III YEAR - V SEMESTER

COURSE CODE: 7BCH5C2

CORE COURSE - X - PHYSICAL CHEMISTRY – III

Unit I Spectroscopy

1.1. **Fundamentals of spectroscopy:** Definition, fundamentals of light such as wavelength, velocity, frequency, photons and definite energy of a photon. Electromagnetic spectrum. Fundamentals of materials such as equipartion principle and different types of movements of particles in a material and quantization of electronic, rotational, vibrational and spin energies. Selection rule. Beer – Lambert's law. Different types of spectroscopy and their applications.

1.2. **Rotational or microwave spectroscopy:** rigid rotator, derivation of equation for rotational constant for a diatomic molecule. Calculation of bond length and hence dipole moment and percentage of ionic character of a bond.

1.3. **Vibrational spectroscopy:** harmonic oscillator, zero – point energy, force constant. Hook's law. Anharmonicity, overtones, combination bands and Fermi resonance. Different types of vibrations. Factors determining the absorption frequency of a functional group. Effect of hydrogen bonding. Vibrational frequencies of different functional groups.

1.4. **Magnetic Resonance Spectroscopy:** Introduction to Nuclear magnetic resonance (nmr) and electron spin resonance spectroscopy (esr). NMR active elements and esr active species. Larmor precession and larmor frequency. Shielding and deshielding of protons, shielding constant , chemical shift and factors determine chemical shift. Spin – spin coupling and spin coupling constants. Chemically and magnetically equivalent nuclei. Introduction to esr and hyperfine structure.

Unit II Phase rule:

2.1. **Fundamentals:** Definition of phase, component and degrees of freedom. Derivation of phase rule. Phase diagram of one component systems such as water system and carbon dioxide.

2.2. **Two component systems:** Reduced phase rule. Classification of two component systems. Phase diagram of simple eutectic systems such as lead – silver, potassium iodide – water system. Phase diagram of two component systems that forms compounds with congruent melting point and incongruent melting points like ferric chloride – water system, copper sulphate – water system respectively.

2.3. **Solutions of non – electrolytes:** Solution of liquids in liquids. Ideal and non-ideal solutions. Raoult's law. Azeotropic mixtures. Steam distillation. Solubility of different types of partially miscible liquids, critical solution temperature (CST).

2.4. **Distribution law:** Distribution law and its validity. Derivation of distribution law. Deviation from distribution law. Applications of distribution law. Solvent extraction.

Unit III Chemical Kinetics

3.1. **Rate of a reaction:** Law of mass action. Rate and rate constant of a chemical reaction. Definitions and comparison of order and molecularity of a reaction. Rate equation for a zero – order reaction with examples.

3.2. **Rate of a first order reaction:** derivation of rate equation for a first order reaction. Examples for first order reactions. Pseudo first order reaction. Application of first order rate equation to acid catalysed ester hydrolysis and inversion of sucrose.

3.3. **Second order reactions:** derivation of rate equation or a second order reaction involving a single reactant and reactions involving two reactants. Examples for second order reactions. Applications of second order rate equation to saponification of esters.

3.4. Half – life of a reaction, relationship between initial concentration and half – life of reactions of different orders.

3.5. Methods for determining the order of a reaction: by using differential and integral rate equations. Half – life method. Isolation method.

3.6. **Theories of reaction rate:** Collision theory. Effect of temperature on the rate of a reaction – Arrhenius equation. Activated complex formation theory (absolute reaction rate theory) ARRT). Lindemann theory of unimolecular reactions.

Unit IV Photochemistry

4.1. **Fundamentals:** Photochemical reactions. Comparison of photochemical and thermal reactions. Consequences of light absorption – Jablonski diagram. Fluorescence and phosphorescence. Chemiluminescence.

4.2. **Laws of photochemistry:** Beer – Lambert law and its limitations. Grotthus – Draper law of photochemical activation. Stark – Einstein law of photochemical equivalence. Quantum efficiency and reasons for variation of quantum yield. Experimental determination of quantum yield.

4.3. **Kinetics of photochemical reactions:** Derivation of kinetic equation of a photochemical reaction. Rate equations for photochemical reactions between hydrogen and chlorine and hydrogen and bromine.

4.4. Lasers – population inversion, optical pumping, Q – switching

Unit V Group theory

5.1. **Fundamentals:** definition of a group. Various symmetry elements corresponding symmetry operations. Identification of possible symmetry elements molecule. Deduction of point group. Order of a group, sub – groups and classes.

5.2. Group multiplication table. Construction group multiplication tables for C C3V, C2h and D2h with suitable examples.

5.3. Matrix representation of symmetry operations.

5.4. Applications of symmetry operations and group theory in chemistry.

Text Books:

1. Advanced Physical Chemistry –Puri,Sharma & Pathania.
2. Physical Chemistry – G. W. Castellan 7th edition
3. Physical Chemistry – S. Glasstone
4. application of group theory in chemistry - F.A. Cotton

Books for Reference:

1. Physical Chemistry – Iran N Levin 6th edition
2. Physical Chemistry – Peter Atkins 7th edition
3. Physical Chemistry - Paul Monk 4th edition

Unit - I

Spectroscopy

Fundamentals of Spectroscopy :-

Spectroscopy defn :-

Spectroscopy is the study of interaction of light with matter. Spectroscopy is the use of absorption, emission or scattering of EMR by atoms or molecules to quantitatively or qualitatively study the atoms or molecules or to study physical processes.

Molecular spectroscopy is a powerful tool for learning about molecular structure and molecular energy levels.

Fundamentals of light :-

Wavelength :- λ

Distance bet. two successive crest or two successive troughs is called wavelength.

$$\lambda = \frac{1}{\bar{\nu}} = \frac{c}{\nu}$$

unit m, nm, Å, μm.

Wave number $\bar{\nu}$

No of waves per cm is called wave number

$$\bar{\nu} = \frac{1}{\lambda \text{ in cm}} = \frac{1}{a}$$

Unit cm^{-1}, m^{-1}

Frequency:

No of waves or cycles which pass a given point in one second is called frequency

$$\nu = \frac{c}{\lambda} = c\bar{\nu}$$

Unit $= s^{-1}$ Hz

Velocity

Velocity of a wave is defines as the distance travelled by the wave in one second. All electromagnetic radiation travels through vaccum at same velocity 3×10^8 m s^{-1}, but freq. and wavelength are different

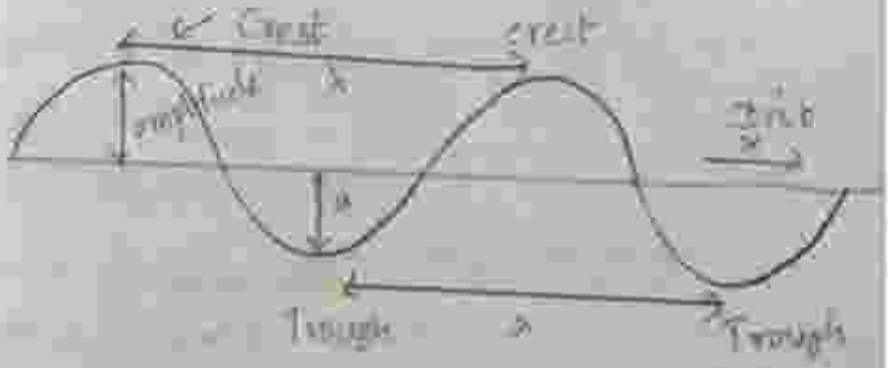
$$c = \nu\lambda = \frac{\nu}{\bar{\nu}}$$

Unit $= m\,s^{-1}$

Electromagnetic radiation EMR

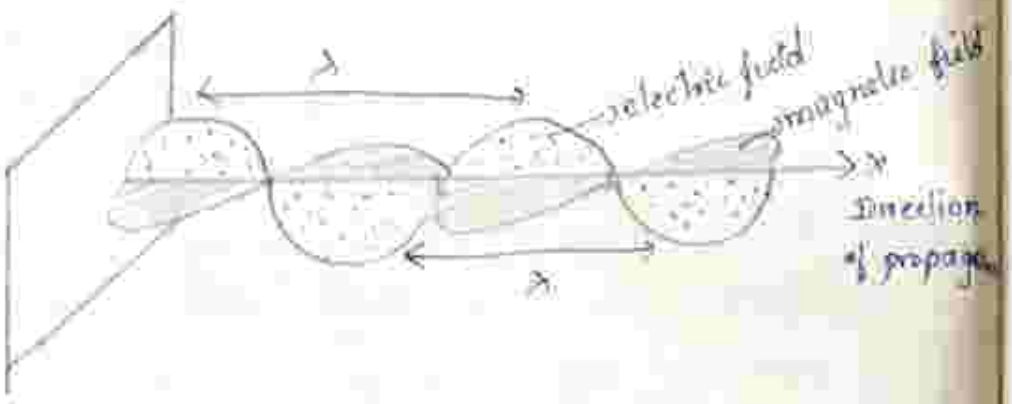
It is a form of energy emitted and absorbed by charged particles which exhibits wave like behaviour as it travels through space. EMR has both electric and magnetic field components which stand in a fixed ratio of intensity to each other and which oscillates in phase ⊥r to each other and ⊥r to the direction of energy and wave propagation. In a vacuum electromagnetic radiation propagates at a characteristic speed, the speed of light

Electromagnetic waves



Electromagnetic waves are self propagating mutual oscillation of electric and magnetic fields. Electromagnetic waves move electromagnetic energy through space and affect regions far remote from the origin of the energy. The propagation of electromagnetic energy is often referred to as radiation.

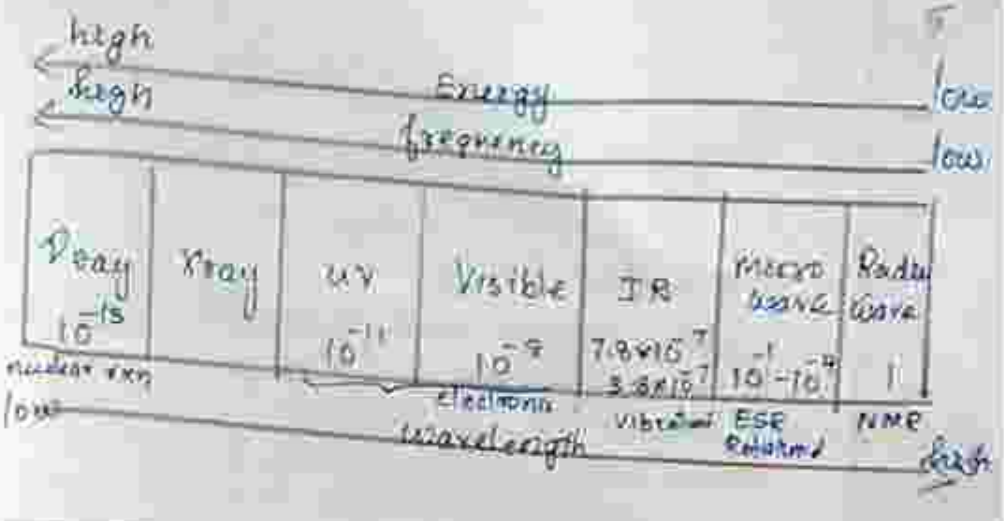
Electromagnetic waves are comprised of oscillating electric and magnetic field at right angles to each other and both are ⊥r to the direction of propagation of the wave. Electromagnetic waves differ in wavelength.



In an electromagnetic wave, the electric field E and magnetic field B oscillate ⊥r to each other and ⊥r to the direction of propagation of wave. It has prop. of a particle and a wave.

Electromagnetic spectrum.

It is the complete range of the wavelength s of electromagnetic radiation beginning with the longest radio waves and extending thro' visible light all the way to the extremely short gamma rays that are product of radio active atoms.



Spectroscopy classification :-

Atomic spectroscopy Molecular spectroscopy

Atomic spectroscopy :-

It is the study of interaction of EMR with atoms. The spectrum is called atomic spectrum.

Molecular spectroscopy :-

It is the study of interaction of EMR with molecules. The spectrum obtained is called molecular spectrum. It gives information about the structure and prop. of molecules such as bond length, bond angles, shapes, dipole moment etc.

A.

Born Oppenheimer approximation :-

Molecules possess different types of Energies

They are

translational energy (E_{trans})

Rotational energy (E_{rot})

Vibrational energy (E_{vib})

Electronic energy (E_{elec})

(i) Translational energy: (E_{tr})

It is the energy due to translational motion of the molecule.

(ii) Rotational energy (E_{rot})

It is the energy associated with the rotation of the molecule about its center of gravity

(iii) Vibrational energy: (E_{vib})

It is the energy associated with the vibrations (stretching, bending etc.) of the constituent atoms.

(iv) Electronic energy: (E_{elec}).

It is the energy associated with the transition of an electron from one level to another energy level.

Born oppenheimer.

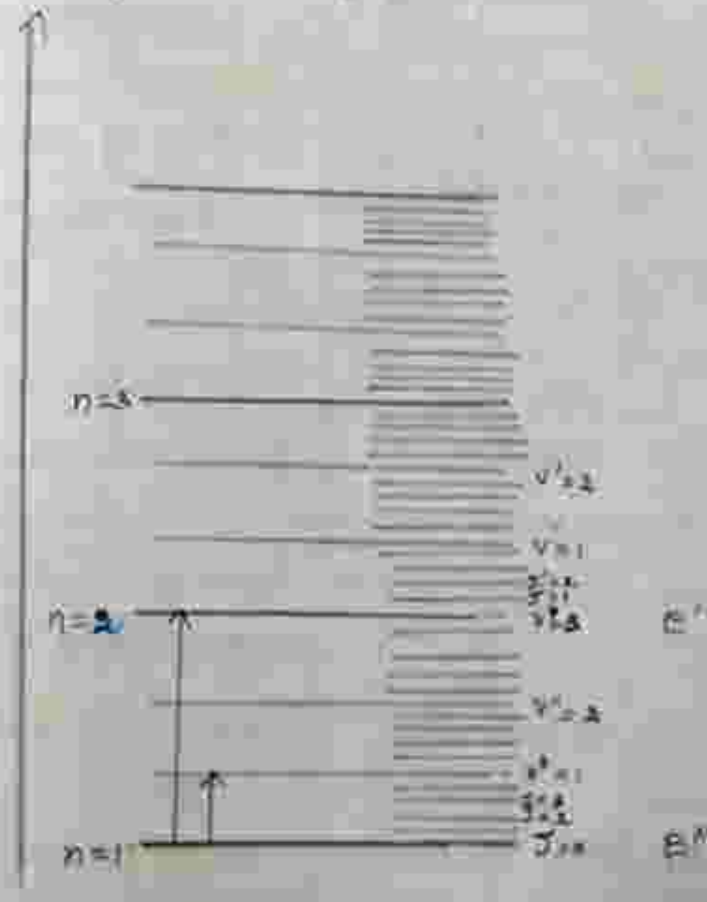
The Total energy of a molecule can be written as the sum of the contributions from the translational, rotational, vibrational, and electronic modes of motion.

$$E_{tot} = E_{tr} + E_{rot} + E_{vib} + E_{elc} \quad \text{— (1)}$$

$$E_{el} > E_{vib} > E_{rot} > E_{tr}.$$

The translational energy E_{tr} is not quantized and hence it is negligible compared with other energies. ∴ eqn (1) becomes $E_{total} = E_{el} + E_{vib} + E_{rot}$.

Energy level diagram.



$n = 1$ Ground electronic state

$n = 2$ excited electronic state

V'', V' = 0, 1, 2, 3 vibrational energy levels.

J'', J' = 0, 1, 2, 3 Rotational energy levels.

In general,

$$E_{elec} >> E_{vib} > E_{rot}$$

Thus energy transition may occur at different regions of the electromagnetic spectrum.

Different types of spectroscopy and its appli

Types	Spectral range	Range in Ems.	Application.
pure rot. (or) microwave	1-100 cm^{-1}	microwave	Moment of inertia, bond length.
Vibration - Rotation	400 - 4000 cm^{-1}	Infra red.	Identification of functio gp in unknown subsla
Electronic spectra	400-800 nm	uv visible	Types of transitions in org comp and inorg complexes
	200-400nm	UV	Presence and nature from π e- sys
	400-800nm	Visible	To detect conjug. sys. shape colour and magnetic natu complexes.

Raman	400 - 800nm	Visible	Structural det - of molecules. Complementary to I.R.
PES	UVPES Esca	uv Xray	Surface analysis Provide the atomic composition of a sample surface as well as the type of the existing che - bond and their distribution
NMR	6-100 MHz	Radio freq	Types of protons, carbon skeleton in a molecule
NQR	6-100 MHz	Radio freq	Information about environment of quadrupolar nuclei in solids
ESR	2-94 GHz	Microwave	Study of any species having at least one unpaired electrons
MB or NRF		Xray	Give information about chemical environment of local magnetic interactions and electric field gradient at nuclei
Mass spectra	70eV		Useful for obtaining at wt - of the molecule and finding molecular formula and its common fragments

Rotational or microwave spectroscopy:

1. Origin:

When the molecules are subjected to a radiation of wavelength 10^2 to 10 cm. the rotational spectra are obtained. It is due to rotational transition of the molecule. The rot spectra are observed in the Far IR region or microwave region

2. Condition:

The condn for obtaining a pure rot-spectrum is that the molecule should possess a permanent dipole moment.

Case - I:

Molecules like H_2, O_2, N_2, Cl_2, CO_2, C_6H_6 etc have no permanent charge separation and hence they have zero dipole moment ($\mu = 0$). Hence these molecules cannot interact with the electrical vector of the radiation. There will be neither absorption nor emission of energy by these molecules. Hence they are inactive in microwave.

Case - II :

Heteronuclear diatomic molecules like HBr, HCl, HI, CO, NO have permanent charge separation and possess permanent dipole moment. Hence these molecules can interact with electrical vector of the radn. This leads to absorption or emission of energy. Hence the molecules are active in microwave.

3. Selection rule :

For the pure rot transition, the selection rule is $\Delta J = \pm 1$ where J is the rot. qn. no.

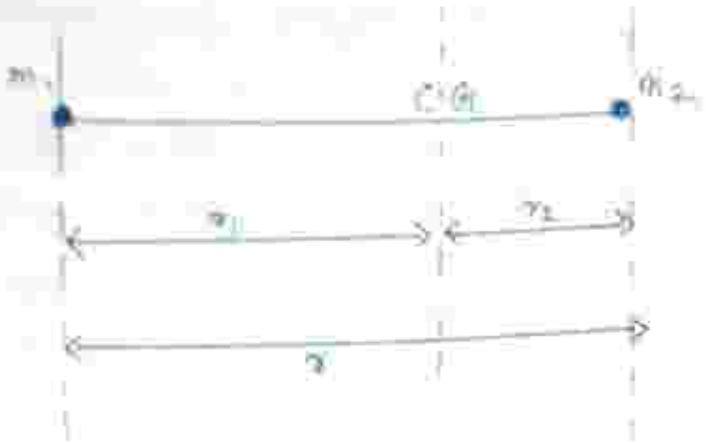
$\Delta J = +1$ absorption

$\Delta J = -1$ emission

Rigid rotator.

Derivation of eqn for rotational const for a diatomic molecule.

Let us consider a rigid diatomic molecule of masses m_1 and m_2 joined by a bond (x). The mole. is rotating about an axis passing thro' centre of gravity in such a way that its internuclear distance is const. It is approximated as a rigid rotator.



r = dist bet two nuclei

m_1 - mass of atom 1

m_2 - mass of atom 2

r_1 - dist bet m_1 and centre of gravity

r_2 - dist bet m_2 and centre of gravity.

The centre of gravity is defined by the following

$$m_1 r_1 = m_2 r_2 \quad \text{---} (1)$$

The moment of inertia I is defined as

$$I = m_1 r_1^2 + m_2 r_2^2$$

$$= m_1 r_1 \cdot r_1 + m_2 r_2 \cdot r_2 \quad \text{---} (2)$$

Sub the value of $m_1 r_1$ and $m_2 r_2$ in (2) we get

$$I = m_2 r_2 r_1 + m_1 r_1 r_2$$

$$I = (m_1 + m_2) r_1 r_2$$

But $r = r_1 + r_2 \Rightarrow r_2 = r - r_1$

$$\therefore m_1 r_1 = m_2 r_2 = m_2 (r - r_1)$$

$$m_1 r_1 = m_2 r - m_2 r_1$$

$$m_1 r_1 + m_2 r_1 = m_2 r$$

$$(m_1 + m_2) r_1 = m_2 r$$

$$r_1 = \frac{m_2}{m_1 + m_2} r$$

Similarly

$$r_2 = \frac{m_1}{m_1 + m_2} \cdot r.$$

Sub the values of r_1 and r_2 in eqn (3)

$$I = (m_1 + m_2)\left(\frac{m_2}{m_1 + m_2}\right) r \cdot \left(\frac{m_1}{m_1 + m_2}\right) r$$

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 \quad \text{— (4)}$$

$$I = \mu r^2 .$$

where μ is called the reduced mass of the molecule $= \frac{m_1 m_2}{m_1 + m_2}$.

By defn the angular momentum 'L' of a rotating molecule is gn by

$$L = I\omega .$$

where ω is its angular velocity. But the angular momentum is quantized whose values are gn by.

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

J = rot. qn. no. $= 0, 1, 2 \ldots$

The energy of rot. mole. is gn by

$$E = \frac{1}{2} I \omega^2 \quad \text{— (5)}$$

Hence the quantized value of the rot energy will be given by.

$$E_J = \frac{1}{2} I\omega^2 = \frac{(I\omega)^2}{2I} = \frac{L^2}{2I} \quad \text{--- (6)}$$

Sub L in (6).

$$E_J = J(J+1)\frac{h^2}{4\pi^2} \cdot \frac{1}{2I}$$

$$E_J = \frac{h^2}{8\pi^2 I} \cdot J(J+1) \text{ Joule} \quad \text{--- (7)}$$

where $J = 0, 1, 2 \ldots$

Div (7) by hc, we get

$$\frac{E_J}{hc} = \frac{h^2}{8\pi^2 I} \cdot \frac{1}{hc} \cdot J(J+1) \quad \text{--- (8)}$$

$$F(J) = \bar{E}_J \text{ or } \bar{\nu} = \frac{h}{8\pi^2 Ic} J(J+1)$$

$$= \bar{B} J(J+1) \quad \text{--- (9)}$$

where $F(J)$ is rot term.

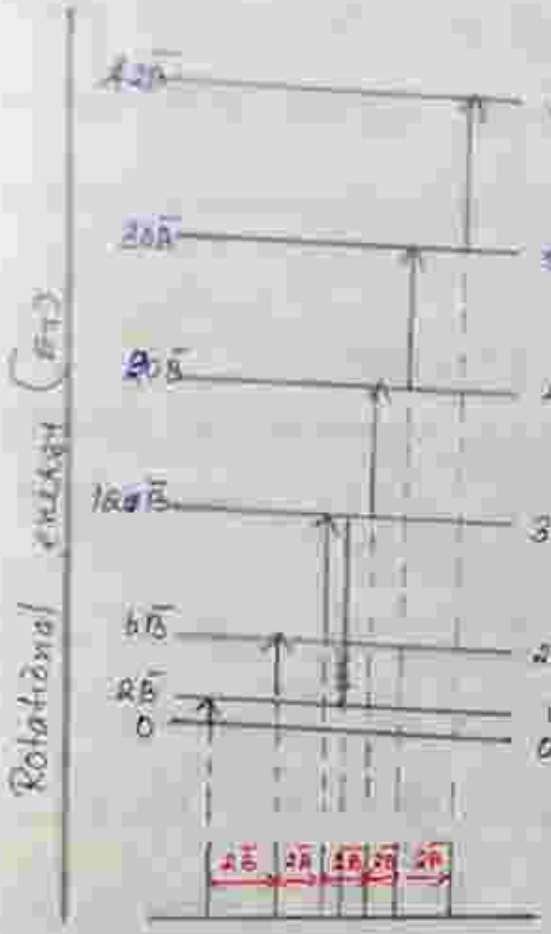
$E(J)$ is rot. energy level in cm^{-1} and

$\bar{B} = \frac{h}{8\pi^2 Ic}$ is rot const.

Sub J in (9) we get

J	0	1	2	3	4	5
E_J	0	$2\bar{B}$	$6\bar{B}$	$12\bar{B}$	$20\bar{B}$	$30\bar{B}$

Energy level of a rigid diatomic molecule is given by



For the transition taking place from J to J+1 the wave freq. is given by

$$\bar{\nu}_{J \to J+1} = \bar{\nu}_{J+1} - \bar{\nu}_J$$

$$= \bar{B}(J+1)(J+2) - \bar{B}J(J+1)$$

$$= \bar{B}(J+1)\,(J+2-J)$$

$$\bar{\nu}_{J \to J+1} = 2\bar{B}(J+1)$$

Thus $\bar{\nu}_{0 \to 1} = 2\bar{B}$

$\bar{\nu}_{(1 \to 2)} = 4\bar{B}$

$\bar{\nu}_{(2 \to 3)} = 6\bar{B}$

$\bar{\nu}_{(3 \to 4)} = 8\bar{B}$

Thus the rot spectrum of a rigid diatomic mole consists of a series of lines at $2\bar{B}$, $4\bar{B}$, $6\bar{B}$, $8\bar{B}$ etc. These lines are separated by $2\bar{B}$. So the lines are equally spaced.

Intensity of rot lines

The relative intensities of spectral lines depend upon the relative populations of the energy levels. It is known that even at room temp. many of the diatomic molecules are present in the excited state energy level. Since the energy level populations is given by the Boltzmann distribution, the intensity of the rot. lines is prop to the degeneracy and the Boltzmann factor i.e

$$\text{Intensity at } \frac{N_J}{N_0} = g_J e^{-E_J/kT} \quad \text{---(1)}$$

where g_J is the degeneracy of the J^{th} level and E_J is the corresponding energy level.

Rot. energy levels are degenerate and its degeneracy is $2J+1$. Hence eqn (1) becomes

$$N_J = N_0(2J+1) \exp\left[\frac{-BhcJ(J+1)}{kT}\right] \quad -(2)$$

Using this eqn. the relative no. of molecules present in any level can be calculated.

Applications of microwave spectroscopy

(1) Det. of bond length of a diatomic molecule:

From the microwave spectrum, the frequency for first band or freq. separation $2\bar{B}$ can be calculated

$$\bar{\nu} = 2\bar{B} = \frac{2h}{8\pi^2 I c} \text{ or } \frac{}{} \text{ in}$$

$$\Delta\bar{\nu} = 2\bar{B} = \frac{2h}{8\pi^2 I c}$$

either $\bar{\nu}$ or $\Delta\bar{\nu}$ the moment of inertia I can be calculated

$$I = \frac{h}{8\pi^2 Bc}$$

then knowing the masses of the atoms present in the diatomic molecule, it is possible to calculate the bond length as follows:

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

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

Dipole moment and % of ionic character

The measure of net molecular polarity is called dipole moment (μ).

It can calculated as the part of the charge and the distance between the charges

$$\mu = Q \times r$$

unit : debye - D

$$1D = 3.336 \times 10^{-30} \text{ C.m.}$$

eg :

The dipole moment of HCl is 1.03 D and the bond length is 127 pm. What is the percent ionic character of the HCl bond.

We can assume that the mole is 100% ionic

$$\therefore \mu = Q \times r$$

$$\mu = (1.60 \times 10^{-19} \text{ C}) \, 1.27 \times 10^{-12} \text{ m}$$

$$= 6.09 \text{ D}$$

The actual D.M measured for this molecule is 1.03 D. So the mole is not completely ionic

$$\frac{1.03 \text{ D}}{6.09 \text{ D}} \times 100\% = 16.9\%$$

D.M are measured experimentally.

	D.M
NaCl	9.0
CH_3Cl	1.87
H_2O	1.85
NH_3	1.47.
CO_2	0
CCl_4	0.

% of ionic character

Fraug ionic compd having some % of covalent character due to Fajans rule. The % of ionic character in a compd having some covalent character can be cal. by the foll eqn.

$$\text{the \% ionic character} = \frac{\text{observed dipole moment}}{\text{Cal. dipole moment assuming}} \times 100$$

Eg:

D.M of KCl is 3.336×10^{-29} Coulomb metre which indicates that it is highly polar molecule. The inter atomic dist. between K^+ and Cl^- is 2.6×10^{-10} m. Cal. D.M of KCl mole if there were opp. charges one fundamental unit located at each nucleus. Cal. % ionic character

D.M of KCl = 3.336×10^{-29} coul

Internal dis bet K^+ & Cl^- = 2.6×10^{-10}

Cal. % ionic char

D.M μ = e x d

= $1.602 \times 10^{-19} \times 2.6 \times 10^{-10}$

= 4.1652×10^{-29}

% of ionic character = $\frac{\text{Ob. D.M}}{\text{Cal. D.M}}$

= $\frac{3.336 \times 10^{-29}}{4.165 \times 10^{-29}}$

= 80.09 %.

Vibrational spectroscopy:

Origin:

When the molecules are subjected to a radiation of wavelength 10^{-3} to 10^{-5} cm. The vibrational spectra are obtained This is due to vibrational transition of the molecule. The spectra are observed in mid and near IR region

Condition:

The condn for obtaining a vibrational spectrum is that the molecules should

possess a dipole moment during vibration. For eg. in case of homonuclear diatomic molecules like H_2, N_2, O_2 etc which have stretching motion of vib. and no bending motion, the dipole moment does not change during vibration hence these molecules do not give vibrational spectra & they are said to be Infrared inactive.

In heteronuclear diatomic molecules like HCl, CO, NO etc and polyatomic molecules like CO_2, H_2O, CH_4, C_2H_4 etc which possess change in DM during some mode of vibration. Hence they give vibrational spectra and are said to be IR active.

3 Selection rule:

$$\Delta V = \pm 1$$

where V is vib qn no $= 0, 1, 2 \ldots$

$\Delta V = +1 \Rightarrow$ Absorption

$\Delta V = -1 \Rightarrow$ Emission

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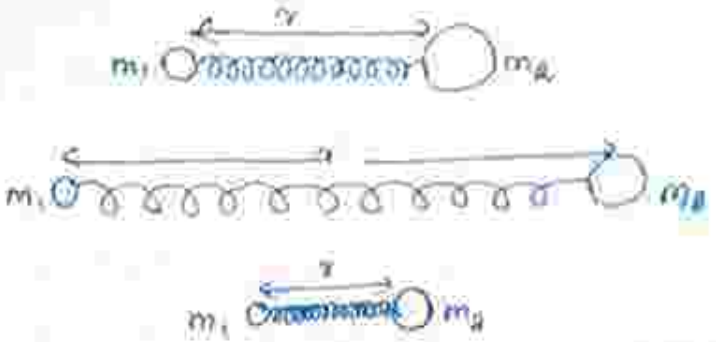
4 SIMPLE HARMONIC OSCILLATOR

Expression for vib energy of a diatomic molecule:

Let us assume that a diatomic mole

masses m_1 and m_2 joined by a chemical bond vibrates as a simple harmonic oscillator (SHO) The masses m_1 and m_2 vibrate back and forth relative to their centre of gravity.



The vibrational freq. of reduced mass μ connected by a spring of force const k is

$$\bar{\nu} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \ s^{-1} \quad — (1)$$

where $\bar{\nu}$ is vib freq.

k - force const. ($N m^{-1}$ or $dyne\,cm^{-1}$)

μ - Reduced mass $= \frac{m_1 m_2}{m_1 + m_2}$

$\therefore$ (1) by c we get

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \ cm^{-1} \quad — (2)$$

The P.E of SHO is a fn. of Hooke law eqn is

$$V_x = \frac{1}{2} k x^2 \quad — (3)$$

$x = r - r_e$ is the displacement

r_e = equilibrium bond length

r = bond length.

From quantum mechanics, the vib energy levels are gn by $E_{vib} = (v + \frac{1}{2}) h\nu$ Joules — (4)

where v is the vib. qm. no $= 0, 1, 2, \ldots$

ν is the vib freq. given by (1)

$\div$ (4) by hc,

$$\frac{E_{vib}}{hc} = \bar{E}_{vib} = \left(v + \tfrac{1}{2}\right) \cdot \frac{h\nu}{hc}$$

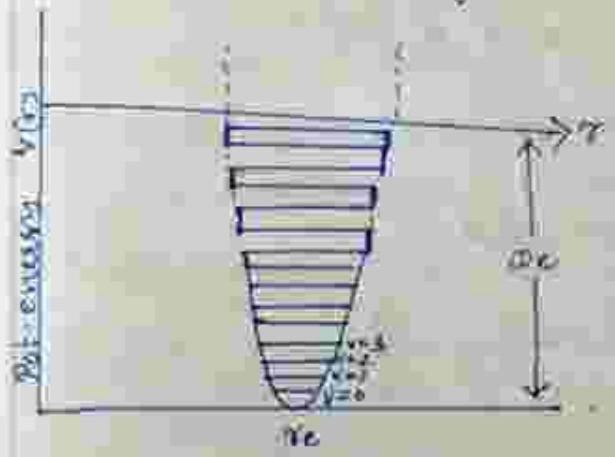
$$= \left(v + \tfrac{1}{2}\right) \frac{\nu}{c}$$

$$G(v) = \bar{E}_{vib} = \left(v + \tfrac{1}{2}\right) \omega_e \text{ cm}^{-1} \quad — (5).$$

where ω_e is the spectroscopic vib freq. and $G(v)$ is called the vibrational term.

v	0	1	2	3	4
E_{vib}	$\frac{h\nu}{2}$	$\frac{3h\nu}{2}$	$\frac{5h\nu}{2}$	$\frac{7h\nu}{2}$	$\frac{9h\nu}{2}$

The vibrational energy levels of a harmonic oscillator are equally spaced



For $v = 0$ the energy is $\frac{1}{2}h\nu = \frac{1}{2}\omega_e$.

The energy is called zero point energy.

For a transition taking place from v'' to v' the vib. ν is given by.

$$\bar{\nu} = \Delta \overline{E}_{\substack{\text{Vib} \\ \nu \to \nu+1}} = \overline{E}_{\text{Vib}}(\nu+1) - \overline{E}_{\text{Vib}}$$

$$= \left(\nu+1+\frac{1}{2}\right)\omega_e - \left(\nu+\frac{1}{2}\right)\omega_e$$

$$\bar{\nu}_{\nu \to \nu+1} = \omega_e \quad \text{— (b)}$$

The vib. freq. corresponding to the transition $0 \to 1$ is called fundamental vib freq.

Force constant :-

W.k.T $\quad \bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ — (3)

where $\bar{\nu}$ is vib. freq. in cm^{-1}

c is the velocity of light

μ is red. mass

Squaring both sides,

$$(\bar{\nu})^2 = \frac{1}{4\pi^2 c^2}\cdot\frac{k}{\mu}$$

$$\therefore k = 4\pi^2 c^2 (\bar{\nu})^2 \mu$$

Thus force const. is calculated.

Hooke's law

Hooke's law describes the relationship of freq to mass and bond length. The freq of bond vibration can be derived from Hooke's law which describes the motion of a vibrating spring

$$F = \ddot{y} = k\sqrt{\frac{f}{m}}$$

f - force const.
m - mass
k = const.

stronger bond = higher ?
smaller mass = higher ?

Anharmonic oscillator

When a molecule is undergoing simple harmonic oscillations, the restoring force of the harmonic vibrations is directly prop. to the displacement and the energy of the harmonic oscillator is given by

$$E_{vib} = (v + 1/2)h\nu$$

$$\text{or } E_{vib} = (v + 1/2)h\omega_e \text{ cm}^{-1}$$

v - vib. qn. no.
ω_e - eq. vib. freq.

But the movement of a real oscillator is not perfectly harmonic. As the displacement increases, the restoring force becomes weaker

and for large amplitude of vibrations, the molecules must dissociate into atoms. Such an oscillator is said to be anharmonic oscillator.

(i) Selection rule:

$$\Delta v = \pm 1, \pm 2, \pm 3 \ldots$$

The transition from $v=0$ to $v=1$ is found to be most intense and is called the fundamental absorption. The transition from $v=0$ to $v=2$ has a very weak intensity and is called first overtone and the transition from $v=0$ to $v=3$ is called second overtone which has still weaker intensity.

(ii) Energy of the anharmonic oscillator.

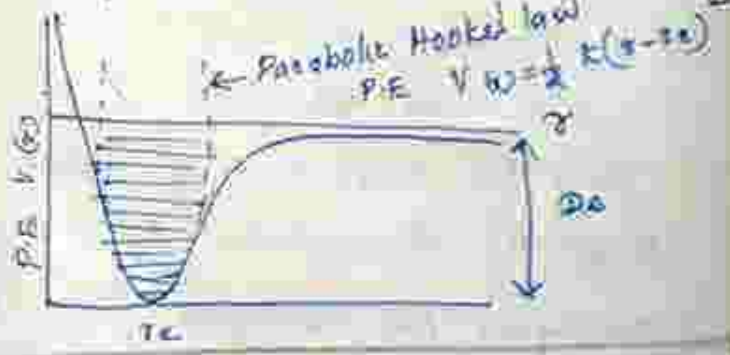
According to Morse, the energy of an anharmonic oscillator is given by

$$E_{vib} = (v+1/2)\omega_e - (v+1/2)^2 \omega_e x_e$$

$\omega_e x_e$ - anharmonicity const

ω_e - eq. vib freq

D_e - eq. diss. energy



Over tones :-

Overtones are bands appeared in IR spectra of molecules due to their anharmonic vibration. These are multiples of a fundamental frequency.

Ex- For H_2O in addn to $\bar{\nu}_1$, $\bar{\nu}_2$ and $\bar{\nu}_3$ $2\bar{\nu}_2$ are observed

Combination band.

Combination bands are other additional band observed in IR spectra due to anharmonic vibration of molecules. These are sum of two or more fundamental frequencies or overtones.

Ex for H_2O, in addition to $\bar{\nu}_1$, $\bar{\nu}_2$ and $\bar{\nu}_3$, $\bar{\nu}_2$, $\bar{\nu}_3$ are observed. These bands have low intensity

Fermi resonance :-

When fundamental mode of vibration becomes degenerate with an overtone or combination band, the intensity of the overtone or combination band is enhanced by a resonance phenomena called Fermi resonance.

Eg

For CO_2, there are 4 vib

$\bar{\nu}_1$, $\bar{\nu}_2$ and $\bar{\nu}_3$ · out of these ·

two are degenerate pair ($\bar{\nu}_2$).

The vibration $\bar{\nu}_2$ corresponds to bending vibration. overtone is $2\bar{\nu}_2 = 2 \times 661 = 1332\ cm^{-1}$

$\bar{\nu}_1$ ⇒ sym. stretching.

But $\bar{\nu}_1$ & $\bar{\nu}_2$ are not observed in IR spectra. But they are observed in Raman spectra.

Due to Fermi resonance, the higher freq. is raised and the lower freq. is depressed i.e $2\bar{\nu}_2$

1334 $2\bar{\nu}_2$ ⟶ 1388 cm^{-1} raised

$\bar{\nu}_1$ = 1285 cm^{-1} lowered

1330

Different types of vibrations :

There are two types of normal modes of vib

① stretching < symmetric stretching
Asymmetric stretching

② Bending < In plane bend vib < Scissoring
Rocking
Out of plane bend vib < Wagging
Twisting

Stretching vibration :

In this type the dist- bet the two atoms (bond length) increases or decreases but the atoms remains in the same bond axis. Stretching vib require higher energy and occur at higher freq. Stretching vibration are 2 types.

① Symmetric stretching

In this type, both the atoms move in and out simultaneously

② Asymmetrical stretching

In this type, one atom moves in and the other moves out as shown here

⑤ Bending vibrations :

Here the distance bet the atoms remains const. but the position of the atom changes relative to the original bond axis. Bending vibrations require lower energy and occur at lower freq.

Bending vib are 4 types

① In plane bending vib.

② Out of plane " "

In plane bending vibrations.

When the atoms bend, finally the atoms remain in the nodal plane of the bgs. Is called in-plane bending.

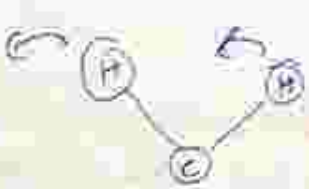
It is of 2 types

① Scissoring deformation

In this type both the atoms swing to the opp side as shown here

② Rocking:

In this type both the atoms swing to the same side



Out of plane bending vibration:

When the atoms bend, finally the atoms remain out of the nodal plane is called out of plane bending.

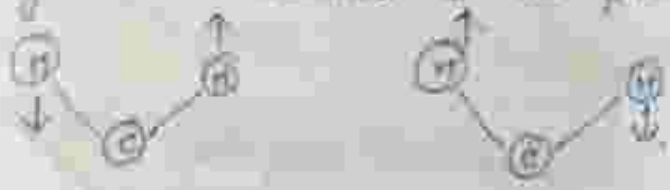
It is two types.

① Rocking deformation

Here both the atoms moving up or down out of the plane of paper

② Twisting deformation

One atom swings up and the other swings down related to the plane of paper



Vibration of polyatomic molecules

① Normal vib modes of CO_2 molecule.

CO_2 - linear molecule.

∴ Normal modes of vib = $3N-5$

$= 3(3)-5 = 4$

These are

① symmetric stretching : $\bar{\nu}_1 = 1330\ cm^{-1}$ IR inactive

② Asymmetric stretching $\bar{\nu}_3 = 2349\ cm^{-1}$ IR active

③ sym. bending and scissoring $\bar{\nu}_2$ } $= 667\ cm^{-1}$ IR active

① O → C ← O 1330 cm^{-1} ④ ↑O — C — ↑O } 667 cm

② O → C → O 2349 cm^{-1} O ↗ C ↘ O } 667 cm

(a) Normal modes of vibration of H_2O

- Non linear molecule — V-shaped

∴ Normal modes $= 3n - 5 = 3$

$\bar{\nu}_1$ = 3651 cm^{-1} symm stretch

$\bar{\nu}_2$ = 1595 cm^{-1} Symm bend

$\bar{\nu}_3$ = 3755.8 cm^{-1} asymstre

Factors determining the absorption frequency of a functional Group.

① Electronic effect.

e⁻ donating gp weakens the carbonyl and lowers its abs. freq.

e⁻ withdrawing gp strengthen C=O bond and raise its freq.

② Conjugation effect:

C=O str. freq. for ~~C=C~~ C=C conjugated

sys. are generally lower by 25–45 cm^{-1} than those of corresponding non-conjugated compounds.

③ Resonance effect:

Resonance weakens the C=O bond and lowers its absorption freq.

④ Ring size effect.

As ring size decreases, the carbonyl stretching freq. increases

⑤ Bond strength and masses of bonded atoms:

(a) The more s character in C-H bond, the stiffer the bond and higher the ν.

−CH	<	=C−H	<	≡C−H
25% s character		33% s		50% s

(b) ab freq. increases with bond multiplicity

C−C < C=C < C≡C

(c) freq. are inversely related to the masses of the bonded atoms.

O−D	<	O−H
2100 cm^{-1}		3600 cm^{-1}.

⑥ H_2 bonding:

H_2 bonded O−H str. appears at lower ν than free O−H str.

Effects of H_2 bonding :

- H_2 bonded O-H str appears at lower freq. than the free O-H str
- The H_2 bonding involves a lengthening of the original O-H bond. This bond consequently weakened & force const is reduced and so the stretching freq is lowered
- The O-H stretching absorption is very characteristics
- In general, intermolecular H_2 bonds give rise to broad bands. while intramolecular H_2 bonds gives sharp and well defined bands.
- Intramolecular H_2 bonding is independent of conc and hence intramolecular H_2 bond remain unaffected on dilution. whereas inter molecular H_2 bonding is conc. dependent. On successive dilution the intensity of the bands due to the intermolecular H-bonding gradually decreases and finally disappears.

- H_2 bonding lengthens and weakens the C=O bond and lowers its absorption frequency. Strong H_2 bonding in the dimer weakens the OH and C=O bonds and leads to broad peaks at lower frequencies.

Vibrational frequencies of different fnal gp.

Below 1000 cm^{-1}

C-H out of plane deformation of aromatic sub-pattern	mono sub benzene 710-690 ortho di sub " 770-735 meta " " 725-680 para " " 840-810
Alkene C-H out of plane bending	c/s alkene 730-665 trans " 990-960
Halogen compds	C-Cl 750-700 C-Br 600-500 C-I ~500

1600 – 1000 NO_2, ether, ester, alcohol

Alcohols C–OH	1° alcohol	~1050
	2° alcohol	~1100
	3° alcohol	~1150
	phenol	1400 – 1200
Ether	C–O–C	1150 – 1060
Aromatic ether		1275 – 1200
Epoxies		1260 – 840
Ester		1250 – 1150
Nitro comp.	NO_2 str. in 1°, 2°	1565 – 1545, 1385–1365
	NO_2 str. – 3°	1545 – 1530, 1365–1345
	" aromatic	1570 + 1500, 1370–1350
Aro C=C str.		1600 – 1585
		1500 – 1450
Amines	1°	1200 – 1220
	2°	1550 – 1280
	2°	1360 – 1810
	aromatic 1° amine	1340 – 1250

1680 – 1620 Alkene C=C

Oxime C=N

1680 – 1620 – C=C str.

1690 – 1630 C=N str.

1900 – 1650 C=O str.

Anhydride	Acyclic anhydrid	1850-1800, 1790-1740
	Cyclic anhydride	1870-1830, 1800-1770
Acidchloride		1815-1775
Ester		1750-1730
Aldehyde	Aliphatic CHO	1740-1720.
	Arom. CHO	1715-1695
Ketone	Aliphatic ketone	1725-1700
	cyclic ketone	1740-1700
	Alkyl aryl ketone	1700-1680
	Diaryl ketone	1670-1660
Amide		1690-1630
Acid	Aliphatic acid	1725-1700.
	Arom. acid	1700-1680

2300 – 2100 C≡C, C≡N

R C ≡ C H	2140-2100
R^1 C ≡ C – R^2	2190-2260
C ≡ N (Nitrile)	2260-2240
N = C = O (Isocyanate)	2275-2250

3000 - 2500 CH str presence of COOH

COOH	very broad band	3000 - 2500
	Two weak band	2900 - 2700
	2720 2820 (CH str of CHO)	
CH str of methyl and methylene		2975 - 2935

3200 - 3000 = CH, Ar-H str

= CH due to alkene, cycloalkene	3040 - 3010
= CH str aromatic	3080 - 3030

3600 - 3003 (OH NH2 NH, ≡CH)

≡ CH str	3310 - 3300
OH str alcohol phenol	3670 - 3580
OH of acid	3560 - 3500
oxime	3 650 - 3500

Magnetic Resonance Spectroscopy.

Principle of NMR

Nuclei with a resultant nuclear spin behaves as tiny bar magnets producing a magnetic moment $m_s = +\frac{1}{2}$. Such nuclei exist in diff energy levels when placed in an external magnetic field. If the diff. in nuclear energy levels is so small that nuclear transitions involve absorption of energy of a few joules in the radio freq. region. Thus, nuclear magnetic resonance (NMR) spectroscopy is exhibited by nuclei in the radio freq region.

Condition for a molecule to be NMR active.

Only nuclei with a resultant nuclear spin give rise to NMR spectra.

Eg.

① Nuclei of atoms with odd mass number
— H^1, B^{11}, C^{13}, N^{15}, O^{17}, F^{19}, P^{31}

② Nuclei of atoms with even mass number but odd atomic number — $_1H^2$, $_7N^{14}$

③ Nuclei of atoms with even mass no. and even at. no — $_6C^{12}$, $_8O^{16}$, $_{14}Si^{28}$, $_{16}S^{32}$) have no resultant spin and hence NMR inactive.

Types of NMR spectroscopy

PMR - Proton magnetic resonance

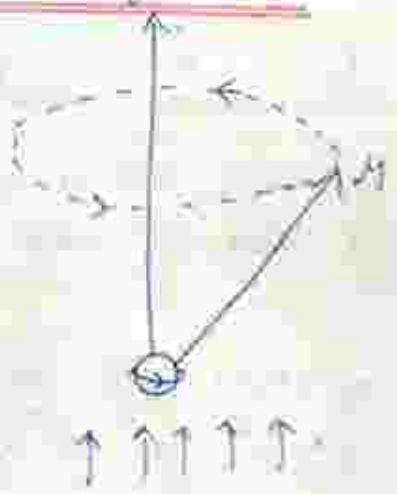
CMR - Carbon magnetic resonance.

Theory of NMR Spectroscopy

(a) Spinning of nuclei.

Like e⁻, atomic nuclei are spinning about an axis. The spinning nucleus behaves like a tiny bar magnet possessing north and south poles. Consequently it acquires a mag moment M.

(b) Precession of nuclei.



When a spinning nucleus is placed in an external magnetic field of strength Ho, the magnetic axis of the nucleus will precess (moves in circular path) about the

axis of the external magnetic field of strength H_0 the magnetic axis of the nucleus is through an angle α. It is analogous to the precession of a spinning gyroscope (top) under the influence of gravity.

The freq. of precession often called Larmor freq. is given by the expression

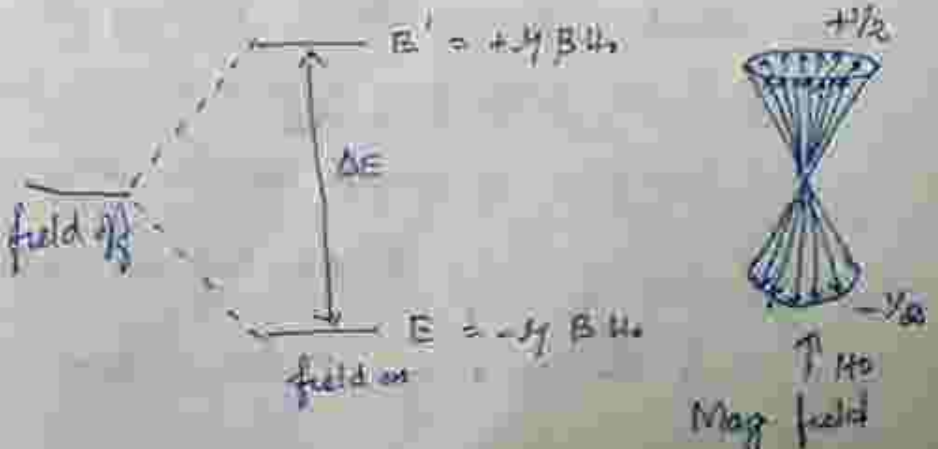
$$\nu = \gamma H_0$$

γ = a const called gyromagnetic ratio

H_0 - strength of external mag. field

In the absence of a magnetic field, the magnetic moments are oriented in a random fashion. However the magnetic moments may be oriented along with or opposite to the direction of the applied field.

For nuclei such as H^1, C^{13}, F^{19} etc, the spin quantum no. I may be $+1/2$ or $-1/2$ and two nuclear energy levels are possible for them.



When the magnetic moments are aligned with the external field, the nucleus is at a lower energy level (E). If the magnetic moments are aligned against the external field, the nucleus will be at a higher energy level (E')

$$E = -\frac{1}{2} \beta \mu H_0$$

$$E' = +\frac{1}{2} \beta \mu H_0$$

$$\Delta E = E' - E = \beta \mu H_0$$

Where μ = mag moment of the nucleus.

β - Nuclear magneton

$= (5.049 \times 10^{-24}$ erg gauss$)$

(c) Resonance:

The energy gap bet. two nuclear levels is very small and to flip a nucleus from a lower energy level to a higher energy level, energy ($\Delta E = h\nu$) in the radio freq region is absorbed. Absorption of energy occurs only when the freq. of radn is equal to the lormour freq of the spinning nucleus. Now, the freq

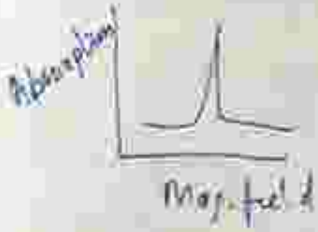
of radn. is said to be in resonance with the freq. of the spinning nucleus. This happens at a definite magnetic field strength applied.

$$\Delta E = h\nu = \beta_N H_0$$

$$\nu = \frac{\beta_N H_0}{h}$$

ν = freq. of radn absorbed

When the freq. of radn. absorbed is plotted against the field strength an absorption peak called signal is obtained



Number of NMR signals.

The NMR signals are due to the proton the molecule possess. Not all protons experience the same external field. Protons of different environment give signals at diff. field strength. ∴ The no. of signals depends upon the type of H atoms present in the molecule.

To illustrate this consider the NMR Spectra of C_2H_6O (CH_3OCH_3) and ethyl alcohol (CH_3CH_2OH).

The six H-atoms in dimethyl ether are in identical environment and ∴ ~~Cannot~~ show one signal. On the other hand, the H atoms in ethyl alcohol exist in three distinct environments and consequently 3 signals are obtained.

other ex.

1) CH_3-CH_2-Cl 2 signal

2) $Cl\,CH_2-CH_2-CH_2\,Cl$ 2 signal

Position of NMR signal:

The position of an NMR signal is det. from the electronic environment of the proton. The electrons around a H-atom shielded it from the applied field

$$H_{eff} = H_0(1-\sigma)$$

where σ is called the shielding constant which is a measure of the e⁻ density around the proton. The shielded

proton will experience a weaker mag. field. Consequently, it requires a higher magnetic field for absorption to take place. That is the proton signal appears at a higher mag. field on the right side of the spectrum. The deshielded proton gives low-field or down field signal on the left side of the spectrum.

Consider the NMR spectrum of methyl alcohol (CH_3OH). The spectrum shows two signals indicating that there are two types of protons - 3 protons of one kind (CH_3) and one proton of another kind (OH) of in the mole

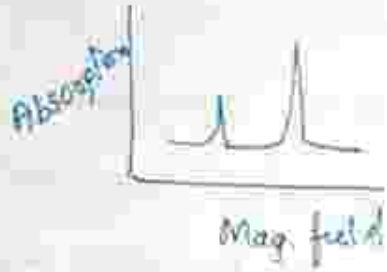
$$\underset{(a)}{CH_3} - \underset{(b)}{OH}$$

Since oxygen is more electronegative than carbon, the e^- density around the H atom in OH bond is lower than that in C-H bonds. That is, the H-atom in OH group is deshielded whereas the H atom in CH_3 group are shielded.

$$\sigma_{CH} > \sigma_{OH}$$

$$H_{CH} \quad H_{OH}$$

Thus the deshielded CH_2 signal appears at down field while the shielded CH_3 signal appears at up field.



Chemical shift:

The position of absorption peaks for different types of protons are normally measured relative to the peak of a ref. compound. In PMR spectroscopy Tetramethyl silane $(CH_3)_4Si$ commonly abbreviated as TMS. It meets the criteria of a good standard as given below.

(1) TMS is chemically inert, and hence does not affect the environment of protons in the sample.

(2) It is a volatile liq. miscible with most organic solvents. It can be removed easily from precious sample after use.

③ It is magnetically isotropic

④ It is added to the sample only in small quantity and hence acts as an Internal standard

⑤ It shows signal as a sharp and intense line due to the presence of 12 equivalent H atoms

⑥ Its signal is conveniently located at the extreme right (upfield) of the spectrum.

The NMR spectrometers are designed in such a way that the radio freq is kept const and the magnetic field strength H₀ is varied. The absorption band appears at a definite field strength measured in H_0. It is conventionally expressed in terms of δ which is defined by the expression

$$\delta = \frac{\nu_{sample} - \nu_{TMS}}{\nu_{applied}} \times 10^6 \text{ ppm}$$

For 60 MHz instrument (for eg.

$$\delta = \frac{\nu_{sample} - \nu_{TMS}}{60 \times 10^6} \times 10^6 \text{ ppm}$$

$$= \frac{\nu_{sample} - \nu_{TMS}}{60} \text{ ppm}$$

For a band appearing at 176 Hz downfield from TMS

$$\delta = \frac{176 - 0}{60} = 2.93 \text{ ppm.}$$

This value of δ is usually in the range 0-10. The position of TMS signal is taken as $\delta = 0$ and most protons have δ values bet 0 and 10.

The proton signals always appear to the left of the TMS signal. The separation or shift in the position of a proton signal in terms of δ value from the TMS signal is called chemical shift

	δ
CH_3	— 2.7
CH_2	— 3.5
OH	5
C_6H_5	7.23
CHO	9.5

(5) CH_3-Cl one peak

CH_3CH_2Br 2 peak

↓

deshielded by Br atom

CH_3 - no deshielding

CH_3CH_2OH 3 peak

↓ ↓

deshielded by −I effect of OH

−I of O, it deshield CH_2 protons

H bonding.

∴ appear (↓).

Factors affecting Chemical shift.

① Inductive effect

1) Electronegativity - higher the magnitude of ENG, higher the deshielding (downfield shift)

Electronegative groups (ENG) near a nucleus will pull e^- away and decrease the shielding of the nucleus.

2) Cumulative effect:

The effect increases with greater no. of electronegative atoms. The deshielding effects are nearly additive.

3) Electronegativity effects decrease with increasing ~~decrease~~ distance.

iii. S character

As s character of C atom ↑, the electronic cloud is held closer to the nucleus and provides less e^- density for shielding of protons ∴ δ increases. (shifted downfield)

$Sp^2 > Sp > Sp^3$

iv. Magnetic Anisotropy

This effect is due to π bonded e^- in molecule.

v. H_2 bonding.

If bonded proton is deshielded and obtains at down field.

vi. Isotopic effect:

When one substitutes a nuclide in a chemical group with a heavier isotope then all other nuclides in the gp. become a bit more shielded.

Splitting of signals

Spin - Spin - coupling.

In the low resolution spectrum, the NMR signals of different equivalent sets of proton appear as single absorption peaks at different applied fields. But in the high resolution spectrum, the signals split into several absorption peaks. This is due to spin-spin coupling.

An NMR signal split into $(n+1)$ peaks when n number of protons are present adjacent to it. This is called $(n+1)$ rule. Thus a doublet results from one adjacent proton, a triplet results from two adjacent protons, a quartet results from three adjacent protons and so on. The peak area or intensity of the lines in multiplet is given by the binomial coefficients of order n and pascals triangle

n	n+1	Relative intensity
0	1 singlet	1
1	2 doublet	1 : 1
2	3 triplet	1 : 2 : 1
3	4 quadet	1 : 3 : 3 : 1
4	5 quintet	1 : 4 : 6 : 4 : 1
5	6 sextet	1 : 5 : 10 : 10 : 5 : 1

Eg

① Ethyl bromide :

$CH_3 - CH_2 - Br$

(a) (b)

In ethyl bromide CH_3-CH_2-Br there are two kinds of hydrogens i.e. methyl (CH_3) and methylene (CH_2). The three hydrogens of the methyl group have two neighbouring protons (CH_2 group). Thus the CH_3 proton signal splits $2+1=3$ peaks (triplet). This is due to three spin orientations.

↑↑

↑↑ ↑↓

↑↓

1 2 1

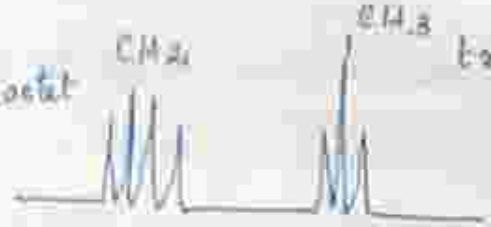
Similarly, the two identical protons of the methylene group couple with the neighbouring three protons of the methyl gp giving rise to $3+1=4$ peaks. This is due to four spin orientations.

↑↑↓ ↑↓↓

↑↑↑ ↑↓↑ ↑↓↑ ↓↓↓

↓↓↑ ↑↑↓

1 3 3 1



② ethyl alcohol.

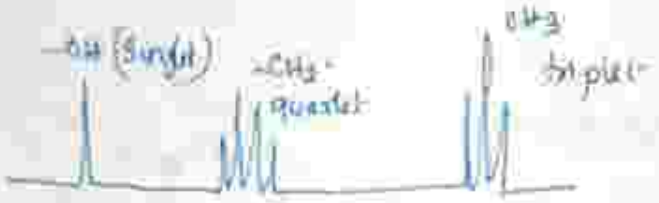
CH_3CH_2OH
a b c

a - triplet
b - quartet
c - singlet.

In ethyl alcohol, CH_3CH_2OH, there are three kinds of protons ie methyl (CH_3) methylene (CH_2) and hydroxyl (OH). The methyl proton signal splits into a triplet due to coupling with the neighbouring two protons of the CH_2 gp. Similarly the CH_2 ~~gp~~ proton signal splits into a quartet due to coupling with the three protons of the CH_3 group.

Splitting is not observed in the OH signal. The hydroxyl proton appears as a singlet ie no spin-spin coupling is seen between the hydroxyl proton and the neighbouring methylene protons. This is due to exchange of OH protons bet ethanol molecules. A particular proton thus does not reside for a sufficiently long time on the O atom to be seen by the neighbouring

proton for the nuclear coupling to be observed



Coupling const.

The spacing between the peaks in a multiplet is usually const - and is called the coupling const & expressed in Hertz. Unlike the chemical shift, the values of coupling const are independent of the external field. It is usually between 1 to 20 Hz.

Illustration

Consider the proton attached to two neighbouring carbon atoms Ha and Hb

The signal for H_a proton split into a doublet by H_b proton and the H_b proton signal is split by H_a proton. The splitting is designated by the code J_{ab}

Significance:

The value of J depends upon the position of the coupling protons. For eg, the magnitude of J differs for cis and trans H_2. IIIrd ortho, para and meta H_2 have different J values. Thus J is useful in distinguishing cis-trans isomers and deciding the orientation in benzene ring.

Ste.	J in H_2
cis	5-12
trans	11-19
ortho	7-10
meta	2-3
para	0-1

ESR Spectroscopy

Origin

Electrons possess a spin of ½ and behave as tiny bar magnets producing a magnetic moment. When an atom or ion or molecule containing one or more unpaired electrons is placed in a magnetic field. Its electron magnetic moment is aligned with or against the direction of the applied field. This leads to the separation of the electron spin energy levels. The energy difference between two e^- spin states is equal to $g\beta_e H_0$

$$\Delta E = E' - E$$

$$= \frac{1}{2} g\beta_e H_0 - \left(-\frac{1}{2} g\beta_e H_0\right)$$

$$= g\beta_e H_0$$

where g = a const called bohr magneton.

μ_e = mag. mom. of the e^-

$$= \frac{eh}{4\pi mc}$$

e = electronic charge.

m = mass of e^-

c = velocity of light

When $g\mu_e H_0 = h\nu$

$$\nu = \frac{g\mu_e H_0}{h}.$$

The freq. of electron spin is said to be in resonance with the freq. of radn absorbed and a signal is obtained. This is known as electron spin resonance (ESR) spectrum. It is also known as Electron paramagnetic resonance (EPR) or Electron magnetic resonance (EMR) spectrum.

Condition for an atom or ion or molecule to be ESR active.

Only atoms or ions or molecules with a resultant electron spin due to unpaired e^- give rise to ESR spectra

Eg -

① Atoms like H^1, H^3

② Molecules like NO, O_2, NO_2

③ Free radicals like $H^{\bullet}$, $\dot{C}H_3$

④ Ions of transition metals and their complexes Fe^{3+}, $Fe(CN)_6^{3-}$ etc

Interpretation of ESR Spectrum

As in NMR, the ESR spectrum is obtained by plotting the intensity of radn. absorbed against the strength of the magnetic field applied. However, the ESR spectrum is usually recorded as the first derivative of the absorption curve.

Absorption curve

First derivative curve

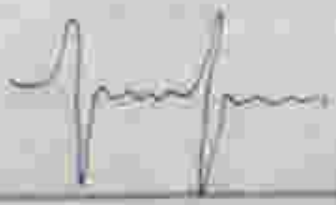
Also, similar to NMR, high resolution ESR signals appear as multiplets. This is called hyperfine splitting which is caused by the interaction between the nuclear spin

and the spin of the odd electron. This can be illustrated by considering the ESR spectrum of H₂ atom. It consists of a single peak corresponding to the transition between the two e⁻ spin energy states

The single e⁻ in H-atom can have 2 possible spin ↑ I way
↓ II way.

The hyperfine str of H atom will consists of n+1 = 2 peaks due to interaction bet e⁻ spins and nuclear spins.

Thus the ESR signal of H atoms splits into two peaks and appear as a doublet in its high resolution spectrum



Application :

① To detect free radicals
② to det - the valence state of metal ions in inorganic complexes

③ to detect conduction e^- in metals

④ to detect biradicals and triplet states

⑤ to study e^- exchange reactions.

Hyperfine str in ESR spectra.

If a species, atom, mole or ions contain free e^- and an active nucleus then the magnetic interaction bet electronic spin S and nuclear spin I occurs. Due to this, first derivative curve of ESR signal undergoes splitting which is called hyperfine splitting. This interaction or splitting is analogous to nuclear spin-spin interaction in NMR spectra.

The no. of ESR lines obtained using the selection rule

$\Delta m_s = \pm 1 \qquad \Delta m_I = 0$ i.e.

$$N = (2I_1 + 1)(2I_2 + 1)$$

In the case of equal I's, the no. of splitting is given by $2nI + 1$ where n is the no. of equivalent nuclei interacting with free e^- and I is spin quantum of interacting nuclei.

The relative intensity of ESR lines for an odd electron interacting with 'n' equivalent protons can be obtained from the coeff. of the binomial expansion of $(1+x)^n$. The coeff. can be arranged in pascals triangle

① H_2 atom

It contains unpaired e^- $S = 1/2$ and a proton with $I = 1/2$.

Thus $m_S = \pm 1/2$ $m_I = \pm 1/2$. In the absence of magnetic field, the e^- spin energy level are degenerate. When magnetic field is applied, the degeneracy is removed i.e

$m_S = \frac{1}{2}$ level is raised and

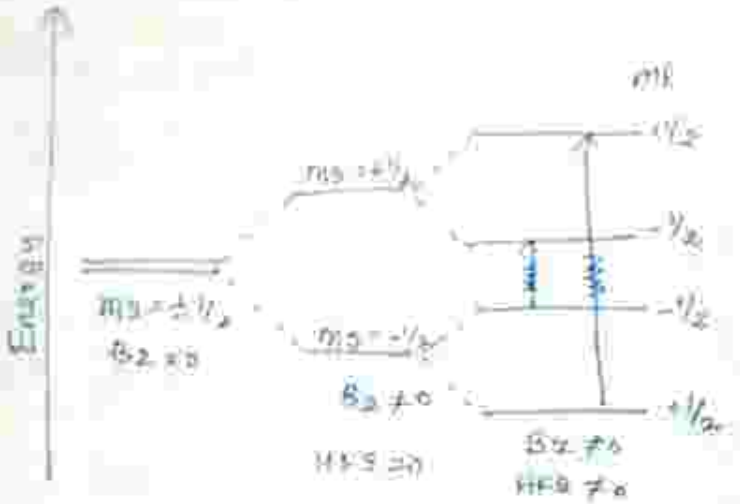
$m_S = -\frac{1}{2}$ level is lowered in energy

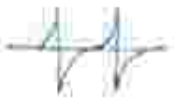
These e^- sublevels interact with the nucleus giving four sub levels This is hyperfine interaction.

No. of ESR lines (acc to $2nI+1$) $= 2$

where no. of equivalent protons $n=1$ and $I = 1/2$

As in Pascal's triangle, the ESR spectrum consists of 2 lines (doublet) of equal intensity (1:1).





Spectrum

The spacing between the lines is known as hyperfine coupling const - 'a'. It is expressed in units of tesla or millitesla

② Methyl radical $^{12}CH_3$:

It contains an unpaired e^- with $S = 1/2$ and three equivalent protons.

$$N = 2nI + 1$$

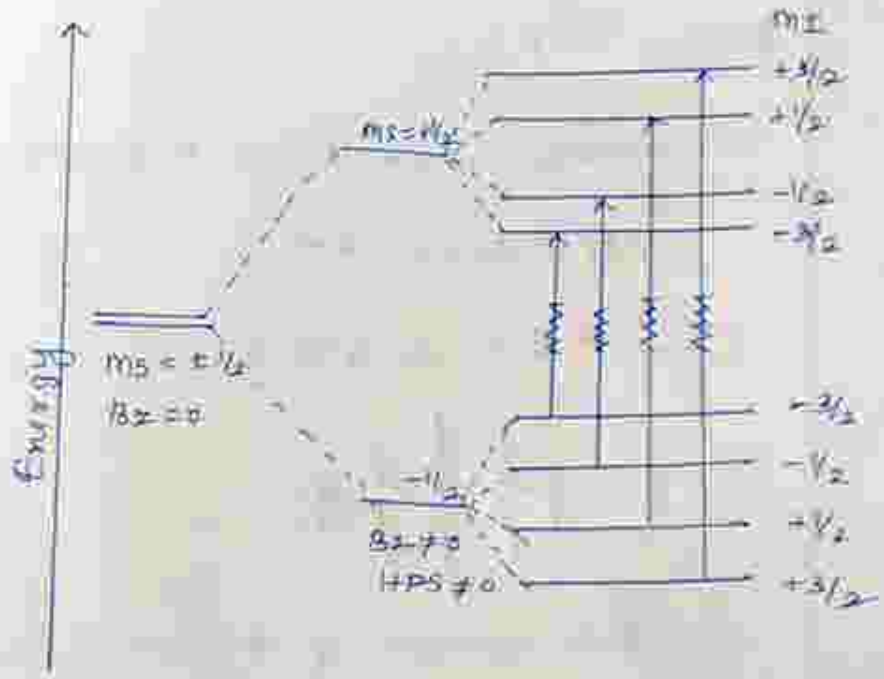
$$= 2 \times 3 \times \frac{1}{2} + 1$$

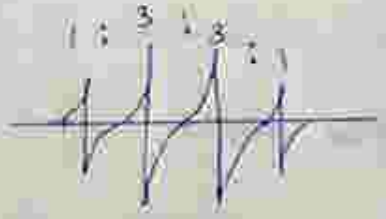
$$= 4$$

m_I value is $+3/2, +1/2, -1/2, -3/2$ and

m_S value is $\pm 1/2$

The ESR spectrum consists of 4 equally spaced (quartet) in the ratio of 1:3:3:1 and a is 22.9 gauss first.





Spectrum

The ESR spectrum of ^{13}C consists of eight lines since ^{13}C interaction produces a doublet and the H_3 a quartet. The value of 'a' is 41 G. and it leads to a planar sp. sp^2 hybridization.

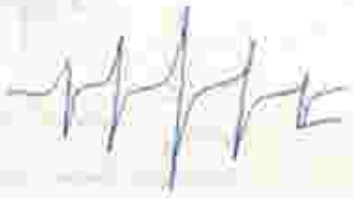
(10) Benzene radical anion

Benzene anion can be formed by the reaction of an alkali metal with benzene THF

In benzene radical anion n=6 and I = ½

$$N = 2nI + 1 = 7$$

m_I = 3, 2, 1, 0, -1, -2, -3



ESR spectrum of benzene anion

The spacing between the lines given by hyperfine coupling const = 3.76 G.

Unit - II

Phase rule :-

Phase rule is an expression, deduced purely from thermodynamic consideration by Willard Gibbs in 1876. It explains the behaviour of heterogeneous systems in ⇌. With the application of phase rule, it is possible to predict qualitatively, by means of diagram, the effect of changing P, T and C on a heterogeneous sys in equilibrium. Phase rule is best expressed mathematically as follows:

$$P + F = C + 2$$

$$\boxed{F = C - P + 2}$$

F = No. of degrees of freedom

C = No. of components

P = No. of phases.

Definition :-

1) Phase (P)

The term phase is defined as "any homogeneous and physically distinct part of a system having all physical and chemical prop the same throughout"

A sys consisting of one phase only is called homogeneous sys. A system consisting of two or more phases is called heterogeneous system.

(eg)

liq. $H_2O \rightleftharpoons H_2O$ water vapour = 2

Solid $CO_2 \rightleftharpoons$ liq $CO_2 \rightleftharpoons$ Gas CO_2 = 3

---

2. Component :-

It is defined as the least no. of independent chemical constituents by means of which the composition of each phase of the system can be expressed in the form of a chemical equation.

$$C = N - E$$

N = No. of chemical species.

E = No. of independent chemical equation relating their concentrations

(eg). Water system

Solid (Ice) $\rightleftharpoons$ liq. $H_2O \rightleftharpoons$ Water vapour

$N = 3$

$E = 2$

$\therefore C = 1$

3. Degrees of freedom (F)

It is defined as 'the least no of variable factor (cons. pr. T) which must be specified so that the remaining variables are fixed automatically to define the system completely.

eg: Pure gas.

No. of components = 1

No. of phases. = 1

No. of degrees of freedom = F = C − P + 2

= 2.

Water sys.

Solid ice ⇌ liq water ⇌ Water vapour

No. of components = 1

No. of phases = 3

No. of deg. of freedom = 0.

Derivation of phase rule:

Consider a heterogeneous sys consisting of 'C' components distributed in 'P' phases at equilibrium in order to describe the

composition of each phase. $c-1$ conc variables must be known. for P phases. this becomes $P(c-1)$. Besides these conc variables. pr. and Temp must also be known. Hence the total no of independent variables required to describe the system is $P(c-1)+2$

No. of conc variables $= P(c-1)$

No. of pr. variable $= 1$

No. of Temp variable $= 1$

Total $= P(c-1)+2$

From T.D point of view, the chemical potential of a component is the same in all the phases of the system. Suppose that a 1-comp sys. has two phases 1 and 2. Now Thermodynamics puts the condition

$$\mu_1 = \mu_2$$

Hence there is one equilibrium relation that gives the distribution of the component between two phases. Similarly for a one component system having three phases 1, 2 and 3

We have two equilibrium relation

$$\mu_1 = \mu_2 = \mu_3$$

In general, there will be $P-1$ equilibrium relations for a component distributed in P phases. Thus the total number of relations required to describe the distribution is C. The components in P phases will be $C(P-1)$.

Degree of freedom F = Tot. no. of variable − Tot. no. of relations

$$F = [P(C-1)+2] - [C(P-1)]$$

$$= PC - P + 2 - CP + C$$

$$= C - P + 2$$

$$F = C - P + 2$$

Phase diagram:

The condn under which different phases would coexist in a heterogeneous sys. can be predicted and described conveniently with the help of a graph called phase diagram. A two dimentional phase diagram may be constructed by plotting any two variables such as P-T, P-C or T-C. However, when three variables are concerned, a solid - 3D phase diagram is

needed to interpret the equilibrium condition of the system.

A phase diagram consists of

① area ② curves (or) lines ③ points. The areas represent one-phase equilibria. The curves or lines which divide the area represent two phase equilibria. The points where three curves meet indicate the co-existence of three phases.

The system is bivariant in the areas. univariant in the curves and invariant at the points.

One - Component system

Water system:

Under ordinary circumstances, water exists in S, L and G phase. The phase diagram or plot of P versus T, of water is shown below.

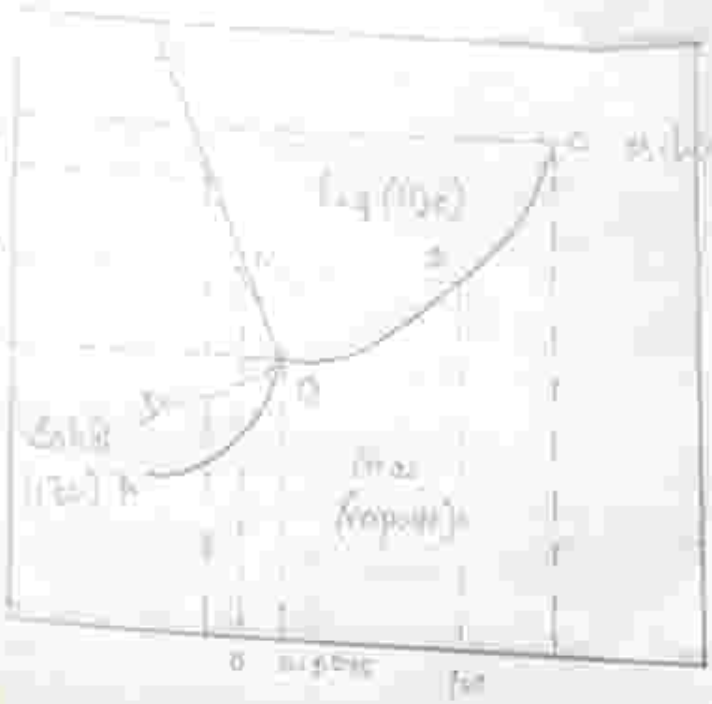
The phase diagram consists of

① Three areas - AOB, BOC and AOC

② Three stable curves: AO, OB and OC

③ one metastable curve - OD

④ one point - O.



(4) The Areas.

The phase diagram consists of three areas AOB, BOC and AOC and each one represents a single phase.

Area	Phase
AOB	Solid
BOC	Liquid
AOC	Vapour

It is necessary to specify both T and P to define the state of the sys. within the area. Hence the sys. is bivariant

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

(b) The Curves.

A curve (or line) separates two phases and the phys. would be invariant along the curve.

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

(c) Curve AO

The curve AO separates the solid (ice) and gas phases. It is the sublimation curve of ice.

Ice $\rightleftharpoons$ Water vapour
(s) (g).

(d) Curve OB:

The curve OB represents the equilibrium between ice and water. Thus it is the melting point curve for ice or the freezing point curve for water.

Ice $\rightleftharpoons$ Water

The curve has a negative slope as it is inclined to the pr. axis. This is due to the fact that the molar vol. of liq. water is lower than that of solid ice. The negative slope of the curve predicts that the M.P. of ice is lowered with increase of pressure

(iii) Curve oc

The curve oc is the vapour pr. curve of water. Along the curve, water and its vapour exist in equilibrium at different temp. C is the critical point (P = 217 atm and T = 374.3°c) above which only the vapour phase exists, whatever may be the pr.

Water ⇌ Water vapour

(iv) Meta-stable curve OD.

It is possible to cool water below its freezing point without solidification along OD. Now water is said to be in supercooled state. The curve OD is a continuation of OC and hence. It is the vapour pr. curve of supercooled water.

The curve OD is above AO, the vapour pr. curve of ice. This shows that the vapour pr. of the supercooled water is higher than that of ice. This means that the supercooled liquid is energetic and not quite stable. It is usually known as a metastable state and is readily changed into the stable state by slight disturbances.

At the triple point :

The three stable curves AO, OB and OC meet at the point O where all the three phases coexist in equilibrium. This is called triple point. At the triple point, the sys is invariant

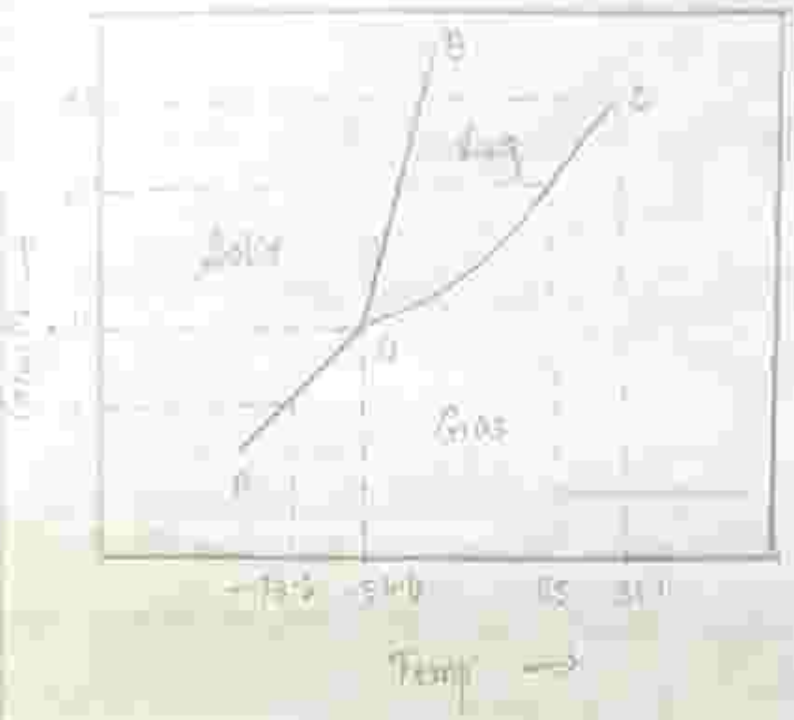
$$\therefore F = C - P + 2$$
$$= 1 - 3 + 2$$
$$= 0$$

At the triple point P = 4.58 torr and T = 0.0075°C. When P or T of the system is changed at the triple point, one of the phases would disappear and the system will no longer be invariant.

Effect of temp. on the equilibrium

At 1 atm pr., water is in the form of ice at the point M. When ice is heated at const pr., the sys. shifts along MN@. At N, ice melts. It is the melting point of ice. Beyond N, there is no solid phase and we get liq. water upto @. At @ water begins to boil. It is the normal B.Pt of water (100°C)

Carbon dioxide system



The general feature of the diagram are quite similar to those of water sys. except that the melting point curve of solid CO_2 has a positive slope. The phase diagram consists of

1. Three areas - AOB, BOC and AOC.
2. Three curves - AO, OB and OC
3. one point - O

(1) The areas :

The phase diagram consists of three areas AOB, BOC and AOC and each one represents a single phase.

Area	phase
AOB	solid
BOC	liquid
AOC	Vapour

The sys is bivariant in the areas

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

(5). The Curves:

The curve separates two phases and the system would be univariant along the curves

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

(i) Curve AO:

AO is the sublimation curve of solid CO_2. It represents the coexistence of solid CO_2 and CO_2 gas. If we raise the temp at const pr, the dry ice will pass into vapour phase without passing thro' liquid phase. In other words, sublimation would occur.

(ii) Curve OB:

The curve OB is the melting point curve of solid CO_2 because it indicates the effect of pr on melting point of solid CO_2. Along the curve, solid

and liquid phases are in equilibrium and the curves slopes away slightly from the pressure axis (+ve slope). This is due to the fact that the molar vol. of liq. CO_2 is larger than that of solid CO_2. As a consequence of the positive slope, the m.pt of solid CO_2 is increased with increase of pr.

(ii) Curve OC :

It is the vapour pr curve of liquid CO_2. C is the critical point (P = 73 atm and T = 31.1°C) of CO_2 gas liquid CO_2 exists below 31.1°C. Above this temp, CO_2 exists only as gas whatever may be the pressure.

(iii) The point O

The point O is the triple point (P = 5.11 atm and T = −56.6°C) From the diagram, it is clear that liquid CO_2 can exist at pr above 5 atm. Hence under ordinary pr (1 atm) solid CO_2 can be vapourised without wetting the surrounding. For this reason, solid CO_2 is called dry ice.

Liq. CO_2 is stored in cylinder at room temp (25°C) and 67 atm pr. When it comes out of the cylinder, the pr is reduced to 1 atm. and dry ice is formed in the form of dense white clouds.

Two component system

For a two component sys $C = 2$, and the phase rule may be written as

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

For a two component sys having one phase, the no of degrees of freedom would become three. $F = 4 - 1 = 3$

This means that in order to describe a two component sys all the three variables - pressure, temp and conc must be specified. This obviously requires a three dimensional figure which is rather difficult to construct. In order to remove this difficulty one of the three variables usually P or T is kept const. It is then possible to construct a two dimensional phase diagram P-C or T-C diagram.

The various equilibria possible for a 2-component sys are

1. liq-gas equilibria
2. L - L "
3. S - G "
4. S - L "
5. S - S "

Reduced phase rule:-

This is formed in S-L sys of two comp. sys. If the sys. exists in one phase, the no. of deg. of freedom will be

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

This means that all the three variables must be specified to describe the sys. This requires a three dimensional phase diagram. However, by keeping either P or T const, it is possible to construct a two dimensional phase diagram.

Since the effect of pr. on S-L equilibria is very small, such sys are studied at atm. pr. Here the gas phase is ignored. These sys having no gas phase are known as condensed sys. Since pr is kept const, the phase rule takes the form.

$$\boxed{F = C - P + 1}$$

This is known as the reduced phase rule and the condensed S-L sys are rep. by T - Comp diagram.

Classification of two component

Solid - liquid equilibria

Suppose that that two components are completely soluble in the molten or liquid state then, based on the nature of the solid phases that separate out on cooling, the solid-liquid Equilibria are classified into three types.

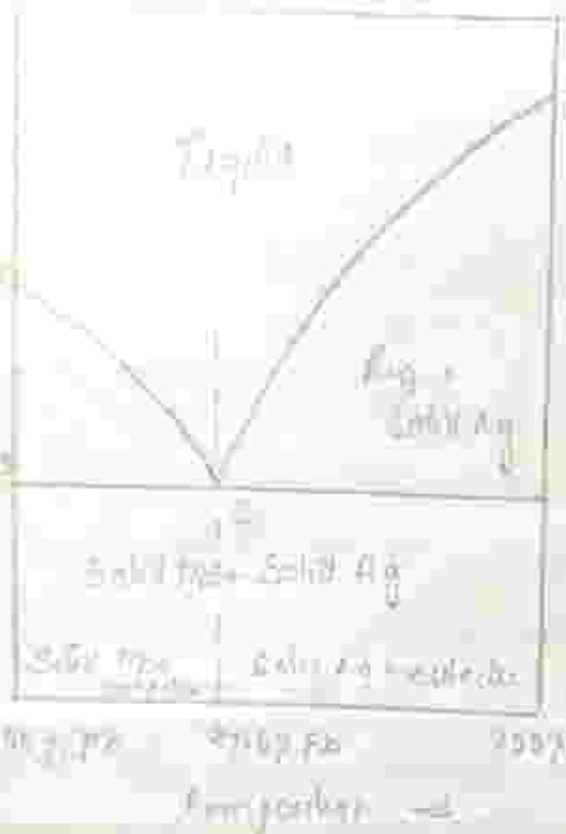
1. Sys forming simple Eutectic mixture
2. Sys. forming compd with congruent M.pt
3. Sys. forming compd with incongruent M.pt
4. Sys. forming solid solution.

Simple Eutectic system.

Lead - Silver system.

The most X eg. of a simple eutectic sys is the lead-silver sys. The phase diagram of the gn. here

1. Point A is the melting point of lead (327°C)
2. Point B is the melting point of silver (951°C)
3. Curve AC is the melting or freezing pt Curve of lead



The addition of Ag lowers the M.Pt of lead along AC. Along this curve, solid lead and liquid melt are in equilibrium. Hence these are two phases and the sys is univariant

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

(4) Curve BC is the melting or freezing pt curve of silver. Along this curve, the M.Pt of silver falls by the addition of lead. Along BC, solid silver and liquid melt coexist and the sys is univariant

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

(5) - Point C : is the eutectic point at which curve AC and BC intersect. At this point, three phases namely solid Pb,

solid Ag, and liquid melt coexist in equilibrium. Thus the sys is invariant at C.

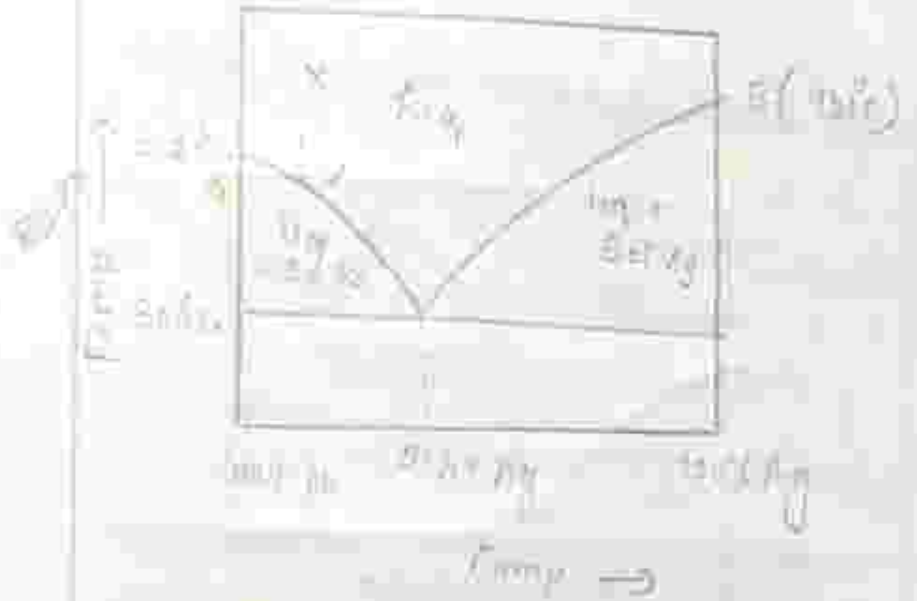
$$F = C - P + 1$$
$$= 2 - 3 + 1$$
$$= 0$$

Below this point, the sys is completely solidified and the temp corresponding to this point is the lowest temp at which any liq. mix can exist. This is known as the eutectic temp. The Pb-Ag sys has the eutectic temp of 300°c and the eutectic mixture has the comp of 97.6% Pb and 2.4% Ag. The region below the line DC represents solid Pb + Eutectic and the region below the line CE represents solid Ag + Eutectic. The characteristic of a eutectic mixture is that it melts sharply at a fixed temp without change of comp.

Pattinsons process of desilverisation of lead:

Argentiferrous lead contains a very small % of Ag. Hence it is not economical to extract silver from this ore. However, the ore may be enriched with Ag by a process called pattinsons process of desilverisation of lead. The principle underlying the process

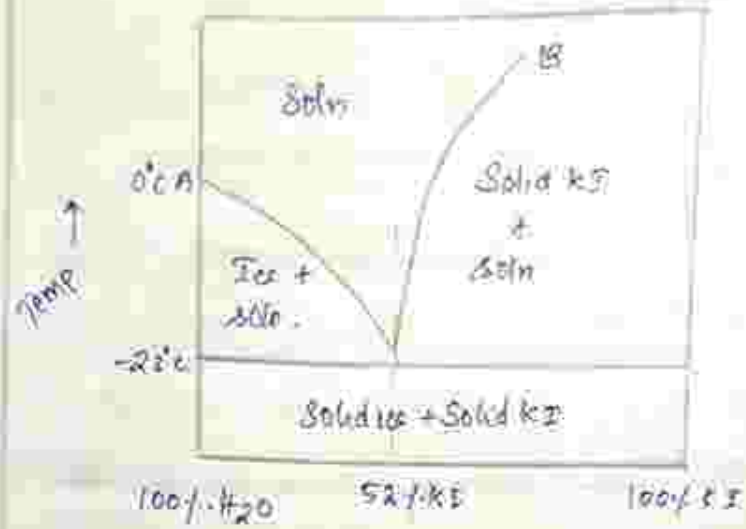
Can be understood from the phase diagram of lead silver sys.



The argentiferous lead is heated to get a homogeneous melt represented by the pt. X. It is then allowed to cool. The temp of the melt will fall along xy and lead begins to separate out at point y. If cooling is continued further, more and more of lead crystallises out and the composition of the liq. melt varies along YC. Consequently the melt becomes richer in silver. On cooling upto the eutectic temp of 300°C the max conc of silver (2.4%) in the ore is obtained

KI - H_2O system

The phase diagram is given below.



① Point A is the M.Pt of ice or the freezing point of H_2O (0°C)

② Curve AC is the freezing point curve of H_2O. Addition of the salt (KI) lowers the freezing point of water along (AC). Along AC ice and salt soln coexist and the sys is univariant

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

③ Curve BC is the solubility curve of KI. It predicts the effect of temp on the solubility

of KI in water. KI is not soluble in water in all proportions. The components are completely miscible at a very high temp which cannot be realised in the phase diagram that is why the curve BC cannot meet the temp axis. Along BC, solid KI is in equilibrium with the solution and the sys is univariant.

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

The steep rise of the curve shows that the solubility of KI increases slowly with temp.

(iv) Point C is the eutectic point. At this point curves AC and BC meet three phases ice, solid KI and soln. are in equilibrium. Hence the sys is invariant at C

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

The eutectic point lies much below the M.Pt of the individual components. For this reason, the eutectic point in the case of salt-water sys. is called cryohydric point this point corresponds to a definite temp called cryohydric temp. For KI - H_2O sys it is $-23^\circ C$. The salt-water mix (60% KI + 40% H_2O) at this point is termed as cryohydrate which is used as a freezing mixture.

Freezing mixture:

Ice melts at 0°C. When a salt like KCl, NaCl or NaNO$_3$ is added to ice, a lowering in temp. is observed. That is a mixture of ice and salt is capable of producing low temp much below 0°C. Such mixtures in general, are called freezing mixture.

Systems in which a compd. with congruent melting pt and incongruent M.pt is formed:

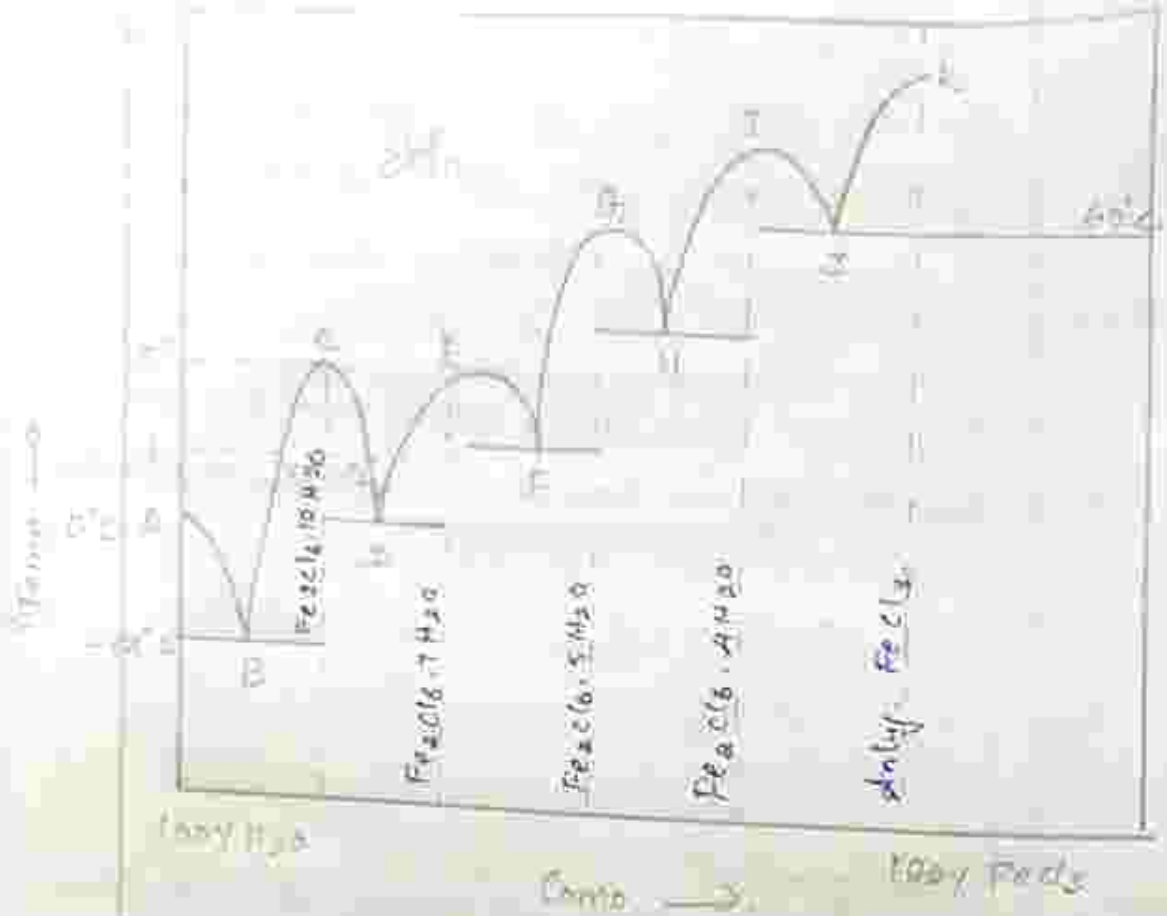
A compd. is said to possess congruent M.pt if it melts sharply into a liquid having the same comp as that of a solid.

$FeCl_3 - H_2O$ system:

Ferric chloride - water forms a two component sys. which involves the formation of more than one compd with congruent M.pt. It forms 4 stable compds. They are

1. Dodecahydrate $Fe_2Cl_6 \cdot 12H_2O$
2. Heptahydrate $Fe_2Cl_6 \cdot 7H_2O$
3. Pentahydrate $Fe_2Cl_6 \cdot 5H_2O$
4. Tetrahydrate $Fe_2Cl_6 \cdot 4H_2O$

The phase dia is as below.



① Eutectic points:

The phase dia consists of five minima at B, D, F, H and I. These are called eutectic points. Since in $FeCl_3$-H_2O sys, one component is water, these eutectic points are usually called cryohydric points. At these points, three phases coexist and hence the sys. is invariant

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

② Congruent M.Pt: There are 4 maxima in the phase diagram at C, E, G and I, corresponding to the formn. of some

compds. these points represent the congruent M.Pt of salt hydrates. In the case of salt-H2O sys. the congruent M.Pt are known as eutectic points. At these points, the two component sys. becomes one comp sys as the two compounds have the same composition both in the solid and liq. phases. Thus the sys is invariant at the eutectic points.

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

③ Curves:

In the phase diagram, A is the M.Pt of ice or freezing point of H_2O. When $FeCl_3$ is added, the freezing point of water decreases along AB. Hence AB is called freezing point curve of H_2O. Along AB, ice and soln are in equilibrium. Hence

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

The comp. of the soln. changes along AB till pt B is reached. At pt. B solid $FeCl_3$ @ H_2O begins to separate as a new phase. Hence at this point ice, solid $FeCl_3 \cdot 12H_2O$ and soln. are in equilibrium

Transition B is called eutectic (cryohydric) point and the sys is invariant-

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

On further addn of $FeCl_3$ and also the soln is heated, the curve BC is traced. This represents the solubility curve of $Fe_2Cl_6 \cdot 12H_2O$ with a max. at C (37°C). At this point, the solid and liq phases have the same comp i.e. $Fe_2Cl_6 \cdot 12H_2O$. Hence C is called congruent melting point. (dystectic)

Addn of $FeCl_3$ beyond pt C causes a lowering of solubility of $Fe_2Cl_6 \cdot 12H_2O$ along CD. It is ∴ to note that the solubility of $Fe_2Cl_6 \cdot 12H_2O$ decreases along CD due to decrease in amt of $FeCl_3$. The result is that at temp below 37°C, the $Fe_2Cl_6 \cdot 12H_2O$ show distinct solubilities x_1 and x_2. Such a phenomenon is called retrograde solubility

On continued addn of ferric chloride phase $Fe_2Cl_6 \cdot 12H_2O$ disappears and the sys follows the curve DE. At E, a new solid $Fe_2Cl_6 \cdot 7H_2O$ crystallises out. Thus DE is the solubility curve of $Fe_2Cl_6 \cdot 7H_2O$ and E is its congruent M.Pt

In a similar manner, the formn of

$FeCl_3 \cdot 5H_2O$ at 6 and $FeCl_3 \cdot 6H_2O$ at 1 may be explained. The curves PQ and H_2 represent the solubility curves of $FeCl_3 \cdot 5H_2O$ and $FeCl_3 \cdot 6H_2O$ resp. The curve Je indicates the solubility of anhy. ferric chloride in H_2O

Gas - Solid sys.

$CuSO_4 - H_2O$ sys:

$CuSO_4$ - takes up water molecules during crystallisation and form salt hydrates or crystallohydrates. It forms three types of crystallohydrates under different vapour Pr. of H_2O

Crystallohydrate	V. Pr. of H_2O
$CuSO_4 \cdot H_2O$	4.5 mm Hg
$CuSO_4 \cdot 3H_2O$	30.9 mm Hg
$CuSO_4 \cdot 5H_2O$	45.5 mm Hg.

When anhydrous $CuSO_4$ is taken in a closed vessel at 50°C and water vapour is gradually introduced, hydration occurs. This can be explained by the vapour Pr. comp. diag.

Comp → (moles of H_2O)

Point D

At this point, anhydrous $CuSO_4$ exists.

Point A :

When water vapour is introduced into the sys, the V.P rises along the line OA. The anhy. $CuSO_4$ begins to absorb H_2O and forms $CuSO_4.H_2O$ at a V.Pr. of 4.5mm of Hg at pt. A

$$CuSO_4 + H_2O \rightleftharpoons CuSO_4.H_2O$$

The process is represented by the line AB, along which $CuSO_4$, $CuSO_4.H_2O$ and water vapour are in equilibrium and the sys would be invariant.

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

The vapour pr. remains const along AB until all the anhy. salt is converted into the monohydrate at pt. B

iii) Point C :

Further addn of water vapour increases the vapour pr and at a pr of 36 mm of Hg, $CuSO_4 \cdot H_2O$ begins to be converted into $CuSO_4 \cdot 3H_2O$

$$CuSO_4 \cdot H_2O + 2H_2O \rightleftharpoons CuSO_4 \cdot 3H_2O$$

This process is represented by the line CD. Along this line, three phases $CuSO_4 \cdot H_2O$, $CuSO_4 \cdot 3H_2O$ and water vapour coexist in equilibrium. So the sys is invariant

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

The vapour pr remains const along CD upto the complete conversion at D.

iv) Point E :

The pr again rises when all $CuSO_4 \cdot H_2O$ is converted into $CuSO_4 \cdot 3H_2O$ on addition of H_2O. When the vapour pr becomes 45.5 mm of Hg at pt E, $CuSO_4 \cdot 3H_2O$ begins to be converted into $CuSO_4 \cdot 5H_2O$. This is represented by the line EF. Along the line, three phases $CuSO_4 \cdot 3H_2O$, $CuSO_4 \cdot 5H_2O$ and water vapour are in equilibrium and its sys would be invariant one $F = C - P + 1 = 2 - 3 + 1 = 0$.

Solutions of non electrolytes

Liq – Liq systems

A homogeneous or heterogeneous mixture of two liquids called solution is a two component sys. The mutual solubilities of the two liquids depend upon ① P ② T of the binary liquid mixture. The effect of P or T on the comp of a binary solution can be explained by the P – C or T – C phase diag respt.

Depending upon the mutual solubility of the two liquids the binary liquid sys are classified into 3 Types

1. Completely miscible liq. sys.
2. Partially miscible liq. sys.
3. immisible liq. sys.

1. Completely miscible liq. sys.

When two liquids are soluble in each other in all proportions, a completely miscible binary solution is formed (eg) benzene and toluene alcohol and water, HCl and H_2O

Ideal soln:

An ideal soln is one where in the

molecules attract one another with equal force irrespective of their nature. Thirdly A dissolves in B forming an ideal soln. the force bet A and A, B and B, A and B will be the same.

Characteristics of an ideal solution.

① Ideal solutions obey additivity rule. This is the property of an ideal soln. is the sum of the prop of the component liquids

② There is no interaction bet the molecules of the components of an ideal soln.

③ There is no vol. change of mixing for an ideal soln. ie $\Delta V_{mix} = 0$

④ There occurs no heat change during mixing of components $\Delta H_{mix} = 0$

⑤ Mixing of components of an ideal soln makes increase in entropy $\Delta S_{mix} > 0$

⑥ In an ideal soln, the activity of a component is equal to its mole fr

⑦ An ideal soln obeys Raoult law

eg. ① Benzene and toluene

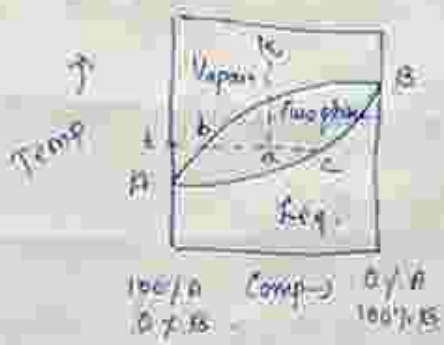
② Benzene and ether

③ Hexane and heptane

④ Chlorobenzene and bromobenzene.

Level rule

To det the relative amt of the two phases in a sys. & the relative amt of the relative amounts of the two phases in a sys, a horizontal line called Tie line is drawn through the pt describing the comp of that sys. to intersect the lines confining the given phase region. The section of that line between the given pt and the points determining the phase composition are inversely proportional to the quantities of the phases.



If pt a describes the composition of the sys, pt b at which the tie line meets the vapour curve gives the composition of the vapour. That pt c represents the comp of the liq. phase.

Acc. to level rule:

$$\frac{\text{Amt of liq phase}}{\text{Amt of vapour phase}} = \frac{ba}{ac}$$

Raoult's law of ideal solutions.

A quantitative relationship between the vapour pr of a liq and its conc in soln was deduced by Raoult. This is known as Raoult's law.

Defn:

The partial v.p of any volatile liq in a liquid solution is equal to the product of the vapour pr of the pure liquid and its mole fraction in the solution.

If an ideal soln is formed bet A and B

$$P_A = P_A^\circ x_A$$

$$P_B = P_B^\circ x_B$$

P_A - partial v.p of A in soln.

P_A° = v.p of pure A.

P_B = Partial v.p of B in soln.

P_B° = v.p of pure B

x_A = Mole fr of A in the soln

x_B = Mole fr of B in the soln.

Thermodynamical derivation of Nernst law

Consider any component A both in the gas and solution phase. Then the chemical potential of A is given by

(i) In gas phase $\mu_{A(g)} = \mu^0_{A(g)} + RT \ln f_A$

(ii) In soln phase $\mu_{A(l)} = \mu^0_{A(l)} + RT \ln a_A$

where μ^0_A - std chemical pot of A

f_A = fugacity of A

a_A - Activity of A.

At equilibrium

$$\mu_{A(g)} = \mu_{A(l)}$$

or) $\mu^0_{A(g)} + RT \ln f_A = \mu^0_A + RT \ln a_A$

or $\frac{f_A}{a_A} = z$ (a const.)

In the pure state of the component

$f_A = f^0_A$ and $a_A = 1$

hence, $z = f^0_A$

$\therefore \frac{f_A}{a_A} = f^0_A$

or $a_A = \frac{f_A}{f^0_A}$ — (1)

When the soln is ideal, fugacity may be replaced by partial pr and activity may be replaced by mole fr. now (1) becomes

$$x_A = \frac{P_A}{P^\circ_A} \quad \text{— (2)}$$

P_A = V.P of A in soln.

P°_A = V.P of A in pure state

x_A = Mole fr. of A

eqn (2) is written as

$$P_A = P^\circ_A \cdot x_A .$$

Azeotropic mixtures.

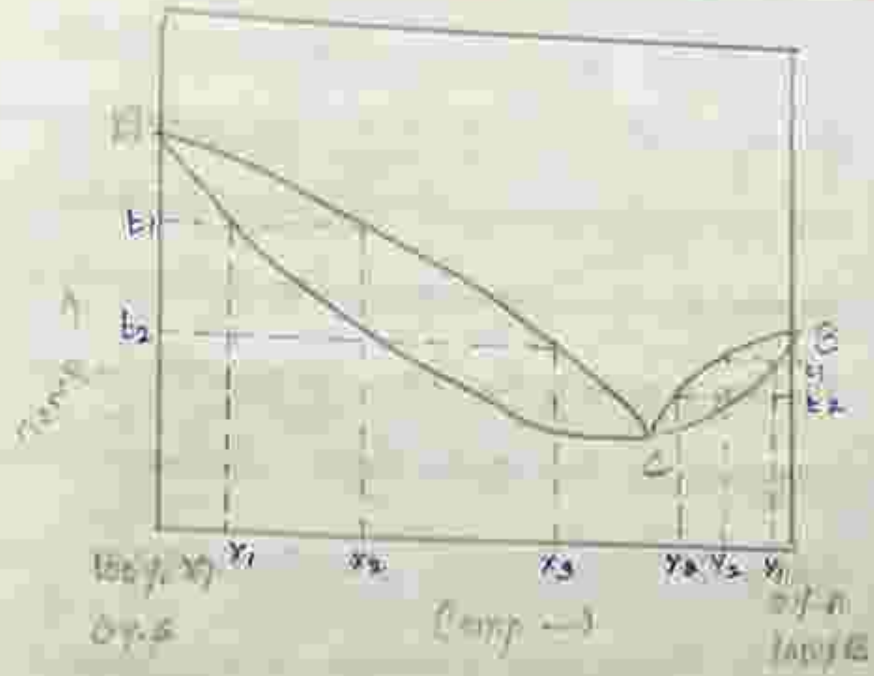
Boiling point - Composition diagram for a Non-Ideal binary solution.

(Theory of Azeotropic distillation)

The complete separation of the components of a non-ideal binary sys. is not possible by fractional distillation. At best it can be resolved into one pure component and a Mixture of two components which like resulting

mixture is heated, it distill over without any change in comp. Mix of this type are known as const Boiling mixtures or azeotropic mixtures or azeotropes. Fractional distillation which results in the formn of an azeotropic mixture is called azeotropic distillation. The principle of azeotropic distillation can be understood from the B.Pt - composition curve of a non-ideal sys.

① TYPE - I : B.Pt - comp curve with a minimum



If a binary soln. (AB) of comp x_1 is distilled, it boils at t_1 and vapours in equilibrium will have the comp x_2. This is richer in the more volatile component B. Consequently, the residual liquid

mixture will be enriched with the less volatile component A.

When the vapour of composition x_2 is condensed and redistilled, the distillate with comp. x_3 is obtained. The proportion of B in the 2nd distillate is greater than that in the 1st one. If the process is repeated several times, a distillate of comp. C is obtained ultimately. This distillate is a mix. of the two liquids which boils without any change in comp. i.e it is an azeotropic mix. The residual liq is pure A.

In a similar manner, distillation of a binary solution of comp y_1 yields pure B and the azeotropic mix. C. Thus fractional distillation of a non ideal liq. pair yields an azeotropic mix of the two components and one component in the pure state. Ethanol and water form a binary azeotropic mix containing 95 % by. alcohol. The absolute alcohol (100 % ethanol) cannot be prepared by distilling the alcohol-water mixture. It may however, be obtained by extractive distillation with a third component like benzene. This give rise to 3 fractions

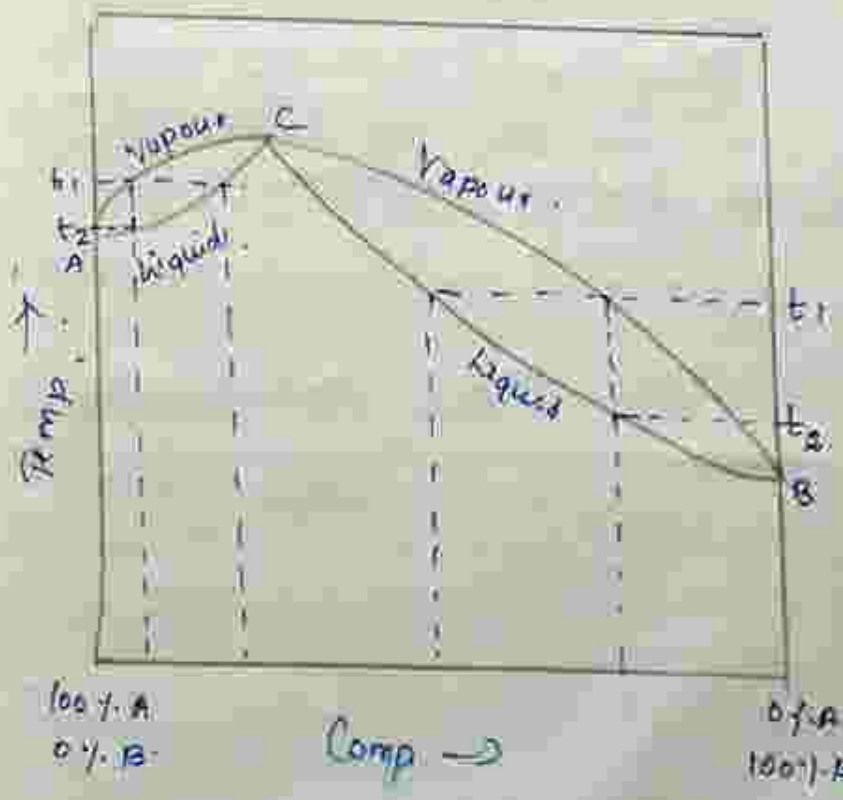
① A binary azeotrope of ethanol and benzene and water distills over first at 64.5°C

② A binary azeotrope of ethanol and benzene distills over 67.8°C and

③ pure ethanol 100% is left in the flask as the residual liq. it distills over at 78.3°C

TYPE : B : B.Pt - Comp. curve with a maximum

The behaviour of non-ideal soln. having a maximum B.Pt is analogous to type A soln. As in type A sys. repeated distillations of a binary soln of comp x_1 will yield comp. A in the distillate and a const Boiling azeotropic mixture C in the residual liquid.



Similarly repeated distillation of a binary soln having comp Y will yield pure B as the distillate and a const boiling mixture C as the residual liquid. HCl and H_2O form a binary azeotropic mixture containing 80.2 % HCl

Azeotropic mixture.

Binary mix of completely miscible liq. which distil without any change in comp- are called const boiling mixture or azeotropic mix or azeotropes

eg

I High boiling azeotropes

HCl 20.2 % — H_2O 79.8 %.

Phenol 42 %. — Aniline 58 %.

II low boiling azeotropes

Water 4 % — ethanol 96 %.

CCl_4 79.5 % - Methanol - 20.5 %.

Completely immiscible liq. sys.

There are certain liq. pairs, eg) nitro benzene and water, liquid paraffin and water, mercury and water, CS_2 and water in which the mutual solubility is so small that they are considered to be completely immiscible liquid system.

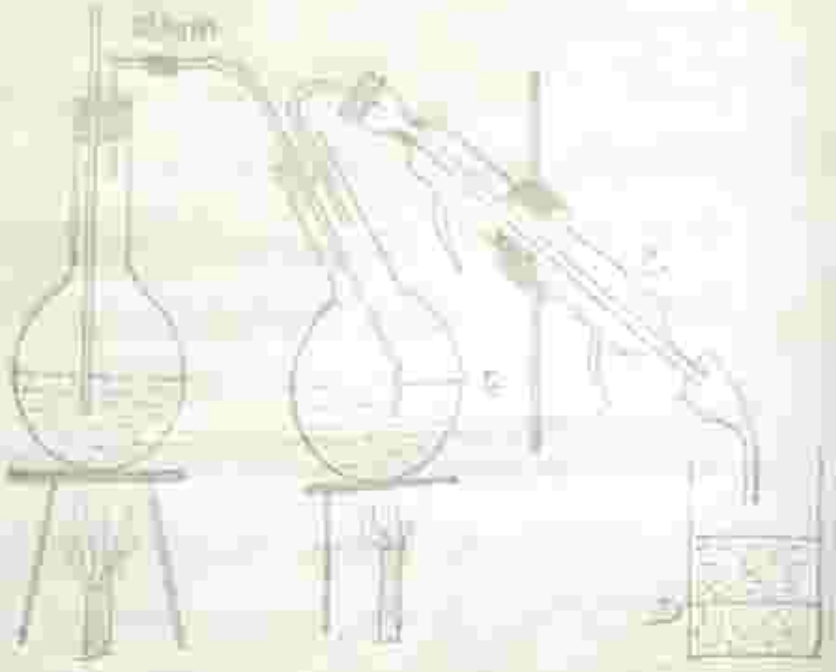
Theory of steam distillation.

Distillation of an organic liquid in a current of steam is called steam distillation. If the organic liquid is completely immiscible with water, the two liquids would behave independently to each other. That is each liquid would exert its own vapour pr. at the given temp independent of the other liquid. If p°_A and p°_B are the vapour pressure of the pure liquid, then the total pr. p, of the mixture is gn by $p = p^\circ_A + p^\circ_B$

liq A and B will boil when their vapour pr. $p^\circ_A + p^\circ_B$ becomes equal to the external pressure.

Since $p > p^\circ_A$ or p°_B, a mixture of two immiscible liq. boils at a temp much lower than the boiling point of either of two liquids. This is the basic principle of steam distillation.

The apparatus set up is given below



The organic liq. is distilled in a current of steam. The liquid boils below its boiling point and gets vapourised. The vapours along with steam are condensed and collected in a receiver. An immiscible liquid pair of the organic liquid and water is formed. They are separated by means of a separating funnel.

Application of steam distillation.

① Steam distillation is used for the purification of ⓐ organic liquids with very high B.pt and ⓑ org. liq. which decompose when

Rusted using their normal B.Pt.

(c) It is useful in determine the molecular weights of organic substances.

Let P^*_A and P^*_B be the partial vapour pr. of the two components with mole fr. x_A and x_B resp.

$$P = P^*_A + P^*_B$$

$$P^*_A = x_A P$$

$$P^*_B = x_B P$$

Where P is the tot vapour pr.

Now $$\frac{P^*_A}{P^*_B} = \frac{x_A}{x_B} \quad - (1)$$

Since $x_A = \frac{n_A}{n_A + n_B}$ and $x_B = \frac{n_B}{n_A + n_B}$

$$\frac{x_A}{x_B} = \frac{n_A}{n_B}$$

Sub. the value of $\frac{x_A}{x_B}$ in (1)

$$\frac{P^*_A}{P^*_B} = \frac{n_A}{n_B} \quad - (2)$$

Where n_A and n_B are the no. of moles of the component A and B in the vapour phase

$$\frac{P^*_A}{P^*_B} = \frac{w_A/M_A}{w_B/M_B}$$

$$= \frac{w_A \cdot M_B}{w_B / M_A}.$$

$$\frac{w_A}{w_B} = \frac{M_B \cdot P^*_A}{M_B P^*_B}$$

If the vapour pr and the weight ratio of the steam distillate of the two components are known, the molecular weight of the organic liq. can be det. knowing the molecular wt of water as 18.

Partially miscible liquid sys.

There are some liq pairs which dissolve in each other only to a limited extent. They constitute partially miscible liq. sys. In such a sys, a liq will completely dissolve in a large quantity of the other to form a completely miscible liq. sys. If the quantity of the liquid is gradually increased and exceeds the saturation limit, two liq. layers are formed. The two liq. layers in equilibrium are known as conjugate solutions. It has been found that the mutual solubility of the two liquids changes with temperature. The temp at which a pair of partially miscible liq becomes completely miscible is called the critical soln temp (CST) or consolute

temp. The study of mutual solubility of partially miscible liq. pairs with temp has revealed that there are three types of such sys. They are.

① Sys with upper C.S.T eg: Phenol with H_2O

② Sys with lower C.S.T (eg) Triethylamine and H_2O

③ Systems with upper and lower C.S.T (eg) Nicotine and water.

Type:1 Phenol - Water sys: (System with upper C.S.T).

Phenol and water are partially miscible in each other. Their mutual solubility, however increases with temp as shown in the Temp- comp curve.

The solubility of phenol in H_2O increases along the curve AB with temp. Similarly the solubility of water in phenol increases along CB. At any definite temp, the composition of the conjugate solutions are given by points on the curves Thus at a temp T_1 the tie lines xy gives the compositions of the conjugate solution- point x represents composition of water rich layer and point y represents composition of phenol rich layer. At any point d, the relative amounts of the two layers can be

calculated by the lever rule.

$$\frac{\text{Amt. of water rich layer}}{\text{Amt. of phenol rich layer}} = \frac{dr}{xd}$$

As the temp. is raised, the compositions of the two curves meet smoothly at the maximum point B. The temperature corresponds to this point is 66°C. At and above this temp, phenol and water would be totally miscible in all proportions. This temp is called upper critical solution temp. of the given sys. The composition of the solution at the CST is 33% by weight of phenol.

There will be two layers within the area ABC and the sys. is heterogeneous. Outside ABC, the sys. is homogeneous and there is only one liq layer.

System with upper CST

Phenol - Water 66°C

Aniline - Water 167°C

Aniline - Hexane 59.6°C

Type II Triethylamine - Water system (system with lower C.S.T.)

Triethylamine and water are partially

miscible liquids in which the mutual solubility decreases with increasing temperature. For such system, the shape of the curve is reverse to type-I. This leads to a lower critical solution temp. (18.5°C). At and below this temperature the two liquids are completely miscible in all proportions. The comp. of the solution at the C.S.T is 30% by weight of triethylamine.

Sys. with lower C.S.T

Triethylamine – Water 18.5°C

Diethylamine – Water 43°C

Methyl piperidine – Water 48°C

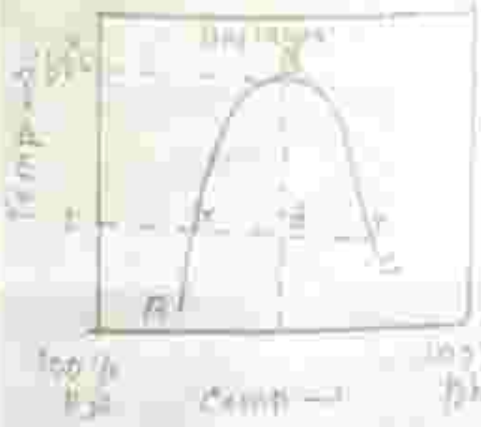
Type: III Nicotine – water system (System with lower and upper CST)

This system has a closed solubility curve with both upper and lower critical solution temp. 208°C and 61°C. Within the enclosed area, the sys is heterogeneous and the liquids are partially miscible. But outside the area the liquids are completely miscible and the system becomes homogeneous. Thus Nicotine and water are completely miscible in all proportions above 208°C and below 61°C.

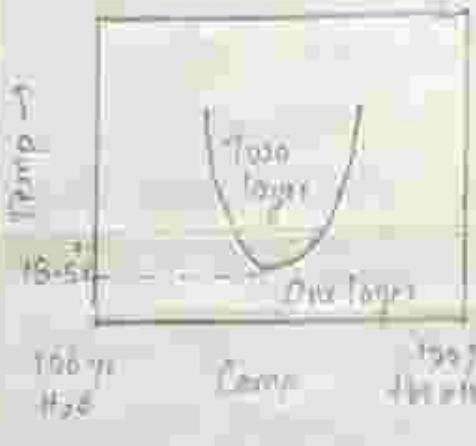
Systems with upper and lower CST

Nicotine – Water 208°C / 61°C

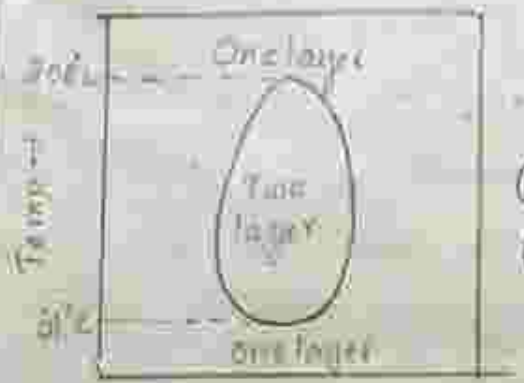
ethylmethyl ketone – water 13.8°C / 68°C



Phenol - water sys.
(sys with upper CST)



Triethylamine - Water sys.
(sys with lower CST)



Nicotine - H_2O sys.
(sys with upper and lower CST)

Temp →

Effect of impurities on CST

The impurities have a marked effect on the critical soln temp. The effect of impurities on CST was first studied by Crismer. He found that CST varies linearly with the conc of impurities.

If an impurity is soluble in one of two liquids, the mutual solubility decreases further so that the upper CST rises and the lower CST decreases. For eg. if a small amt. of 1% solution of sodium chloride is added, the CST of phenol-water sys is raised by 12°.

When the impurity dissolves in both the liquids, the mutual solubility increases in such a way that the upper CST is lowered and the lower CST is raised. For eg. a few ml of 1% sodium oleate or sodium stearate lower the CST of phenol-water sys by 44°. This means that phenol dissolves in water smoothly at room temp in the presence of a little soap solution.

Application of CST measurements:

It can be used to test the purity of phenol and other liquid which are partially miscible with water. This is referred as 'crismertest'

DISTRIBUTION LAW:

The Nernst distribution law deals with the distribution of a solid between two immiscible liquids. Benzene is immiscible with water and iodine is soluble in both the liquids. When a sat. soln. of I_2 in benzene is shaken with water, iodine distributes itself between the two liquids in a fixed ratio. If C_1 and C_2 are the conc. of iodine in benzene and water resp. then at const temp.

$$\frac{C_1}{C_2} = K_D$$

where K_D is a const., called the distribution or partition coefficient. This is the mathematical form of the distribution law which states that when a solute is added to a system of two immiscible liquids, it distributes itself between the two liquids in a constant ratio.

Experimental verification of the law:

A sat solution of iodine in benzene is shaken with water for half an hour. On standing, the mixture separates into two layers. The conc. of iodine in each layer is determined separately by titration against standard thio. The ratio of the concentration of iodine in benzene and water is found to be a const.

$$\frac{\text{Conc. of iodine in benzene}}{\text{Conc. of iodine in water}} = K_D \text{ (Constant)}$$

Thermodynamic derivation of Distribution law:

Consider the distribution of iodine between benzene and water at Tc. If μ_1 is the chemical potential of iodine in benzene and μ_2 is its chemical potential in water then

$$\mu_1 = \mu_1^\circ + RT \ln a_1$$

$$\mu_2 = \mu_2^\circ + RT \ln a_2$$

where a_1 and a_2 are the activities of iodine in benzene and water layer respt.

At equilibrium,

$$\mu_1 = \mu_2$$

$$\mu_1^\circ + RT \ln a_1 = \mu_2^\circ + RT \ln a_2$$

$$\ln \frac{a_1}{a_2} = \frac{\mu_2^\circ - \mu_1^\circ}{RT} \quad \text{— (1)}$$

At a given temp, the standard chemical potential of a substance in a solvent is const and hence eq (1) becomes

$$\ln \frac{a_1}{a_2} = \text{const} \quad \text{---} (2)$$

For ideal sys, the activity is almost equal to conc, Hence eqn (2) reduces to

$$\frac{C_1}{C_2} = K_D \text{ (const)},$$

Conditions for distribution law:

The distribution law is valid only under the foll condition.

1. The temp remains constant throughout the experiment
2. The solvents are perfectly immiscible. This means that their mutual solubility remains unaltered by the addition of the solute.
3. The solution is dilute
4. The solute does not react with the solvents.
5. The solute remains in the same molecular state in both the solvents. That is the solute does not undergo association or dissociation.

Limitations of the law

The distribution law does not hold good if the solute undergoes association or dissociation in any one of the solvents. In such cases, the law is applied with some modifications.

1. Association of solute

Let C_1 and C_2 be the conc. of the solute in two solvents. If the solute gets associated in solvent 2, then the distribution law is modified as

$$\frac{C_1}{\sqrt[n]{C_2}} = K_D$$

where n is the no. of molecules present in the associated species. eg. When benzoic acid is distributed between water and benzene it is associated in benzene medium to form a dimer. (n=2)

$$2\,C_6H_5COOH \longrightarrow (C_6H_5COOH)_2$$

Dimer

2. Dissociation of solute.

Let C_1 and C_2 be the conc. of the solute in the two solvents. If the solute undergoes dissociation in solvent 2, then the distribution coeff is given by

$$\frac{C_1}{C_2(1-x)} = K_D$$

where x is the degree of dissociation of the solute eg when oxalic acid is distributed between water and ether. it suffers dissociation in the aq. layer.

$$H_2C_2O_4 \longrightarrow 2H^+ + C_2O_4^{2-}$$

Oxalic acid.

Solvent extraction.

The process of removing a substance from its aqueous solution by shaking with a suitable organic solvent is termed solvent extraction. It works on the preferential solubility of the substance in the organic solvent. It can be shown by the distribution law that the process of extraction is much more complete and economical if it is carried out in several operations with a given vol of the solvent

Let us consider a solution containing w gms of a solute in V ml of the solution. Suppose this solution is extracted with v ml of an organic solvent. If the extracting solvent has been used in a single operation

the amount of solute left unextracted is given by

$$W_1 = \left(\frac{kV}{kV+v}\right) W \quad \text{——} (1)$$

where $K = \frac{C_{H_2O}}{C_{solvent}} = \frac{1}{K_D}$

If on the other hand, the extracting solvent is used in several operations, the amt of solute left unextracted at the end of n extractions is gn by

$$W_n = \left(\frac{kV}{kV+v}\right)^n W \quad \text{——} (2)$$

where, n = No. of extractions, Since $n > 1$, it is obvious from eq (2) that the magnitude of W_n is small.

That is $W_n < W_1$

$$\left.\begin{matrix}\text{Amount of substance} \\ \text{extracted}\end{matrix}\right\} = \begin{matrix}\text{Initial amount} - \\ \text{Amount extracted}\end{matrix}$$

$$= W - W_n$$

Thus

$$W - W_n > W - W_1$$

Application of Distribution law

① To find the state of molecules

The distribution law is used to find out whether the molecules of a substance are in the normal state or associated or dissociated in a particular solvent.

② To determine the equilibrium constant

The principle of distribution is conveniently used to determine the equilibrium const of a reaction which involves complex forms.

$$KI + I_2 \rightleftharpoons KI_3$$

$$K = \frac{[KI_3]}{[KI][I_2]}$$

③ To determine the hydrolysis const

The distribution experiment can be employed in evaluating the hydrolysis const. of a salt like aniline hydrochloride

$$C_6H_5NH_2.HCl + H_2O \longrightarrow C_6H_5NH_2 + HCl$$

$$K = \frac{[C_6H_5NH_2][HCl]}{[C_6H_5NH_2.HCl][H_2O]}$$

Hydrolysis const $k_h = K\,[H_2O]$

$$= \frac{[C_6H_5NH_2][HCl]}{[C_6H_5NH_2 \cdot HCl]}$$

$$= \frac{C_{aniline} \times C_{HCl}}{C_{salt}}$$

4. Use of distribution indicators:

When a very dilute solution of I_2 in water is titrated against thiosulphate solution, the end point cannot be noticed sharply as the reaction mixture produces only a pale blue colour with starch. But addition of few drops of CS_2 or CCl_4 produces a deep blue colour. The organic solvent extracts most of the iodine which gives blue colouration with starch.

5. Extraction of substances:

The process of solvent extraction is generally used to separate and purify organic substances from their aqueous solution. Here multistep extraction is more effective than the single step extraction.

6. To estimate the solubility of a substance:

When two immiscible solvents are saturated with a solute, the ionic become

equal to the solubilities

$$\frac{S_1}{S_2} = k_D$$

The solubility of a substance can be calculating knowing its solubility in another solvent immiscible with the first one.

7. Washing of precipitate

In gravimetric analysis, the ppt is washed several times with small volumes of washing liquids. The impurities get distributed between the free and occluded solvent layers and the ppt is purified

(8) Partition chromatography:

It is an excellent analytical technique used to separate organic sub. This is based on the principle of distribution of the sub. between a stationary phase and a moving phase.

Unit - III Chemical Kinetics

Introduction :

Chemical kinetics is concerned with the study of the speed or rate at which a reaction proceeds. Such studies help to elucidate the reaction mechanism and reveal the influence of different factors which control the progress of the reaction.

Law of mass action

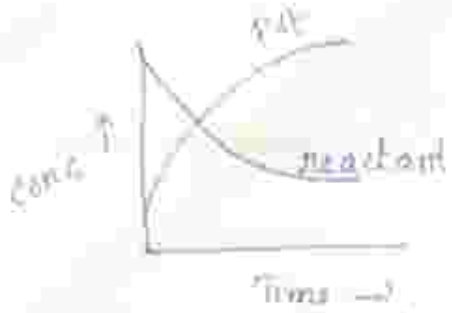
This gives the relation between the rate of the chemical reaction and the conc of the reactant.

The rate of a chemical reaction at a given temp is directly proportional to the pdt of the active masses of the reactant at that instant

This law is applicable to all reactions occuring in the gas phase or in the liquid phase.

Rate of a reaction :

The rate of the reaction is defined as the change in conc of the reactant or products per unit time. With the progress of time, the conc of the reactant decreases while that of the pdt increases.



For a reaction of the type:

$$A \rightarrow B$$

$$\text{Rate of the reaction} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

The negative sign implies that the conc. of the reaction is decreasing with time. If dx is the change in conc. at a time interval of dt, then

$$\text{Rate of the reaction} = \frac{dx}{dt}$$

Rate constant:

Consider the reaction

$$A + B \rightarrow \text{product}$$

If C_A and C_B are the molar conc. of the reactant A and B at any time 't', then the rate

$$\frac{dx}{dt} \propto C_A \cdot C_B$$

$$\frac{dx}{dt} = k\, C_A \cdot C_B$$

Where k = rate const. It is defined as the rate of the reaction when the molar conc. of

each reactant is unity. It is also known as specific reaction rate. The unit of rate constant is $k = lit\ mole^{-1} sec^{-1}$

Characteristics:

1) Greater k, faster the reaction

2) k depends on nature of the reactant.

3) k does not depend on conc. of reactant

4) k changes with Temp

5) unit of k depend on order of rxn.

Order of the reaction

The rate of a chemical reaction is proportional to the conc. of the reacting substances. The no. of conc. term which determine the rate of a rxn is called order of the reaction. It is equal to the sum of the powers to which the conc. terms are raised in the differential rate equation.

(Eg:) 1) $A \rightarrow$ pdt.

$$\frac{dx}{dt} = k[A]$$

order = 1 ∴ I order rxn

2) $A + B \rightarrow$ pdt

$$\frac{dx}{dt} = k[A][B]$$ II order rxn.

order = 2

(3) $2A \rightarrow$ pdt

$$\frac{dx}{dt} = k[A]^2$$

order = 2

∴ (2) and (3) are II order reactions.

(4) $aA + bB + cC \rightarrow$ pdt

$$\frac{dx}{dt} = k[A]^a[B]^b[C]^c$$

order = a+b+c.

If the rate of the reaction is independent of the conc of the reactant, the reaction is said to be zero order. Besides I, II, III order reactions, there are reactions of fractional order.

Molecularity of a reaction

The molecularity of a reaction is defined as the minimum no of reacting molecules required to bring about a chemical reaction.

When one, two or three molecules are involved in a chemical reaction, the reaction is said to be unimolecular, bimolecular or trimolecular rxn resp.

Differences bet Molecularity and order of rxn.

	Molecularity	Order
1.	It is equal to the no. of molecules of reactant which take part in a single step chemical reaction	It is equal to the sum of molar conc. of the reactant in the rate expression
2.	It is a theoretical concept which depends on the rate det. steps for a rxn mixn.	It is experimentally det. quantity which is obtained from the rate of the overall rxn
3)	It is always a whole no.	It may be whole no., Zero or fractional Value
4.)	It is obtained from a single balanced chemical equation	It cannot be obtained from a balanced chem. Equation
5)	It reveals some basic facts about rxn mixn	It does not reveal anything about reaction mixn.

Zero order rxn:

Zero order rxn is one in which the rate of the rxn does not depend on the conc. of the reactant

Derivation of Rate equation

Let us consider the reaction

$A \longrightarrow$ product

Rate of the reaction $r = -\frac{d[A]}{dt} = k[A]^n$ — (1)

or $\frac{dx}{dt} = k(a-x)^n$

$\frac{dx}{dt} = k$

$dx = k \cdot dt$

Integrating $\int dx = k \int dt$

$x = kt + c$ — (2)

The value of c can be det using $x = 0$ when $t = 0$

$0 = k(0) + c \Rightarrow c = 0$

$x = kt$

$k = \frac{x}{t}$

where k is rate const of zero order rxn

characteristics

1) Unit mol lit^{-1} sec^{-1} or mol dm^{-3} sec^{-1}

2) Half life time $t_{1/2}$ of a

3) (eg) Thermal decomp of HI on gold surface

$2HI \xrightarrow{Au} H_2 + I_2$

(2) Photochemical combination of H_2 and Cl_2 in presence of sunlight

3.4 Rate of first order reaction

A first order reaction is one in which the rate of the reaction depends only on one conc. term.

Consider the rxn :

$A \longrightarrow$ pdt

Rate of the reaction $r = -\frac{d[A]}{dt} = k_1[A]$ — (1)

where k_1 is the rate const of the I order rxn. This eqn. is called as differential rate expression for the first order reaction

(a) Derivation of rate const.

Let the initial conc of A be 'a' mol dm^{-3}. After time 't', let 'x' mol dm^{-3} of A has reacted. Then the conc of A remaining after time 't' is $(a-x)$ mol dm^{-3}

$$-\frac{d(a-x)}{dt} = k_1(a-x) \quad \text{— (1)}$$

$$\frac{dx}{dt} = k_1(a-x) \quad \text{— (2)}$$

$$\text{i.e.} \quad \frac{dx}{a-x} = k_1\,dt$$

On integration, $\int \frac{dx}{a-x} = k_1 \int dt$

$$-\ln(a-x) = k_1 t + c \quad \text{— (4)}$$

where 'c' is the integration const. The value of 'c' is det using boundary condn

when $t = 0$, $x = 0$.

eqn (a) becomes

$$-\ln a = k_1(0) + c$$

or $c = \ln a$

substituting the value of c in eqn (a), we get

$$-\ln(a-x) = k_1 t - \ln a$$

$$\ln a - \ln(a-x) = k_1 t$$

$$\ln \frac{a}{a-x} = k_1 t$$

$$k_1 = \frac{1}{t} \ln \frac{a}{a-x}$$

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{——— (5)}$$

Eqn (5) is the integrated rate eqn for the rate const of a first order reaction

Characteristics:

(1) The overall rate of the reaction depends only on the conc of one of the reactant

(2) Unit of K:

For the first order reaction, the rate const is

$$k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$$

unit $= \text{time}^{-1}$ [sec^{-1} / min / Year]

(iv) Graphical representation

The first order rate const equation can be rewritten as

$$\frac{k_1 t}{2.303} = \log a - \log(a-x)$$

$$\log(a-x) = \frac{-k_1 t}{2.303} + \log a$$

On plotting of $\log(a-x)$ against t a straight line is obtained with a negative slope equal to $\frac{k_1}{2.303}$

Time for half change $t_{1/2}$ (Half life period for zero)

Half life period of a reaction is defined as the time required for 50% completion of the reaction. It is represented by notation $t_{1/2}$

When $t = t_{1/2}$ $x = \frac{a}{2}$ then the rate const of the first order reaction is

$$\therefore k_1 = \frac{2.303}{t_{1/2}} \log \frac{a}{a/2}$$

$$t_{1/2} = \frac{2.303 \times \log 2}{k_1} = \frac{0.693}{k_1}$$

$$t_{1/2} = \frac{0.693}{k_1}$$

The $t_{1/2}$ for the first order rxn does not depend on conc terms.

Ex. for first order:

① Decomposition of H_2O_2

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

② Thermal decomp. of N_2O_5

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

Pseudo First order reaction or Pseudo Unimolecular reaction:

The reaction with molecularity greater than or equal to 2 but order is one are called Pseudo unimolecular or pseudo first order rxn.

eg: ① Hydrolysis of ethyl acetate in acid medium

② Inversion of cane sugar

③ Hydrolysis of Acetic anhydride.

Application of first order rate equation to

① Acid catalysed ester hydrolysis

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

ethyl acetate → acetic acid, ethyl alcohol

There:

(iii) Inversion of Sucrose

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

glucose fructose.

Both the above reactions are bimolecular and follow the kinetics.

$$\text{Rate} = k[CH_3COOC_2H_5][H_2O]$$

or $$\text{Rate} = k[C_{12}H_{22}O_{11}][H_2O]$$

but reactions are found to be of I order. experimentally it is observed that it is usually carried out taking dilute aqueous solution of ester or sugar and acid (H+) such that in the reaction mixture water exists in large excess as compared to ester. It is also say that H_2O has almost its maximum conc. of 55.5 mol L^{-1}, so there is no appreciable change in its conc and the same remains practically const.

$\therefore$ $\text{Rate} = k[H_2O][CH_3COOC_2H_5]$

becomes $\text{Rate} = k'[CH_3COOC_2H_5]$ where (k') called pseudo rate const. Thus the molecularity of the above reaction is two. but its order is one.

Second order reaction:

A second order rxn is one in which the rate of the reaction depends on two conc. terms.

When both reactants are same:

Consider the rxn

$2A \rightarrow$ pdt.

Rate, $r = -\frac{1}{2}\frac{d[A]}{dt} = \frac{dx}{dt} = k_2[A]^2$ — (1)

k_2 = rate const of II order rxn.

This eqn is known as differential rate expression for the second order rxn.

Derivation:

Let the conc. of A at time 't' sec is $a-x$ mol/lit

then $\frac{dx}{dt} = k_2(a-x)^2$ — (2)

i.e $\frac{dx}{(a-x)^2} = k_2\,dt$

Integ, $\int \frac{dx}{(a-x)^2} = k_2 \int dt$

$$\frac{1}{a-x} = k_2 t + C$$

where C is the integration const. The value of C is determined using boundary condn. when $t=0, x=0$. eqn (3) becomes.

$$\frac{1}{a} = k_2(0) + C$$

$$C = \frac{1}{a}.$$

sub. the value of c in eqn (2), we get

$$\frac{1}{a-x} = k_2 t + \frac{1}{a}$$

$$k_2 t = \frac{1}{a-x} - \frac{1}{a}$$

$$k_2 = \frac{1}{t}\left[\frac{a-(a-x)}{a(a-x)}\right]$$

$$k_2 = \frac{x}{t\,a(a-x)} \quad \text{——(4)}$$

eqn (4) is the integrated rate eqn for the rate const of a second order rxn.

(6) Characteristics of II order rxn

(1) Unit of k_2

For the II order rxn, the rate const is

$$k_2 = \frac{1}{t}\,\frac{x}{a(a-x)}$$

Writing the units of t, x, a and a-x in the above expression, then

$$k_2 = \frac{1}{s}\,\frac{\text{mol dm}^{-3}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}$$

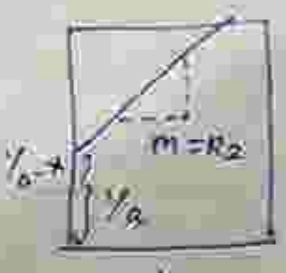
$$\therefore \text{Unit} = \text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}.$$

(2) Graphical representation

The second order rate const can be represented as

$$\frac{1}{t}\left[\frac{1}{a-x} - \frac{1}{a}\right] = k_2$$

$$\frac{1}{a-x} = k_2 t + \frac{1}{a}$$



On plotting $\frac{1}{a-x}$ against t, a straight line is obtained with +ve slope equal to k_2.

(iii) Time for half change $t_{1/2}$

$$k_2 = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$$

At $t_{1/2}$, $x = \frac{a}{2}$ $\quad a-x = \frac{a}{2}$

$$t_{1/2} = \frac{1}{k_2}\left[\frac{a/2}{a-a/2}\right] = \frac{1}{k_2 a}$$

$$\therefore t_{1/2} \propto \frac{1}{a}$$

The $t_{1/2}$ of second order reaction is inversely proportional to its conc. term.

eg:) Conversion of Ozone to oxygen.

$$2O_3 \rightarrow 3O_2$$

② Saponification of ester -

$$CH_3COOC_2H_5 + KOH \longrightarrow CH_3COOK + C_2H_5OH$$

When reactants are different:

Consider a second order rxn.

$$A + B \longrightarrow \text{product}.$$

$$\text{Rate } r = \frac{-d[A]}{dt} = \frac{-d[B]}{dt} = \frac{dx}{dt} = k_2[A][B] \quad \text{—①}$$

where k_2 is the rate const of II order rxn.

Derivation:

Let the initial conc. of A is a mol dm^{-3}

and that of 'B' is 'b' mol dm^{-3}. After time t, 'x' mol dm^{-3} of A and 'x' mol dm^{-3} of B react to form 'x' mol dm^{-3} of the pdt. Thus the conc. of A and B remaining after time 't' is (a-x) and (b-x) mol dm^{-3} resp.

$$\frac{dx}{dt} = k_2 (a-x)(b-x) \quad \text{——} (1)$$

(or)
$$\frac{dx}{(a-x)(b-x)} = k_2 dt$$

(or)
$$\frac{dx}{a-b}\left[\frac{1}{b-x} - \frac{1}{a-x}\right] = k_2 dt$$

using partial fraction (assuming $a > b$)

$$\frac{1}{(a-x)(b-x)} = \frac{1}{a-b}\left[\frac{1}{b-x} - \frac{1}{a-x}\right]$$

On integration.

$$\frac{1}{a-b}\left[\int \frac{dx}{b-x} - \int \frac{dx}{a-x}\right] = k_2 \int dt.$$

$$\frac{1}{a-b}\left[\int -\ln(b-x) - (-\ln(a-x))\right] = k_2 t + c$$

$$\frac{1}{a-b} \ln\left(\frac{a-x}{b-x}\right) = k_2 t + c \quad \text{——} (2)$$

where C is the integration const.

The value of C is det. using $t = 0, x = 0$

Eqn (2) becomes

$$\frac{1}{a-b} \ln \frac{a}{b} = k_2 (0) + c$$

$$c = \frac{1}{a-b} \ln \frac{a}{b}$$

sub, the value of C in eqn (1), we get

$$\frac{1}{a-b} \ln\left(\frac{a-x}{b-x}\right) = k_2 t + \frac{1}{a-b} \ln \frac{a}{b} \quad -(4)$$

$$k_2 t = \frac{1}{a-b} \ln\left(\frac{a-x}{b-x}\right) - \frac{1}{a-b} \ln \frac{a}{b}$$

$$k_2 t = \frac{1}{a-b}\left[\ln\left(\frac{a-x}{b-x}\right) - \ln\left(\frac{a}{b}\right)\right]$$

$$k_2 = \frac{1}{t(a-b)} \ln\left(\frac{b(a-x)}{a(b-x)}\right) \quad -(5)$$

(5) is the integrated rate expression for the rate const of a second order rxn. Now for $b > a$, the rate expression is changed to.

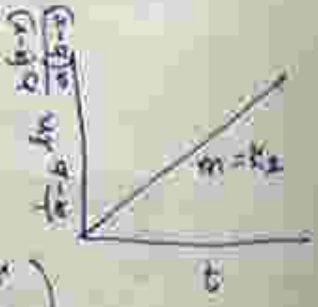
$$k_2 = \frac{1}{t(b-a)} \ln \frac{a(b-x)}{b(a-x)}$$

Characteristics :

(1) Graphical representation.

The second order rate const can be represented as.

$$k_2 t = \frac{1}{a-b} \ln\left(\frac{a-x}{b-x}\right)$$



On plotting $\frac{1}{a-b} \ln\left(\frac{a-x}{b-x}\right)$ against t, a st line passing through the origin is obtained.

With +ve slope equal to k_2

③ Units

Unit of k_2 is $dm^3 mol^{-1} s^{-1}$

Eqs

1) $K_2S_2O_8 + 2KI \longrightarrow 2K_2SO_4 + I_2$

2) $H_2 + I_2 \longrightarrow 2HI$

3.5. Methods for determining the order of a reaction:

(1) Use of integral rate expression (or) integration method.

* This is a trial and error method
* In the method the conc. of reactant at different time intervals are det experimentally
* The data obtained from the expt. are substituted in different integral rate eqn.

The rate equation which gives a constant value corresponds to the order of the reaction.

I order rxn, $k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$

II order rxn $k_2 = \frac{1}{t}\left[\frac{x}{a(a-x)}\right]$ and

$$k_2 = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}.$$

II order rxn $k_2 = \frac{1}{2t}\left[\frac{x(2a-x)}{a^2(a-x)^2}\right]$

* It is applicable for simple reactions but fails in case of complex reactions ie side or reversible reactions etc.

* In this method it is necessary to study the reaction over a wide time intervals.

Vant Hoff's differential method:-

Order of a rxn can be det. using differential rate eqn. The rate of n^{th} order reaction is gn by

$$r = k_n c^n.$$

If r_1 and r_2 are the rates at two diff. reactant conc. c_1 and c_2 then

$$\therefore r_1 = k_n c_1^n$$

$$r_2 = k_n c_2^n$$

$$\frac{r_1}{r_2} = \left(\frac{c_1}{c_2}\right)^n$$

Taking log, $\log \frac{r_1}{r_2} = n \log \frac{c_1}{c_2}$

$$\therefore n = \frac{\log r_1 - \log r_2}{\log c_1 - \log c_2}$$

r_1 and r_2 are the rates corresponding to the conc c_1 and c_2. Hence order of the reaction (n) can be calculated

Half - life method

Order of a reaction can be determined with the help of half life and initial molar conc

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

where n is the order of reaction

For two different initial conc a_1 and a_2, the half lives $(t_{1/2})_1$ and $(t_{1/2})_2$ are given by

$$(t_{1/2})_1 \equiv t_1 = \frac{1}{(a_1)^{n-1}}$$

$$(t_{1/2})_2 \equiv t_2 = \frac{1}{(a_2)^{n-1}}$$

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking log

$$\log \frac{t_1}{t_2} = (n-1) \log \frac{a_2}{a_1}$$

$$n-1 = \frac{\log t_1 - \log t_2}{\log a_2 - \log a_1}$$

$$n = 1 + \frac{\log t_1 - \log t_2}{\log a_2 - \log a_1}$$

Thus the order of rxn 'n' can be det.

(a) Ostwald's isolation method

This method is based on the principle that the rate of a reaction depends only on the conc. of the reactant which is present in small quantities. The reactant present in large excess do not affect the rate of reaction.

Consider a reaction:

$$A + B \longrightarrow \text{product}$$

To find out the order of this reaction, first of all, a small quantity of A and a large excess of B are taken. The order of the reaction is det. by any one of the above methods. This corresponds to the order w.r.t. A (n_A). Then the same reaction is carried out by taking small quantity of B and excess of A. Order is again determined. This corresponds to the order w.r.t B (n_B). The total order of the reaction is $n_A + n_B$.

(Eg) $H_2 + I_2 \rightleftharpoons 2HI$

When I_2 is in excess, the order of the reaction is pseudo first order w.r.t H_2. IInd order when H_2 is in excess. The order is pseudo I order w.r.t I_2.

∴ overall order is II order reaction.

5.6 Theories of reaction rate:

Temperature dependence of reaction rate:

The Arrhenius equation:

The rate of a reaction increases with T. In 1889, Arrhenius derived a mathematical expression for the variation of reaction rates with temp from Vant Hoff's reaction isochore.

$$\frac{d\ln K}{dT} = \frac{\Delta E}{RT^2} \quad \text{---(1)}$$

K = Eq. const

ΔE = Energy change.

$K = \frac{k_1}{k_2}$ and $\Delta E = E_1 - E_2$

Where k_1 and k_2 are the rate const of the forward and backward reactions respt.

Now (1) may be written as

$$\frac{d\ln k}{dt} = \frac{E_1}{RT^2}$$

$$\frac{d\ln k}{dt} = \frac{E_2}{RT^2}$$

In general, $\frac{d\ln k}{dt} = \frac{E_a}{RT^2}$

On integration, $\ln k = \frac{E_a}{RT} + \ln A \quad \text{---(2)}$

where A is the integration constant

eqn (2) may be written as

$$k = A e^{-E_a/RT}$$

This is called Arrhenius equation. In this equation A is a const called frequency factor and E_a is the energy of activation.

Significance of Arrhenius equation

i) Cal. of energy of activation

The Arrhenius equation may be used to calculate the activation energy of a reaction

$$k = A e^{-E_a/RT}$$

Taking logarithm.

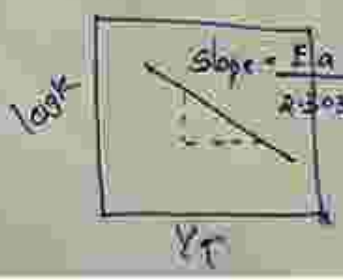
$$\ln k = \ln A - \frac{E_a}{RT}$$

(or) $2.303 \log k = 2.303 \log A - \frac{E_a}{RT}$

$$\therefore \log k = \log A - \frac{E_a}{2.303RT}$$

A plot of $\log k$ versus $\frac{1}{T}$ gives a st-line with a slope equal to $\frac{-E_a}{2.303R}$.

Knowing the slope E_a can be evaluated



2 Calculation of Reaction rate

$$\frac{d\ln k}{dt} = \frac{E_a}{RT^2}$$

∫ bet limits.

$$\int_{k_1}^{k_2} \frac{d\ln k}{dt} = \int_{T_1}^{T_2} \frac{E_a}{RT^2}$$

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\text{or } 2.303 \log \frac{k_2}{k_1} = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$= \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Thus if the reaction rate at one temp is known that at another temp can be cal. with a known value of E_a.

Collision theory:

This is the earliest theory of reaction rates. This was developed by Arrhenius and Vant Hoff.

Assumptions :

(1) The reactant molecules must come nearer and collide with each other.

(2) The reactant molecules must possess adequate energy at the time of collision. The collision must be effective

(3) Reactant molecules must be properly oriented at the time of collision

Derivation of rate const. of a bimolecular reaction :

Acc. to collision theory, the reactant molecule must collide with each other. On collision they must acquire sufficient energy to get themselves activated. Then a chemical reaction takes place.

Let us consider a reaction in gas phase at temp. T.

$$A + B \longrightarrow \text{pdt}$$

m_{AB} m_A m_B

mol. diameter σ_{AB} σ_A σ_B

No. of mole/cm^3 n_A n_B.

If A moves with an average velocity C_{av} it will travel C_{av} dist/sec and collide with B.

The collision of A and B looks like a cylinder.

Then Vol of cylinder $= \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 c_{av}$.

Then all the molecules of B within this volume will collide with the moving molecule A.

The no. of collisions per sec per cm^3 bet A and B $\Big\}$ $Z_{AB} = \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 n_A n_B c_{av}$

where $c_{av} = \sqrt{\frac{8RT}{\pi M_{AB}}}$, M_{AB} - reduced mass $= \frac{m_A m_B}{m_A + m_B}$.

Eqn ① becomes.

$$Z_{AB} = \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 n_A n_B \sqrt{\frac{8RT}{\pi M_{AB}}} \quad \text{——— ②}$$

Acc to Maxwell's distribution law of Molecular velocities.

$$n^* = n e^{-E_a/RT} \quad \text{——— ③}$$

Where n^* is the no. of activated molecules and n is the total no. of molecules.

$$\frac{n^*}{n} = e^{-E_a/RT}$$

$\propto$ Fr. of effective collision is $e^{-E_a/RT}$

∴ The rate of formn. of pdt

= Collision no (Z_{AB}) × fr. of effective collisions

Rate $= \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 n_A n_B \sqrt{\frac{8RT}{\pi M_{AB}}} \times e^{-E_a/RT}$ ——— ④

For a II order rxn,

rate $= k[A][B] = k n_A n_B$.

Comparing eqn. (A) and (B).

$$k n_A n_B = \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 n_A \cdot n_B \sqrt{\frac{8RT}{\pi M_{AB}}} e^{-E_a/RT}$$

$$k = \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8RT}{\pi M_{AB}}} e^{-E_a/RT} \quad \text{—— (6)}$$

$$k = Z' e^{-E_a/RT} \quad \text{—— (7)}$$

where $Z' = \text{Const} = \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8RT}{\pi M_{AB}}}$

For several rxn, the cal. value from eqn (7) and experimental value of rate const. 'k' differ widely. Hence the eqn (7) is modified into

$$k = p Z' e^{-E_a/RT} \quad \text{—— (8)}$$

where p is the probability factor or steric factor. The value of p varies from unity to about 10^{-9} acc. to the nature of the reactant.

Comparing eqn (8) with the Arrhenius equation $k = A e^{-E_a/RT}$ we get.

$$A = p Z$$

$$= p \pi \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\frac{8RT}{\pi M_{AB}}}$$

$$= \sqrt{8R\pi} \times P (d_{AB})^2 \left(\frac{T}{M_{AB}}\right)^{1/2} \quad \text{—— (9)}$$

where m_{AB} is reduced mass

$$\frac{m_A m_B}{m_A + m_B} \quad (\text{unit} = g\,mol^{-1})$$

sub the value of A, π in eqn (9) we get

$$A = \sqrt{8 \times 8.314 \times 3.14}\; p (d_{AB})^2 \left(\frac{T}{M_{AB}}\right)^{1/2}$$

$$= 14.452\; p (d_{AB})^2 \left(\frac{T}{M_{AB}}\right)^{1/2} \quad \text{---(10)}$$

Unit = $\sqrt{1000}\; m^3 s^{-1}$

For 1 mole,

$$A = 2.753 \times 10^{29}\; p (d_{AB})^2 \left(\frac{T}{M_{AB}}\right)^{1/2} dm^3 mol^{-1} s^{-1}$$

Failure of Collision Theory:

1) not able to explain the unimolecular rxn
2) not applicable for complex molecule
3) rate of certain rxn are extremely high. This is not explained by this theory
4) The rate const expression do not contain any entropy terms
5) This theory simply ignores vib. and rot. energy terms. It could be properly justified

Lindemann's theory :

It is a unimolecular rxn.

consider a reaction

$$A \longrightarrow \text{pdt } (P)$$

Mean

1. $A + A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^* + A$ —— (1)

activated mole.

2. $A^* \xrightarrow{k_3}$ Product (P) —— (2)

When two molecules of A collide with each other, the activated molecule A^* is produced. This activated molecule A^* may undergo either deactivation by collision with a normal molecule or spontaneous reaction to form products.

Rate of formation or appearance of A^*

$$+\frac{d[A^*]}{dt} = k_1[A][A] = k_1[A]^2 \quad \text{—— (3)}$$

similarly, rate of decomp. or disapp. of A^*

$$-\frac{d[A^*]}{dt} = k_2[A^*][A] + k_3[A^*] \quad \text{—— (4)}$$

Rate of formn of pdt. P

$$\frac{d[P]}{dt} = k_3[A^*] \quad \text{—— (5)}.$$

Acc. to steady state approximation

Rate of formn = Rate of decomp.

$$k_1[A]^2 = k_2[A^*][A] + k_3[A^*]$$

$$k_1[A]^2 = [A^*]\{k_2[A] + k_3\}$$

$$[A^*] = \frac{k_1[A]^2}{k_2[A] + k_3} \quad \text{——— (5)}$$

Sub the value of $[A^*]$ in eqn (5), we get

$$\frac{d[P]}{dt} = k_3\left[\frac{k_1[A]^2}{k_2[A] + k_3}\right] \quad \text{——— (7)}$$

From eqn (7), the rate of rxn has no definite order. Hence two condn. may be imposed

(1) At high pr $k_2[A] \gg k_3$

i.e $k_2[A] + k_3 = k_2[A]$

(7) is modified into, $\frac{d[P]}{dt} = k_3 \frac{k_1[A]^2}{k_2[A]}$

$$= \frac{k_3 k_1}{k_2}[A] \quad \text{——— (8)}$$

From eqn (8) the rxn is of first order.

(2) At low pr $k_2 \gg k_2[A]$

i.e $k_2[A] + k_3 = k_2$

(7) is modified into $\frac{d[P]}{dt} = k_3 \frac{k_1[A]^2}{k_2} = k_1[A]^2$

$$\frac{dP}{dt} = k[A]^2 \quad \text{——— (9)}$$

∴ Hence the reaction is of second order.

(TST).

Transition state theory (or) Absolute reaction rate theory (ARRT) or Activated complex theory (ACT)

Postulates:-

① The reactant molecules first excited to form an activated complex. This activated complex is in equilibrium with the reactants.

$$\text{Reactant} \rightleftharpoons [\text{Activated complex}]$$

② Activated complex is having four translational degrees of freedom along the reaction coordinate and one vib. degree of freedom less than that of the normal molecule. The extra translational degree of freedom is formed from one vib. degree.

③ The rate of the reaction is given by the rate of decomp. of pdt.

$$[\text{Activated complex}] \longrightarrow \text{pdt}$$

Derivation:-

Let us consider a bimolecular rxn.

$$A + B \longrightarrow \text{pdt}.$$

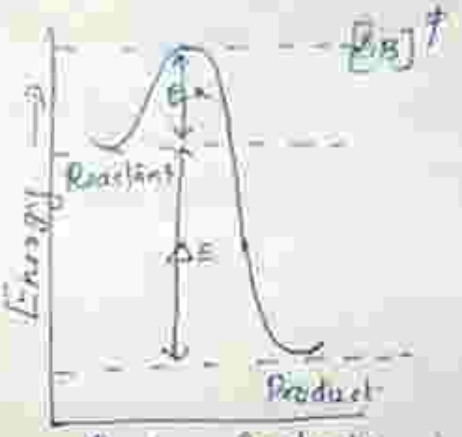
$$\text{rate} = k[A][B].$$

According to ARR, the mech is

$$A + B \underset{\text{React}}{\rightleftharpoons} \underset{\text{Activated complex}}{[AB]^{\neq}} \xrightarrow{k_a} \text{product}$$

where $k^{\neq}$ is the equilib const bet the reactant and activated complex.

The rate of the rxn will depend upon 2 factors



① The conc of $[AB^{\neq}]$.

(Cal. by using statistical mechanics).

② The rate at which $[AB]^{\neq}$ breaks up to yield products.

$$A + B \underset{}{\overset{k^{\neq}}{\rightleftharpoons}} [AB]^{\neq}$$

On applying the law of mass action

$$k^{\neq} = \frac{[AB]^{\neq}}{[A][B]} \quad \text{— (2)}$$

where $k^{\neq}$ is the equilibrium const bet the reactant and activated complex.

From classical mechanics,

$$\text{Energy of vib} = \frac{RT}{N_A} = k_B T \quad \text{— (3)}$$

where k_B is Boltzmann const R/N_A.

From quantum mechanics :

energy of vib = $h\nu$ — (4)

where h is plancks const

ν = freq. of vib

comp (3) & (4) we get.

$$k\nu = \frac{RT}{N_A}$$

$$\nu = \frac{RT}{hN_A} \quad \text{— (5)}$$

$$\nu = \frac{k_B T}{h} \quad \text{— (5a)}.$$

The vibrational freq. ν is the rate at which the activated complex molecule move across the energy barrier. The rate const $k^{\neq}$ can be identified with ν.

$$\text{rate} = \nu [(AB)^{\neq}] \quad \text{— (6)}.$$

Substituting the value of $[(AB)^{\neq}]$ from (2) we get

$$\text{rate} = \nu [A][B] k^{\neq} \quad \text{— (7)}$$

Compare (1) and (7) we get

$$k [A][B] = \nu [A][B] k^{\neq}.$$

$$k = \nu k^{\neq} \quad \text{— (8)}.$$

Sub the value of ν from (5) and 5(a).

we get

$$k = \frac{k_B T}{h} \cdot k^{\neq} \quad \text{or} \quad \frac{RT}{h N_A} \cdot k^{\neq} \quad \text{—(9)}$$

The equilibrium const $k^{\neq}$ can be expressed in terms of the standard Gibbs free energy for the activation process.

$$(\Delta G^{\circ})^{\neq} = -RT \ln k^{\neq} \quad \text{—(10)}$$

and $(\Delta G^{\circ})^{\neq} = (\Delta H^{\circ})^{\neq} - T(\Delta S^{\circ})^{\neq}$ —(11)

From (10) we get

$$-\frac{(\Delta G^{\circ})^{\neq}}{RT} = \ln k^{\neq}.$$

(or) $k^{\neq} = e^{-(\Delta G^{\circ})^{\neq}/RT}$ —(12)

sub $(\Delta G^{\circ})^{\neq}$ from eqn (11) we get

$$k^{\neq} = e^{-(\Delta H^{\circ})^{\neq}/RT} \cdot e^{(\Delta S^{\circ})^{\neq}/R} \quad \text{—(13)}$$

eqn (9) becomes

$$k = \frac{k_B T}{h} \cdot e^{-(\Delta H^{\circ})^{\neq}/RT} \cdot e^{(\Delta S^{\circ})^{\neq}/R} \quad \text{—(14)}$$

eqn (14) is known as Eyring eqn.

$(\Delta S^{\circ})^{\neq}$ std entropy of activation

$(\Delta G^{\circ})^{\neq}$ std free energy of activation

$(\Delta H^{\circ})^{\neq}$ std enthalpy of activation

Significance :

$$k = \frac{k_B T}{h} \cdot e^{-(\Delta G^\circ)^\neq / RT} \quad \text{— (35)}$$

This involve 2 factors $\frac{k_B T}{h}$ and $e^{-(\Delta G^\circ)^\neq / RT}$

(1) the first factor $\frac{k_B T}{h}$ is const at const Temp

(2) second factor $e^{-(\Delta G^\circ)^\neq / RT}$ contains a negative sign. Hence the rate of the reaction depends on free energy of activation. i.e At particular temp, greater the value of $(\Delta G^\circ)^\neq$, the slower will be the reaction.

Unit - IV Photochemistry

Fundamentals

It has been found that some substances are sensitive to light. They undergo chemical reaction when exposed to light. Such reactions are called photochemical reaction or photolysis.

Photochemistry mainly concerns with the physical change and chemical reactions brought about the low frequency electromagnetic radiations such as visible and u.v. rays. The chemical reactions produced by the high frequency radn. like x-rays are studied under Radiation chemistry. Such reactions are called radiolysis.

Photochemical reactions.

These are chemical reaction which are initiated by activation due to absorption of light. They proceed only in light. These are the combination of 1° photochemical process and 2° thermal chemical process.

(eg) $H_2 + Cl_2$ dark no rxn

$H_2 + Cl_2$ light 2 HCl. (Cloud explosion).

Acetone vapour $\xrightarrow{\text{light}}$ $CH_3CH_3 + CO$

$\lambda = 313nm$.

Comparison of photophysical and thermal reaction

	Thermal or dark reaction	Photochemical reaction
1.	are initiated by activation due to molecular collision	are initiated by activation due to absorption of light
2.	are temp. dependent	are temp. independent
3	can occur in darkness	proceed only in light
4	Rxn rate changes with T	Rxn rate changes with the intensity of radn.
5.	have high T. Co efficient	have negligible T coeff.
6.	are always accompanied by ↓ of free energy $\Delta G = -ve$	some of them involve ↑ of free energy ΔG = +ve or −ve.
7.	Some of them cannot take place at ordinary temp.	occur invariably at ordinary temp.

Consequences of light absorption.

There are substances which are capable of absorbing light. The light energy so absorbed lifts the atoms or molecules of the materials into an excited state. This is a physical change which is referred to as the primary process

Since the excited state are unstable, the atom or molecule returns to its original or ground state with emission of light. This is a photophysical process. Sometimes, the excited atoms or molecules may enter into chemical reaction due to thermal collision. This is called 2° process. Thus a photochemical reaction is the combination of a 1° photophysical process and a 2° thermochemical process.

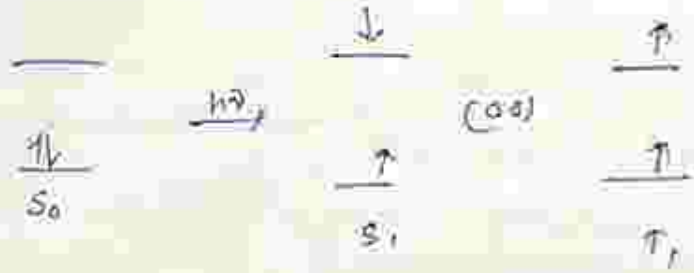
	1° process	2° process
1.	involves activation of atoms or molecules by absorption of light	involves activation of atoms or molecules by thermal collision
2.	is independent of T	& temp. dependent
3.	obeys Einsteins law of photochemical equivalence	does not obey Einsteins law of photochemical equivalence
4.	has unit quantum efficiency.	has quantum efficiency greater or less than unity

Jablonski diagram:

Photochemical process:-

Mechanism and energy transfer in photophysical process:-

Molecules in their G.S have spin paired e⁻. It is represented as S_0 (↑↓). They absorb light (visible or uv) and get excited by raising one of the paired electrons to a higher energy level. The spin orientations of the two electrons may be either parallel (↑↑) and antiparallel (↑↓). If the spins are antiparallel then the molecules are said to be in singlet excited state (S_1). If the spins are parallel then the molecules are said to be in triplet excited state (T_1).



The excited molecule return to the ground state dissipating the energy by any one of the following transition.

(i) Non radiative transitions

The activated molecule suffers vibrational deactivation thro' molecular collision between the singlet state and energy is dissipated in the form of heat. This is a non radiative transition called internal conversion (IC)

The molecules may also lose energy by involving transition between singlet and triplet states. This type of transition called intersystem

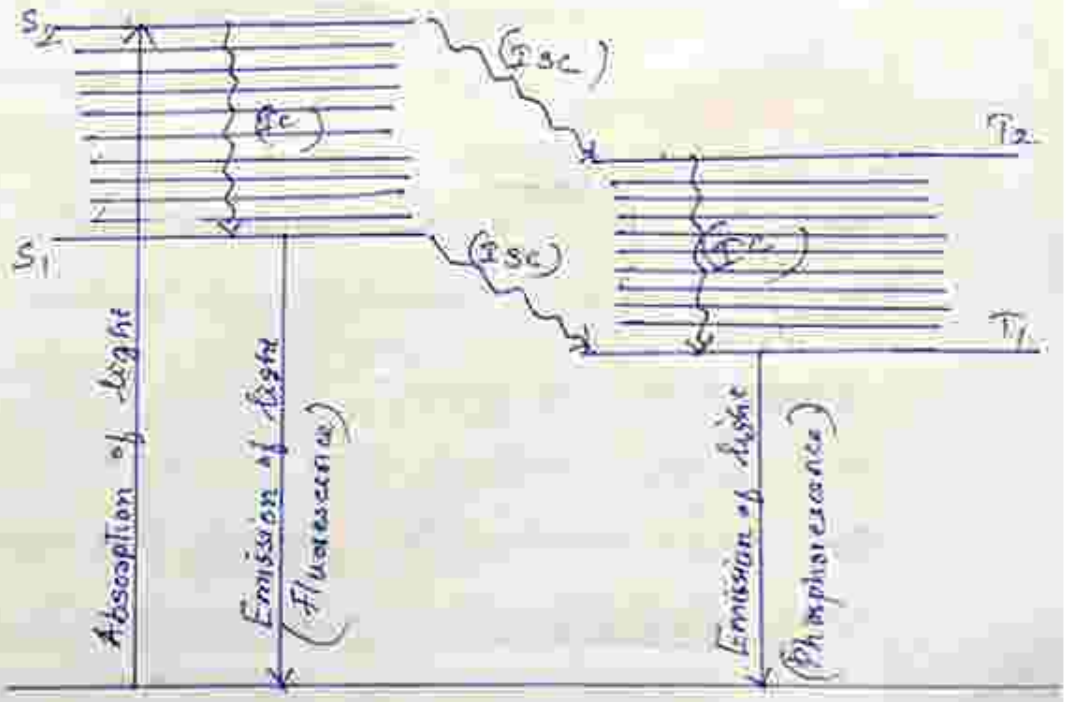
crossing (ISC) is also non radiative.

(ii) Radiative transitions:-

When the molecules return from the singlet excited state to the G.S, visible light is emitted. This radiative process is called fluorescence.

The transition from the triplet excited state to the G.S is accompanied by emission of visible light called phosphorescence. This is also a radiative power.

The various non-radiative and radiative transitions are best explained with the help of Jablonski diagram.



IC - Internal conversion

ISC - Intersys. crossing

Types of photophysical process.

1. Fluorescence:

Defn:

When a beam of light (visible or uv) is allowed to fall on certain substances, they emit visible light which ceases as soon as the incident light is cut off. This phenomenon of instantaneous emission of light is known as fluorescence.

Types:

① Normal fluorescence.

It is observed mostly in organic substances like fluorescein, eosin, petroleum, chlorophyll, aniline, rhodamine, vitamin A, etc. A few inorganic substances like fluorite (natural CaF_2) uranyl sulphate, ultramarines etc also exhibit fluorescence. The light re-emitted as fluorescence is of longer wavelength than the incident light. This phenomenon is called normal fluorescence or simply fluorescence.

Different substances fluoresce with light of different wavelength and hence colour.

Fluorspar - Blue light
Chlorophyll - Red light
Uranyl sulphate - Green light.

① Resonance fluorescence:

In certain cases, the fluorescent light has the same wavelength as that of the incident light. This phenomenon is known as prompt or resonance fluorescence.

The vapours of Hg, Na etc exhibit resonance fluorescence when it is exposed to light of wavelength 2537 Å.

② Sensitized fluorescence:

A substance which does not normally exhibit fluorescence may be made fluorescent in the presence of other fluorescent substance. This phenomenon is called sensitized fluorescence. Zn, Cd, Ag, Thallium etc fluoresce in the presence of Hg vapour (photo sensitizer)

Mech:

Molecules in their ground state (S_0) are spin paired. When such a molecule absorbs light (visible or uv) one of the paired e^- goes to a higher energy level (S_1, S_2 or S_3). From the excited state the molecule returns to the ground state through the following processes.

① From the higher excited state, the molecule returns to the first excited state, the molecule returns to the S_1 state through vibrational deactivation (internal conversion) by thermal collision

② From the S_1 state, the mole. returns to the G.S (S_0) liberating the absorbed radiation as

fluorescence

Salient features.

① Since the spin orientation of the two single electrons is antiparallel, the transition from S_1 to S_0 is spectroscopically allowed. Hence the absorbed light is re-emitted as fluorescence instantaneously (within 10^{-8} sec)

② Some energy is dissipated during vibrational deactivation. Hence the freq. of the fluorescent light is slightly less than that of the incident light.

③ Since atoms do not suffer vibrational deactivation, they exhibit resonance fluorescence.

Phosphorescence:

Defn:

When a beam of light (visible or UV) is allowed to fall on certain substances, they emit visible light which persists for some more time even after the incident light is cut off. This phenomenon of delayed emission of light is called phosphorescence.

(ex). phosphors (sulphides of Ca, Sr, Ba).
ruby, dyes dissolved in fused boric acid.
organic sub. like aspirin, cocaine, procaine nicotine etc.

Mech:

When a substance is irradiated, its molecules absorb light and get excited by shifting one of the paired electrons from the G.S (S_0) to the excited singlet state ($S_1, S_2 S_3$ etc)

From the excited state, the molecule returns to the G.S thro' the following processes.

(1) The life time of the excited singlet state is relatively lower (10^{-9} sec), than the excited triplet state (10^{-3}). The molecule loses from the singlet state to the more stable triplet state and relax there for sometime. This is called intersystem crossing (ISC).

(2) From the heighest excited state (S_3, S_2, T_3, T_2 etc) the molecule returns the first excited state (S_1 and T_1) thro' vibrational deactivation (IC).

(3) From the T_1 state, the molecule returns to the G.S (S_0) liberating the absorbed radiation as phosphorescence.

Solvent features:

(1) In the excited triplet state, the e^- has spin parallel to that of the ground state electron. That is, the transition involves spin inversion which needs time for its occurrance. This is spectroscopically forbidden and hence the absorbed light is re-emitted slowly after a time lag.

(2) Some energy is dissipated during vibrational deactivation. Hence phosphorescent radn is of shorter freq. than the incident light (i.e) $\lambda_a < \lambda_e$.

3 Chemiluminescence:

Defn:

The phenomenon of emission of visible light as a result of chemical reaction at a temp. at which a black body normally does not emit visible light is known as chemiluminescence. It is the reverse of photochemical reaction which occurs by absorption of light.

Eg:

1) Yellow phosphorus glows with a greenish yellow light. It is due to the oxidation of Phosphorus vapour by atmospheric oxygen.

$$4P + 5O_2 \longrightarrow 2P_2O_5 + h\nu.$$

2) When a solution of $SnCl_2$ is added to dil. H_2SO_4 in the dark, a feeble glow is observed.

$$SnCl_2 + H_2SO_4 \longrightarrow SnSO_4 + 2HCl + h\nu.$$

(3) A red light is emitted when Cl_2 or hypochlorite ion is oxidized by alkaline H_2O_2 solution.

Mech:

Chemiluminescence can be explained by electron transfer reaction.

① large polycyclic hydrocarbon undergo ionisation which interact to give excited molecule

$$A_2^- + A_3^+ \longrightarrow A_2^* + A_1$$

This is illustrated by MO theory as under.

① ABMO ↓ — ↓ —

BMO ↑↓ + ↑ + ↑ ↑↓

A_0^- A_3^+ A_0^+ A_2

② The excited molecule is deactivated by the emission of light

$$A_2^* \longrightarrow A_2 + h\nu$$

4.2. Laws of photochemistry :

Beer lambert law:

Defn:

When a beam of monochromatic light is passed thro a homogeneous solution containing an absorbing substance, the rate of decrease of intensity of radn. with the thickness of the solution is proportional to the intensity of the incident light and the conc. of the solution.

Mathematically:

$$\frac{-dI}{dx} \propto I_c$$

$$\frac{-dI}{dx} = k I_c$$

$$\frac{dI}{I} = -k c dx \quad \text{——} (1)$$

I - intensity of incident light

x - thickness of medium in metre

c - conc. of soln. in moles dm^{-3}

k - proportionality constant.

$\int$ (1) between the limits

$$\int_{I_0}^{I} \frac{dI}{I} = -k \int_0^x dx$$

$$\ln \frac{I}{I_0} = -k c x$$

$$\ln \frac{I_0}{I} = k c x \quad \text{——} (2).$$

$$2.303 \log \frac{I_0}{I} = k c x$$

$$\log \frac{I_0}{I} = \frac{k}{2.303} c x$$

$$\log \frac{I_0}{I} = \epsilon c x$$

$\epsilon = \frac{k}{2.303}$ = molar extinction coefficient

$\log \frac{I_0}{I}$ = absorbance (A)

$\therefore A = \epsilon c x$

$\frac{I}{I_0}$ = transmittance T

$\therefore \boxed{A = -\log T}$

Recalling eqn (2)

$$I = I_0 e^{-kcx} \quad \text{——(3)}$$

From (3) it is obvious that the intensity of light decreases exponentially with the conc and thickness of the medium. This is another form of Beer lambert's law.

Significance :

Basis of colorimetric analysis.

Grotthus - Draper's law :

When light falls on a substance a fr. of light is absorbed and the remaining is transmitted. It is only the absorbed light that can bring about a chemical change. This is known as Grotthus - Draper law.

This law is purely qualitative and gives no quantitative relationship. bet the amt of light absorbed and the no of molecules reacted.

Stark - Einstein law of photochemical equivalents

The law state that each molecules taking post in a photochemical reaction absorb only one quantum of light.

The law implies a quantitative relationship between the no. of reacting molecule and the no. of quanta of light absorbed.

① Energy of one quantum of light = ϵ

$$\epsilon = h\nu$$

h = planks const (6.626×10^{-34} J/sec)

ν = freq. of light.

② Energy of one Einstein of light is E

$$E = N\epsilon = Nh\bar{\nu}$$

where N = Avagadro no. (6.023×10^{23})

Quantum Yield:

The efficiency of a photochemical reaction is often expressed in terms of quantum yield which is defined as the no. of molecule reacting per quantum of light absorbed.

$$\Phi = \frac{\text{No. of molecules reacting in a given time}}{\text{No. of quanta of light absorbed in the same time}}$$

$$\Phi = \frac{\text{No. of moles reacting in a given time}}{\text{No. of Einsteins of light absorbed in the same time}}$$

Deviations in Quantum yield:

The Einsteins law of photochemical equivalence implies that the quantum yield of photochemical reactions should be unity ($\Phi = 1$). But in most cases, Φ is greater or less than unity. This is due to secondary thermal reactions.

Acc. to Bodenstein, molecules are activated, each molecule absorbing one quantum of light. This is called primary process. The molecule thus activated undergo a series of thermal reactions without further absorption of light. These are called 2° processes. The quantum yield of a reaction is determined by the nature of the 2° process

① Reactions with $\Phi = 1$

When the activated molecules instantaneously decompose into the product without entering into 2° processes, the quantum yield becomes unity.

① $Cl_2 + O_2 \longrightarrow Cl_2O_2$ $\quad \Phi = 1$

② $H_2 + O_2 \longrightarrow H_2O_2$ $\quad \Phi = 1$

② Reactions with $\Phi < 1$

In this type of reactions, the activated molecules get deactivated to certain extent by collision in the secondary process. That is, the active species of the primary process reunite to give back the reactant molecules in the secondary process. Thus the quantum yield of the reaction is less than unity.

eg

$2NH_3 \longrightarrow N_2 + 3H_2$ $\quad \Phi = 0.2$

$H_2 + Br_2 \longrightarrow 2HBr$ $\quad \Phi = 0.01$

③ Reactions with $\Phi \geq 1$

These are photochemical reactions in which the activated molecules produce free radicals in the primary process. The free radicals may then start subsequent secondary reactions with other molecules without the use of light. As a result, for every quantum of radiation absorbed more than one molecule can enter into reactions. Thus the quantum yield of such reactions is greater than unity.

$$3O_2 \longrightarrow 2O_3 \qquad \Phi = 2$$

$$2HI \longrightarrow H_2 + I_2$$

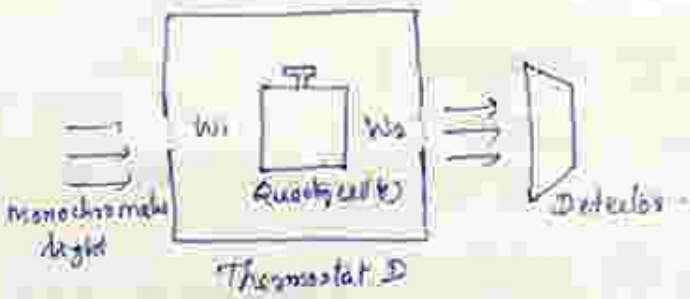
In some cases, a series of secondary processes involving several thousands of molecules may take place. This leads to a chain rxn with very high quantum yield

$$CO + Cl_2 \longrightarrow COCl_2 \qquad \Phi = 10^3$$

$$H_2 + Cl_2 \longrightarrow 2HCl \qquad \Phi = 10^4 - 10^6$$

Determination of Quantum Yield

The experimental arrangement for the measurement of quantum yield is gn. below



The reaction mixture is taken in a glass or quartz cell x with optical plane window W_1 and W_2. The cell is kept in thermostat D. A narrow beam of monochromatic light is allowed to pass thro' the reaction mixture for a known time. The reaction mixture absorbs a portion of light. The residual portion of light is then allowed to enter a detector which measures the light intensity. Thermopiles or chemical actinometer are

generally used as detectors.

When the intensity of light is determined keeping the reaction vessel empty. In case of solutions, it is filled with the solvent. The diff. bet the two readings will give the amt. of light energy absorbed by the reaction mixture.

(iv) The rate of reaction of the mixture under investigation is determined by the usual methods used in chemical kinetics. This gives the no. of moles reacting in a given time

$$\Phi = \frac{\text{No. of moles reacting in a gn time}}{\text{No. of einsteins absorbed in the same time}}$$

$$= \frac{\text{Rate of the reaction}}{\text{Amount of energy absorbed}}$$

Chemical actinometer:

It is a device used to estimate the no. of Einsteins of light absorbed in photochemical reactions. The commonly used chemical actinometer is uranyl oxalate actinometer. It consists of a dilute solution of oxalic acid mixed with uranyl sulphate. Uranyl sulphate acts as the

photosensitized in the decomposition of oxalic acid on exposure to light. The extent of decomposition of oxalic acid is determined by titrating against pot. permanganate. The amt of decomposition is proportional to the product of the intensity of light of a given wavelength and the time of exposure.

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

$$(UO_2^{2+})^* + \begin{matrix} COOH \\ | \\ COOH \end{matrix} \longrightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

KINETICS OF PHOTOCHEMICAL REACTIONS:

The kinetics of photochemical reactions may be studied by measuring either the quantum yield or the order of reaction. For that, a suitable mechanism is proposed and a mathematical rate eqn is derived. If it gives the quantum yield or order of reaction in agreement with the experimental value the mechanism will be accepted.

In most cases, the rate equation for a photochemical reaction is derived with Bodenstein's steady state principle which states that the rate of formn of an intermediate is equal to the rate at which it is used up.

This means that the conc. of an intermediate is const. at any instant mathematically

$$\frac{d(R)}{dt} = 0$$

where R is the intermediate usually free radical in photochemical reaction.

Photochemical combination of H_2 and Cl_2.

$$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

Mxn

i) $Cl_2 + h\nu \xrightarrow{k_1} 2Cl$ Rate $= k_1 I_a$.

ii) $Cl + H_2 \xrightarrow{k_2} HCl + H$ Rate $= k_2[Cl][H_2]$

iii) $H + Cl_2 \xrightarrow{k_3} \{HCl\}^* + Cl$ Rate $= k_3[H][Cl_2]$

iv) $Cl + Cl \xrightarrow{k_4} Cl_2$ Rate $= k_4[Cl]^2$

HCl is formed by means of step (ii) and (iii).

∴ The rate of formn of HCl is gn by

$$\frac{d[HCl]}{dt} = k_2[Cl][H_2] + k_3[H][Cl_2] \quad \text{—(1)}$$

In this reaction, $H^\cdot$ and $Cl^\cdot$ radicals are formed as intermediates

Applying steady state principle to Cl-radical

$$k_1 I_a + k_3 [H][Cl_2] = k_2 [Cl][H_2] + k_4 [Cl]^2 \quad \text{---(2)}$$

for H radical,

$$k_2 [Cl][H_2] = k_3 [H][Cl_2] \quad \text{---(3)}$$

Add (2) and (3)

$$k_1 I_a = k_4 [Cl]^2$$

$$[Cl] = \sqrt{\frac{k_1 I_a}{k_4}} \quad \text{---(4)}$$

Comparing (1) and (3)

$$\frac{d[HCl]}{dt} = 2k_2 [Cl][H_2] \quad \text{---(5)}$$

Sub [Cl] in (5)

(4)

$$\frac{d[HCl]}{dt} = 2k_2 \sqrt{\frac{k_1 I_a}{k_4}} [H_2] \quad \text{---(6)}$$

putting $2k_2 \sqrt{\frac{k_1}{k_4}} = k'$ eqn (6) becomes

$$\frac{d[HCl]}{dt} = k'[H_2]\sqrt{I_a}$$

Quantum yield $\phi = \frac{\frac{d[HCl]}{dt}}{I_a} = \frac{k'[H_2]\sqrt{I_a}}{I_a}$

$$= \frac{k'[H_2]}{\sqrt{I_a}}$$

The Cl radical formed in step (1) is used in step (2) to generate HCl molecules and H radical. The H radical in turn generates Cl-radical in step (3). Thus step (2) and (3) are repeated a large no. of times leading to chain rxn with high ϕ ($10^4 - 10^6$)

5. Kinetics of HBr reaction

Reaction bet H_2 and Br_2

$$H_2 + Br_2 \xrightarrow{h\nu} 2HBr$$

Mech:

1) $Br_2 + h\nu \xrightarrow{k_1} 2Br$ — Rate $= k_1 I_{ab}$

2) $Br + H_2 \xrightarrow{k_2} HBr + H$ — Rate $= k_2 [Br][H_2]$

3) $H + Br_2 \xrightarrow{k_3} HBr + Br$ — Rate $= k_3 [H][Br_2]$

4) $H + HBr \xrightarrow{k_4} H_2 + Br$ — Rate $= k_4 [H][HBr]$

5) $Br + Br \xrightarrow{k_5} Br_2$ — Rate $= k_5 [Br]^2$

k_1, k_2, k_3, k_4, k_5 — specific rate constant.

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \quad (1)$$

$$\frac{d[Br]}{dt} = k_1 I_{ab} + k_3[H][Br_2] + k_4[H][HBr] - k_2[Br][H_2] - k_5[Br]^2 \quad (2)$$

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] \quad (3)$$

When steady state is reached

$$(2) = (3) = 0 \implies (2) + 3 = 0$$

$$\frac{d[Br]}{dt} = \frac{d[H]}{dt} = 0.$$

$$k_1 I_{ab} + k_2 [H][H_2] + k_4 [H][HBr] - k_2 [H_2][Br] - k_5 [Br]^2 + k_2 [Br][H_2] - k_2 [H][HBr] - k_4 [H][HBr] = 0$$

$$\therefore k_1 I_{ab} - k_5 [Br]^2 = 0$$

$$k_5 [Br]^2 = k_1 I_{ab}$$

$$\boxed{[Br] = \sqrt{\frac{k_1}{k_5} I_{ab}}} \quad \text{---} \quad (4)$$

Sub (4) in (3)

$$k_2 \sqrt{\frac{k_1}{k_5} I_{ab}} [H_2] - k_3 [H][Br_2] - k_4 [H][HBr] = 0$$

$$\therefore k_2 \sqrt{\frac{k_1}{k_5} I_{ab}} [H_2] = k_3 [H][Br_2] + k_4 [H][HBr]$$

$$= [H] \{ k_3 [Br_2] + k_4 [HBr] \}$$

$$\boxed{[H] = \frac{k_2 \sqrt{\frac{k_1}{k_5} I_{ab}} \cdot [H_2]}{k_3 [Br_2] + k_4 [HBr]}} \quad \text{---} \quad (5)$$

Sub (4) and (5) in (1)

$$\frac{d[HBr]}{dt} = k_2 \left(\sqrt{\frac{k_1}{k_5} I_{ab}} \right) [H_2] + k_3 \left(\frac{k_2 \sqrt{\frac{k_1}{k_5} I_{ab}} [H_2]}{k_3 [Br_2] + k_4 [HBr]} \right) [Br_2]$$

$$- k_4 \left(\frac{k_2 \sqrt{\frac{k_1}{k_5}} [H_2]}{k_3 [Br_2] + k_4 [HBr]} \right) \cdot [HBr]$$

$$= k_2 \sqrt{\frac{k_1}{k_5} I_{ab}} [H_2] \left\{ 1 + \frac{k_3 [Br_2]}{k_3 [Br_2] + k_4 [HBr]} - \frac{k_4 [HBr]}{k_3 [Br_2] + k_4 [HBr]} \right\}$$

$$= k_2\sqrt{\frac{k_1}{k_5}}\, I_{ab}\, [H_2] \left\{ \frac{k_3[Br_2] + k_2[HBr] + k_3[Br_2] - k_4[HBr]}{k_3[Br_2] + k_4[HBr]} \right\}$$

$$\frac{d[HBr]}{dt} = \frac{k_2\sqrt{\frac{k_1}{k_5}}\, I_{ab}\, [H_2] \cdot 2k_3[Br_2]}{k_3[Br_2] + k_4[HBr]} \quad \text{---(1)}$$

∴ Numerator and denominator by $k_3[Br_2]$ in (1)

$$\frac{d[HBr]}{dt} = \frac{2k_2[H_2]\sqrt{\frac{k_1}{k_5}}\, I_{ab}}{1 + \frac{k_4[HBr]}{k_3[Br_2]}}$$

$k_2 = k_1$ and $\frac{k_3}{k_4} = m$ $\qquad \frac{k_4}{k_3} = \frac{1}{m}$

$$\therefore \frac{d[HBr]}{dt} = \frac{k_1[H_2]\sqrt{\frac{k_1}{k_5}}\, I_{ab}}{1 + \frac{1}{m}\frac{[HBr]}{[Br_2]}}$$

Here ϕ value is very low.

Here step (2) in mxn for former reaction is exothermic and hence takes place simultaneously. Reaction (2) in mxn for latter reaction is endothermic and takes place extremely slowly at ordinary temperature.

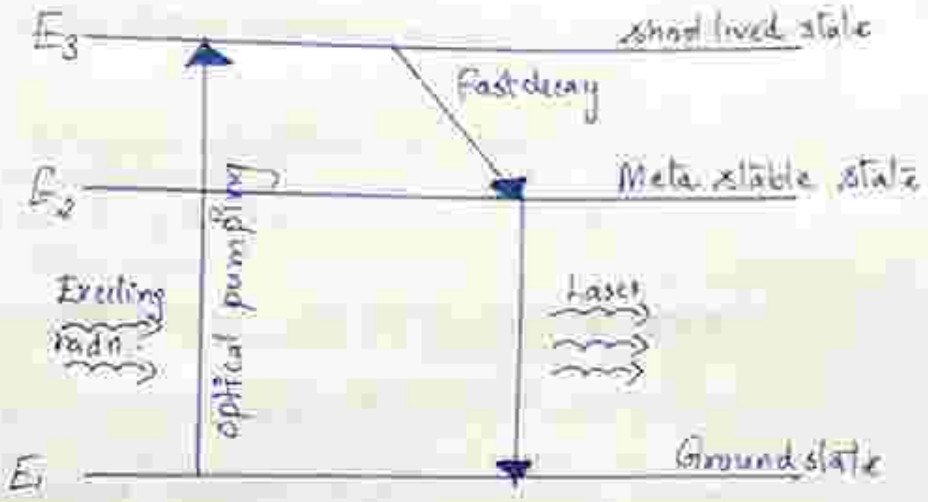
4.4

LASER:

The word LASER is the abbreviation for Light Amplification by stimulated Emission of Radiation.

Laser is a device which produces a highly concentrated monochromatic, coherent and unidirectional beam of light. The operating frequency of laser beam is 10^{15} Hz

Principle



Let E_1 E_2 and E_3 be the energy levels of atoms with ↑ value of energy. Let N_1, N_2 and N_3 be the no. of atoms at the energy level E_1, E_2 and E_3 respt. E_1 - G.S and E_3 - short lived state E_2 - intermediate metastable state

Consider an exciting radn. of the right freq, ν_0 with energy $h\nu_0 = E_3 - E_1$ strikes the atom at E_1. Now the optical pumping action

takes place and hence the atoms at E_1 are pumped to E_3 by the process of stimulated absorption.

The excited atoms at E_3 are short lived ($t = 10^{-8}$ sec) a good no. of excited atoms in level E_3 quickly drop to the intermediate level E_2 by a fast decay process.

E_2 is a meta stable state, the atoms remain in this excited state for longer time of 10^{-3} sec. as compared to short lived state E_3 (10^{-8} sec)

This results in population inversion between the levels E_1 and E_2 i.e $N_2 > N_1$.

atoms at E_2 decay by spontaneous emission or stimulated emission. It emits radiation of freq. ν with energy $h\nu = E_2 - E_1$. This photon of energy $(E_2 - E_1)$ incident on another atoms to produce two coherent photons moving in the same direction. These two photons produce two more photons and so on. This process continues as a chain reaction producing an amplified continuous laser beam.

One of the X feature of Lasers is Q-switching

1) A laser can generate radn as long as population inversion is maintained.

2) It can operate continuously when heat is easily dissipated, although the population in upper level is filled up again by pumping.

3) If overheating occurs, lasers can be operated only in pulses (ie microsec or millisec) so that the medium gets a chance to cool. Such pulses can be achieved by Q-switching. The modification of the characteristics of the resonant cavity.

4) The aim of Q-switching is to achieve a healthy population inversion in the absence of resonant cavity then to plunge the population inverted medium into a cavity and hence to obtain a sudden pulse of radn.

5) To achieve Q-switching, we use pockel cell to convert plane polarised light to circularly polarised light when an electrical pot-diff is applied.

Q-switching is a technique by which a laser can be made to produce a pulsed output beam. This technique allows the production

of light pulses with extremely high peak power much higher than would be produced by the same laser if it were operating in a continuous wave mode.

Population inversion and optical pumping.

The process of making the population of atoms in a higher energy state more than that of lower energy state is known as population inversion. The method by which population inversion is obtained is called optical pumping.

Optical pumping.

It is a process in which light is used to raise e^- from lower Energy level in an atom or molecule to a higher one. It is commonly used in laser construction to pump the active lasers medium so as to achieve population inversion.

Unit V - Group theory

Symmetry elements

A sym. element is a geometrical entity such as a line, a plane or a point about which a symmetry operation of rotation, reflection or inversion may be done.

Symm operations

A symm operation is a movement of a body such that the resulting configuration of the molecule is indistinguishable from the original. The resulting configuration may be an equivalent or identical configuration.

(Eg)

Consider H_2 molecule of conf. I. It can be rotated by 180° to give an equivalent conf. II. Application of the rotation operation twice produces an identical conf. III

Types of symm. ele.:

Plane of symm (σ):

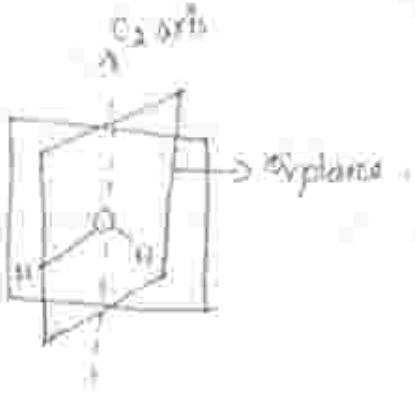
It is an imaginary plane within the molecule which divides into two halves one is the mirror image of the other. If reflection of any atom of the molecule is carried out on the plane of symmetry, it coincidences with another equivalent atom. Thus the plane of symm. is nothing but a reflection plane.

The reflection planes can be classified into 3 types based on their relation with the principal axis.

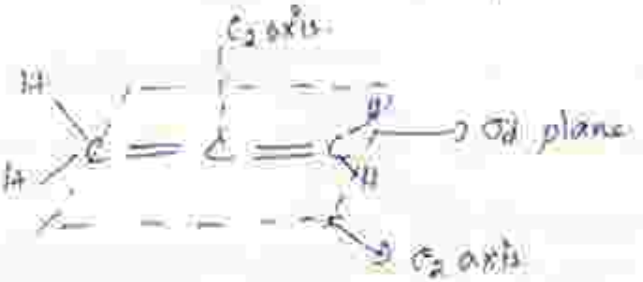
① A plane is referred to as horizontal plane (σ_h). If it is ⊥r to the principal axis

② A reflection plane drawn vertically thro' the principal axis is called a vertical plane (σ_v). for eg. H_2O molecule has a σ_v plane which passes thro' the principal axis containing O atom and bisecting a line.

bet. the H atoms



③ A vertical plane which bisects two ⊥r C_2 axis is called a dihedral plane σ_d



② Proper axis of symmetry (C_n). It is an imaginary line passing thro' the molecule about which rotation can be carried to obtain an equivalent confn. In general, the symbol for proper axis of symmetry is C_n, where n is known as the order of the axis. It is gn by the formula.

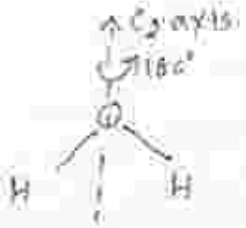
$$n = \frac{360^\circ}{\theta}$$

where θ is the minimum angle of rotation to obtain the equivalent configuration.
The proper axis of symm. is nearly a rotation axis

Eg.

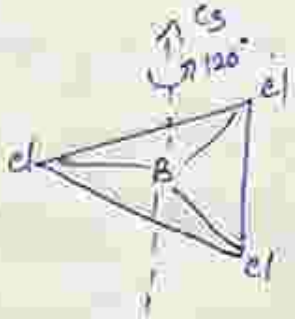
① Water mole. is rotated by an angle of 180° about an axis to get an equivalent or identical configuration. Now the order of the axis is 2 and the axis is known as C_2 axis of symmetry.

$$n = \frac{360^\circ}{\theta} = \frac{360}{180} = 2$$



② BeI_3 has the C_3 axis of symmetry. The minimum angle of rotation (θ) to obtain the equivalent confi is 120°

$$n = \frac{360^\circ}{\theta} = \frac{360}{120} = 3$$



③ $[PtCl_4]^{2-}$ ion has a C_4 axis of symmetry. The equivalent configuration is obtained by rotating the ion thro 90° about this axe.

iii Benzene molecule has a C_6 axis of symmetry

3. Improper axis of symm (S_n)

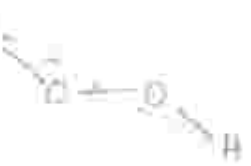
It is an imaginary line passing thro' the molecule about which rotation followed by reflection in a plane ⊥r to the rotation axis can be performed to attain an equivalent configuration. Thus an improper axis of symm is a rotation-reflection axis. Trans dichloroethylene provides an example of molecule with S_2 axis of symm. This molecule posses C_2 axis and σh plane

4. Centre of symmetry: (i).

This is a point such that any line drawn thro' it meets the same atom at equal distances in opp. direction. Thus the centre of symmetry is a centre of inversion.

eg C_2H_4

(3) H_2O_2



(x) Identity

A symm operation which brings back the molecule to its original orientation is called identity operation. This is the operation of doing nothing. The corresponding symm ele is called the identity which is denoted as E. All molecules possess identity.

Group, Subgroup and classes.

Groups:-

A gp is a collection of symm. elem. which are interrelated according to certain rules. Gps may be either finite or infinite. That is they may contain a limited or an unlimited no. of ele. The symm gps are mostly finite. The no. of elements in a finite gp is called its order and the conventional symbol for order is 'h'. A gp in which all elements commute is called an Abelian gp. In an Abelian gp the order of addn is immaterial.

Prop of group:

1) The prod of any two elem. in the gp and the squares of each element from another ele of the gp. If A, B and C are three ele of a gp

$$A \times B = C$$
$$A^2 = B$$
$$A^2 = C$$

2) One element in a gp commutes with all other elements and leave them unchanged. This element is known as the identity element (E).

$$EX = XE$$

3) Every element of the group obeys the Associative law of multiplication. If A, B, C are three ele of the gp then

$$(AB)C = A(BC).$$

4) Every element has an inverse or reciprocal which is also an element of the gp. The ele R is the reciprocal of the element S if $RS = SR = E$ where E is the identity. Obviously, if R is the reciprocal of S then S is the reciprocal of R. Also E is its own reciprocal.

Types of group

1. Finite group

A gp containing finite or limited no of ele is called a finite group. The sym gps with which we shall be concerned are mostly finite. The no of elements in a finite gp is called its order and is rep. as h. pt group. orders is the no of sym operations possible. Thus in C_{2v} m.p, the order is 4 and in C_{3v} order is 6.

2) Infinite group:

A group containing infinite or unlimited no. of element is called an infinite group.
Eg. Linear mole.

3) Abelian group.

A gp. in which all the elements commute is called an Abelian group. Two ele. A and B commute if $AB = BA$. The set of no: bet $-\infty$ and $+\infty$ form an Abelian gp under the multiplication process. The set of sym. operations of water mole. represents an Abelian gp since they obey the commutative law.

4) Non Abelian gp:

A gp is said to be non Abelian if all the elements do not commute with one another. The sym operation of the ammonia molecule provide an eg for the non-Abelian gp as $E, C_3^1, C_3^2, \sigma_v, \sigma_v'$ and σ_v'' do not obey the commutative law.

5) Cyclic law:

A gp is said to be cyclic if all the elements of a gp can be generated from one element $A, A^2, A^3, \ldots A^n$ form the elements of a cyclic gp with A^n as the identity element. Hence n refers to the tot no. of elements and is called the order of the gp. H_2O_2 - eg.

Sub groups:

Smaller groups which may be found within a larger group are called sub groups. The elements of a subgroup should obey the following condition.

① The elements should satisfy all the rules of the group

② If 'g' is the order of the group and 'a' is the order of the subgp, then g/a is a +ve integer other than zero

Eg the subgp. in H_2O molecule.

① E

② E and C_2

③ E and σ_v

④ E and σ_v'

Classes:

A complete set of elements which are conjugate to one another is called a class of the group. Conjugate elements are related by the equation

$$X^{-1} A X = B$$

where X is another ele. of the gp. X is known as the similarity transformation element. The similarity transformation of one element by another may be used to find whether a set of elements form a class. For eg. H_2O has four sym. operation $E, C_2, \sigma_v, \sigma_v'$. The similarity transform of a particular operation is obtained with all the operation as follows:

$$E^{-1} C_2 E = C_2$$

$$\sigma_v' C_2 \sigma_v = C_2$$

$$(\sigma_v')^{-1} C_2 \sigma_v' = C_2$$

$$C_2^{-1} C_2 C_2 = C_2.$$

Order:

The order of a elem must be an integral factor of the order of the group.

Point groups:

All the symm operations present in a mole. form a gp. A gp is generally called point gp. Since all the elemts of sym. present in the molecule intersect at a common point and this point remains fixed under all the sym. operations of the molecule. The point gps of mole. are denoted by specific symbols

Classification of point groups:

① C_{nv} point gps:

C_{2v} pt gp

eg. H_2O.

sym. oper.: $E, C_2, 2\sigma_v$.

C_{3v} pt gp.

eg. NH_3

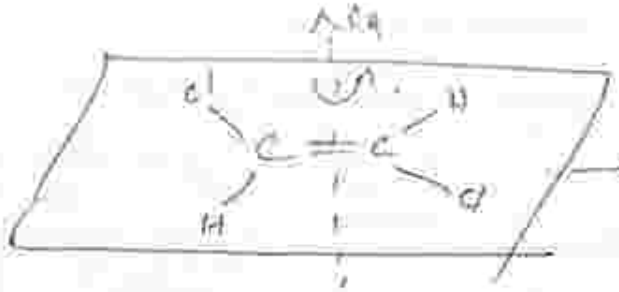
sym op: $E, 2C_3, 3\sigma_v$

2) C_{2h} pt gp:

C_{2h} pt gp

Eg: Trans dichloroethylene
4 sym operation.

pt gp: E, C_2, σ_h and i.



3)

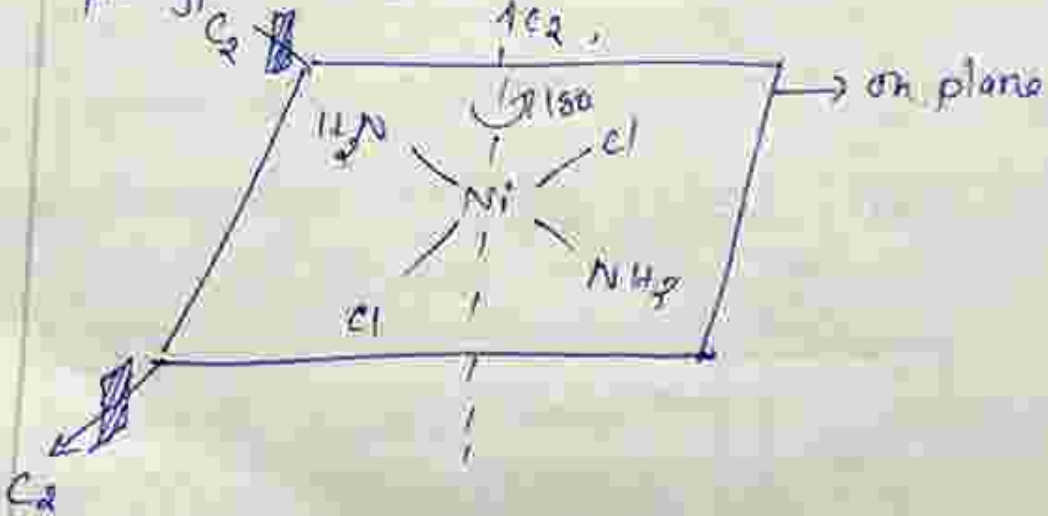
D_{nh} point group.

D_{2h} D_{3h} D_{4h} D_{6h} $D_{\infty h}$.

D_{2h}:

Eg Trans dichlorodiammine Ni(II).
8 sym. operation:
$3C_2$, i σ_v, σ_h and i.

pt. gp:



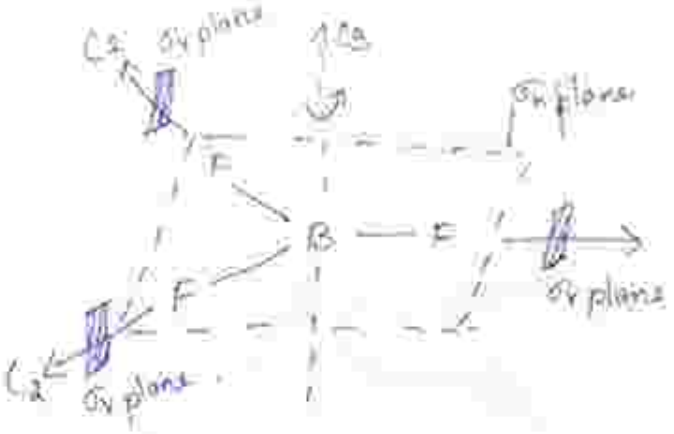
D_{3h}

Eg: BF_3

Trigonal planar mol.

12 sym operation

pt-gp: E, $2C_3$, $3C_2$, $3\sigma_v$, σ_h, $2S_3$

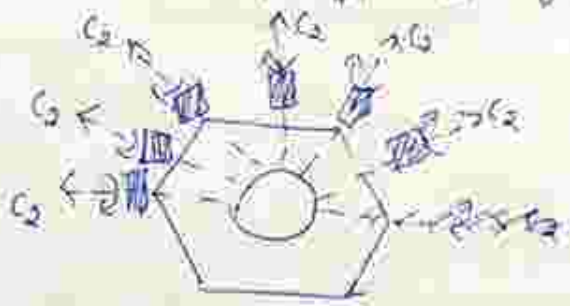


D_{6h} point gp:

Eg: Benzene

24 sym operation

pt gp: E, $5C_6$, $6C_2$, $2S_3$, $2S_6$, $6\sigma_v$, σ_h and i



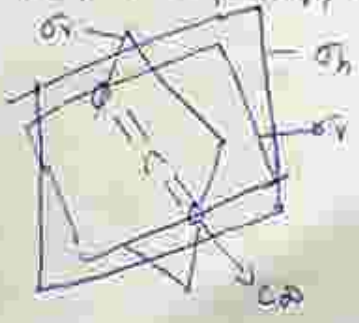
C_6

$6\sigma_v$

$D_{\infty h}$ point gp

Eg: CO_2, linear mole.

pt gp: E, $2C_\infty$, $\infty\sigma_v$, σ_h, i, $2S_\infty$ and ∞C_2

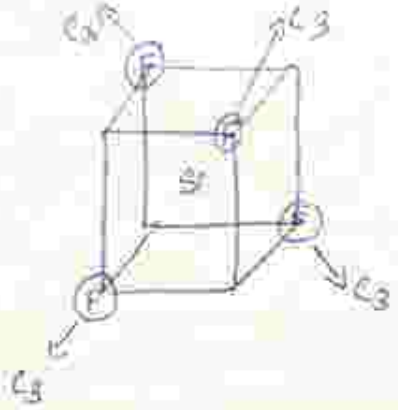


4) Td pt gp

eg SF_4, CF_4

24 sym operation

pt gp $E, 8C_3, 3C_2, 6S_4$ & $6\sigma_v$

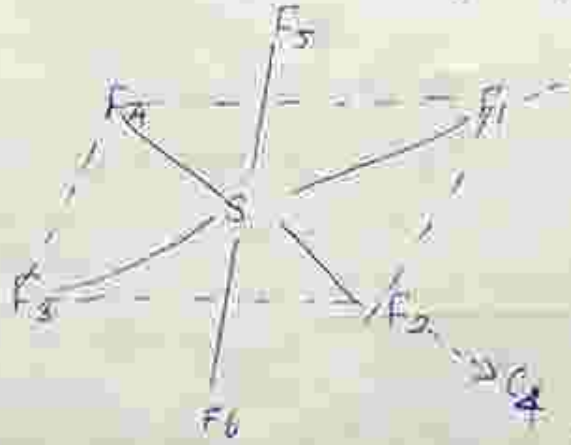


5) Oh point gp

48 sym operation

pt gp: $E, 8C_3, 6C_4, 6C_2, 3C_2 (=C_4^2), i, 6S_4, 8S_6$

$3C_4$ and $6\sigma_d$



Group multiplication table

Defn:

The elements of a gp can be listed in a table known as group multiplication table. This table reveals the different relations between the elements of angle is one another there must necessarily be a third at right angles to both.

Construction of gp multiplication table

C_{2v} point gp

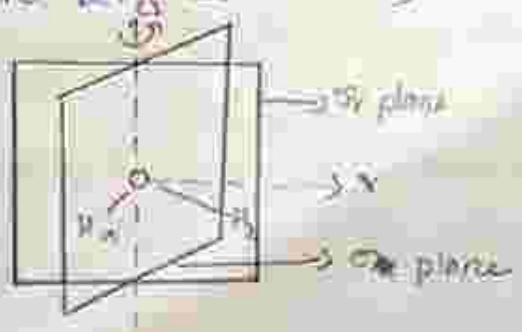
Eg: water

Water belongs to C_{2v} point gp which contains 4 sym operation - E, C_2 and $2\sigma_v$.

* The mole has a two fold C_2 axis of symmetry which passes thro' O atom and in bet the two H atoms.

* The molecule has two vertical σ_v planes. One is the molecular plane containing O and H atoms and the other is passing through C_2 axis ⊥r to the molecular plane (i.e thro O-atom and bet two H atom)

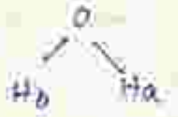
Str



C_2V	E	C_2	σ_{xz}	σ_{yz}
E	E	C_2	σ_{xz}	σ_{yz}
C_2	C_2	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2
σ_{yz}	σ_{yz}	σ_{xz}	C_2	E

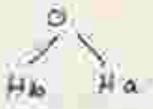
I

C_2



σ_{xz}

σ_{yz}



II

C_2

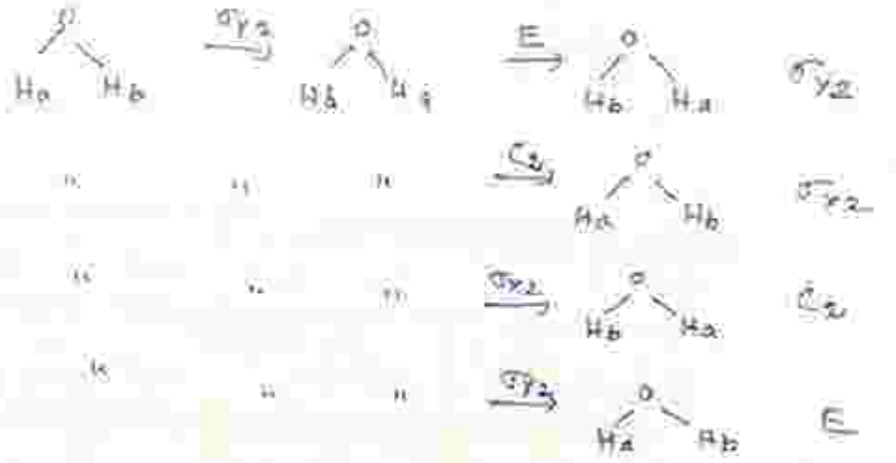
E

σ_{xz}

σ_{yz}

(iii)

(iv)



C_{3V} point group

Eg: NH_3

Ammonia belongs to C_3 point gp.

Six symm. operation E, $2C_3$ and 3 σ_v.

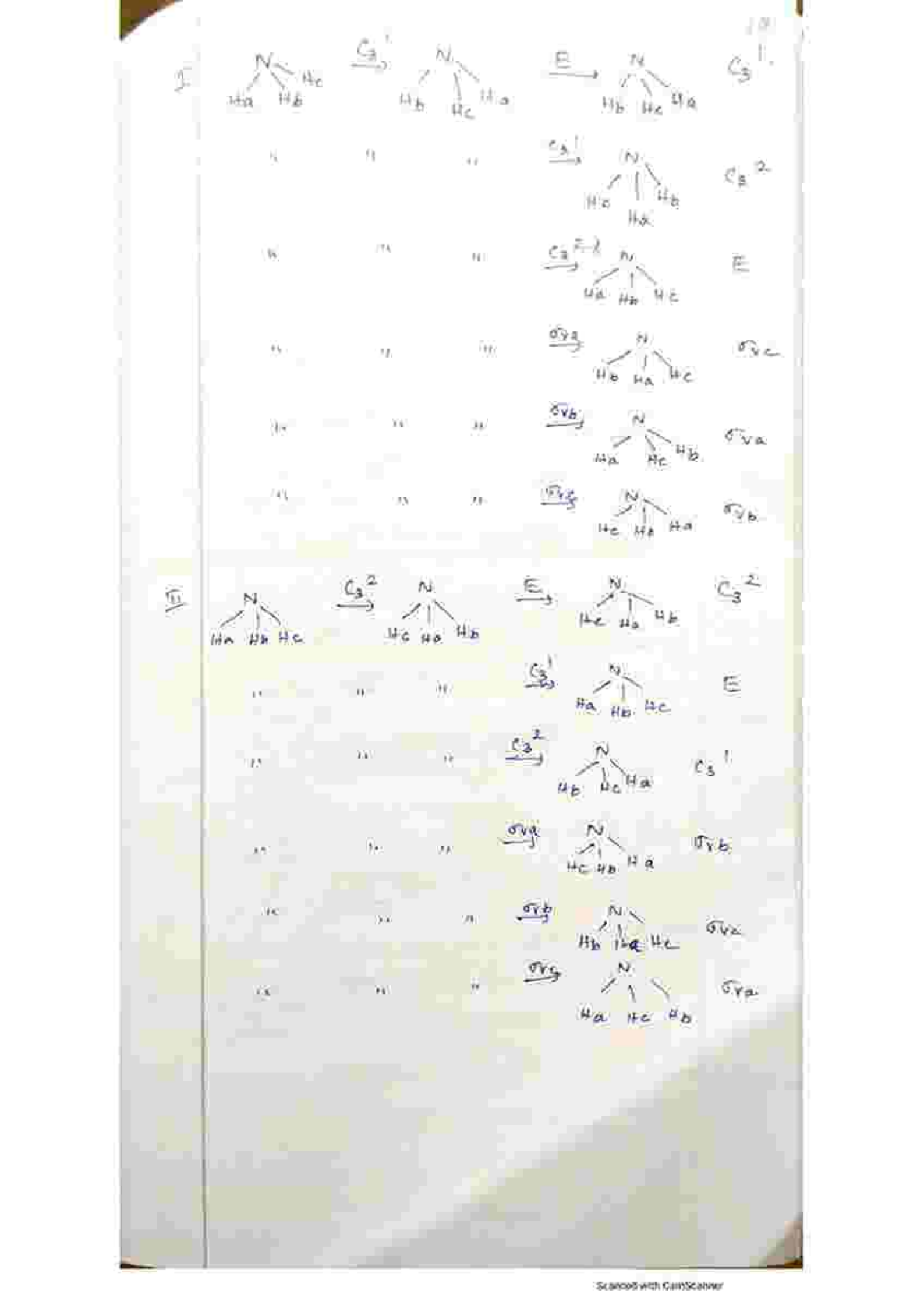
The axis passing thro N atoms and three centre of triangle passing thro N atoms.

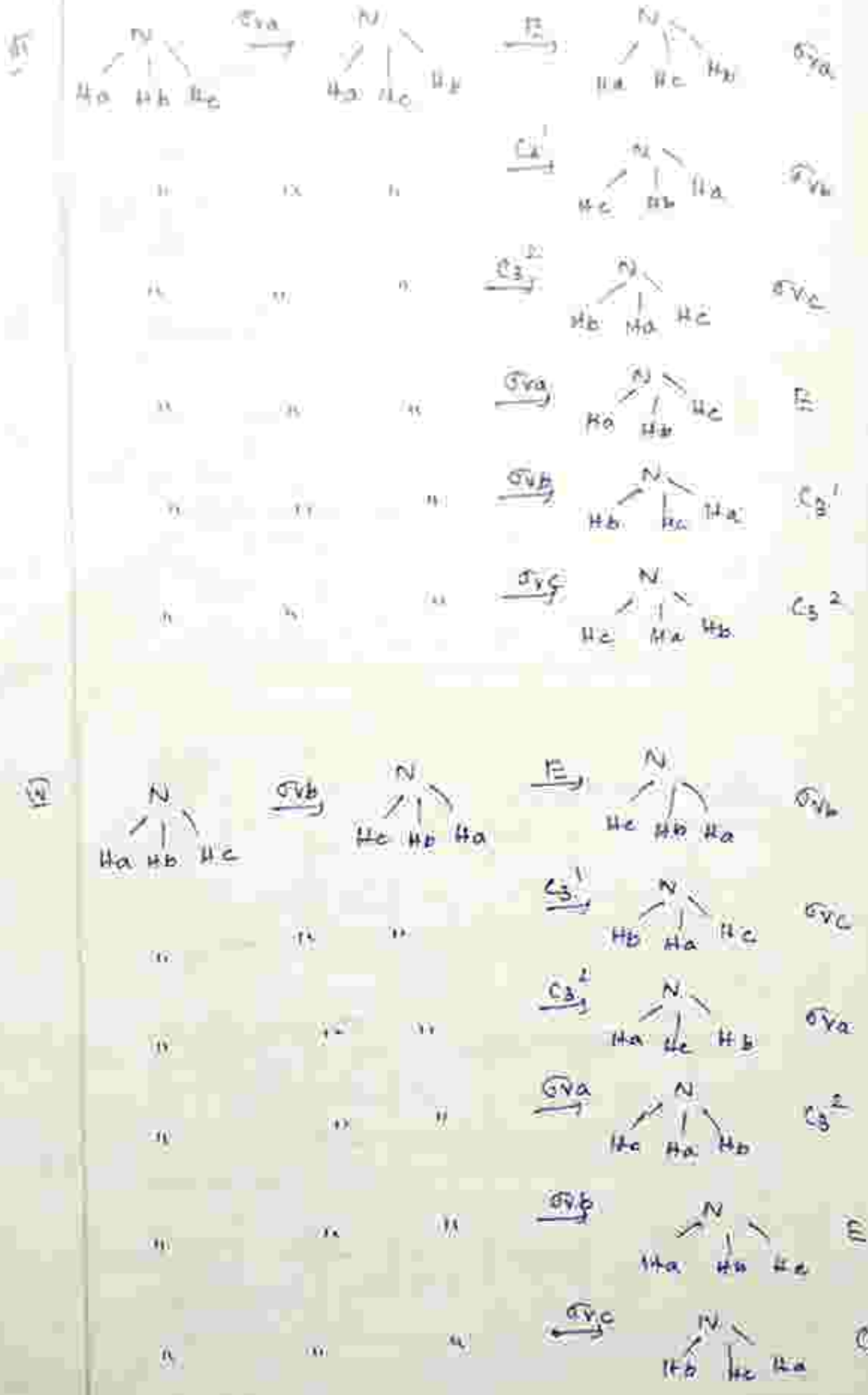
Containing three H atoms is a three fold C_3 axis.

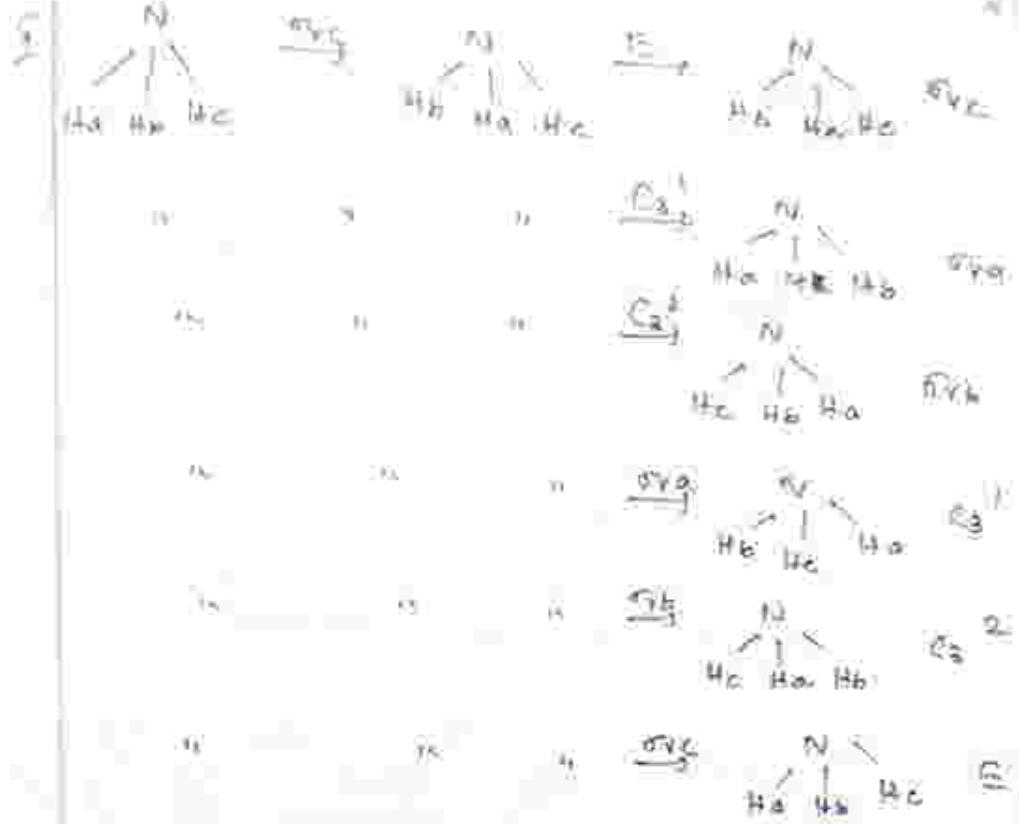
There are three σ_v planes each passing thro N atoms and one of the H atoms.

they are designated as σ_v^a, σ_v^b and σ_v^c.

C_{3v}	E	C_3^1	C_3^2	σ_v^a	σ_v^b	σ_v^c
E	E	C_3^1	C_3^2	σ_v^a	σ_v^b	σ_v^c
C_3^1	C_3^1	C_3^2	E	σ_v^c	σ_v^a	σ_v^b
C_3^2	C_3^2	E	C_3^1	σ_v^b	σ_v^c	σ_v^a
σ_v^a	σ_v^a	σ_v^b	σ_v^c	E	C_3^1	C_3^2
σ_v^b	σ_v^b	σ_v^c	σ_v^a	C_3^2	E	C_3^1
σ_v^c	σ_v^c	σ_v^a	σ_v^b	C_3^1	C_3^2	E







C_{2h} Group multiplication table

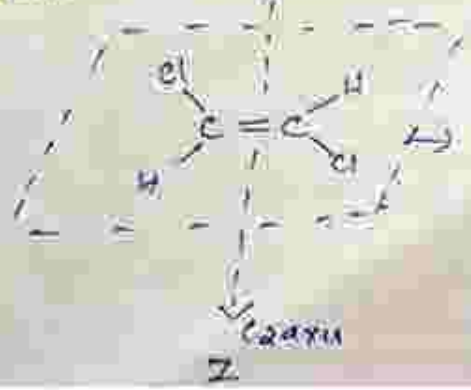
(eg) Trans dichloroethylene.

The pt. gp. consists of four sym. operations

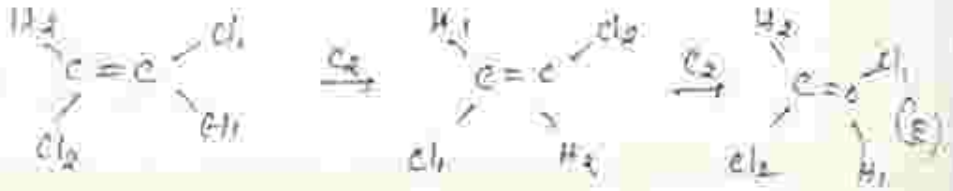
E, C_2, σ_{xy}, i

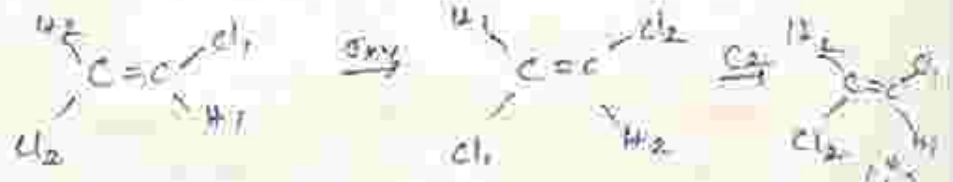
The molecule has a centre of sym. (i).

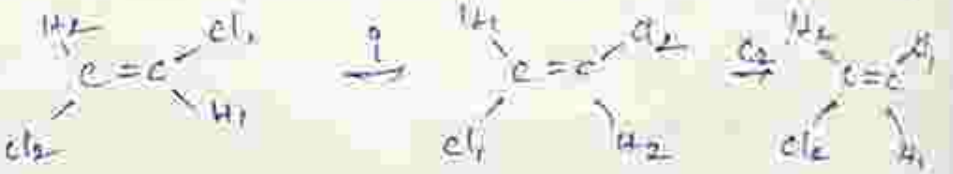
There is a two fold axis of sym. C_2. This axis is to the molecular plane. This molecular plane passing thro' the Cl and H atom is the horizontal σ_{xy} plane.



C_{2h}	E	C_2	σ_{xy}	i
E	E	C_2	σ_{xy}	i
C_2	C_2	E	i	σ_{xy}
σ_{xy}	σ_{xy}	i	E	C_2
i	i	σ_{xy}	C_2	E







Dah:

eg: Trans dichlorodiamine Ni^{II}

8 sym: operations

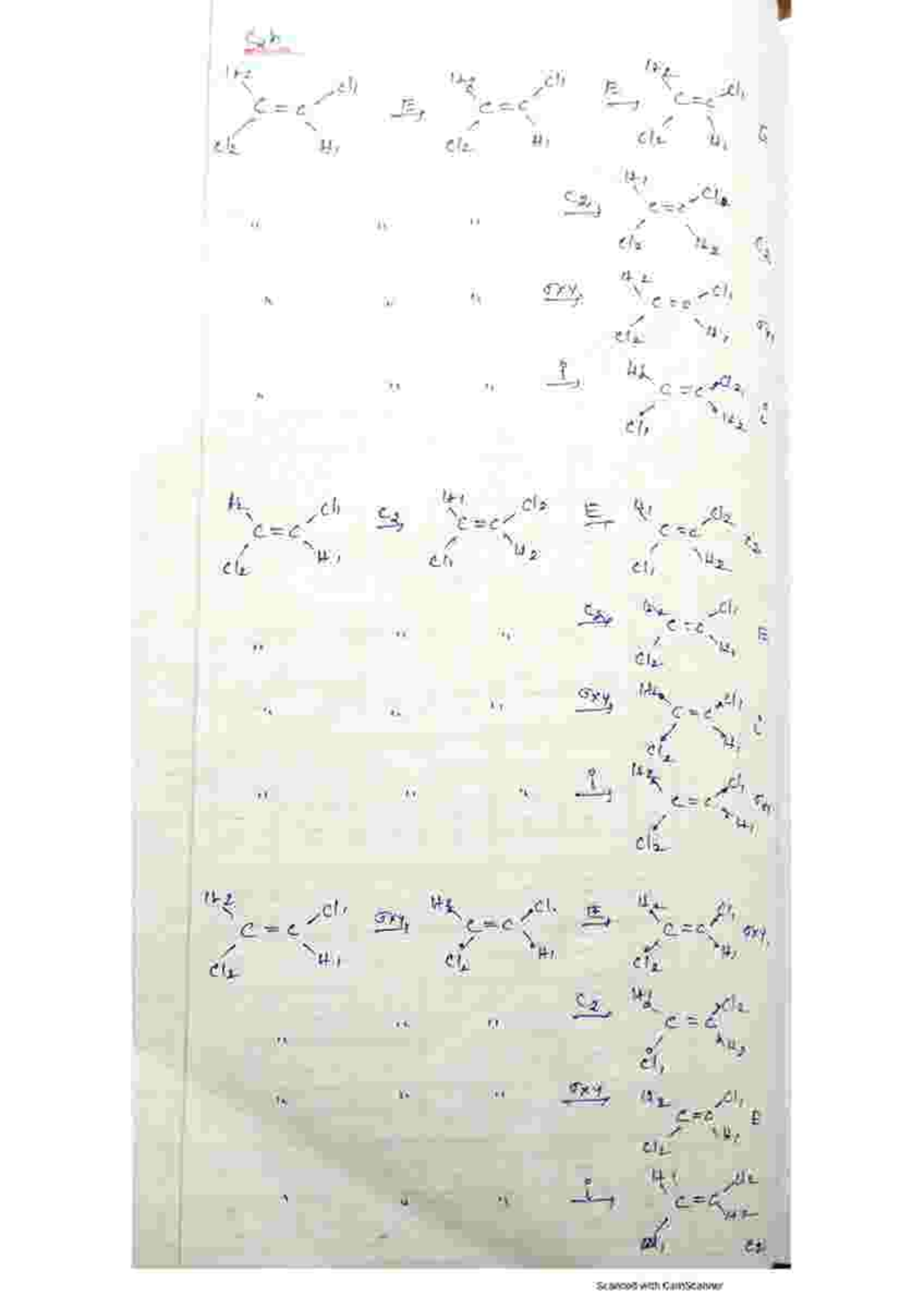
E $3C_2$, $2\sigma v$, σh and i.

There are three C_2 axis of sym. one passing thro the Cl atoms another passing thro the NH_2 gp and the third is ⊥r to the

plane of the molecule

There are 2 σ_v plane and one σ_h plane inversion centre i

D_{2h}	E	C_{2z}	C_{2y}	C_{2x}	i	σ_{xy}	σ_{xz}	σ_{yz}	Raman for relations	quadratic term	cubic term
A_g	+1	+1	+1	+1	+1	+1	+1	+1	—	x^2, y^2, z^2	1
B_{1g}	+1	+1	−1	−1	+1	+1	−1	−1	R_z	xy	xyz
B_{2g}	+1	−1	+1	−1	+1	−1	+1	−1	R_y	xz	xyz^2
B_{3g}	+1	−1	−1	+1	+1	−1	−1	+1	R_x	yz	xyz^2
A_u	+1	+1	+1	+1	−1	−1	−1	−1	—	—	xyz
B_{1u}	+1	+1	−1	−1	−1	−1	+1	+1	z	z	z^3, xyz^2
B_{2u}	+1	−1	+1	−1	−1	+1	−1	+1	y	y	y^3, yz^2
B_{3u}	+1	−1	−1	+1	−1	+1	+1	−1	x	x	x^3, xz^2



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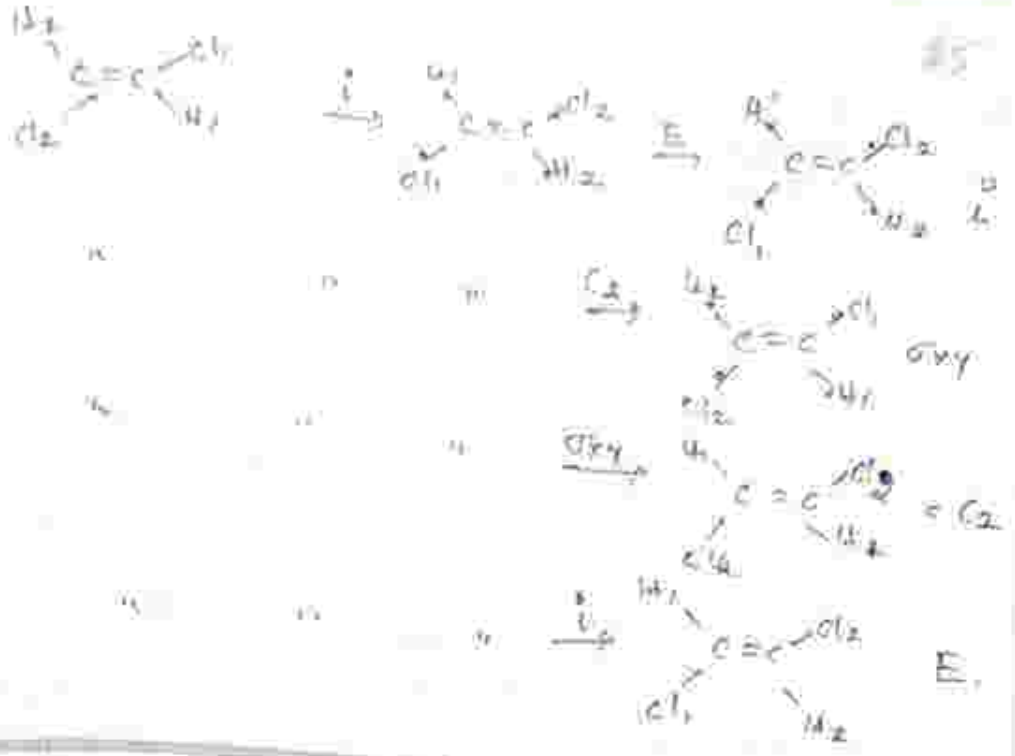

Matrix representation of sym. operations

Any sym. operation about a sym. ele. in a mole. involves transformation of a set of coordinates x, y and z of an atom into a set of new coordinates x', y' and z'. The two sets of coordinates of the atom can be related by a set of equations. This set of equations may also be formulated in matrix notation. Thus each sym operation can be represented by a specific matrix.

Matrices :

A matrix is a rectangular array of nos. or symbols for numbers

eg. $\begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \end{bmatrix}$ $\begin{bmatrix} x \\ y \\ z \end{bmatrix}$.

Matrix for rotation operation about Cn axis

Consider a vector r in the 2D coordinate sys. The vector r can be expressed as a column matrix as $r = \begin{bmatrix} x \\ y \end{bmatrix}$ — (1)

where x and y are the components the vector r. Let the vector be rotated thro' an angle θ such that the components of the vector become x' and y'. The resulting vector r' is expressed as another column matrix

$$r' = \begin{bmatrix} x' \\ y' \end{bmatrix} \quad -(2)$$

x' and y' are related to x and y by eqn

$$x' = x\cos\theta + y\sin\theta \quad -(3)$$

$$y' = -x\sin\theta + y\cos\theta \quad -(4)$$

(3) and (4) are rep. in matrix

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \times \begin{bmatrix} x \\ y \end{bmatrix} \quad -(5)$$

$$r' = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \times r.$$

If C_n represents rotation about the axis by angle θ, then the rotation operation can be expressed as $r' = C_n \times r$ — (7).

Comparing (6) and (7)

$$C_R = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

C_R represents the matrix for rotation operation. In three dimension, the matrix $C_R(z)$ which represents rotation about z axis is written as

$$C_R z = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Matrix for reflection operation.

Consider a vector r with components x and y. By reflection across the y axis (yz plane) the components x and y become x' and y'. The components x' and y' are related to x and y by the equation

$$x' = -1x + 0y \quad \text{—(1)}$$

$$y' = 0x + 1y \quad \text{—(2)}$$

The above equation are represented in matrix form as follows

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \times \begin{bmatrix} x \\ y \end{bmatrix} \quad \text{—(3)}$$

$$r' = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \times r \quad \text{—(4)}$$

$$y' = \sigma_{yz}\, x \quad \text{--- (5)}$$

From (4) and (5) we get

$$\boxed{\sigma_{yz} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}}$$

Extending to 3D, we get

$$\sigma_{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_{xy} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$\sigma_{zx} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Matrix for improper rotation about S_n axis

The matrix for improper rotation is given by the pdt of $C_n(z)$ matrix and σ_{xy} matrix. Thus the matrix S, which represents improper rotation about the z axis is written as.

$$S = \begin{bmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$S = \begin{bmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Matrix for inversion operation.

The x, y and z components of a vector r are transformed into their respective negatives by the inversion operation. The components x, y and z are related to -x, -y & -z by the equation

$$I.x = -1x + 0y + 0z$$

$$I.y = 0x - 1y + 0z$$

$$I.z = 0x + 0y - 1z$$

Where I_x, I_y, I_z refer to "inversion operation on the components x, y and z. In matrix form, these equation become

$$I\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

From the above equation, we get the matrix for inversion i as

$$\underline{I} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

5) Matrix for identity operation.

By identity operation, the component x, y and z of a vector remains unchanged. The equation which represent the effect of identity operation on the vector a are gn below.

$$E.x = 1x + 0y + 0z$$

$$E.y = 0x + 1y + 0z$$

$$E.z = 0x + 0y + 1z$$

Ex. Ey and Ez in the above eqn represents the identity operation on the components x, y and z. In matrix form these equations become.

$$\underline{E} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

From this equation we get the matrix for identity operation E as

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

5.4 Applications of sym. operations and group theory in chemistry.

* To predict whether or not a molecule has a dipole moment
* To predict if a molecule will show optical activity
* To derive selection rules for spectroscopic transitions
* To determine which AO's to be used to construct hybrid orbitals
* to predict which molecular vibrations lead to IR spectra
* To label and designate MOs, etc.