - \alpha}{1} + \frac{\alpha}{n}$$

$$i = \frac{n(1-\alpha) + \alpha}{n}$$

or

$$in = n - n\alpha + \alpha$$

or

$$n\alpha = n + \alpha - in$$

or

$$n\alpha - \alpha = n - in$$

or

$$\alpha(n-1) = n(1-i)$$

or

$$\alpha = \frac{n(1-i)}{n-1}$$

Here α = degree of association
 i = Van't Hoff factor

S.No.	Osmosis	Diffusion
1.	Only solvent molecules passes through semi permeable membrane.	Solvent and solute both the particle flow from the high concentration to low concentration.
2.	Solvent flows from lower concentration solution to higher concentration solution.	Solvent and solute molecules flow from higher concentration of solution to lower concentration of solution till equilibrium.
3.	Osmosis takes place only in liquids.	Diffusion takes place in solutions as well as in gases.
4.	This process takes place only in one direction.	This process may takes place in any direction.

Q.8. What is the difference between Osmosis and diffusion.

Ans. Osmosis and diffusion has following differences:

Q.9. Numericals (1 to 4)

1. A solution is prepared by dissolving 43.0 gm of Naphthalene (Mm = 128.0 gm mol⁻¹) in 117.0 gm of benzene (Mm = 73 gm Mol⁻¹). Calculate the Mole fraction of the two components of the solution.

Ans. Number of Moles, $n = \frac{\omega}{M}$

ω = given mass of solute

M = Molar or molecular weight of solute

$$n_1 = \frac{117}{78} = 1.50 \text{ mol}$$

$$n_2 = \frac{43}{120} = .34 \text{ mol}$$

$$\text{Mole fraction of } n_1 (x_1) = \frac{n_1}{n_1 + n_2}$$

or

$$= \frac{1.50}{1.50 + .34}$$

$$= \frac{1.50}{1.84} = 0.8152$$

$$\text{Mole fraction of } n_2 (x_2) = \frac{n_2}{n_1 + n_2}$$

$$= \frac{.34}{1.50 + .34}$$

$$= \frac{.34}{1.84} = 0.185$$

2. Calculate the mole fraction of water in a mixture containing 9.0 gm water ($M_m = 18 \text{ gm mol}^{-1}$), 120 gm acetic acid ($M_m = 60 \text{ gm Mol}^{-1}$) and 115 gm ethanol ($M_m = 46 \text{ gm mol}^{-1}$).

Ans. n_1 (water) = $\frac{9}{18} = \frac{1}{2}$ mol

$$n_2 = (\text{acetic acid}) = \frac{120}{60} = 2 \text{ mol}$$

$$n_3 = (\text{ethanol}) = \frac{115}{46} = \frac{5}{2} \text{ mol}$$

$$n = n_1 + n_2 + n_3$$

$$= \frac{1}{2} + \frac{2}{1} + \frac{5}{2}$$

$$= \frac{1 + 4 + 5}{2}$$

$$= \frac{10}{2} = 5 \text{ mol}$$

$$\text{Mole fraction of water} = \frac{n_1}{n}$$

$$= \frac{1/2}{5}$$

$$= \frac{1}{2} \times \frac{1}{5} = \frac{1}{10} = .10$$

3. Concentrated hydrochloric acid contains 37% (by mass) HCl the density of its solution is 1.18 gm/ml. Calculate the molarity and molality of the

solution.

Ans. Weight (mass) of the solution = 100 gm.

$$\text{Density of the solution} = \frac{\text{Mass}}{\text{Volume}}$$

$$\begin{aligned} \text{So Volume of the solution} &= \frac{\text{Mass}}{\text{density}} \\ &= \frac{100}{1.18} = 85 \text{ml} \\ &= 85 \text{ cm}^3 = 0.085 \text{ dm}^3 \end{aligned}$$

$$n(\text{HCl}) = \frac{w}{M} = \frac{37}{36.5} = 1.01 \text{ mole}$$

$$\begin{aligned} \text{Molarity of HCl} &= \frac{\text{No. of moles}}{\text{Volume of solution}} \\ &= \frac{1.01}{.085 \text{ dm}^3} = 12.0 \text{ mol dm}^{-3} = 12.0 \text{ M} \end{aligned}$$

$$\begin{aligned} \text{Molality of HCl} &= \frac{\text{No. of moles}}{\text{Weight of solvent in kg}} \\ &= \frac{1.01}{.063} \\ &= 16.03 \text{ Mol Kg}^{-1} \\ &= 16.03 \text{ M} \end{aligned}$$

4. The density of 2.0 M solution of acetic acid ($M_m = 60 \text{ gm mol}^{-1}$) in water is 1.02 g mol^{-1} . Calculate the mole fraction of acetic acid.

Ans. Mass of acetic acid in 2.0 M acetic acid

Solution = 120 gm per dm^3 of the solution

$$\begin{aligned}\text{Mass of solution} &= \text{Volume} \times \text{density} \\ &= (1.00 \text{ dm}^3) (1.02 \text{ Kg dm}^{-3}) \\ &= 1.02 \text{ kg}\end{aligned}$$

$$\begin{aligned}\therefore \text{Mass of solvent (water)} &= 1020 \text{ gm} - 120 \text{ gm} \\ &= 900 \text{ gm}\end{aligned}$$

$$n(\text{acetic acid}) = \frac{120 \text{ gm}}{60 \text{ gm mol}^{-1}} = 2.0 \text{ mol}$$

$$n(\text{water}) = \frac{900 \text{ gm}}{18 \text{ gm mol}^{-1}} = 50.0 \text{ mol}$$

$$\text{Mole fraction of acetic acid} = \frac{2.0}{(50.0 + 2.0)} = 0.038^{-1}$$

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