

Syllabus

Module - 1

- * Bonding
- Crystal field Theory
- Electronic spectra & ligands (strong & weak fields)
- Phosphorescents & fluorescents
- Taborski diagram
- Hydrogen bonding & their effect on physical properties
- Metallic bonds
- Classification & applications of liquid crystals
- Band theory of solids & superconductors.

* Spectroscopy

- Basic principles and instrumentation and application of UV, visible & IR spectroscopy.

Module - 2

- * Chemical Kinetics
- 2nd order reactions
- Determination of order
- fast & slow reactions
- Steady state approximation.
- Temperature effect
- Concept of activated complex / transition state : energy of activation.

- Potential energy surface.
- Theories of reaction rate : collision & transition state theory in terms of enzyme catalysis

Module - 3

- * Electrochemistry
 - Dry E' Fuel cells
 - Electrochemical cell
 - Solar cells
 - Dsensitized cell
 - Photovoltaic cell
- * Environmental chemistry
 - Air E' water pollution
 - Analysis of gaseous effluents
 - Oxides of Nitrogen, Sulphur & hydrogen sulphite
 - Chemical analysis of effluents liquid streams
 - BOD
 - COD
 - Control of pollution
 - Depletion of ozone layer.

Module - 4

- * Stereochemistry
 - Stereoisomerism of organic compounds

containing 1 E' 2 chiral centres.

- Enantiomers & diastereomers
- E-Z nomenclature
- R-S configuration
- Atropisomerism
- Optical isomerism in alenes, biphenyls & spiranes
- Circular dichroism

* Reaction mechanism

- Inductive, electromeric & mesomeric effects
- Study of reaction intermediates (carbanions, carbocations, carbene, nitrene & benzyne)
- Mechanism of electrophilic & nucleophilic substitution sec^n .
- Mechanism & application of foll. $\text{sec}^{n, s}$ →

 - a)- Suzuki- Miyaura cross coupling sec^n
 - b)- Fries & photo fries rearrangement
 - c)- Wagner- Meerwein rearrangement
 - d)- Umpolung reactions
 - e)- Reaction of vision.

Module - 5

* Polymers

- Introduction & their classification
- Types of polymerisation
- Free radical anionic & cationic polymerisation
- Preparation, rheological properties & uses

of some common polymers

- Synthetic polymers (Carbon framework, silicon framework, fluorinated framework).
- Biodegradable polymers.

* Water analysis

- Introduction
- Hardness of water - cause, types, units.
- Disadvantages of using hard water for industrial & domestic purposes.
- Softening of hard water.
- Chemical analysis of water - estimation of free chlorine, total alkalinity, hardness,
- Numericals based on determination of hardness.

Spectroscopy

(4R sharma)

(P.S. Kalse)

spectro + scope

(Silverstein)

↓
radiation

(LDS Yadav)

↓
measurement

That branch of science which deals with measurement of radiation i.e. determination of unknown compound through radiation is kya spectroscopy.

Spectroscopy is that branch of science which deals with determination of structure of unknown compound through interaction of EM radiation with matter

OR

It is the analysis of EM radiation absorbed, emitted or scattered by molecule

Advantages →

- * Takes less time
- * Less amt. of substance
- * can be reused repeatedly
- * More accurate & reliable.

Spectrometer - Spectrometer or spectrometre measures the energy change or frequency of an EM radiation emitted or absorbed. [The separation or analysis of a composite radiation into diff wavelengths of frequency constitutes a spectrum.]

(2) Emission spectrum - when dissociation occurs.

Wavelength (λ) \rightarrow dist.
2 crest. or 2 troughs

Wave no. ($\bar{\nu}$ or \perp) \rightarrow no. of waves per unit dist.

Frequency \rightarrow (ν) \rightarrow no. of waves from a point in 1 sec.

Energy \rightarrow $E = h\nu$

$$E = \frac{hc}{\lambda}$$

$$E \propto \frac{1}{\lambda} \propto \nu \propto \bar{\nu}$$

Electromagnetic Spectrum

The increasing order of wavelength or decreasing order of frequency of EM waves is $\underline{\text{energy}}$ \rightarrow $\underline{\text{wavelength}}$.

γ	X	UV	Vis	IR	Microwave	Radiowaves
0.001 nm	0.1 nm	10-400 nm	400-800 nm	800 nm - 1 cm	1 cm - 100 cm	> 100 cm

UV-Vis
spectroscopy

Range - 200-800 nm

10-200 not

considered bcz

it is for saturated

compds.

to test for unsaturation

& conjugations

molecular

spectroscopy.

IR spectroscopy



4000 - 667 cm⁻¹

to find functional groups

in any compd.

type of bond. (C=C)

Spectroscopy associated with EM waves

- ① Radiowaves → Nuclear Magnetic Resonance (NMR spectroscopy)

In this, spinning of nucleus causes resonance so we can find nature of proton or type of carbon present.

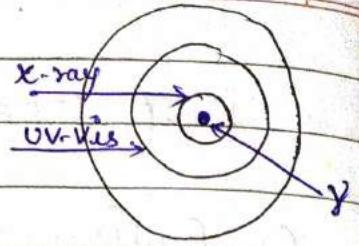
types → proton-NMR, C^{13} -NMR, P-NMR etc

- ② Microwaves → Rotational Spectroscopy
used to determine bond length & angle.
Due to higher energy than radiowaves, they also cause rotation along with resonance.

- ③ Infrared → Infrared Spectroscopy or Vibrational Rotational Spectroscopy.
When IR radiation is passed through a molecule it starts rotating faster & vibrates (compression & expansion).
Used to determine functional group & type of bond.

- ④ UV-Vis → Electronic Spectroscopy
Due to excitation of electrons from ground state to excited state or vice versa.

⑤ X-Rays \rightarrow X-Ray Diffraction
Used to find bond angle.



⑥ γ -Rays \rightarrow Mawbauer spectroscopy.
To find about parent nuclei.

In case of IR \rightarrow Microwave \rightarrow

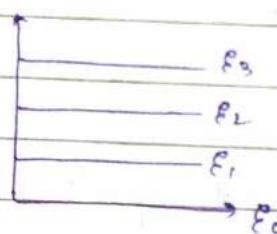
* Gap b/w energy levels of molecules in case of rotational Spectroscopy is 0.2 KJ/mol



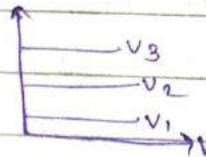
In case of IR \rightarrow

energy gap $\rightarrow 15-40 \text{ KJ/mol}$

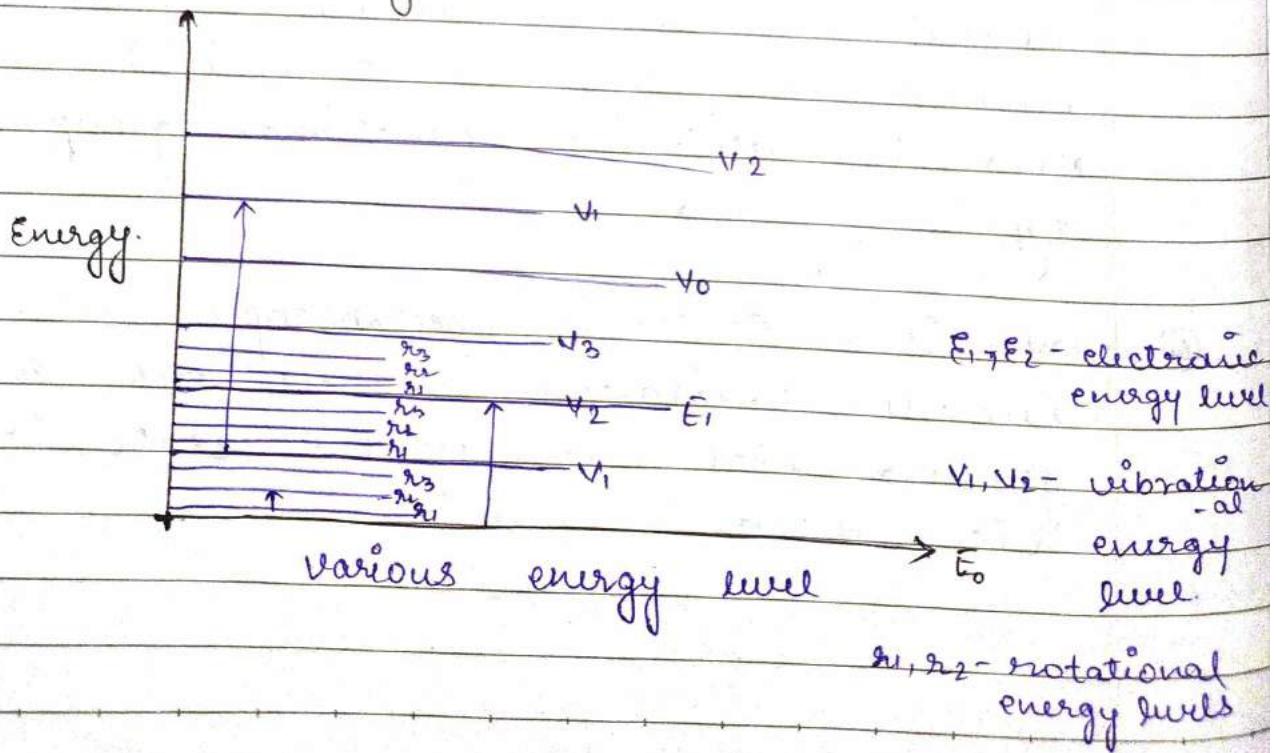
UV-V_{is} \rightarrow



gap - 950 KJ/mol



Combined diagram \rightarrow



Different types of molecular energy →

i)- Translational energy - Energy due to uniform or linear motion of the molecule as a whole is \rightarrow translational energy. Since a molecule can move in any direcⁿ (x, y or z) so it has 3 degrees of freedom. Acc. to KTG,

$$\text{Total } E_{\text{trans}} = \frac{3}{2} KT$$

$$\text{Av. } E_{\text{trans}} = \frac{1}{2} KT$$

ii)- Rotational energy - The energy associated with overall rotation of the molecule (with its atoms) -

$$E_{\text{rot}} = \frac{1}{2} I \omega^2$$

Acc. to quantum mechanics,

$$E_{\text{rot}} = \frac{J(J+1)\hbar^2}{8\pi^2 I}$$

J = rotational quantum number.

I = moment of inertia

iii)- Vibrational energy - This energy is due to vibration of the atoms of the molecule about equilibrium position

$$E_{\text{vib}} = \left(v + \frac{1}{2}\right) h\nu_0$$

v = vibrational quantum no.

ν_0 = frequency of vibration.

If $v=0$ - the $E_{\text{lib}} = \frac{1}{2} h\nu_0$ (K/a zero point energy).

- (iv) Electronic energy - This type of energy is due to the motion of electrons i.e. due to various electronic arrangements.

$$E_{\text{elec}} > E_{\text{lib}} > E_{\text{rot}} > E_{\text{trans}}$$

$$E_{\text{total}} = E_{\text{elec}} + E_{\text{lib}} + E_{\text{rot}}$$

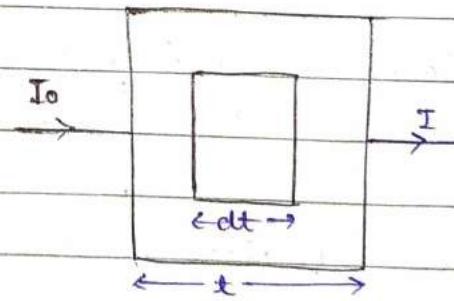
E_{trans} is negligible.

UV-Visible Spectroscopy

→ Laws of Absorption:

① Lambert's law →

When a beam of monochromatic light is passed through an absorbing medium, - the rate of decrease of intensity of absorbing light radiation with the thickness of absorbing medium is directly prop. to intensity of light



$$-\frac{dI}{dt} \propto I$$

$$\frac{dI}{dt} = -KI$$

$$\int_{I=I_0}^I \frac{dI}{I} = -K \int_0^t dt$$

$$[\ln I]_{I_0}^I = -kt$$

$$\ln \frac{I}{I_0} = -kt$$

$$\frac{I}{I_0} = e^{-kt}$$

$$I = I_0 e^{-kt} \quad \text{--- (1)}$$

$$\begin{aligned} I_{abs} &= I_0 - I \\ &= I_0 - I_0 e^{-kt} \end{aligned}$$

$$I_{abs} = I_0 (1 - e^{-kt})$$

$$\ln \frac{I}{I_0} = -kt$$

$$2.303 \log_{10} \left(\frac{I}{I_0} \right) = -kt$$

$$2.303 \log \left(\frac{I_0}{I} \right) = kt$$

$$\underbrace{\log_{10} \left(\frac{I_0}{I} \right)}_{\text{Absorbance}(A)} = \underbrace{\left(\frac{k}{2.303} \right)t}_{\epsilon}$$

Absorbance(A) ϵ = Extinction coeff.
or Absorptivity

$$A = \epsilon t$$

② Beer's law \rightarrow (Beer's Lambert's law) \rightarrow
 When a beam of monochromatic light radiation
 is passed through an ^{absorbing} medium, the rate
 of decrease of intensity of radiation with
 thickness of the absorbing medium is
 directly proportional to the intensity
 of incident radiation as well as concⁿ
 of solⁿ (absorbing medium).

$$-\frac{dI}{dt} \propto I \times c$$

$$\int_{I=I_0}^I \frac{dI}{I} = \int_0^t -Kcdt$$

$$\ln \frac{I}{I_0} = -Kct$$

$$I = I_0 e^{-Kct}$$

$$\Rightarrow A = \epsilon ct$$

ϵ = molar extinction
coeff.

Q A solution of thickness 3 cm transmits 30% incident light. Calculate concentration of solution given extinction coefficient = $4000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

$$A = \epsilon ct$$

$$\text{Transmittance} = 0.3 = \frac{I}{I_0}$$

$$\therefore \text{Absorbance} = \log \frac{I_0}{I} = \log \frac{1}{0.3} = \log \frac{10}{3}$$

$$= 1 - 0.4771$$

$$= 0.5229$$

$$= 0.523$$

$$A = Ect$$

$$0.523 = 4000 \times c \times 3$$

$$c = \frac{0.523}{4000 \times 3}$$

$$c = 4.35 \times 10^{-5} \text{ mol/dm}^3.$$

- Q The %age transmittance of an aqueous solution of unknown compound is 20% at 25°C and 300 nm for a 4×10^{-5} M in a 2cm cell. Calculate -
- ① Absorbance
 - ② molar extinction coeff.
 - ③ %age transmittancy of a 2×10^{-5} molar soln in a 4cm cell.

$$\textcircled{1} \quad A = \log \frac{I_0}{I} = \log \frac{1}{0.2}$$

$$= 1 - 0.301$$

$$= 0.699.$$

\textcircled{2} molar e

$$A = Ect$$

$$0.699 = E \times 4 \times 10^{-5} \times 2$$

$$E = 0.087375 \times 10^4$$

$$E = 8.7 \times 10^3 \text{ mol}^{-1} \text{ cm}^{-1}$$

③ $A = 8.7 \times 10^3 \times 2 \times 10^{-5} \times 4$
 $= 8.7 \times 2 \times 4 \times 10^{-2}$
 $A = 0.696$

$$\boxed{\% T = 20\%}$$

Q An unknown substance transmits 40% of light of wavelength 43.5 nm in a cell of 2cm dimension which has concentration of 20 g/l. Under similar condition, what % of light will be transmitted by a solution containing 40 g/l of same unknown substance.

$$\log \frac{I_0}{I} = \log \frac{10}{4} = 1 - 0.602 \\ = 0.398$$

$$A = Ect$$

$$0.398 = E \times 20 \times 2$$

$$E = \frac{0.398}{20 \times 2}$$

$$= \frac{0.398}{40}$$

Now,

$$A = \frac{0.390}{40} \times 40 \times 2$$

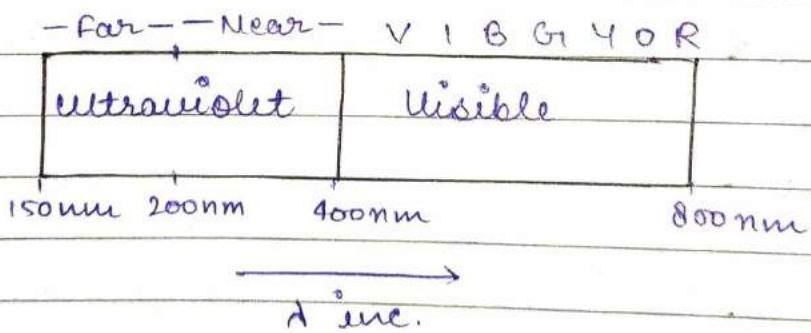
$$= 0.390 \times 2$$

$$A = 0.796$$

$$\% \text{ Transmitted} = 84\%.$$

UV-Visible Spectrum →

Electronic Spectroscopy: → UV-VIS spectroscopy is also known as electronic spectroscopy because it involves the transition of electrons within a molecule or ion from a lower to higher electronic energy level or vice versa by absorption or emission of radiations falling in the UV-VIS range of electromagnetic spectrum respectively.

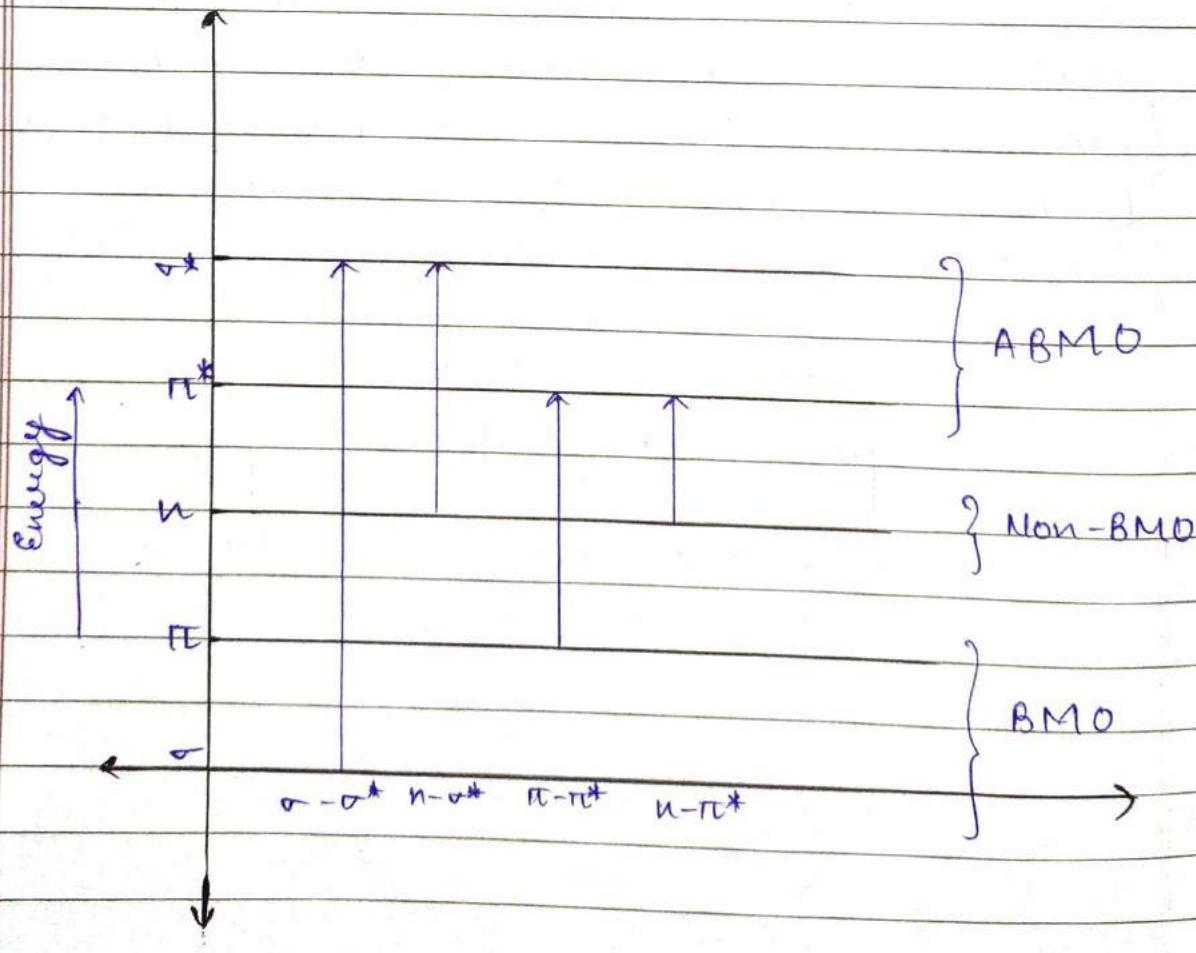


Uses of UV-Vis spectroscopy -

- For determination of mol. wt.
- Detection of impurity
- Determination of dissociation const.
- Determination of kinetics of reaction.
- To find no. of conjugated double bonds and aromatic conjugation.

λ_{max} = wavelength at which a molecule possesses its highest absorptivity coefficient (ϵ_{max}).

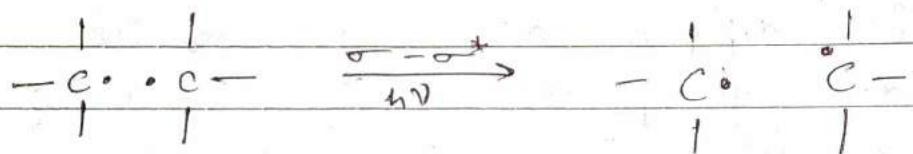
Types of electronic transitions



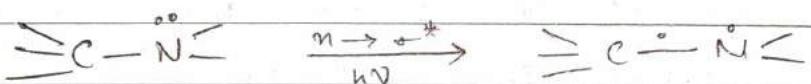
Range →

Types of Electronic transitions -

- ① $\sigma \rightarrow \sigma^*$:- This type of transition takes place in saturated compd. like alkane where only σ bond is present & no atom has non-bonding e⁻s.
Such transitions require energy in range of 120-150 nm.



- ② $n \rightarrow \sigma^*$:- The excitation of an electron from an unshared pair to antibonding σ^* orbital is called $n \rightarrow \sigma^*$ transition.



range = 150-180 nm

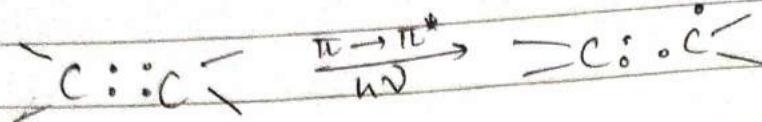
- ③ $\pi \rightarrow \pi^*$:- Range = 180-200 nm

This type of transition takes place in unsaturated compounds containing double or triple bonds.

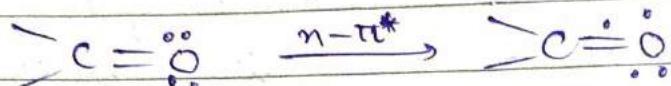
The excitation of $\pi - \text{e}^-$ requires smaller energy & hence transition occurs at longer wavelength.

for conjugated di and trienes → above 200 nm

1,3-butadiene → 217 nm.



④ $n \rightarrow \pi^*$: \rightarrow This type of transition occurs in compds. containing non-bonding e's on hetero atom. (>C=O , >C=S , -N=O)



Range $(> 280 \text{ nm})$.

colour to bear
Chromophores \rightarrow

It is defined as any isolated covalently bonded group that shows a characteristic absorption in ultraviolet or visible region.

e.g. benzene & nitrobenzene
colourless yellow coloured \rightarrow due to presence of chromophores.

enhances colour

Auxochromes \rightarrow Groups which are not chromophores themselves but their presence can cause the increase in colour intensity of compounds are called auxochromes.

They shift the absorption maximum towards red end of spectrum.

Absorption & intensity shift \rightarrow

-OR + 6 nm

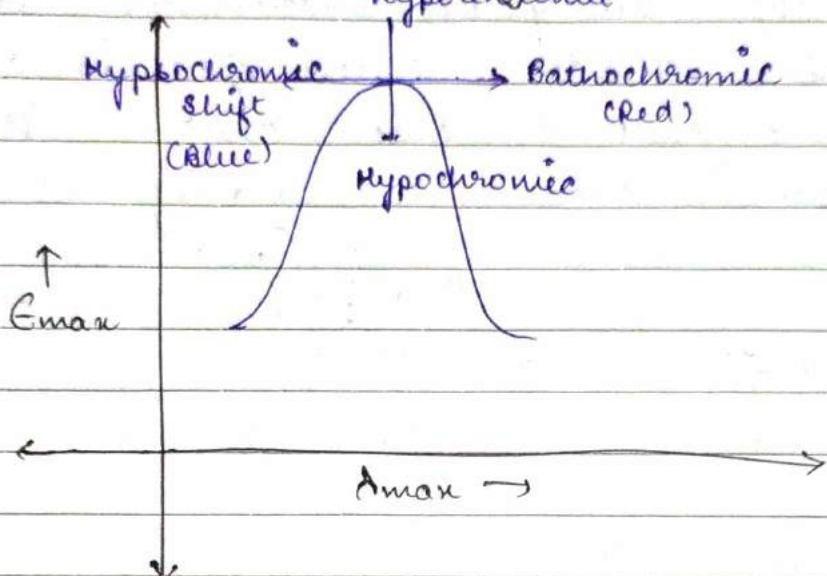
-SR + 30 nm

-Cl, -Br + 5 nm

-NR₂ + 60 nm

-OCOCH₃ 0

Absorption ϵ' intensity shifts →
Hyperchromic



Bathochromic shift (Red shift)-

The shift of an absorption maximum (ΔE_{max}) towards the longer wavelength is called bathochromic shift or red shift. It may be due to presence of aurochrome or change in polarity of solvent.

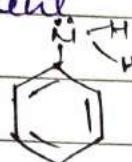
The $n-\pi^*$ transition for carbonyl compounds experiences bathochromic shift when the polarity of solvent is decreased.

Conversion of phenol to phenolate ion causes bathochromic shift bcz - the non-bonding c^- become available for interaction $\pi-e^-$ of the ring.

Hypsochromic shift (blue shift) \rightarrow

The shift of absorption maximum (λ_{max}) towards the shorter wavelength is called hypsochromic shift or blue shift. It may be due to increase in polarity of solvent or removal of conjugation.

e.g.-

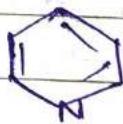


$$\lambda_{max} = 280 \text{ nm}$$

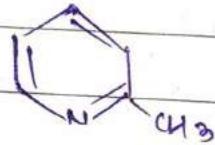
$$\lambda_{max} = 203 \text{ nm}$$

Hyperchromic shift -

It is - the effect leading to increase in intensity of absorption maximum i.e. ϵ_{max} increases. The introduction of auxochromes usually \uparrow es the intensity of absorption maximum.



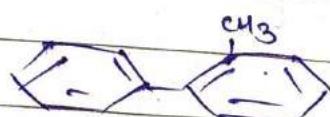
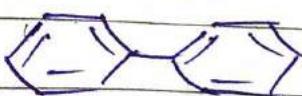
$$\epsilon = 2750$$



$$\epsilon = 365 \quad 3560$$

Hypochromic shift -

The decrease in intensity of absorption i.e. ϵ_{max} is known as hypochromic shift. It is caused by the groups which distort the geometry of the molecules.



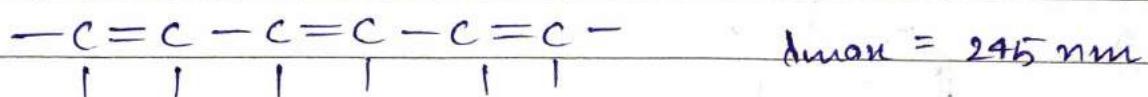
Fischer

Woodward - Fischer Rule →

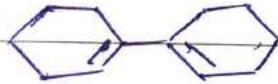
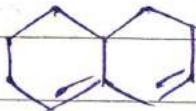
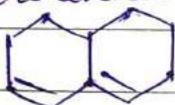
* non-cyclic dienes



* conjugated triene

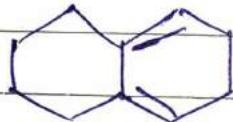


* cyclic diene +
→ heteroannular



$$\lambda_{\max} = 214 \text{ nm}$$

→ homoannular

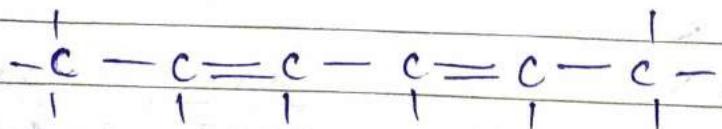


$$\lambda_{\max} = 253 \text{ nm}$$



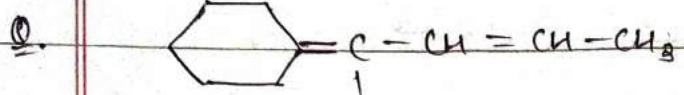
→ +30 (double bond
extending
conjugation).

Q. Calculate absorption max. in UV spec. of
2,4 hexadiene +



$$217 + \underline{5} = 227$$

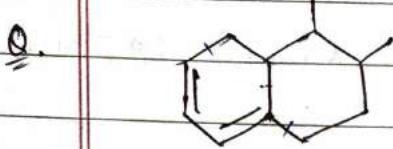
~~ring residue~~
(alkyl grp)



\downarrow
Base value
 CH_3

$$217 + \underbrace{5 + 5 + 5 + 5 + 5}_{\text{ring residue}} = 242$$

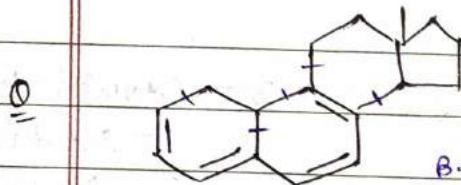
[exocyclic bond]



$$253 + \underbrace{5 + 5 + 5}_{\text{ring residue}} + 5 = 268 + 5 = 273 \text{ nm}$$

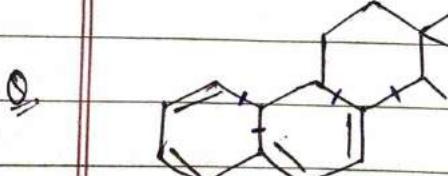


$$214 + 15 + 5 = 234$$



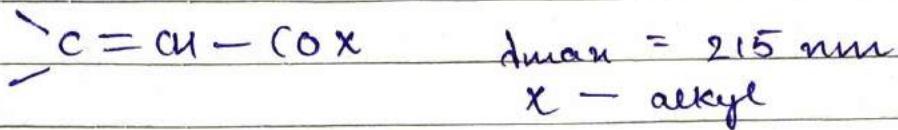
$$253 + \underbrace{30 + 30 + 5 + 25 + 25}_{\text{B.V. } d\text{-B ext congi. } + 20 \text{ ring residue}} = 253 + 80 + 10 = 343$$

$$= 338 + 10 = 348 \text{ nm}$$



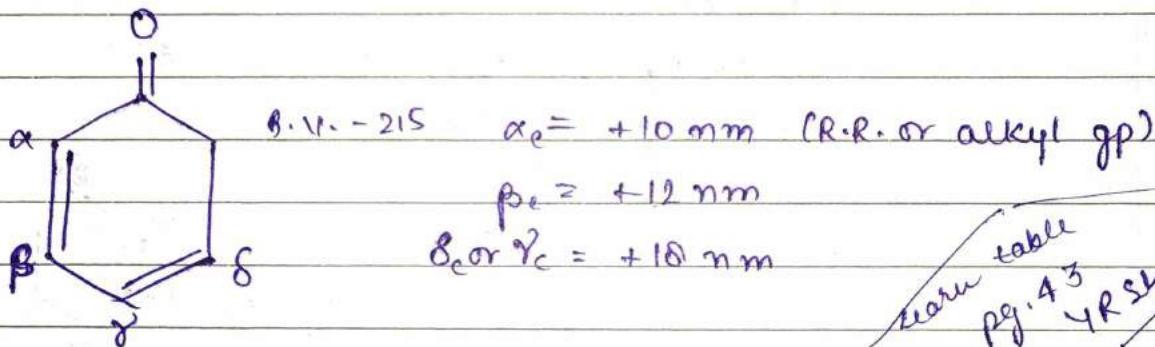
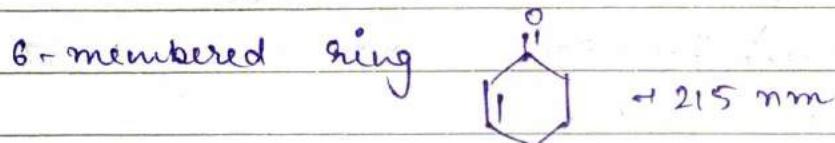
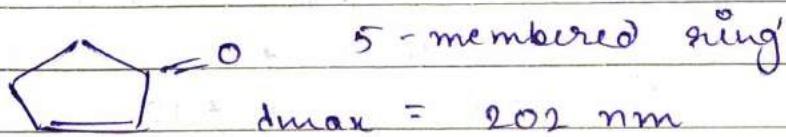
$$253 + \underbrace{30 + 30}_{d\text{-B}} + \underbrace{\frac{20}{4 \times 5}}_{\text{ring residue}} + \underbrace{\frac{10}{2 \times 5}}_{\text{exo}} = 253 + 60 + 20 + 10 = 343$$

UV absorption in α - β unsaturated carbonyl compound:



$X = \text{H}$, $\lambda_{\text{max}} = 207 \text{ nm}$

$X = \text{OH}$, $\lambda_{\text{max}} = 193 \text{ nm}$

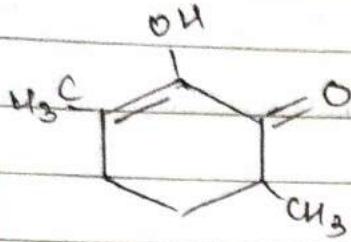


Learn table pg. 43 4F Sharma

If α - β unsaturated carbonyl compd. & homoannular ring are both are present then base value will be of α - β unsaturated carbonyl compd. ϵ' + 39 nm for homoannular ring.

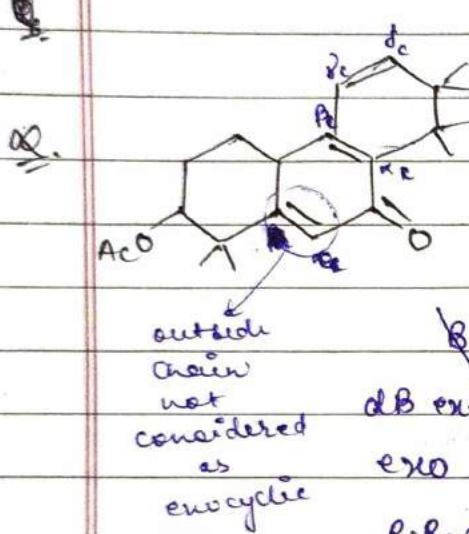


B.V. $215 + \frac{2 \times 12}{100} + 5$
 $= 244 \text{ nm}$



OH $\alpha_c \rightarrow +35$ $\beta_c >$

$$215 + 35 + \overbrace{12 + 12}^{R.R.\ \beta'\text{ CH}_3\text{ gp at } \beta_c} = 262 \quad 274$$



B.V. - 215

IDB ext. conj. - +30

R.R. at $\alpha_c \rightarrow +10$

R.R. at $\beta_c \rightarrow +12$

B.V. $\rightarrow 215$

* R.R. at $\delta_c \rightarrow +18$

dB ext. conj. $\rightarrow +30$

homocyclic $\rightarrow +39$

exo $\rightarrow +5$

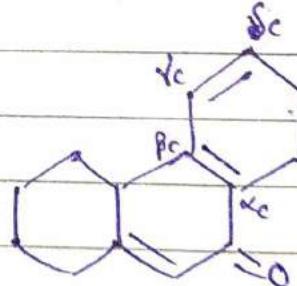
R.R. at $\alpha_1 \rightarrow +10$

R.R. at $\beta_1 \rightarrow -24$

R.R. at $\beta_2 \rightarrow +24$

324

310

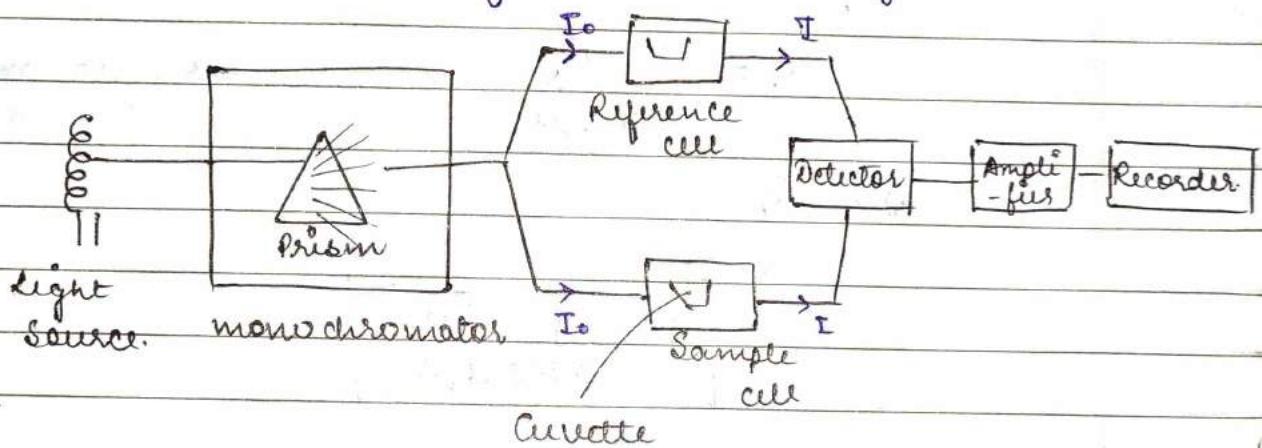


UV - Visible Spectrophotometer

The instrument used in UV-Visible spectroscopy is called as UV-VIS spectrophotometer.

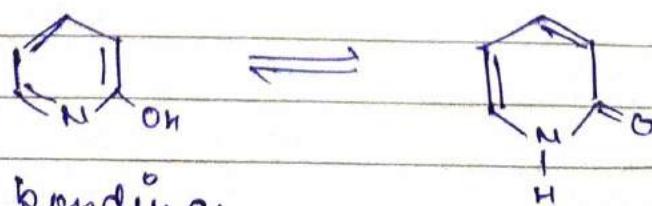
A spectrophotometer is a device which detects the transmittance of radiation when light of certain intensity or frequency is passed through it.

The instrument compares intensity of transmitted light with that of incident light.



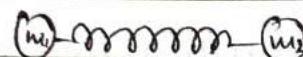
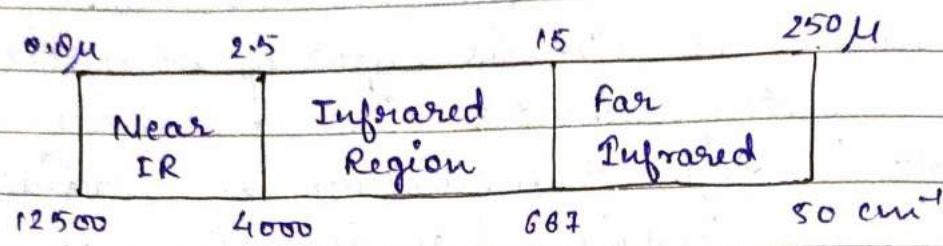
Applications of UV-Visible Spectroscopy →

- To determine presence & extent of conjugation
- To determine geometrical isomers
- To determine functional groups
- To find dissociation constant & kinetics of reaction
- To detect keto-enol tautomerism.



→ hydrogen bonding.

Infrared Spectroscopy



$$\frac{1}{\nu}$$

$$\nu = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}, \quad \text{Here, } \mu = \frac{m_1 m_2}{m_1 + m_2}$$

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

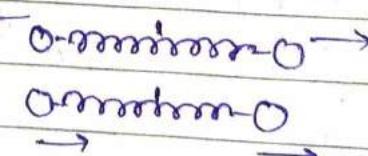
\Rightarrow

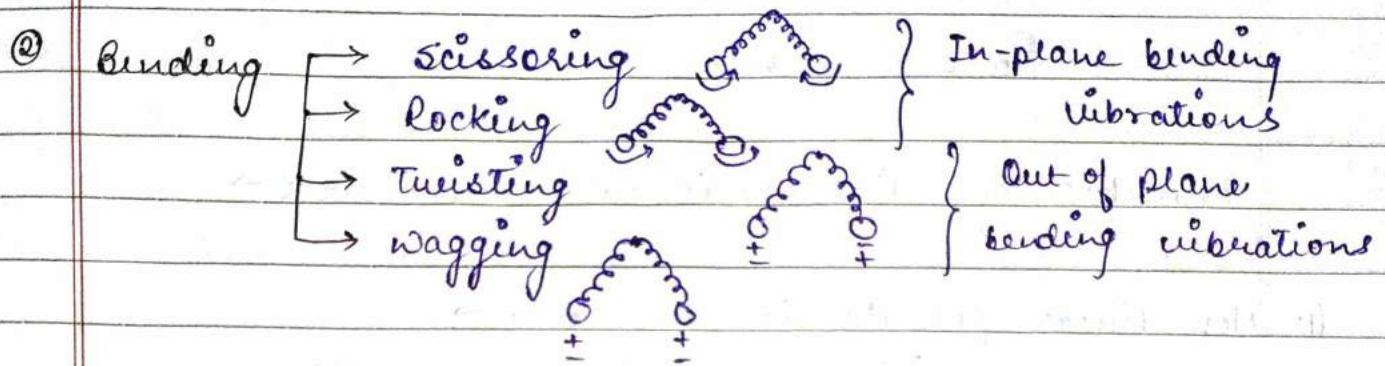
$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Types of molecular vibrations

↓ ↓
 Stretching Bending
 ↓ ↓
 change in change in
 bond length bond angle

① Stretching Symmetric Asymmetric





Fundamental vibrations and overtones →

- * Fundamental vibration - The vibration corresponding to transition from ground state to 1st excited state is ν_0 fundamental vibration.

$$\epsilon_{\text{vib}} = \left(\nu + \frac{1}{2}\right) \hbar \nu_0$$

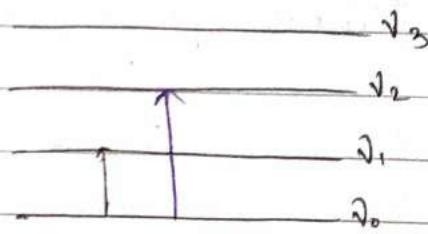
For fundamental vib. →

here, $\nu = 0$ for E_0

$$E_0 \overset{\text{fund}}{=} \left(0 + \frac{1}{2}\right) \hbar \nu_0$$

for E_1

$$E_1 \overset{\text{fund}}{=} \left(1 + \frac{1}{2}\right) \hbar \nu_0$$



$$\epsilon_{\text{vib}} = \frac{E_1 + E_0}{2} - E_0$$

$$\boxed{\epsilon_{\text{vib}} = \hbar \nu_0}$$

1st overtone →

$$E_0 = \frac{1}{2} \hbar \nu_0$$

$$E_2 = \frac{5}{2} \hbar \nu_0$$

$$\therefore \epsilon_{\text{vib}} = 2 \hbar \nu_0$$

$$\text{Error} = 3\%.$$

Number of fundamental vibrations \rightarrow

① Non-linear polyatomic molecule \rightarrow

$n = \text{no. of atoms in molecule}$

Translation degree of freedom = 3

Rotational " " " " = 3

Vibrational " " " " = ?

$$3n = 3 + 3 + V_{DOF}$$

$$V_{DOF} = 3n - 6$$

② Linear polyatomic molecule -

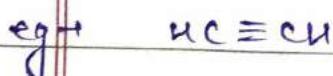
Trans. DOF = 3

Rot. " " = 2

Vib. " " = 9

$$3n = 5 + V_{DOF}$$

$$V_{DOF} = 3n - 5$$



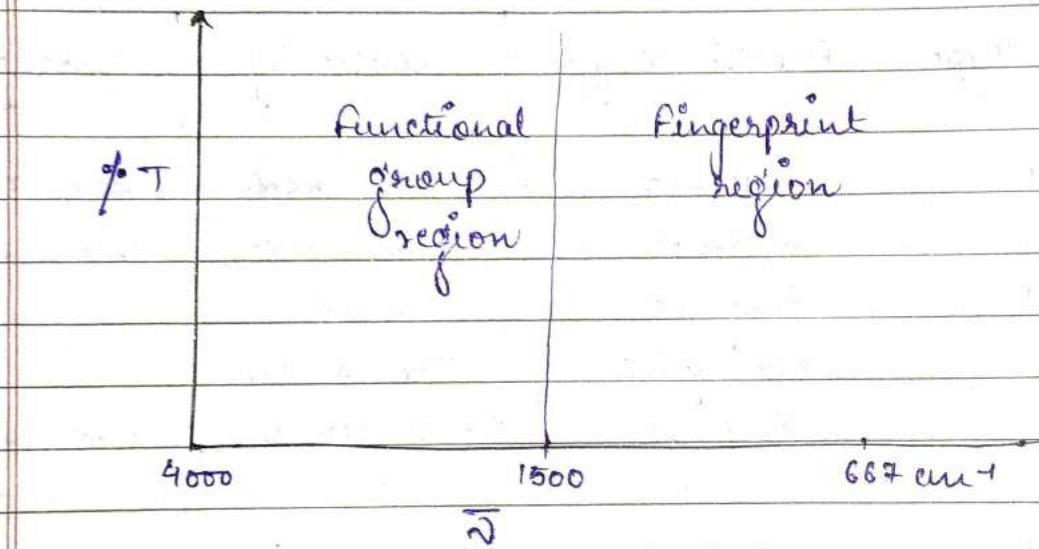
$$\begin{aligned} \Rightarrow V_{DOF} &= 3 \times 4 - 5 \\ &= 7. \end{aligned}$$

$$\begin{aligned} \text{CH}_4 \Rightarrow V_{DOF} &= 3 \times 5 - 6 \\ &= 9. \end{aligned}$$

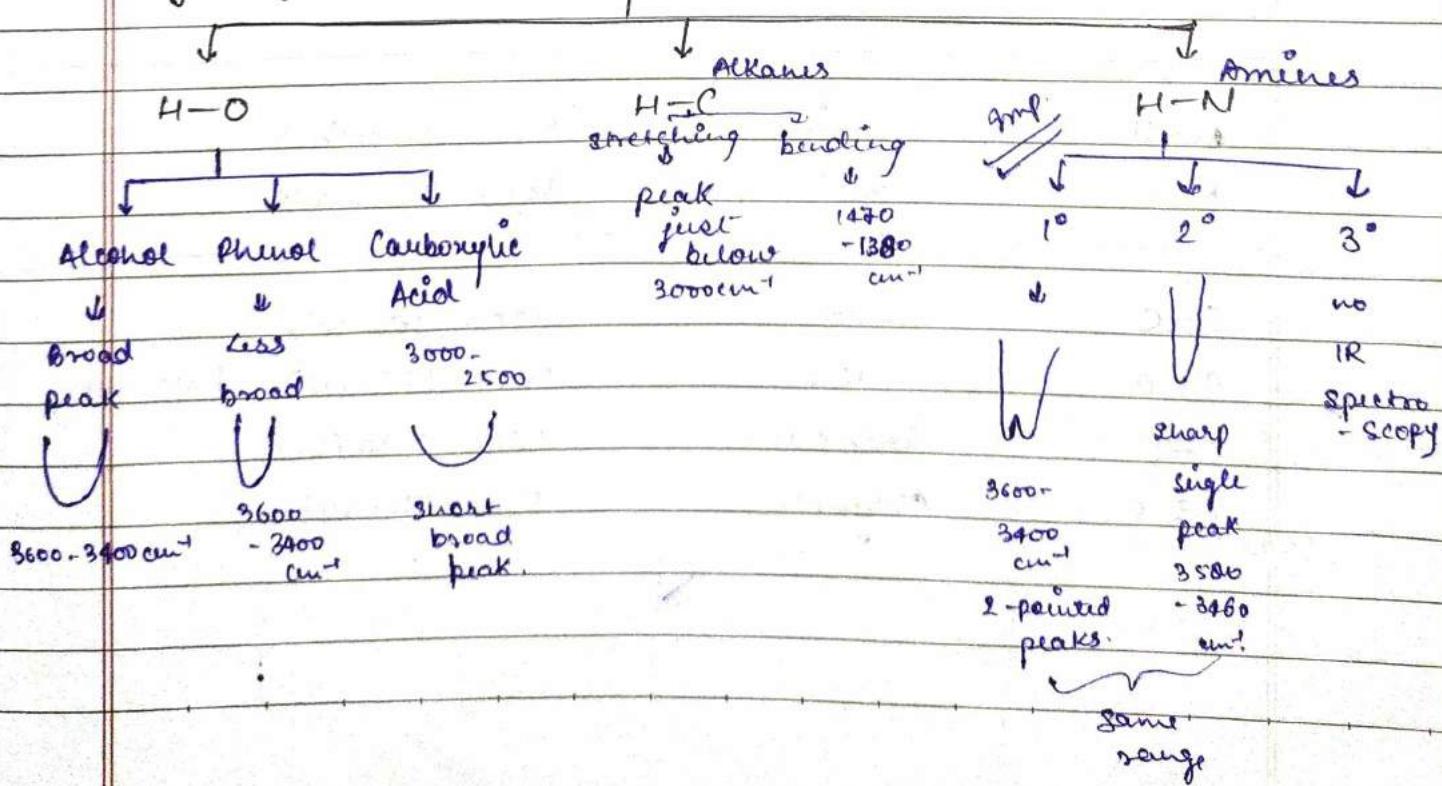
* Molecules having dipole moment zero will be IR inactive & will not show IR spectroscopy.
eg: CO₂, CH₄ etc.

Such molecules will be Raman active.
And vice versa.

IR Spectrum :→



→ Hydrogen attached to sp^3 hybrid atoms →



Hydrogen is attached to sp^2 hybrid atom

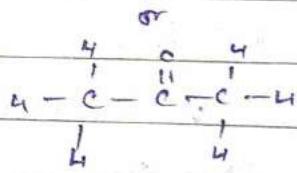
Alkene	Aromatic stren-	Aldehyde
\checkmark stretching \checkmark bending just above \checkmark below 3000	3100 cm^{-1} broad $1000-800\text{ cm}^{-1}$	$2950 \& 2800$

Bond type	Functional gp.	Stretching	Bending
* s - sharp m - medium w - weak			
C-H	Alkanes	$2970-2850\text{ (s)}$	$1420-1350\text{ (s)}$
C-H	Alkenes	$3080-3020\text{ (w)}$	$1000-675\text{ (s)}$
C-H	Alkynes	3300 (s)	
C-H	Aldehydes	$2900/2700\text{ (m)}$	
C-H	Aromatic	$3100-3000\text{ (v)}$	$800-675$
O-H	Alcohol	$3600-3400\text{ (broad)}$	
O-H	Acids	$3000-2500\text{ (s)}$ (broad)	
N-H	Amine	$3500-3300\text{ (m)}$	
N-H	Amide	$3500-3350\text{ (v)}$	
C-C	Alkane	$3000-2800\text{ (w)}$	
C=C	Alkene	$1680-1620\text{ (v)}$	$1000-600$
C=C	Aromatic	$1600-1450\text{ (v)}$	
C≡C	Alkyne	$2260-2100\text{ (v)}$	

$C \equiv N$	Cyanides	2200
$C - O$	Alcohol, ether, ester	1300-1500 (S)
$C = O$	Ketone	1725-1705 (S)
$C = O$	Aldehyde	1740-1720
$C = O$	Ester	1750-1735 (S)
$C = O$	Acid Anhydride	1725-1700 (S) 1690-1650 (S)
$O - H$	Alcohol	3600-3400 (broad)
$O - H$	Acids	3000-2500 (S) (broad)

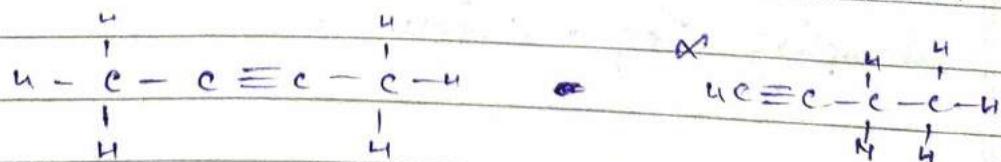
Q. An organic compd. having mol. formula C_3H_6O and has IR absorption freq. at 1760 cm^{-1} determine str. of compd.

- carbonyl group \rightarrow aldehyde or ketone \rightarrow $\text{H}-\overset{\underset{\text{H}}{\text{C}}}{\text{C}}-\overset{\underset{\text{H}}{\text{C}}}{\text{C}}-\text{C=O}$



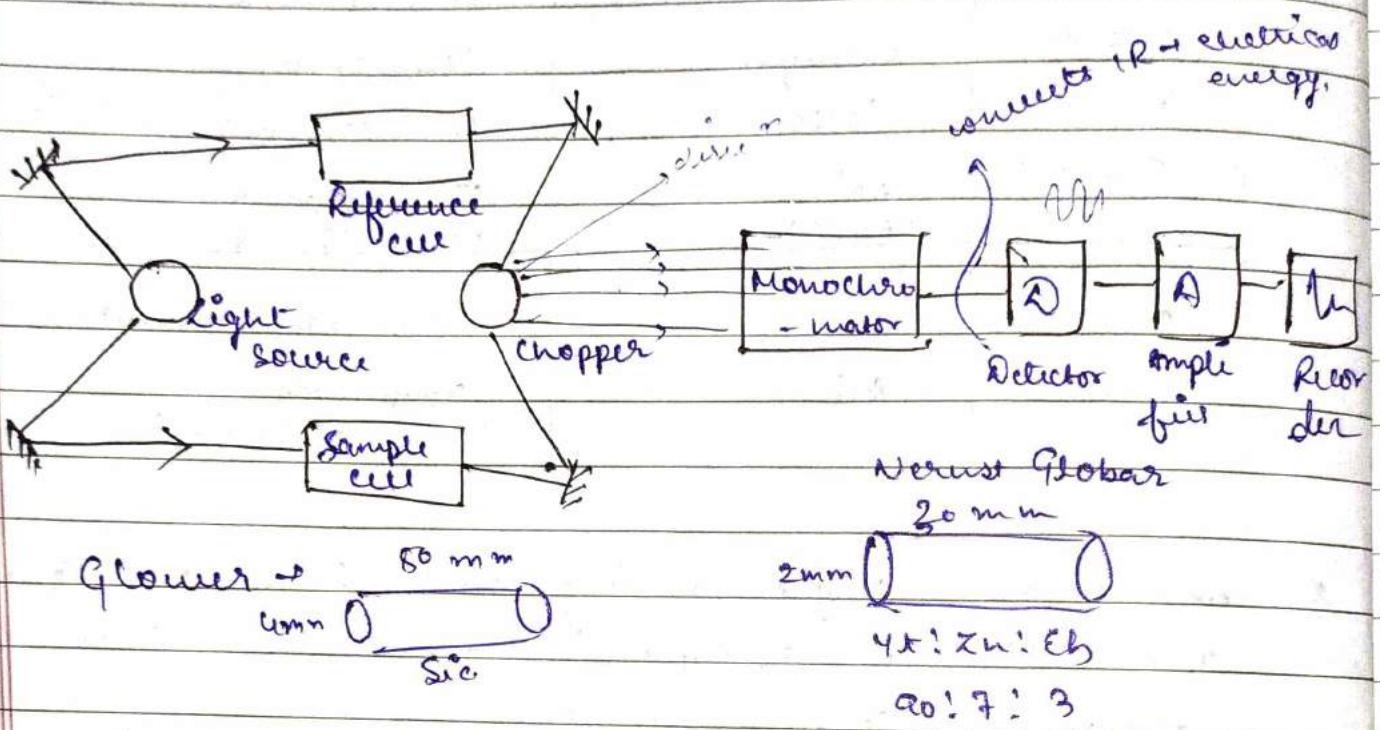
but C-H bond peak (2900 & 2700) of ald. is not given \Rightarrow ketone.

Q. An organic compd. having mol. formula C_4H_6 IR freq.s \rightarrow 2260 & 2950 cm^{-1} . determine str.



bcz C-H (3300) of alkyne is not given.

IR Spectrophotometer →



Applications of IR spectroscopy -

- Determination of force constant (K)
- ✓ → Identification of functional group.
- Distinction b/w intra & intermolecular H-bonding
- Structure elucidation of unknown compd.
- Study of keto-enol form.
- Shape or geometry
- detection of impurities.

Sampling Tech Techniques →

C₁₄H₁₀X₂ Na Oe Sf

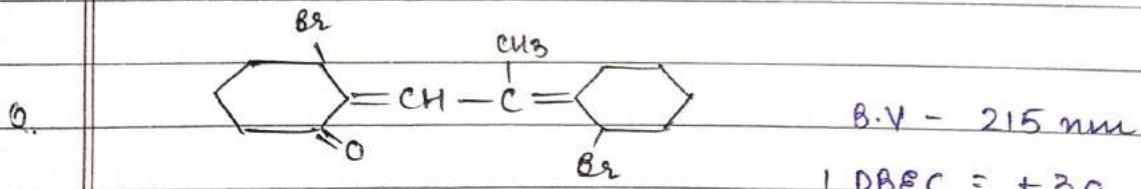
$$\text{No. of Double bonds \& rings} = (a+1) - \frac{(b+c-d)}{2}$$

cg- C₁₄H₁₀NO

$$\text{NDBAR} = (3+1) - \left(\frac{10-1}{2} \right)$$

$$= 4 - 3$$

$$= 1.$$

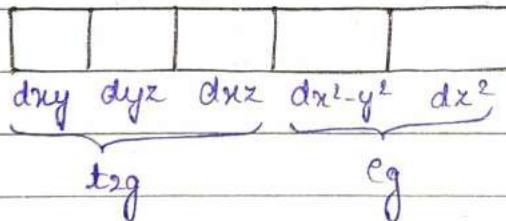
1 R.R. at α = +102 R.R. at δ = +361 CH₃ at γ = +182 ~~cyclic~~ exocyclic = +10

Bonding

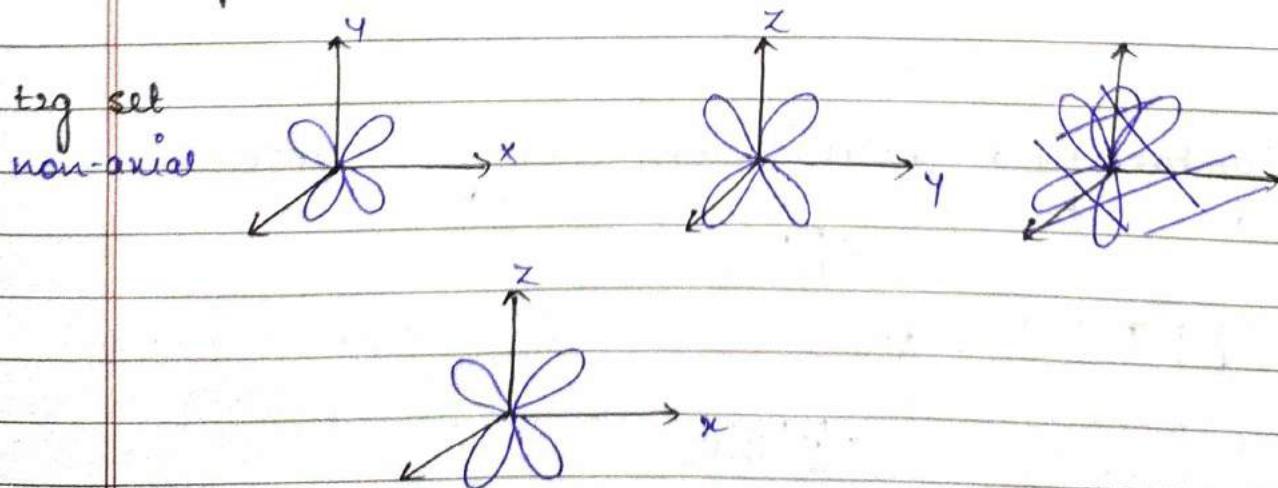
Crystal Field Theory →

- * Postulates
 - Ligands are point charges.
 - Interaction b/w CMA & ligands is electrostatic.
 - d-orbitals are degenerate (have same energy in free atom)
 - degeneracy is disturbed during bond formation i.e. orbitals acquire different energies.

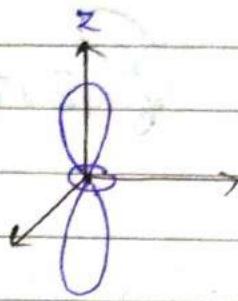
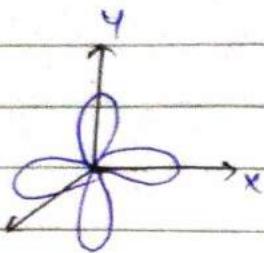
d-orbitals -



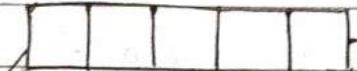
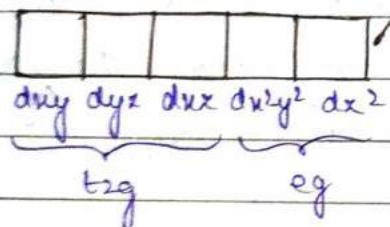
shape - double dumbbell.



cg set
axial



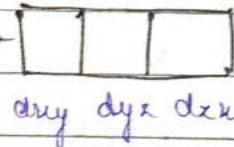
* Four octahedral complexes \rightarrow



$$= \frac{+3}{5} = 0.6$$

Dq (characteristic)

$$= -\frac{2}{5} = -0.4$$



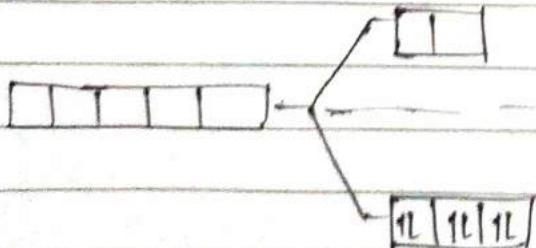
Weak field ligand \rightarrow high spin or spin free complex

eg - F, H₂O

Strong field ligand \rightarrow low spin or spin paired complex.

eg - CN

Crystal field stabilisation energy \rightarrow (CFSE)

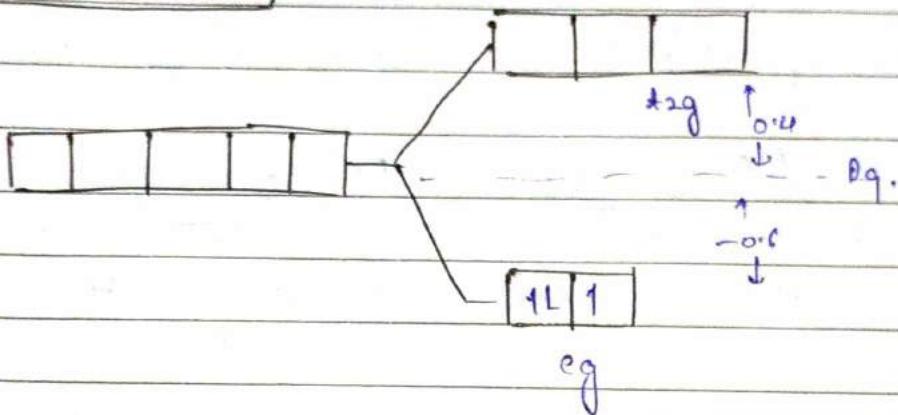


$$\begin{aligned} &= 0.6 \times 0 - 0.4 \times 6 \\ &= -2.4 Dq. \end{aligned}$$

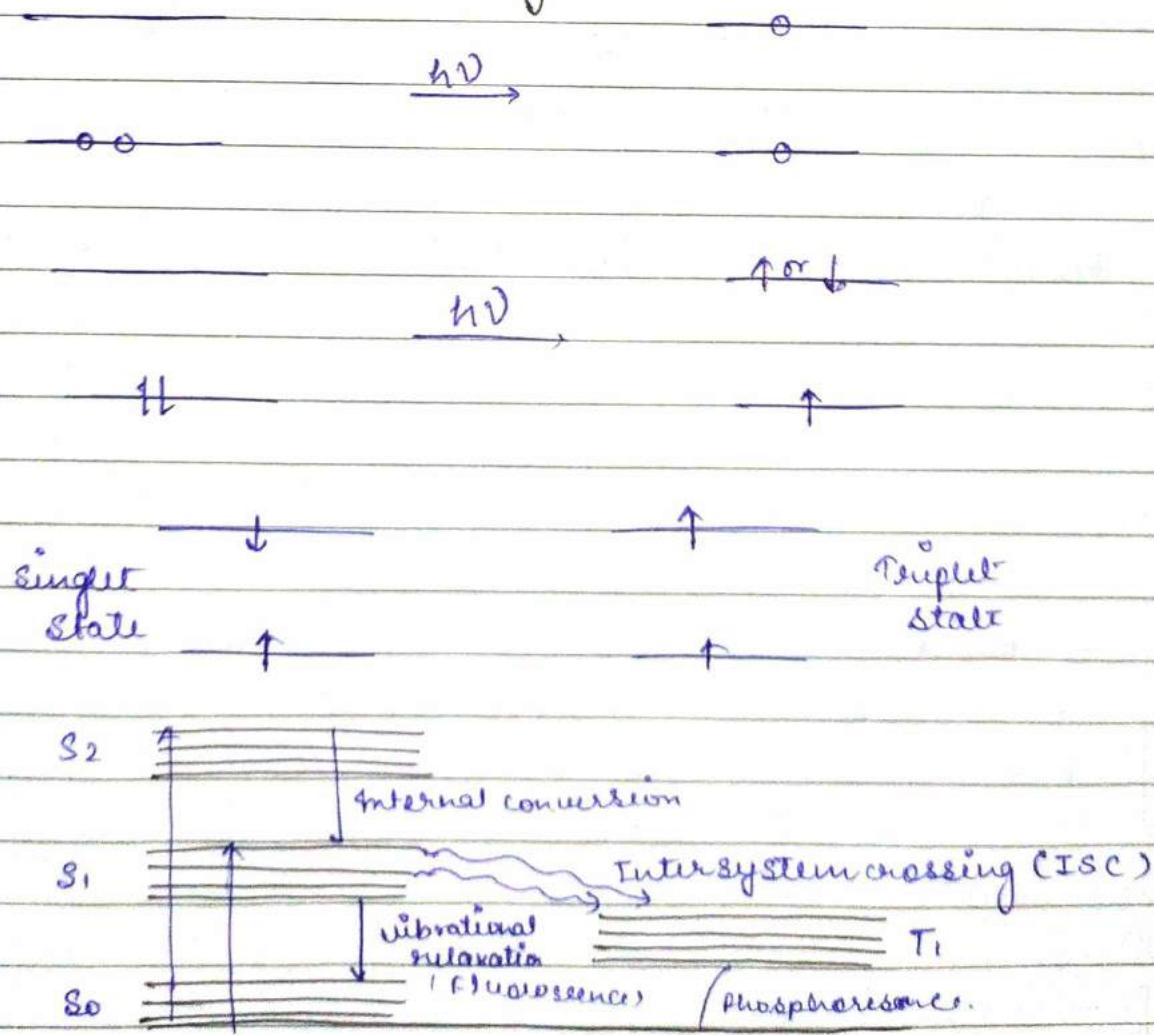
→ Four tetrahedral complexes →

$$\Delta t = \frac{4}{9} \Delta_0$$

(emission)



Jablonski Diagram



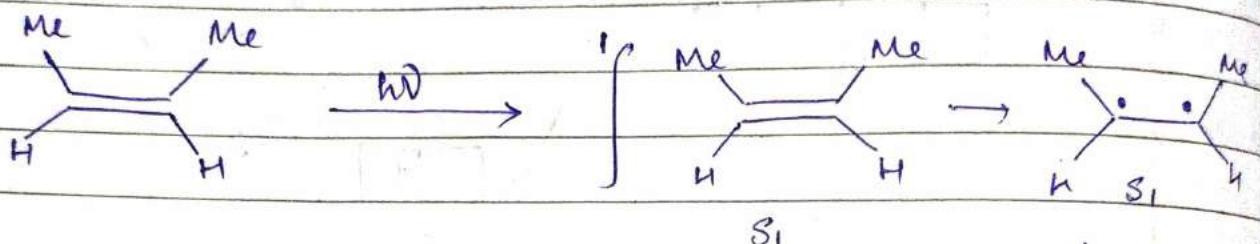
$S_1 \rightarrow S_0$ (Fluorescence) Radioactive process

$S_1 \rightarrow T_1$ (Intersystem crossing) CNRP

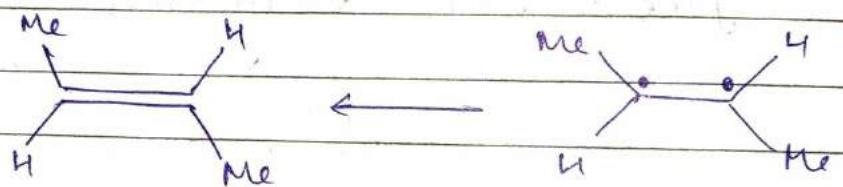
$T_1 \rightarrow S_0$ (Phosphorescence) Radioactive process.

{ Energy Triplet < Energy Singlet }

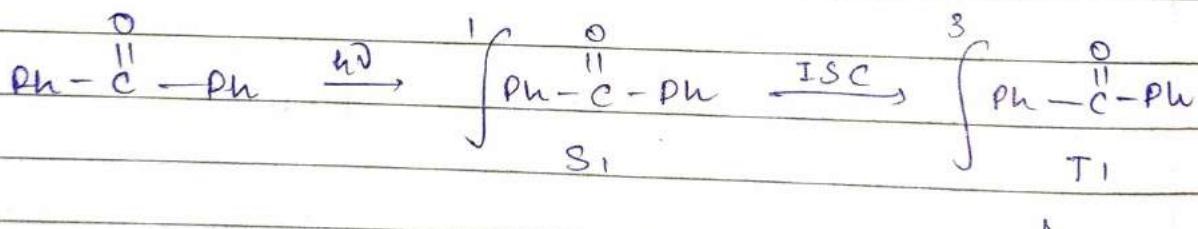
*



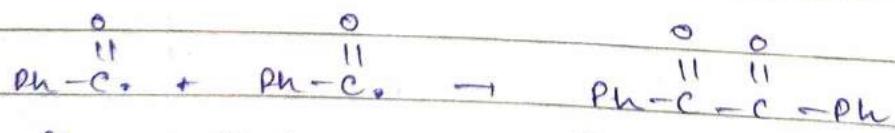
Single bond rotation



*



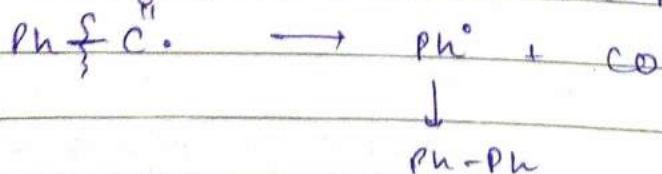
①



②



③



\downarrow



Liquid Crystals →

Solid $\xrightarrow[\text{M.P.}]{\Delta}$ liquid
transition temp. melting temp.
Long chain solid $\xrightarrow{\uparrow}$ liquid crystals $\xrightarrow{\uparrow}$ liquids
(Mesophases)
 \downarrow shows properties
of both solid &
liquid \rightarrow can be called
4th state of matter.

Cholesteryl Benzoate

$\downarrow 146^{\circ}\text{C}$

milky liquid \rightarrow (Turbid liquid)

$\downarrow 179^{\circ}\text{C}$ Anisotropic

Liquid (Isotropic)

Liquid crystalline state is the intermediate state between solids & liquids. The substances which have arrangement like solids & freedom of motion like liquids are called liquid crystals. Liquid crystals are also called mesomorphic form.

Types of Liquid Crystals -

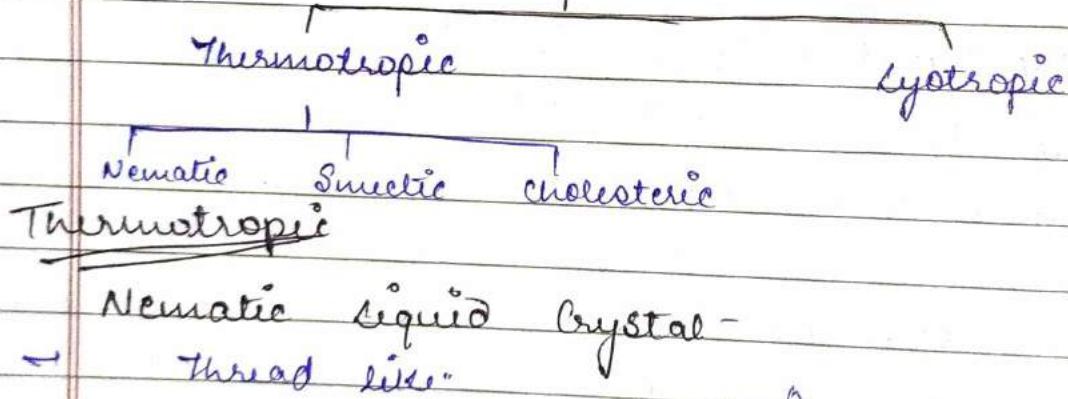
- So liquid crystal materials have several common characteristics. Among these are
- Rod like molecular structure

- Rigidity of long axis
- and strong dipoles and/or easily polarisable
- liquid crystals exhibit anisotropic physical properties (optical, mechanical, symmetrical, etc.)

The molecules can exhibit orientational order such that all the axes line up in a particular direction.

The average direction of the molecules is called the director.

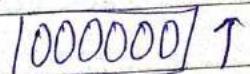
Liquid Crystals



- Orientational behaviour but no positional behaviour.
- Affected by magnetic field
- Shows more properties of liquid than solid
- flows like liquid but is turbid
- ✓ → Newtonian liquid → follows condⁿ of viscosity
- Anisotropic

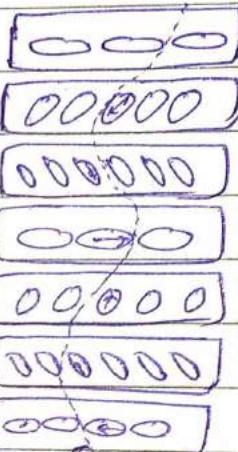
Smectic liquid crystal -

- Soap like
- Non-newtonian → concept of viscosity not applicable.
- crystal lattice exists
- gives x-ray diffraction patterns.
- Uniaxial, → Bragg's eqn applicable
- Not affected by magnetic field
- In presence of polarised light, these appear to be fan like.



Cholesteric liquid crystal -

- In layers but random arrangement
- shows twisting or rotational behaviour
- It basically determines wavelength of light - falls in visible region → shows colours on changing temp
- used in temp. sensors or thermometers.



complete cycle

this twists
or rotates.

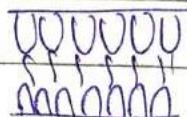
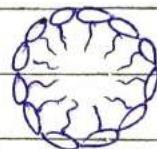
Lyotropic L.C.

When long chain solid is dissolved in polar isotropic liquid, then we

When a high conc. of long organic molecules of rod like shape is dissolved in an isotropic solvent like

water, lyotropic liquid crystals are obtained.

→ Amphiphilic behaviour



① Applications :-

* Temperature sensors

* Sensitive to light, electric & magnetic fields

② Detect potential failure ^{box}

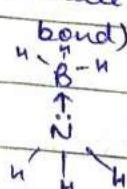
③ Thermometer

④ Diagnosis → detection of tumors

LCD (liquid crystal display)

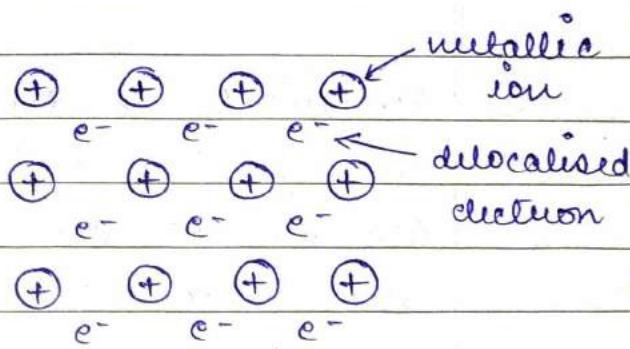
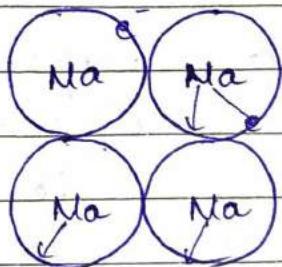
⑤ Chromatographic separation (Can make solvents for chro. sep.)

Bond

Tonic or electrovalent	Covalent → B/w non metals	Coordinate covalent bond B-H	Metallic → B/w metals	Hydrogen
eg - NaCl	eg. N≡N			

Metallic Bond →

A metallic bond is the electrostatic force of attraction that the neighbour positive metallic ion have for the delocalised electrons.



Electron sea model

Properties of metallic bonds -

- ① Electrical conductivity
- ② Heat conductivity
- ③ Ductility
- ④ Malleability
- ⑤ Luster or reflectivity

Relating metallic bond to metallic properties.
Because electrons are delocalised around positively charged nuclei, metallic bond explains many properties of metals.

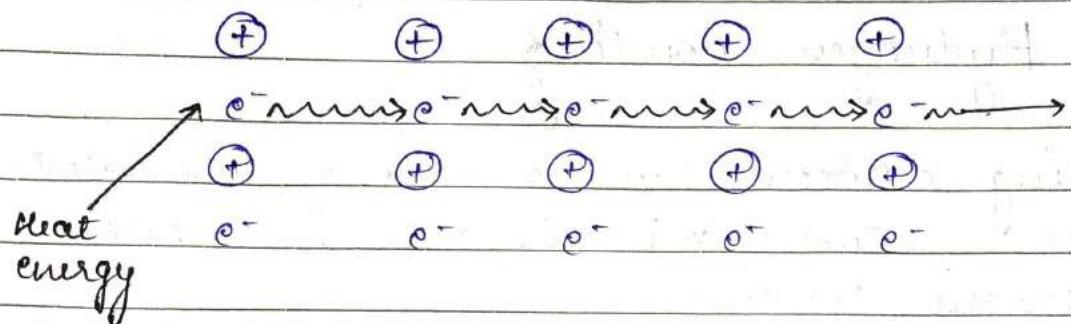
① Electrical conductivity - The metals are a good conductor of electricity.
Acc. to e-sea model, the mobile electrons are free to move to the vacant space b/w metal ions.

When electric voltage is applied at the two ends of metallic wire, it causes the electrons to be displaced in a given direction

The best conductors are the metals which attract the outer electrons the least and thus allow them the greatest freedom of movement.

② Heat conductivity - If a metal is heated at one end, the heat is carried to the other end. The mobile electrons in the electron sea around one end of the metal easily absorb heat energy and increase their vibrational motion. They collide with adjacent electrons and transfer the added energy to them. Thus, the mobility of the e's allows

heat transfer to the other end.



- ③ Ductility & malleability - They can be explained by e⁻ sea model.
 In metals, the positive ions are surrounded by the sea of e⁻s that flows around them. If a layer of the metal ion is forced across another, say, by hammering, the internal structure remains essentially unchanged. The sea of e⁻s adjusts position rapidly and the crystal lattice is restored. This allows the metal to be malleable & ductile.

- ④ Luster or reflectivity - The delocalised mobile electrons of the electron sea account for this property. Light energy is absorbed by these electrons which jumps into higher energy levels and return immediately to ground state. In doing so, e⁻s emit EM radiations (light of same freq.). Since, the radiated energy is of same frequency as that of incident light.

we see it as reflection of original lig.

Hydrogen Bonding

Bonding between hydrogen and an electronegative atom ($\text{H}\cdots\text{F}, \text{H}\cdots\text{O}, \text{H}\cdots\text{N}$) is called hydrogen bonding.

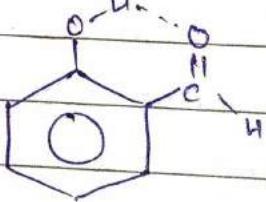
Condition \rightarrow The size of electronegative atom must be small.

It is of two types -

- ① Intermolecular.
- ② Intramolecular.

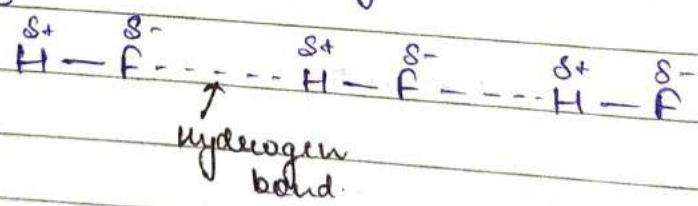
- ① Intramolecular - H-bonding within the molecule.

e.g. -



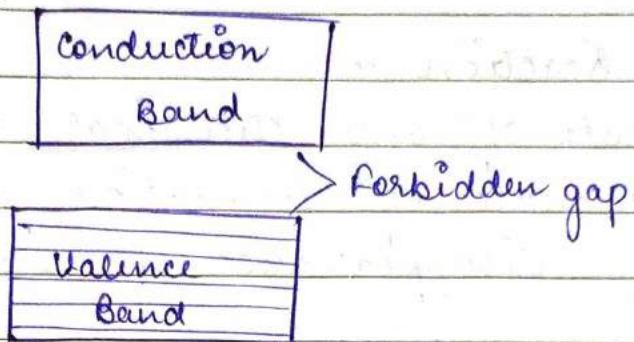
- ② Intermolecular - H-bonding between different molecules.

e.g. -

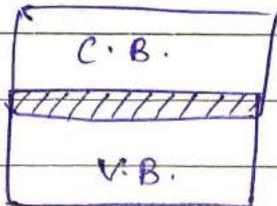


Effect of H-Bonding -

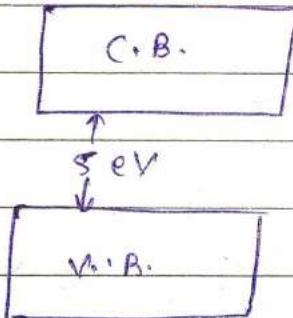
Band Theory



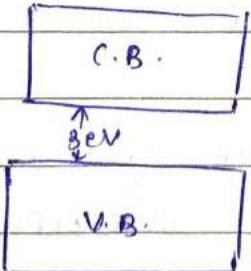
Conductors -



Insulators



Semiconductors



Chemical Kinetics

Rate of Reaction →

The rate of any chemical reaction is equal to rate of formation of product or rate of disappearance of reactants.



$t=0$	a	0
$t=t$	$a-x$	$2x$

$$\frac{-\Delta [N_2]}{\Delta t} = \frac{x}{t}$$

$$\frac{\Delta [NH_3]}{\Delta t} = \frac{2x}{t}$$

$$\left[\text{Rate of reaction} = -\frac{d[N_2]}{dt} = \frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt} \right]$$

unit - mol l⁻¹ sec⁻¹.

Rate law → The rate of reaction is directly proportional to the concentration of reactants raised to some power (order).



$$\left\{ R \propto [A]^2 \right\}$$
$$R = k[A]^2$$

molecularity - no. of molecules involved in aⁿ
order - power of reactants in rate law.

Date _____ Page _____

Rate constant (K) →

$$R = k[A]^2$$

k = rate constant

unit of rate constant -

zero order $\text{g}^{-n} \rightarrow \text{mol l}^{-1} \text{ sec}^{-1}$

1st order $\rightarrow \text{sec}^{-1}$

2nd order $\rightarrow \text{l mol}^{-1} \text{ sec}^{-1}$

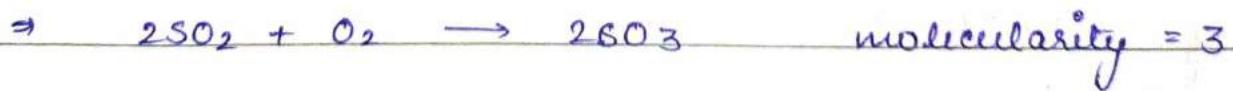
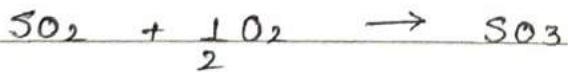
① Determine the order

conc.	0.5	0.49	0.51	0.5	0.49
time (sec)	10	20	30	40	50

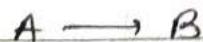
zero order

conc.	1	2	3	4	5
time (sec)	10	20	30	40	50

first order



First Order Reaction →



$$t=0 \quad a \quad 0$$

$$t=t \quad a-n \quad n$$

$$\text{Rate} \propto [A]$$

$$\text{Rate} = k_1(a-x)$$

$$\frac{d[A]}{dt} = -k[A]$$

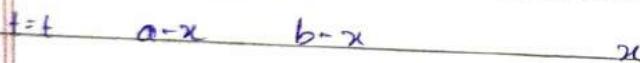
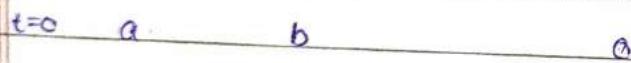
$$\ln[A] - \ln[A_0] = -kt$$

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

Half life + when half of reactant are consumed, $\left\{ t_{1/2} = \frac{\ln 2}{k} \right\} \Rightarrow \left\{ t_{1/2} = \frac{0.693}{k} \right\}$

Second Order Reaction

Case I →



✓ $\frac{dx}{dt} \propto [A][B]$

$$\frac{dx}{dt} = k_2[A][B]$$

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

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

①. $a > b$

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

$$\frac{1}{(a-b)} \int_{0}^x \left[\frac{1}{b-x} - \frac{1}{a-x} \right] dx = \int_0^t K_2 dt$$

$$\frac{1}{a-b} \left[-\ln(b-x) + \ln(a-x) \right]_0^x = K_2 t + \frac{1}{a-b} \ln \left(\frac{a}{b} \right)$$

$$\frac{1}{a-b} \left[\frac{\ln(a-x)}{(b-x)} - \frac{\ln a}{b} \right] = K_2 t$$

$$\frac{1}{a-b} \frac{\ln(a-x) \times b}{(b-x) a} = K_2 t$$

$$K_2 = \frac{1}{t(a-b)} \frac{\ln b(a-x)}{a(b-x)}$$

② $b > a$

$$K_2 = \frac{1}{t(b-a)} \frac{\ln a(b-x)}{b(a-x)}$$

Case II -

\rightarrow Product

$$t=0 \quad a \quad 0$$

$$t=t \quad a-x \quad x$$

$$\frac{dx}{dt} = K PA]^2$$

$$\frac{dx}{dt} = K (a-x)^2$$

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

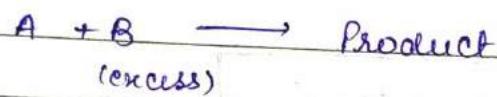
$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$\frac{1}{a-x} - \frac{1}{a} = kt$$

$t_{1/2}$

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

Case III.



→ pseudo unimolecular reaction.

→ same as first order reaction.

Half life of 2nd Order Recn →

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

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

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

$t_{1/2} = \frac{1}{ka}$

For n^{th} order reacⁿ →

$$t^{1/2} = \frac{1}{K(a)^{n-1}}$$

Determination of Order of any reaction →

- ① Integral rate equation method
- ② Graphical method
- ③ Half life method
- ④ Differential method
- ⑤ Oswald's Isolation method

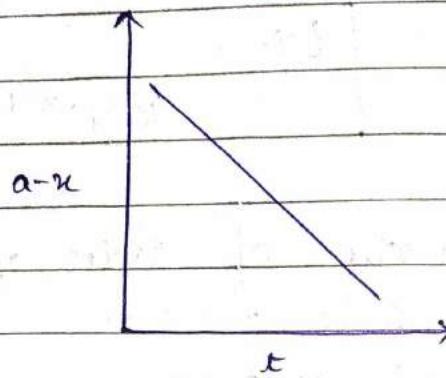
#1. Integral rate equation method-

The reaction under study is performed by taking different initial conc's of the reactants (a) and noting the conc's (a-n) after regular time intervals. The experimental values of a, (a-n) and t are substituted into the integrated rate eqn's for 1st, 2nd & 3rd order reacⁿs. The rate eqn which yields a constant value of 'K' corresponds to the correct order of the reaction.

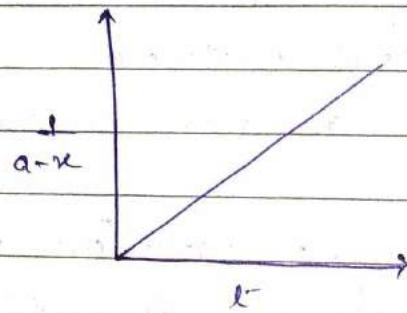
This is a 'hit and trial' method for determining the order of reacⁿ. It is extensively used to find order of reacⁿ.

#2. Graphical Method

First order recⁿ



Second order recⁿ



We can determine the reaction order by seeing whether the graph of the data fits one of the integrated rate equations.

#3. Half life method

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

Here, we take two different initial conc's i.e. we perform two different experiments and then solve them to find n .

$$t_{1/2} = \frac{1}{k[A_1]^{n-1}} \quad \text{--- (1)}$$

$$t_{21/2} = \frac{1}{K[A_2]^{n-1}} \quad \text{--- (2)}$$

$$\frac{t_{21/2}}{t_{21/2}} = \left[\frac{A_2}{A_1} \right]^{n-1}$$

$$\ln \frac{t_1}{t_2} = (n-1) \ln \left(\frac{A_2}{A_1} \right)$$

$$n-1 = \frac{\ln(t_2/t_1)}{\ln\left(\frac{A_2}{A_1}\right)}$$

$$n = 1 + \frac{\ln(t_2/t_1)}{\ln(A_2/A_1)}$$

Q In the reduction of nitric oxide, 50% of A_1 was completed in 108 sec when initial pressure was 336 mm Hg and in 147 sec, initial pressure was 288 mm Hg. Find order.

$$\frac{108}{147} = \left(\frac{288}{336} \right)^{n-1}$$

$$n = 1 + \frac{\ln(108/147)}{\ln(288/336)}$$

$$n = 1 + 2 \\ = 3$$

#4. Differential method (Vant Hoff's differential method) →

The rate of reaction of n^{th} order is proportional to concentration of reaction to the n^{th} power. To find n ($-\frac{dc}{dt}$) in the two

$$\boxed{-\frac{dc}{dt} = kc^n}$$

exp. is determined by plotting conc's against 't'.

The slope ($-\frac{dc}{dt}$) at a

given time
is measured
by drawing
tangents
using the
values
of slopes
 $\frac{dc_1}{dt}$ & $\frac{dc_2}{dt}$
at
mean
be
determined

$$-\frac{dc_1}{dt} = kc_1^n \Rightarrow \ln\left(\frac{-dc_1}{dt}\right) = \ln k + n \ln c_1 \quad \text{---(1)}$$

$$-\frac{dc_2}{dt} = kc_2^n \Rightarrow \ln\left(\frac{-dc_2}{dt}\right) = \ln k + n \ln c_2 \quad \text{---(2)}$$

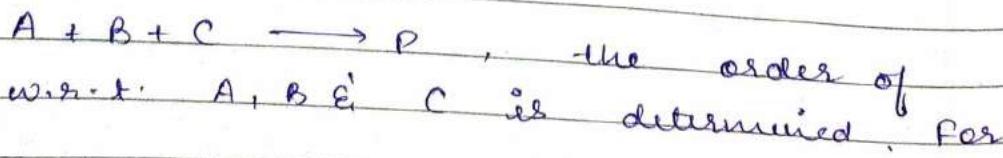
$$(1) - (2)$$

$$\ln\left(\frac{-dc_1}{dt}\right) - \ln\left(\frac{-dc_2}{dt}\right) = n \ln c_1 - n \ln c_2$$

$$\text{then } n = \frac{\ln\left(\frac{-dc_1}{dt}\right) - \ln\left(\frac{-dc_2}{dt}\right)}{\ln c_1 - \ln c_2}$$

#5. Ostwald's Isolation method →

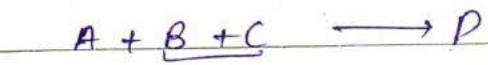
This method is implied in determining the order of complicated reactions by isolating one of the reactants so far as its influence on the rate of reaction is concerned. Suppose the reacⁿ under consideration-



Date: _____ Page: _____

determination of order w.r.t. A, B & C are taken in large excess so that their conc's are not affected during the reacn. Similarly, for determining order of B & C, AE'C and AE'B are taken in excess resp.

given time interval
is measured
by decreasing tangents.
Using the values of slopes
 $\frac{dc_1}{dt}$ & $\frac{dc_2}{dt}$
we can
determine if n_A , n_B & n_C are order w.r.t. to A, B & C
then



order of reaction, $[n = n_A + n_B + n_C]$

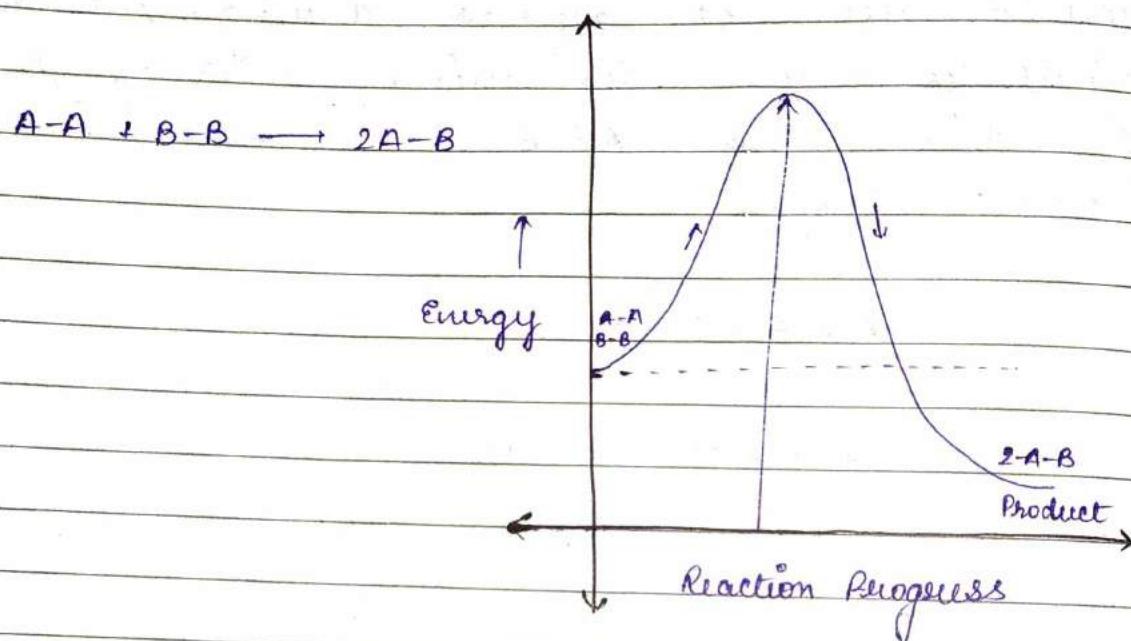
Collision Theory of Reaction Rates

According to this theory, a chemical reacn takes place only by collision b/w reacting molecules. But not all collisions are effective. Only a small fraction of collisions produce a reaction. The two main cond's for a collision b/w 2 molecules to be productive are-

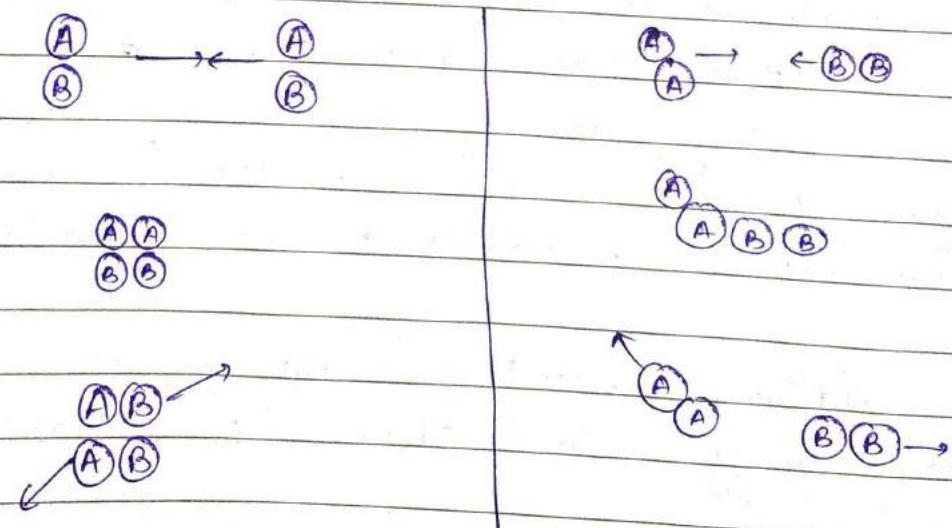
- ① the colliding molecules must possess sufficient kinetic energy to cause a reaction.

②

The reacting molecules must collide with proper orientation.



A chemical reaction occurs by breaking bonds between the atoms of the reacting molecules and forming new bonds in the product molecules. The energy for breaking of bonds comes from kinetic energy possessed by the reacting molecules before collision is known as activation energy.



The correct orientation is that which ensures direct contact b/w atoms involved in the breaking and forming of bonds.

Only the molecules colliding with K.E. greater than A.E. and with correct orientation can cause reaction.



$$\text{rate} = f \times p \times z$$

f = fraction of molecules having sufficient energy for r.

p = probable fraction of collision with effective orientation.

z = collision frequency

Arrhenius Equation \rightarrow

$$K = Ae^{-\frac{E_a}{RT}}$$

$$\ln K$$

$$-\frac{E_a}{R} = m$$

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

$$1/T$$

$$\frac{\ln K_2}{K_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Q The value of rate const. K for the reacⁿ was determined at several temp. A plot of lnK v/s $1/T$ gave a straight line of which the slope was found to be $-1.2 \times 10^4 \text{ K}^{-1}$. $E_a = ?$

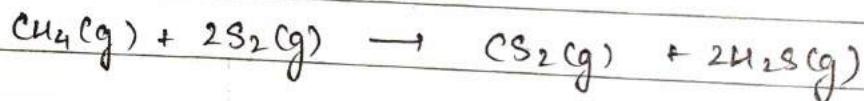
$$\text{Slope} = -\frac{E_a}{R}$$

$$\frac{E_a}{R} = 1.2 \times 10^4$$

$$E_a = 1.2 \times 10^4 \times 0.001$$

- whatever.

Q. The gas phase reacⁿ b/w methane & diatomic sulphur is given by the eqⁿ



At 550°C , the rate const. for reacⁿ is 1.1 L/mol-sec , at 625°C , $K = 6.4$
Calculate E_a .

$$T_1 = 550 + 273 = 823 \text{ K}$$

$$T_2 = 625 + 273 = 898 \text{ K}$$

$$\frac{\ln K_2}{K_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\frac{\ln 6.4}{1.1} = \frac{E_a}{0.001} \left[\frac{1}{823} - \frac{1}{898} \right]$$

$$\begin{aligned}
 E_a &= \frac{\ln 6.4}{1.1} \times 0.814 \times \frac{0.23 \times 0.98}{75} \\
 &= 144271.744 \text{ J/mol} \\
 &= 1.44 \times 10^5 \text{ J/mol}
 \end{aligned}$$

Limitations of Collision theory →

- ① Applicable only for gases
- ② Tells only about K.E. & not rot, vib energy.
- ③ Can't explain rxn for complex molecules, can still only upto & bimolecular rxn.
- ④ orientation unexplained.

~~✓~~ ⑤ The collision-theory of rxnⁿ rates is logical & correct, however, it has been oversimplified and suffers from the following weaknesses

- ⑥ The -theory applies to simple gaseous rxn's only
It is also valid for solutions in which the reacting species exist as simple molecules.
- ⑦ The values of rate const calculated from collision theory expression (Arrhenius eqⁿ) are in agreement with the experimental values only for simple bimolecular rxn's.
- ⑧ For rxns involving complex molecules, the experimental rate constants are quite diff. from the calculated ones.
- ⑨ There is no method for determining the steric effect for a rxnⁿ whose rate const. hasn't been determined experimentally.

- ⑤ In the collision theory, it is supposed that only the K.E. of colliding molecules contributes to the energy required for surmounting the energy barrier.
- ⑥ There is no reason why rotational & vibrational energies of molecules should be ignored.
- ⑦ The collision theory is silent on the cleavage & formation of bonds involved in the reaction.

Potential Energy Surface

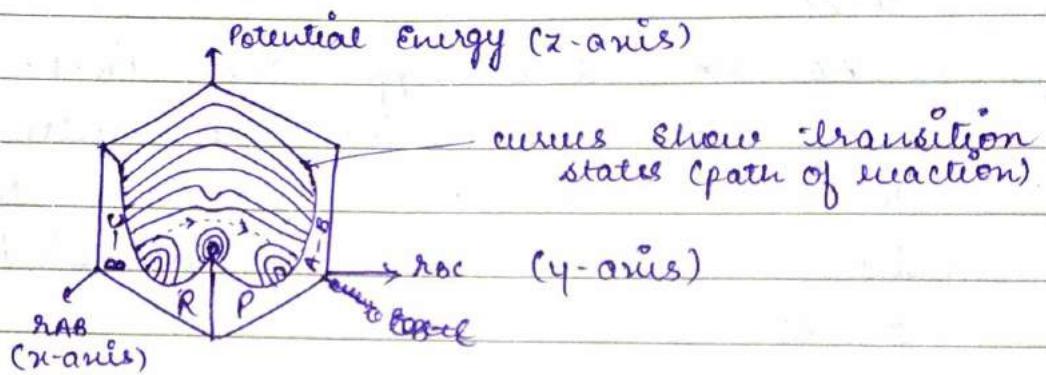
A potential energy surface describes the energy of a system, specially a collection of atoms in terms of certain parameters, normally the position of atoms.

The surface might define energy as a function of one or more coordinates. If there is only one coordinate, then it is a potential energy curve.

Significance of Potential Energy Surfaces

- ① We can easily trace the path of the reaction over this surface.
- ② It is the path from the reactant side to the product side that follows the contours of minimal potential energy.

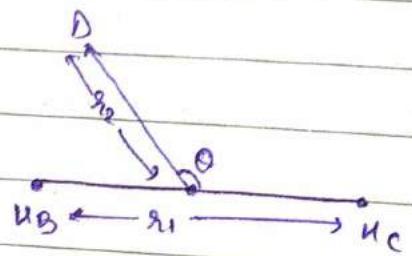
- ③ The potential energy gives a map of chemical reaction from beginning to the end.



Saddle point - point of zero energy

Special coordinates required to describe the reaction pathway on potential energy.

Let us consider the r_{in}



We need 3 special coordinates to describe configuration of above reacting system at any point along the r_{in} path

These coordinates are -

- ① r_1 - internuclear dist b/w HB & He
- ② r_2 - dist of DA from mid pt. of r_3
- ③ θ_1 - angle b/w HB-He & vector from mid pt. of HB-He bond to DA.

One potential approach of DA to Hg-He is energetically more favourable than any other approach in which D approaches H-H along the line joining the centre of Hg-He.

As DA atom approaches Hg-He molecule, along the line joining the centre of atoms Hg & He, the P.E. depends on two coordinates i.e. θ , & only θ is found to be 0° or 180° .

So for the general reacⁿ. $A + BC \rightarrow AB + C$

If r_{AB} is plotted along x-axis & r_{BC} along y-axis (see fig)

the potential energy can be plotted along z-axis normal to xy plane.

and potential energy ($V(x,y)$) of the reacting molecules can be visualised as a surface in 3-dimension as shown in fig.

For the reacⁿ $- A + BC \rightarrow AB + C$

with fixed value of θ (0° or 180°) then

the variation of PE plotted as a fⁿ of r_{AB} & r_{BC} is shown in fig 2

- ① If r_{AB} is large as shown in left phase of fig 2, the PE is essentially of BC molecule. Similarly, the right phase represents energy of AB molecule.

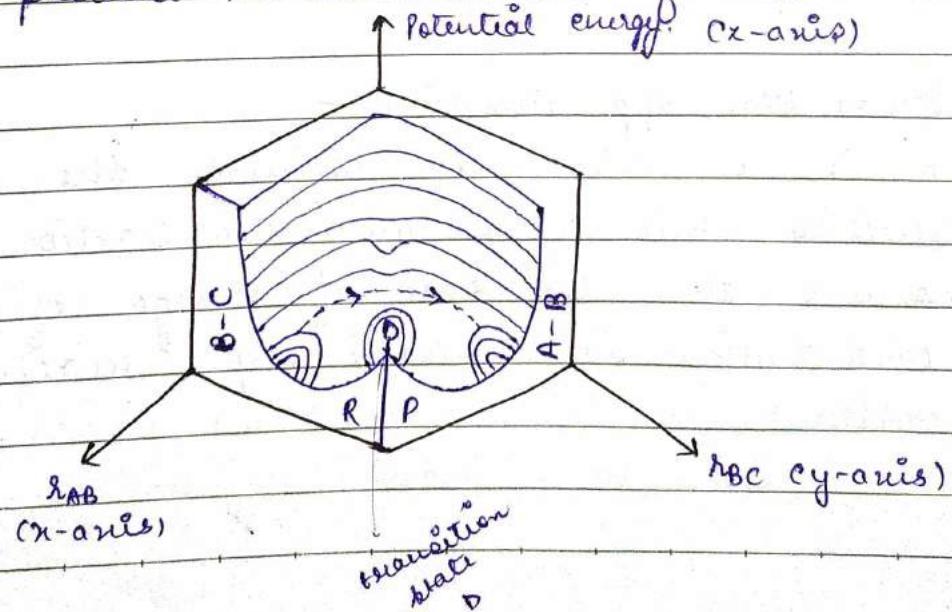
Initially r_{AB} is very large and as A approaches B, the lowest energy path is given by dashed line from reactant R to product P. This dashed line gives a minimum energy path which is also referred to as reaction coordinates.

The highest point along the secⁿ coordinate is the saddle point. It is a point of max p.e. along secⁿ coordinate but min. in a direcⁿ perpendicular to the secⁿ coordinates.

The reacting system ~~and~~ at Saddle point is said to be in the transition state. It is a high plate plateau giving p.e. of the atoms A, B & C when separated from each other.

As A approaches B, r_{AB} decreases and kinetic energy is converted to p.e. as shown in the valley in left in fig 2.

If K.E. is sufficient ^{for the system} to reach saddle point then product AB and C are formed.



Chemical Kinetics

Mechanics



$\text{C}_0 \text{ mmole l}^{-1}$	5.0	8.2	17	30
$R_0 / 10^{-7} \text{ mol l}^{-1} \text{ s}^{-1}$	3.6	9.6	40	130

$$R \propto C^n$$

$$\frac{R_1}{R_2} = \left(\frac{C_1}{C_2} \right)^n$$

$$\frac{3.6}{9.6} = \left(\frac{5.0}{8.2} \right)^n$$

$$\left\{ n=2 \right\}$$

- Q. The half life for hydrolysis of ester with initial conc' of reactant as follows-

$R \rightarrow P$
$[C] / 10^{-2} \text{ mol l}^{-1}$
2.0 5.0 4.0 3.0 240 300 300 400

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

Steady State Approximation \rightarrow

It is a method to estimate the overall reaction rate of a multi-step reaction. It assumes that the rate of change of intermediate concentration in a multi-step reaction are constant.

Q The Michaelis-Menten
rate for enzyme catalyzed reaction is given by $V_0 = \frac{V_{max}[S]}{K_m + [S]}$

If the initial rate is equal to one half of final rate then find K_m .

$$\rightarrow V_0 = \frac{V_{max}}{2}$$

$$\frac{V_{max}}{2} = \frac{V_{max}[S]}{K_m + [S]}$$

$$\frac{K_m + [S]}{2} = \frac{[S]}{2}$$

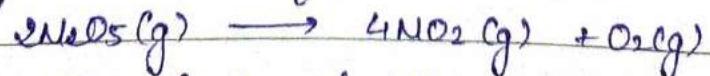
$$\therefore K_m = [S]$$

Q 1×10^{-4} moles of an enzyme carbonic anhydrase dehydrates carbonic acid (H_2CO_3) to produce 0.6 moles of carbon dioxide per second. what is the turnover number of the enzyme

turnover no. = $\frac{\text{no. of moles of substrate reacted}}{\text{no. of moles of enzyme} \times t}$

$$= \frac{0.6}{10^{-4} \times 1} = 6 \times 10^3 \text{ per sec.}$$

Q The value of rate const. for the reaction



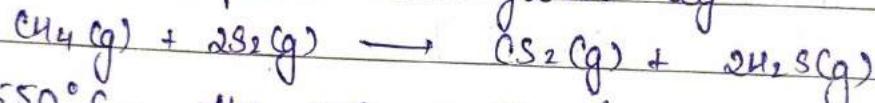
was determined at several temperatures. A plot of $\ln k$ vs $1/T$ gave a straight line of which

The slope was found to be $-1.2 \times 10^4 \text{ K}$
 What is activation energy of such.

$$\frac{-E_a}{R} = -1.2 \times 10^4 \text{ K}$$

$$E_a = 10^5 \text{ J/mol.}$$

Q The gas phase rate between methane and diatomic sulphur is given by



at 550°C , the rate const. is $1.1 \text{ mol}^{-1}\text{sec}^{-1}$
 and at 625°C $\rightarrow 6.41$ $E_a = ?$

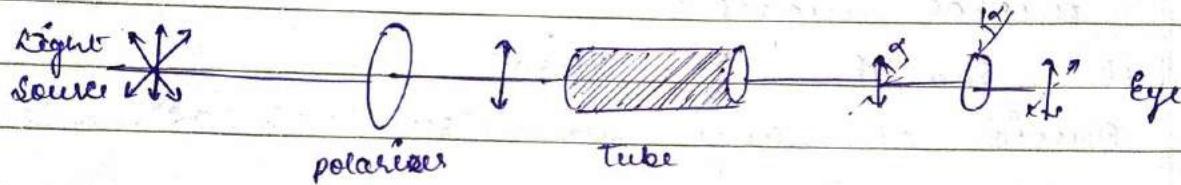
$$\log \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log \frac{6.41}{1.1} = \frac{E_a}{R} \left[\frac{1}{523} - \frac{1}{698} \right]$$

$$\log \frac{64.1}{11} = \frac{E_a}{R} \left[\frac{75}{523 \times 698} \right]$$

$$= 1.4 \times 10^5 \text{ J/mol}$$

Stereochemistry



Polarimeter

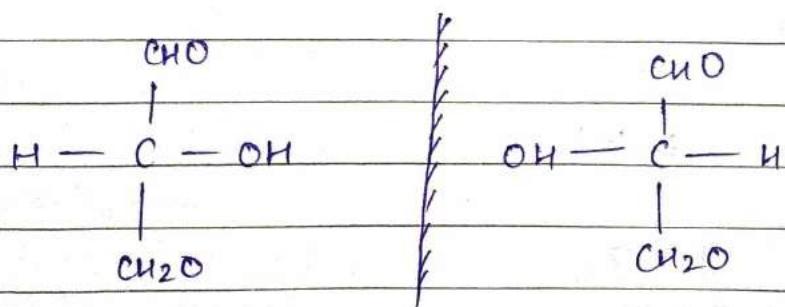
Specific Rotation

The degree of rotation depends upon the number of molecules of the substance encountered by light along its path. Specific rotation is defined as rotation produced by a solution of length l dm & concentration c for the given λ of light at the given temperature.

$$\text{Specific Rotation } [\alpha] = \frac{100\alpha}{l \cdot c}$$

length - decimetres

concⁿ → no. of grams per 100 ml solⁿ.

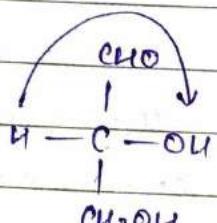


non-superimposable mirror images + enantiomers
 " " " " non " " → diastereomers.

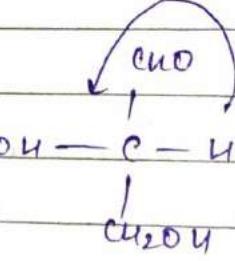
Four compd. to be optically active,

- it should have non-superimposable mirror image
- it should be chiral
- devoid of any symmetry (POS, COS, axis etc.)

D₂O

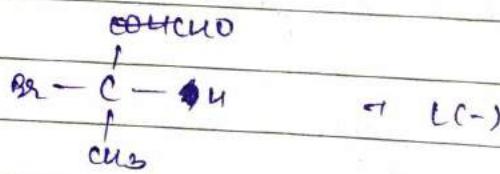


D⁺ 10 mole

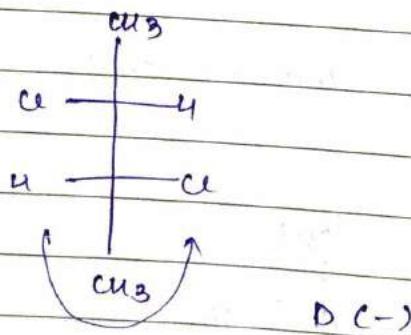


L⁻ 10 mole

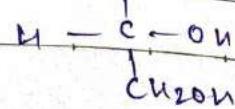
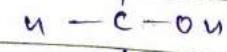
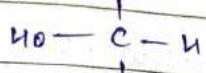
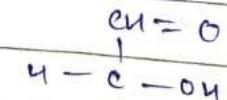
D.



D.



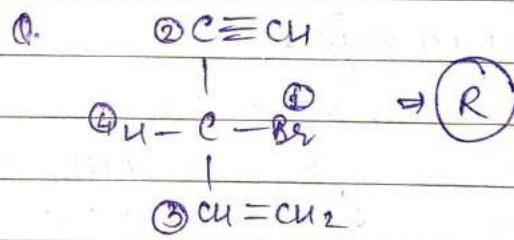
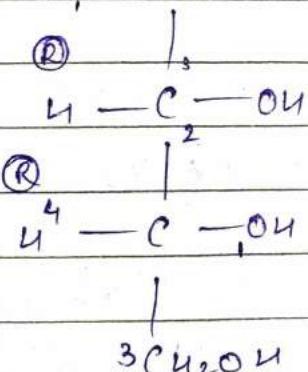
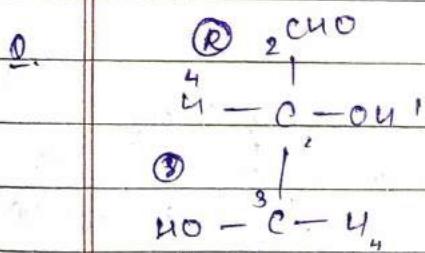
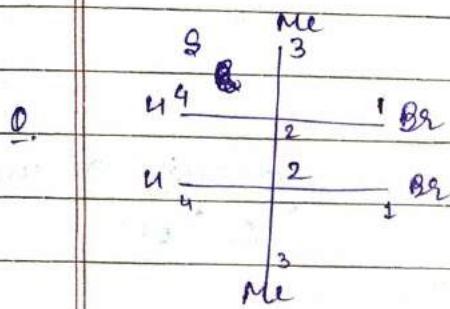
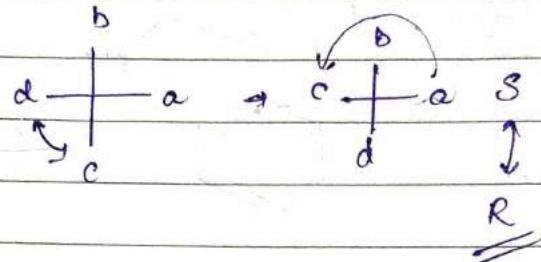
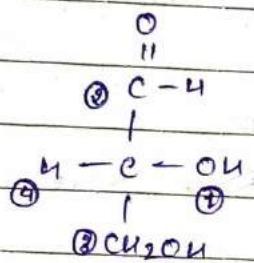
Glucose



D(+)

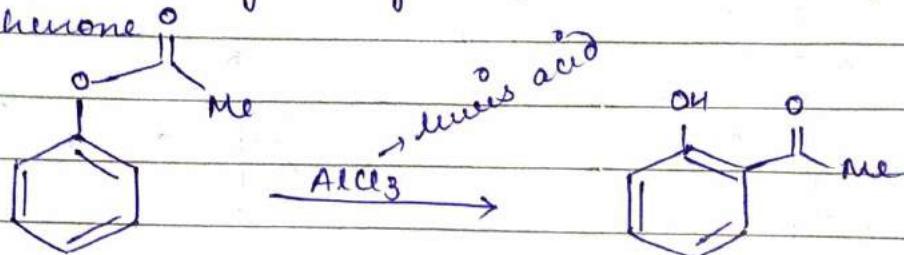
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R-S configuration → (CIP Rule)
Rectus Sinister

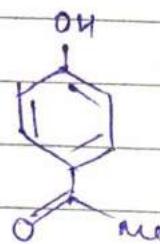


FRIES REARRANGEMENT

When phenyl acetate is treated with AlCl_3 to form orthohydroxyacetophenone and parahydroxy-acetophenone

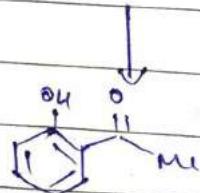
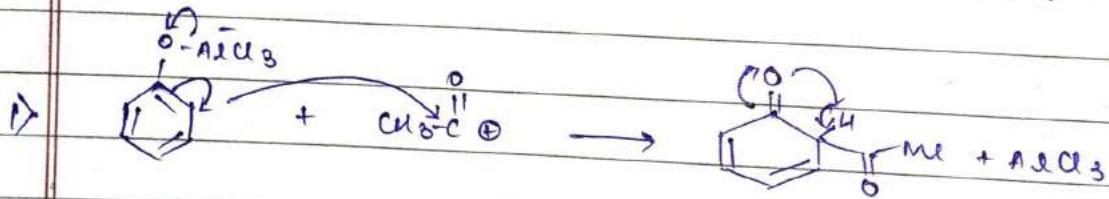
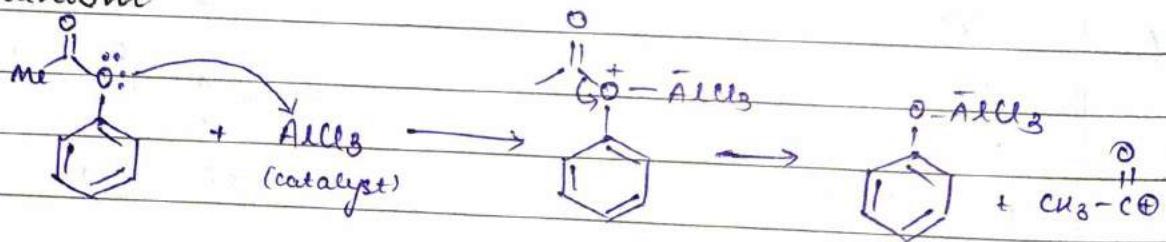


O-hydroxyacetophenone
(major)

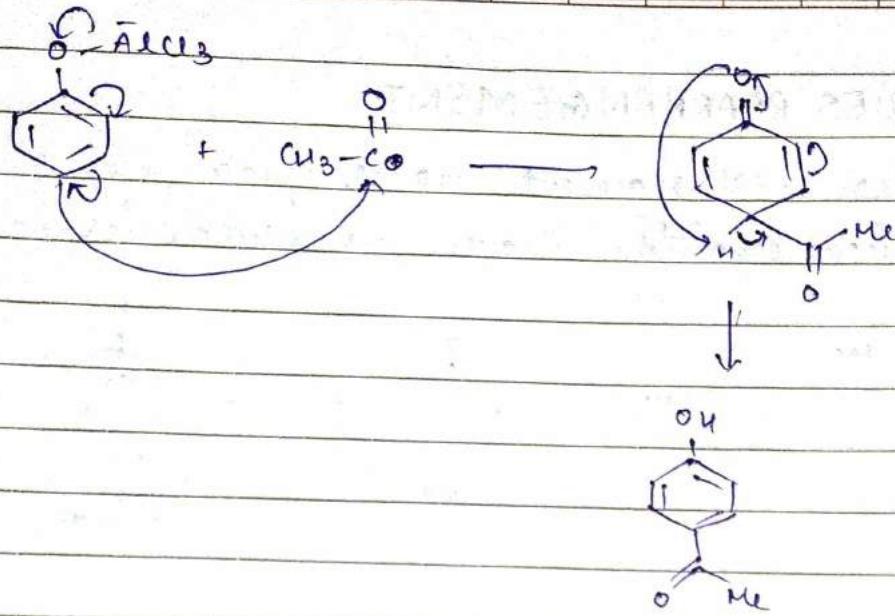


parahydroxyacetophenone
(minor)

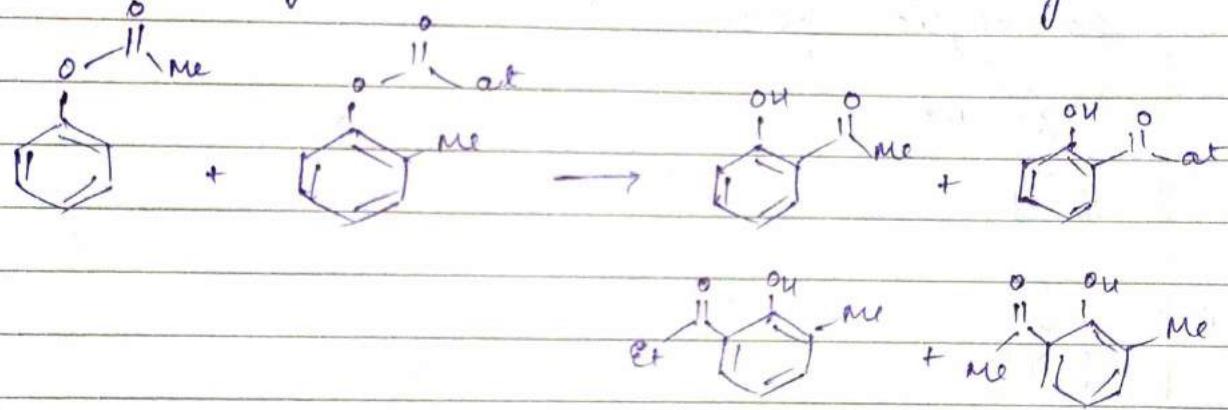
Mechanism



2>



Fries rearrangement takes place intermolecularly.



Applications -

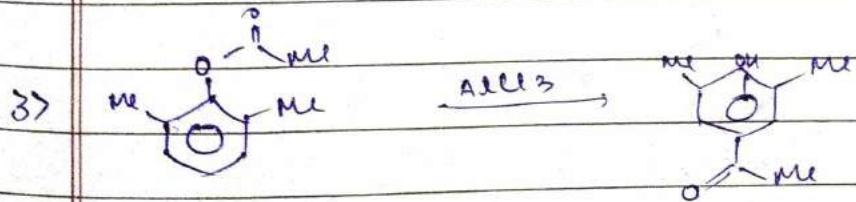
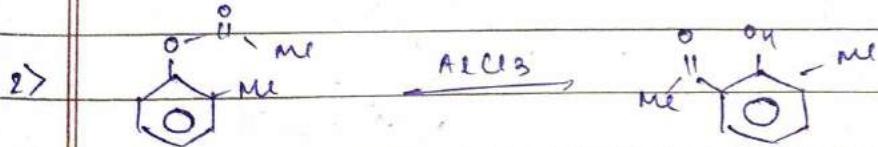
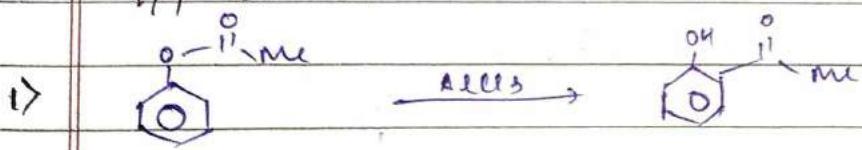
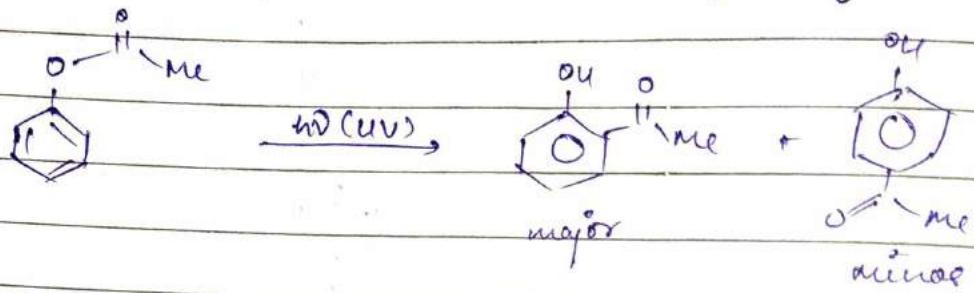
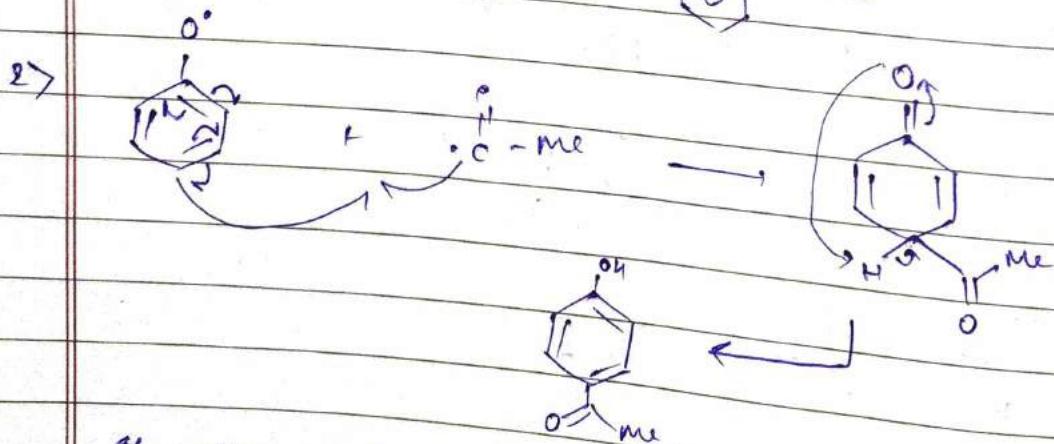
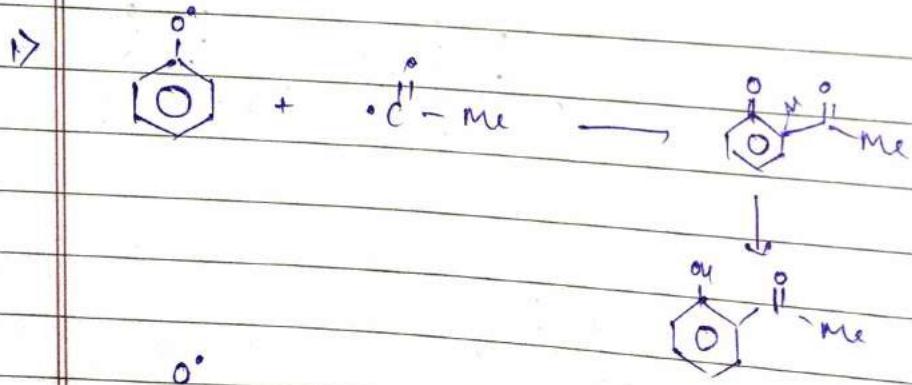
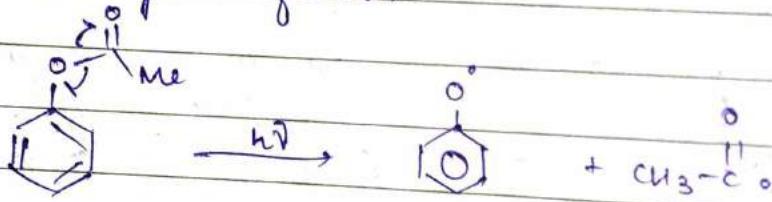


PHOTO FRIES REARRANGEMENT

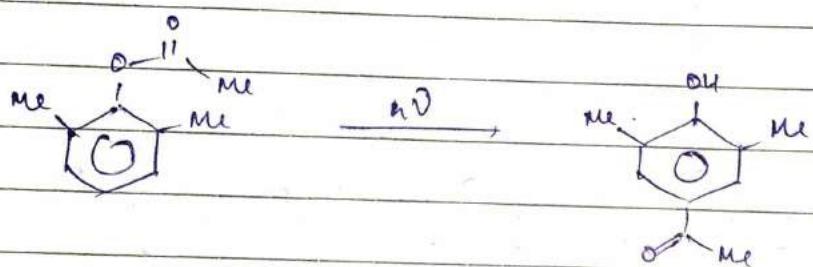
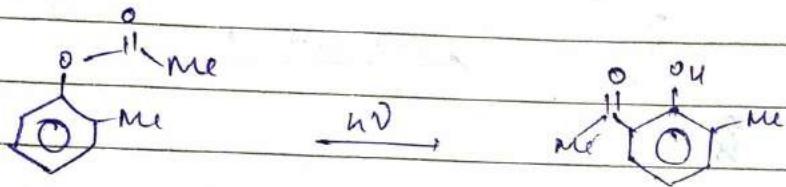
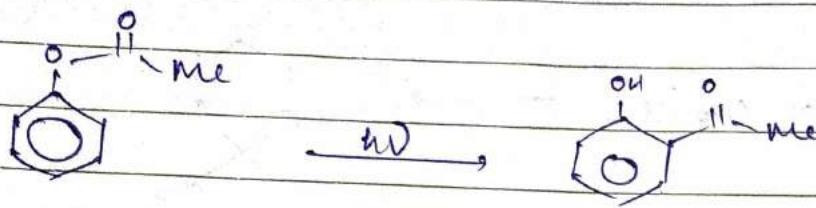
When free rearrangement takes place under photochemical condition known as photofree rearrangement.



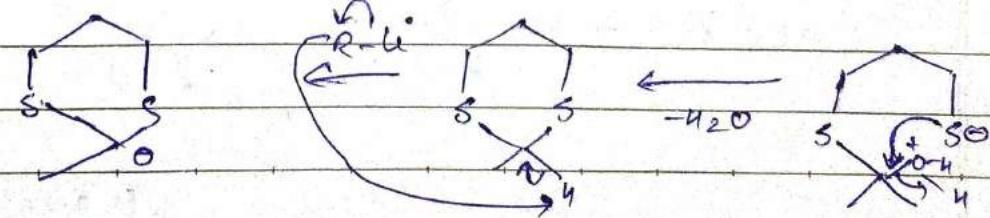
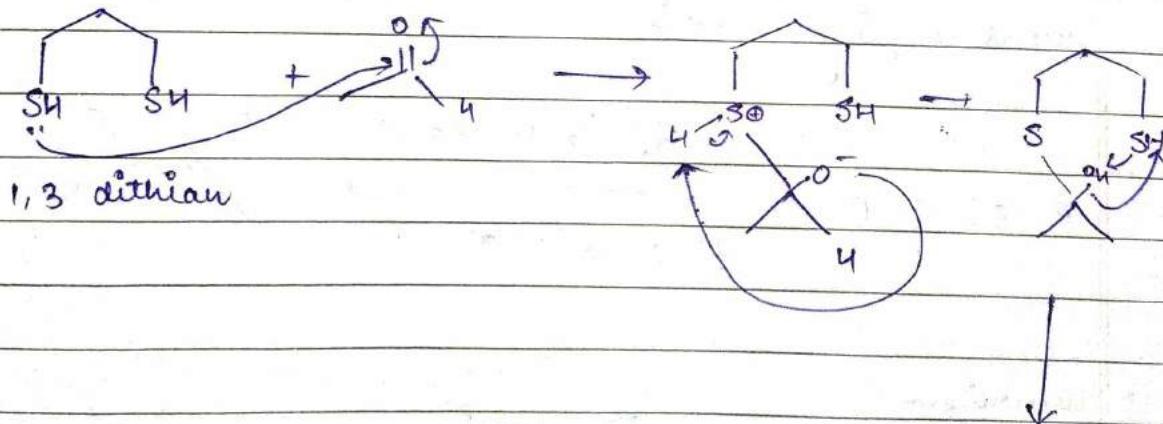
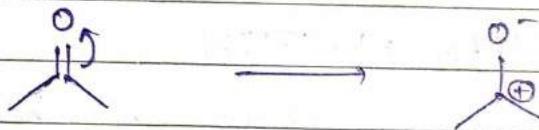
⁴ Mechanism - The mechanism proceeds through homolytic fission.



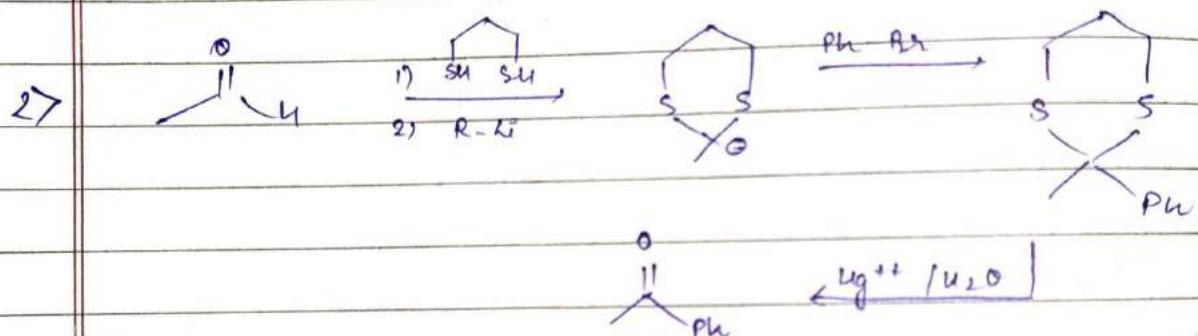
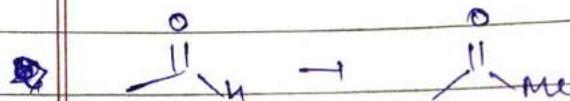
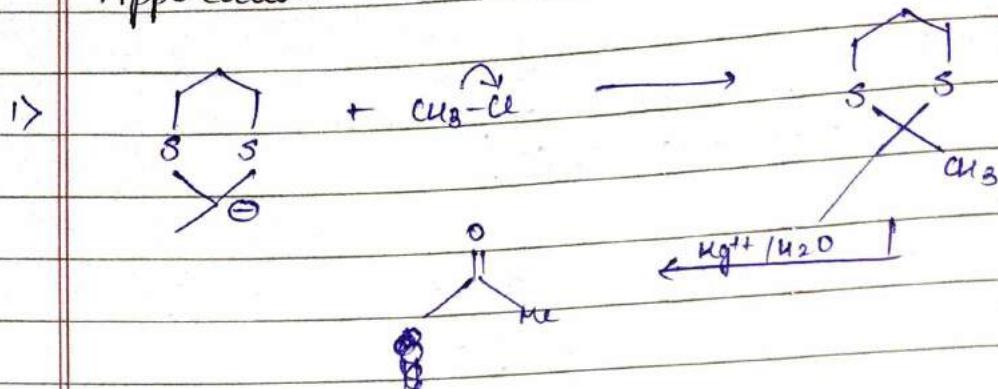
It also takes place intermolecularly

Applications -UMPOLUNG

The reversal of polarity is called Umpolung

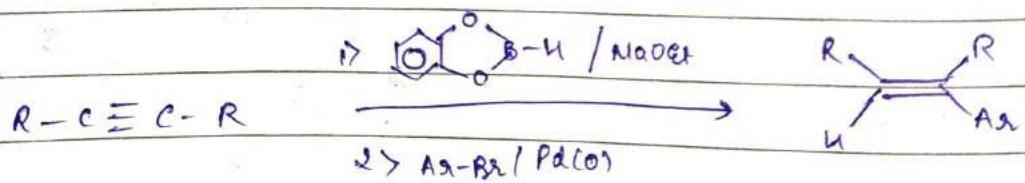


Application -

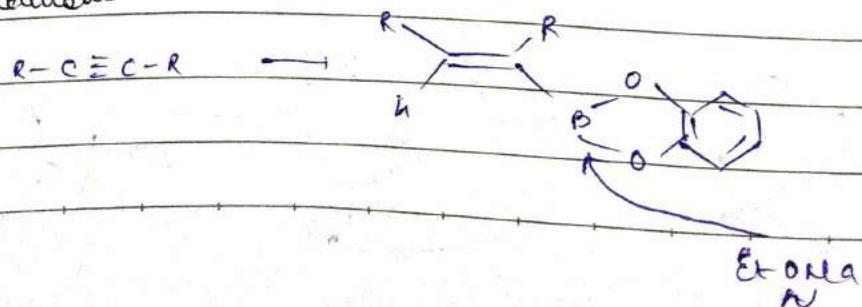


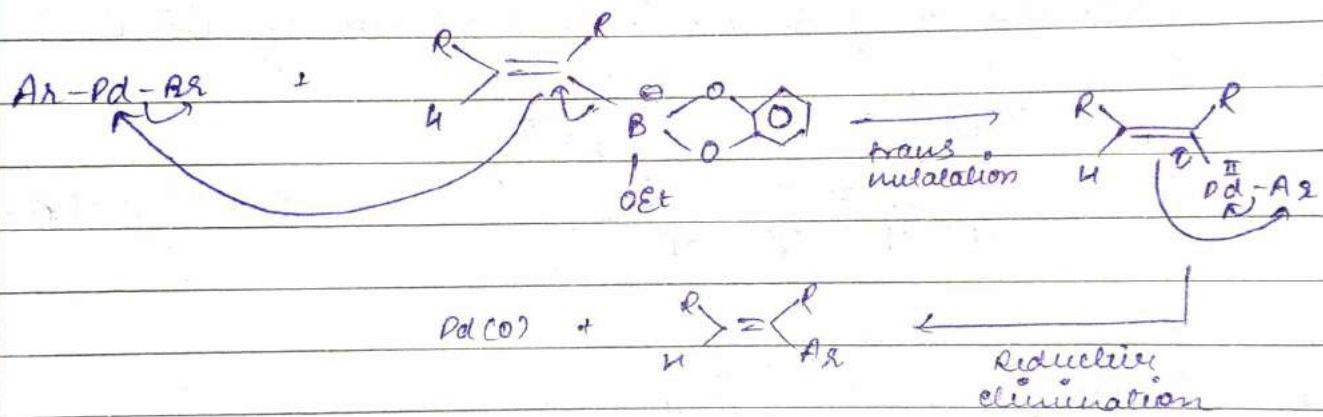
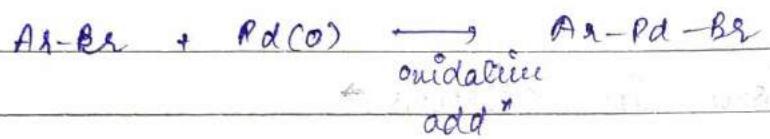
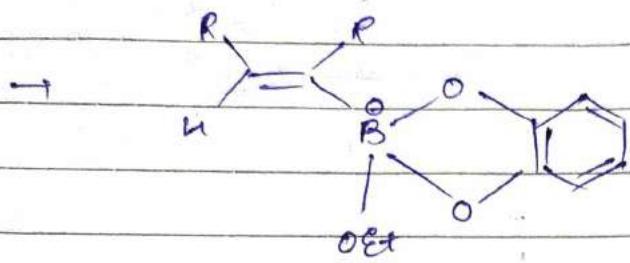
SUZUKI CROSS COUPLING REACTION

Arylation or alkylation of alkyne by boronic ester in presence of NaOEt is called Suzuki cross coupling reaction.

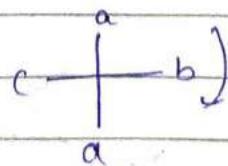
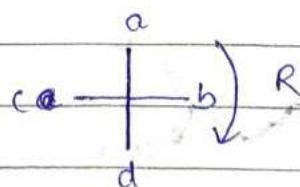
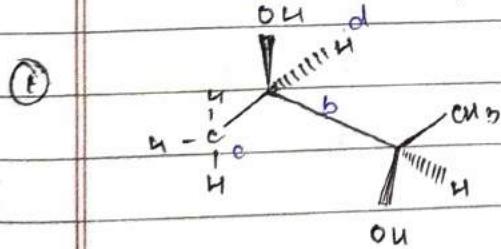


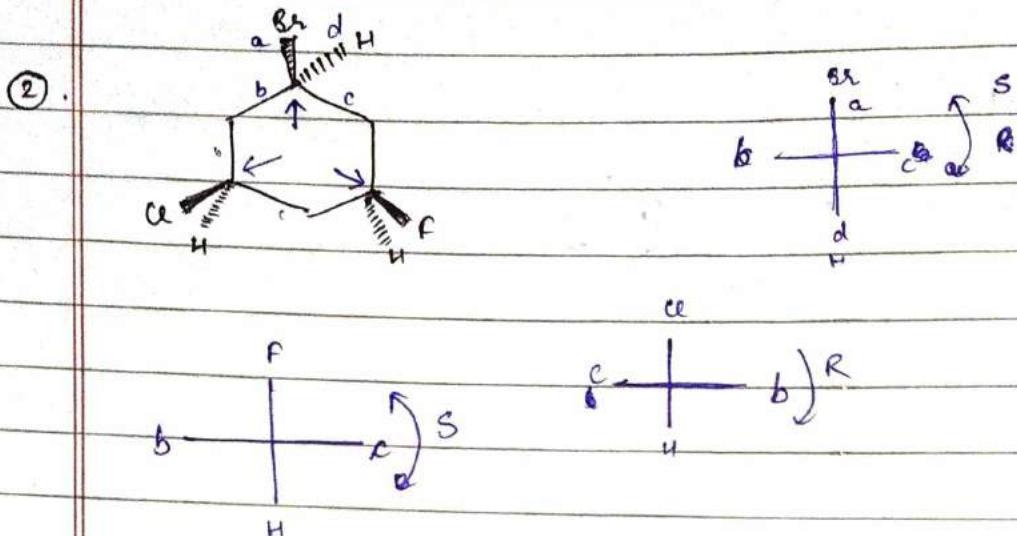
Mechanism





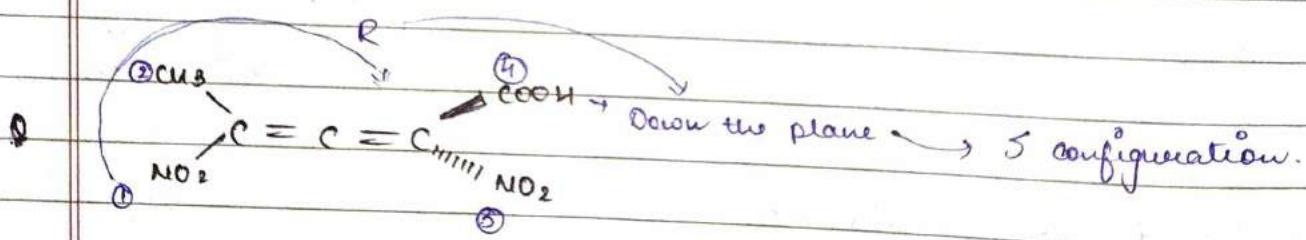
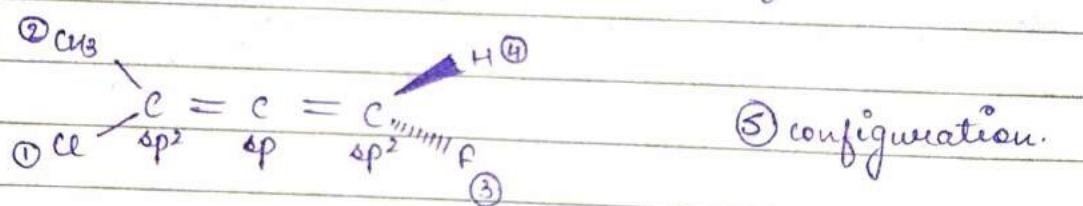
① Find R-S configuration



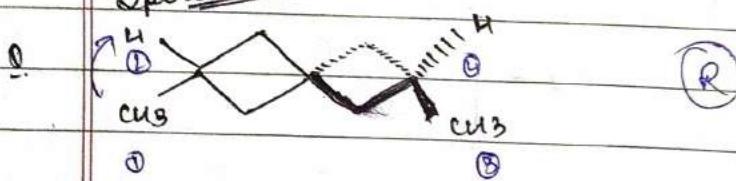


Optical Isomerism in Allenes \Rightarrow

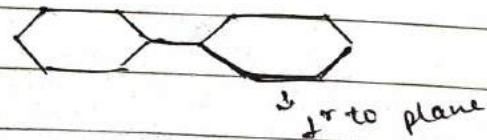
Allenes \rightarrow compds. having even no. of $C=C$ bonds.



Spiranes.

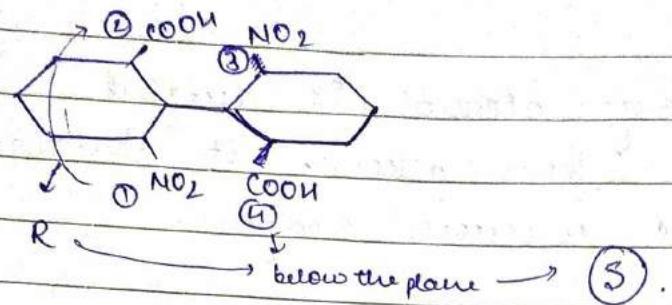


Biphenyls

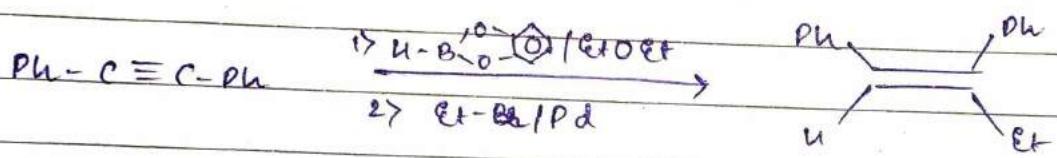
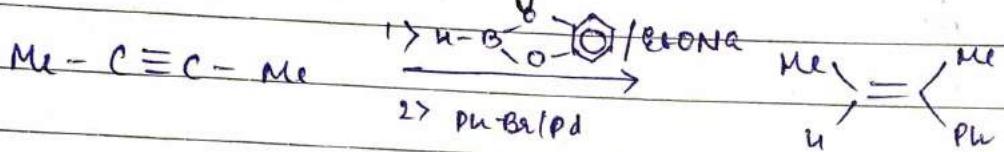


Bulky groups should be present to prevent rotation.

eg.

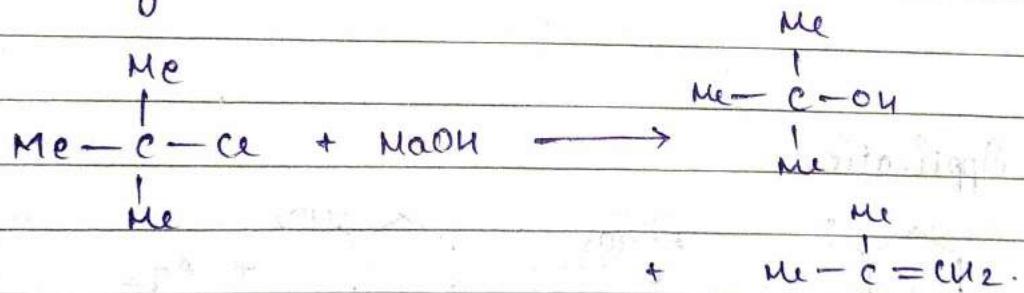


Suzuki cross coupling →

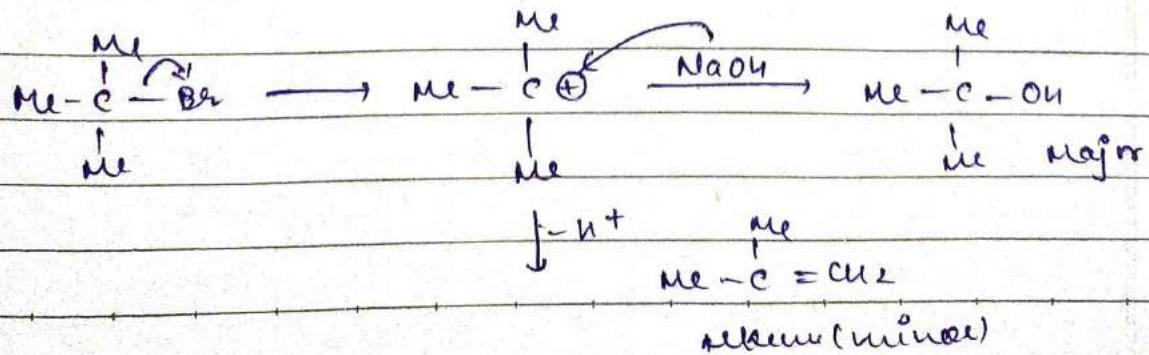


Wagner Meenkin Rn →

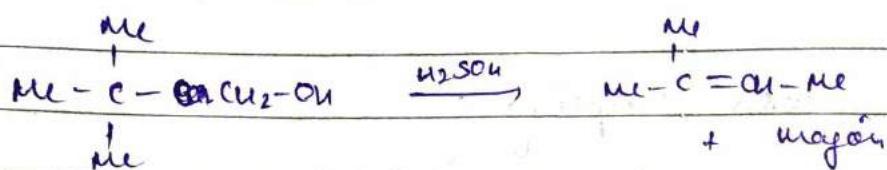
when alkyl halide is treated with base such as NaOH or KOH to form alcohol ~~or~~ alkene is called Wagner Meenkin reac.



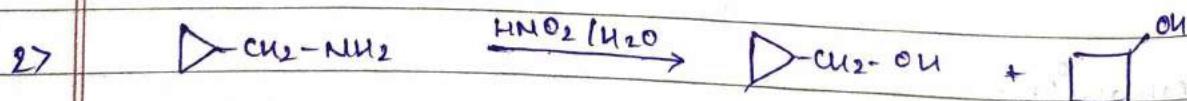
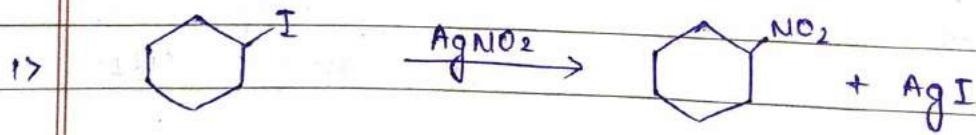
Mechanism -



When primary alcohol is treated with acid (H_2SO_4) to form alkene, it is also called Wagner-Meerwein reagent.

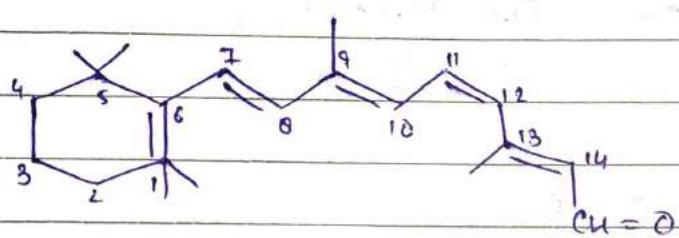


Application

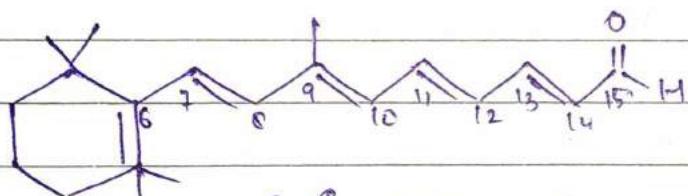


Chemistry of vision

Light strikes the eye and does something in the eye, and brain receives a signal that something is there. In this chemistry, the conversion of cis-retinal into trans-retinal occurs.

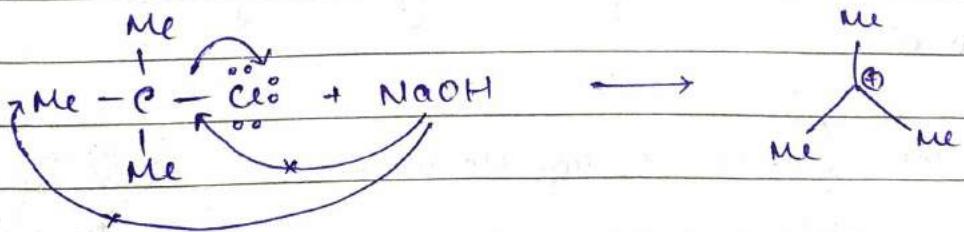


cis-retinal (cis)

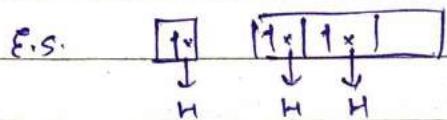
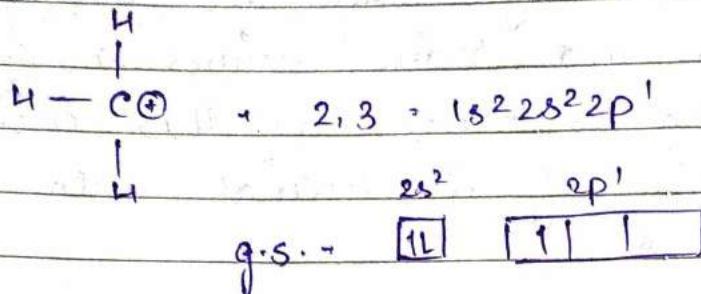


Carbocation

Carbon species containing +ve charge is called carbocation or carbonium ion. It is prepared by reaction of alkyl halide with aqueous KOH.

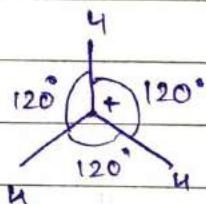


Hybridisation and shape



3 B.P. + 0 LP

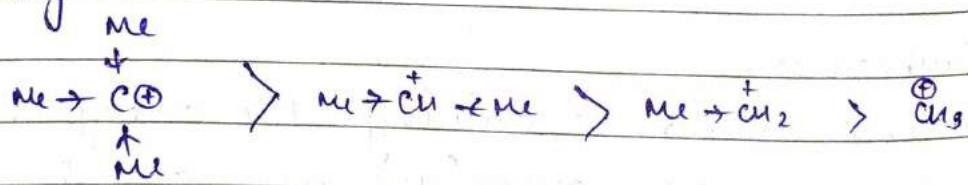
Tetragonal Planar



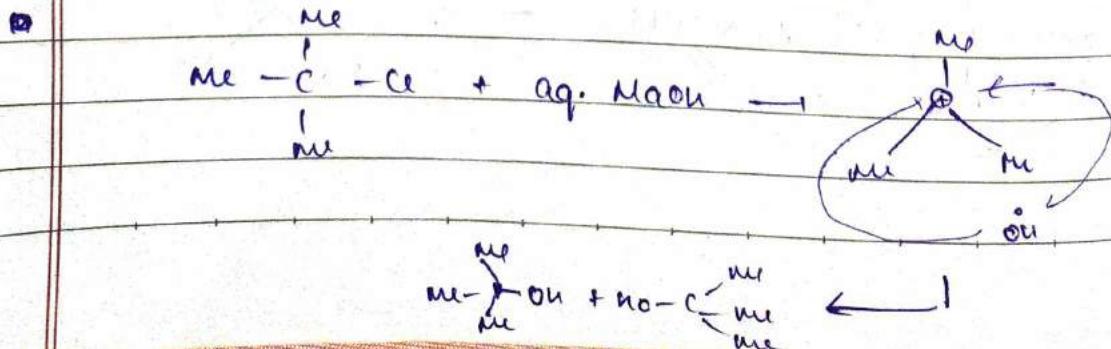
e^- releasing group
enhance the stability
of carbocation.

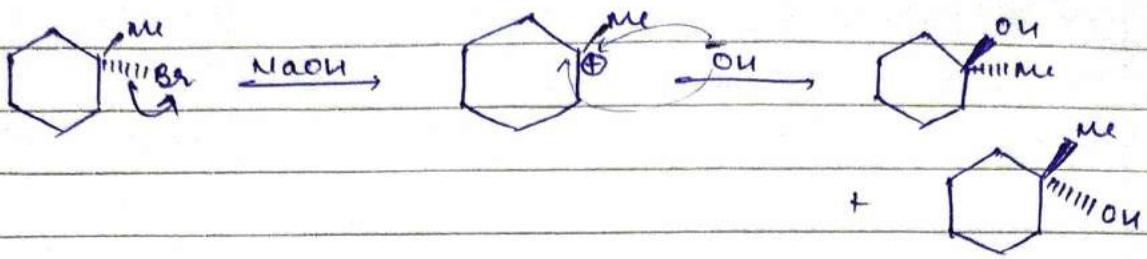
Application \Rightarrow

Stability-



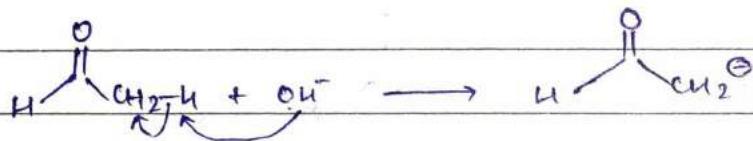
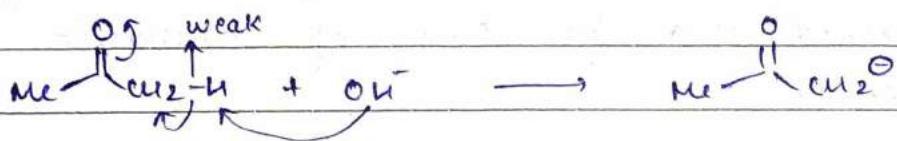
The conversion of tertiary alkyl halide into alcohol



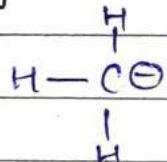


Carbanion

Carbon species containing negative charge is called carbanion. It is formed by the loss of aldehyde or ketone with base.



Hybridisation and shape

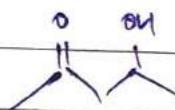
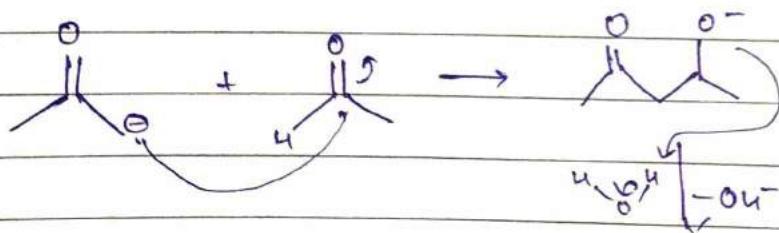
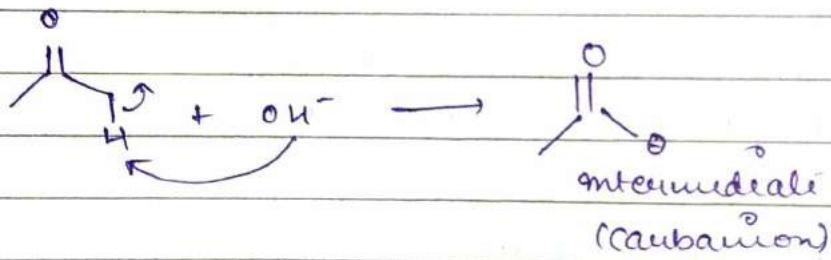


Electron attracting grp stabilizes the carbanion whereas e⁻ releasing gp decreases the stability

Applications

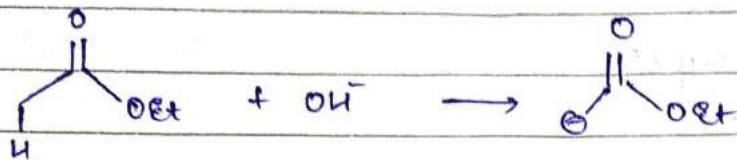
① Aldol condensation

In Aldol condensation, the product is formed via formation of carbanion intermediate.



② Claisen condensation

In Claisen condensation, product is formed by carbanion intermediate.

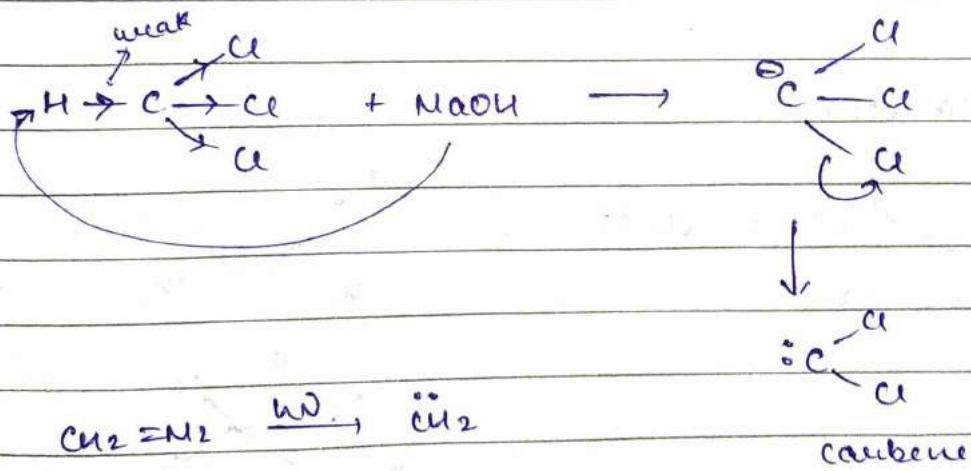


Carbene

When carbon species contain 2 free e⁻s, it is called carbene. It has 6 e⁻s in octet & is e⁻ deficient.

Carbene is formed by sucⁿ of chloroform with NaOH and de

when diazonium is treated in presence of light



It is of two types -

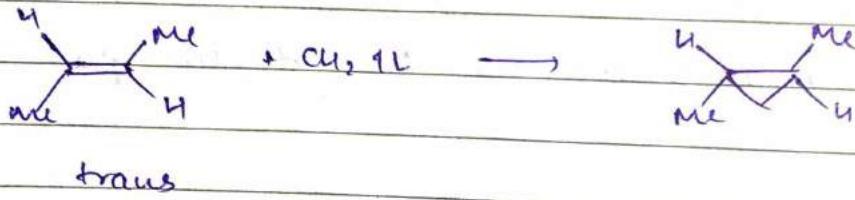
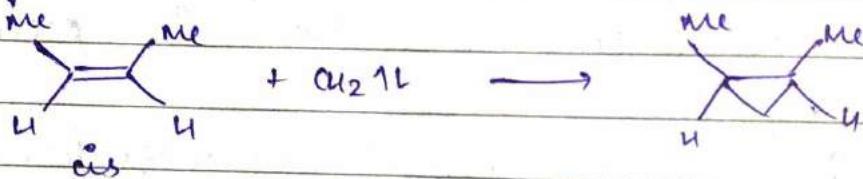
- ① Singlet carbene
- ② Triplet "

Singlet carbene - when both the e's are paired
(Opposite directn)

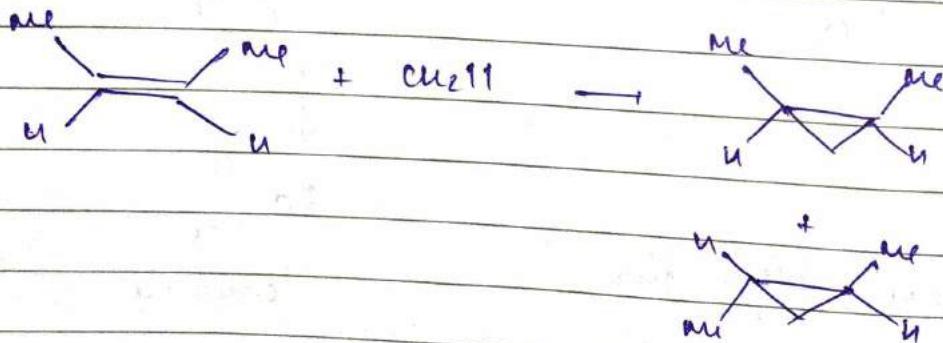
Triplet carbene - when both e's are unpaired
(Same directn)

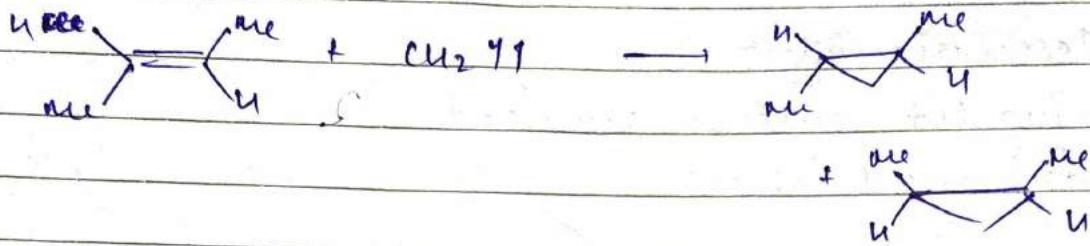
Application

- ① Singlet carbene -



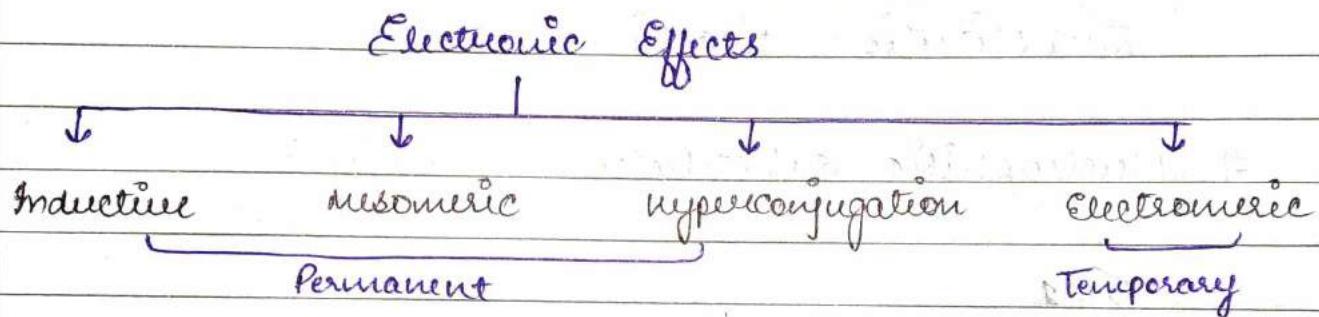
- ② Triplet carbene



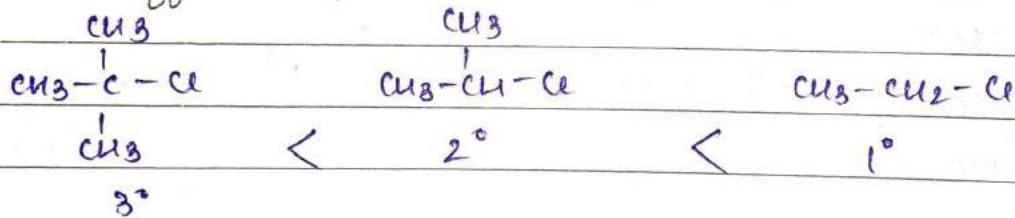


Electronic Effects

Substrate + Reagent → Intermediate → Product



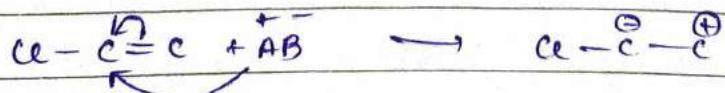
Inductive Effect \rightarrow present in σ bond



- * more s character \rightarrow more I effect (electronegativity)
 - * more \overline{s} I character \rightarrow more acidity

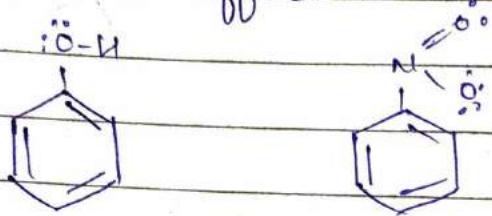
Electromeric Effect → present in π bonds

- * attacking reagent required
 - * complete transfer of e.s.



Mesomeric Effect -

- # conjugated system required
- # permanent effect.



+M group

-M group

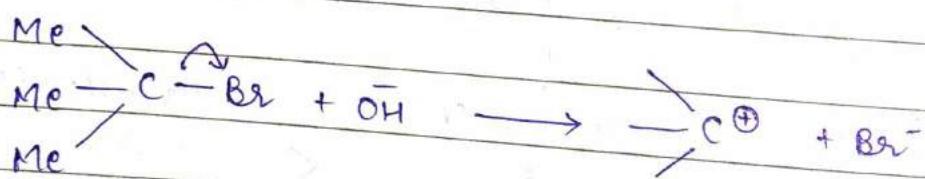
Substitution Reaction

- # Nucleophilic substitution reaction -

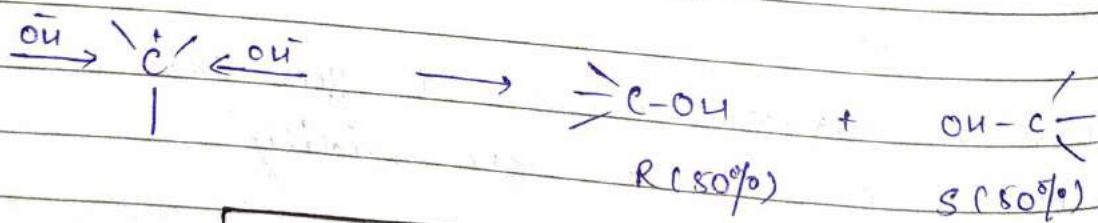
S_N1

Unimolecular nucleophilic substitution

Step 1 -

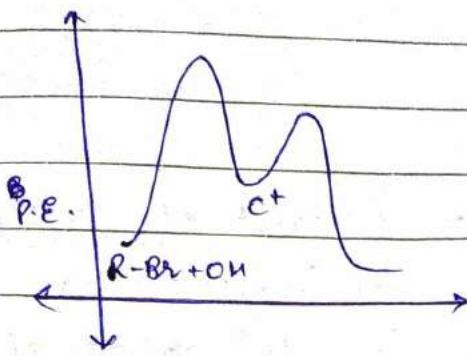


Step 2 -



Rate $\propto [\text{Me}_3\text{C}-\text{Br}]$

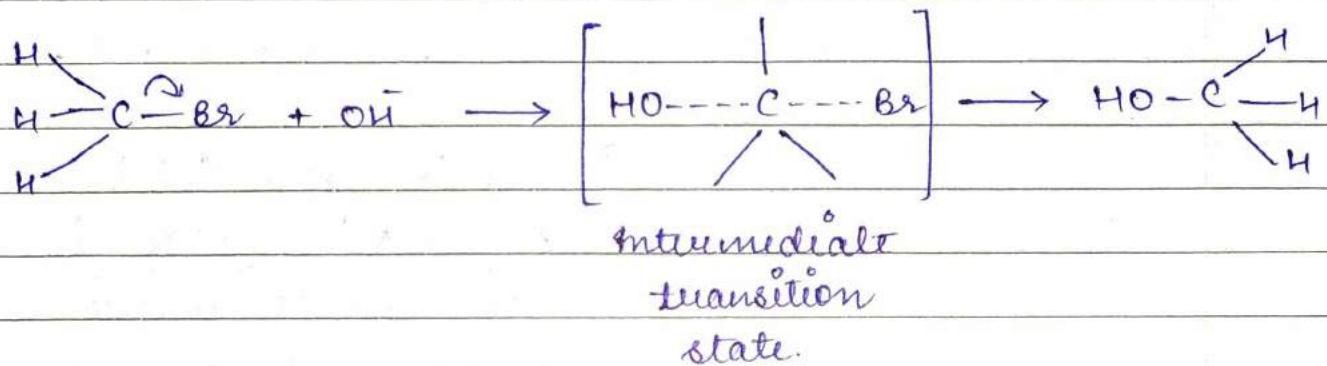
much of reactant



$[3^\circ > 2^\circ > 1^\circ]$

SN_2

Bimolecular nucleophilic substitution



Walden inversion takes place $[1^\circ > 2^\circ > 3^\circ]$

Imp Questions (End-Sem)

Units → CFT (numericals) (theory) ✓ practical

✓ Tablonski diagram

✓ liquid crystals (dkh lena)

spectroscopy → full cache se) ✓ IR + conceptual questions
(IR active, vib. POF etc)

Kinetics → ✓ all derivations (measurement) (steady state)
✓ numericals

Electro- fuel cells detail, photovoltaic cell etc. numericals ✓

✓ Pollution → BOD, COD, sewage treatment, effect of heavy metals on water, eutrophication, NOx, SOx

Structure → ✓ R-S, E-Z, optical isomerism in alkenes,
✓ isomers, etc.

✓ organic rec" mechanism

Polymers - Silicon, biopolymers, conductive poly., rate, aug mol wt. viscosity etc.

HARDNESS OF WATER

units of hardness - ① ppm = 1 part of CaCO_3
equivalent hardness
in 10^6 parts of
water.

② Mg/l

1 Mg/l = 1 mg of CaCO_3
equivalent hardness
in 1 l water.

③ Clark's degree ($^{\circ}\text{Cl}$)

1 parts of CaCO_3 in
70000 parts water or

1 grain of CaCO_3 in
1 gallon water.

or 1 Clark degree = 1 part
of CaCO_3 eq. hardness per
70000 parts of water.

④ Degreee french ($^{\circ}\text{Fr}$)

1 $^{\circ}\text{Fr}$ = 1 part of CaCO_3 eq.
hardness in 10^5 parts of
water.

⑤ Epm (1 mg equivalent per
litre)

1 epm = 50 ppm of CaCO_3 .

Relation -

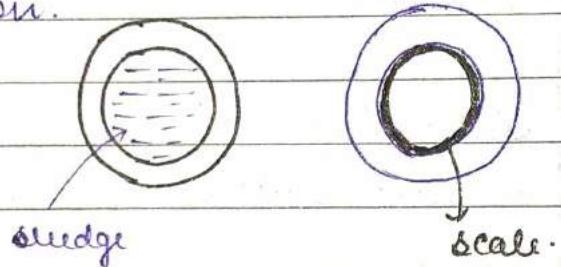
$$1 \text{ ppm} = 1 \text{ mg/L} = 0.07^\circ \text{C} = 0.1^\circ \text{F} = 0.02 \text{ epm}$$

Types of Hardness

- Temporary Hardness (Carbonate Hardness)
- Permanent Hardness (Non-Carbonate Hardness)
due to chlorides, sulphates, nitrates :'

Problems due to use of hard water in
boilers (industries)

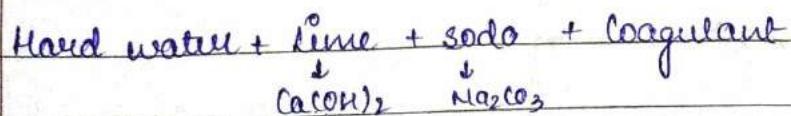
- ① Scale & sludge formation.



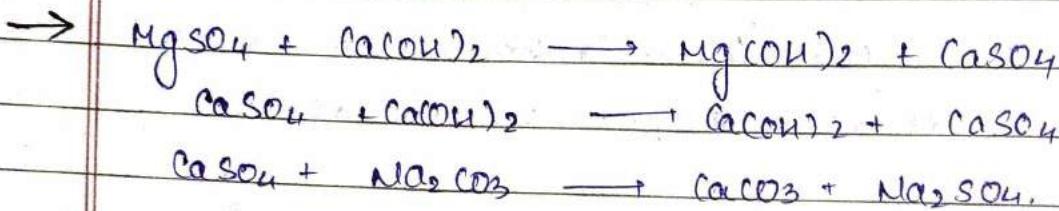
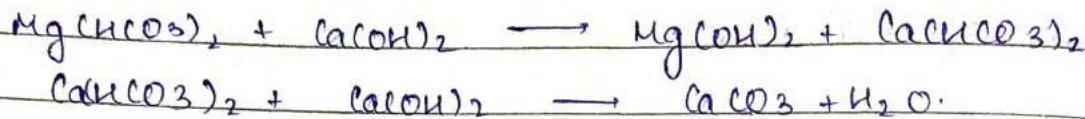
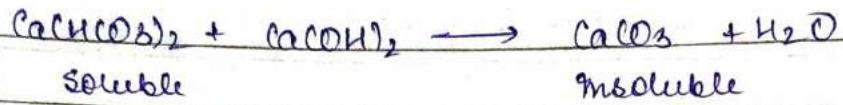
- ② Caustic Embitterment
- ③ Boiler corrosion
- ④ Priming and foaming

Processes for Softening of Hard Water

- ① Lime Soda Process



function of time



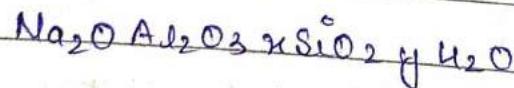
Advantages -

→ Economical

Limitations -

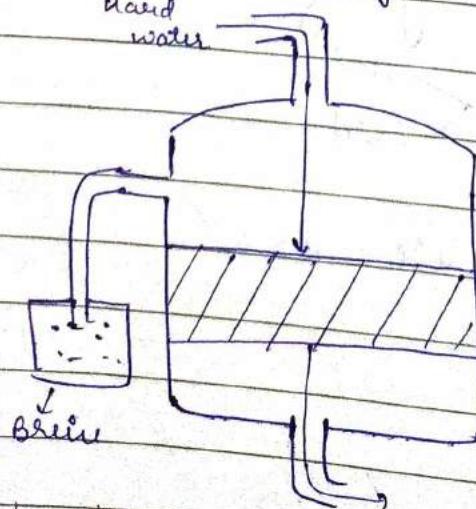
- Requires skilled labour.

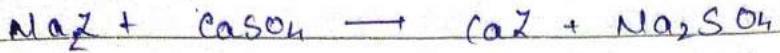
⑨ Zeolite or Pemmitil Process -
Boiling stone



$$(x = 2 - 10) \quad (y = 2 - 6)$$

Naed
wote





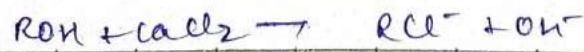
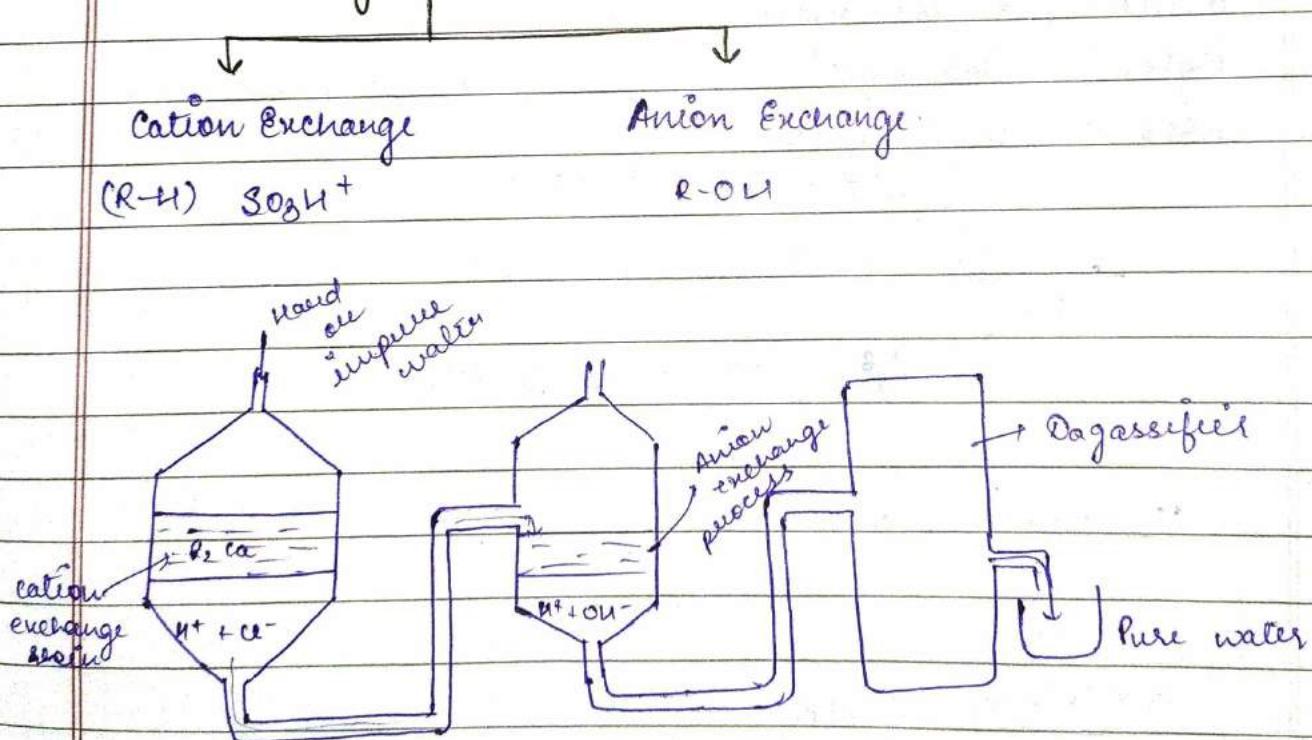
Limitations -

- Turbid water can't be purified.
- can't be easily regenerated.
- If acid is present in water, it will destroy zeolite.
- Coloured substances can't be used.

Advantages

- It removes all Ca & Mg ions.

③ Ion exchange resin method -



Equivalents of CaCO_3

$\text{Eq of } \text{CaCO}_3 = \left[\frac{\text{mass of hardness producing substance}}{\text{chemical Eq. of hardness producing substance}} \right] \times [\text{Chemical Eq. of } \text{CaCO}_3]$

- ① Calculate the temporary hardness & permanent hardness of a sample of water containing $\text{Mg}(\text{COCO}_3)_2 = 4.3 \text{ mg/l}$

$$\text{Ca}(\text{COCO}_3)_2 = 16.2 \text{ mg/l}$$

$$\text{MgCl}_2 = 9.8 \text{ mg/l}$$

$$\text{CaSO}_4 = 13.6 \text{ mg/l}$$

$$\frac{100}{2} = \text{eq. wt of } \text{CaCO}_3$$

$$\textcircled{1} \cdot \frac{4.3 \times 50}{73} = 5$$

$$\textcircled{2} \cdot \frac{16.2}{2} = \text{eq. wt. of } \text{Mg}(\text{COCO}_3)_2$$

$$\textcircled{3} \cdot \frac{9.8 \times 50}{81} = 10$$

$$\textcircled{4} \cdot \frac{13.6 \times 50 \times 2}{95} = 10$$

$$\textcircled{5} \cdot \frac{13.6 \times 50 \times 2}{136} = 10$$

Temporary = addⁿ of bикарбонатов = 15

Permanent = 100 - 20

Q Calculate the quantity of lime & soda required for softening 50000 l of water containing foll. salts per litre.

$$\text{Mg}(\text{C}\text{O}_3)_2 = 7.5 \text{ mg/l}$$

$$\text{Ca}(\text{C}\text{O}_3)_2 = 8.1 \text{ mg/l}$$

$$\text{MgCl}_2 = 2 \text{ mg/l}$$

$$\text{CaSO}_4 = 13.6 \text{ mg/l}$$

$$\text{mg NaOH + coagulant) } \\ \text{mg NaOH} = 12 \text{ mg/l}$$

$$\text{lime requirement for softening} = \frac{74}{100} \left[\begin{array}{l} \text{Temporary Ca ion,} \\ + 2 \times \text{temp. Mg ion} \\ + \text{permanent (Alg}^{+2} \\ + Fe^{+3} + Al^{3+}) + CO_2 \\ + H + (\text{NaCl or Na}_2\text{SO}_4) \\ + UC_03 - \text{NaAlO}_2 \end{array} \right]$$

$$\text{Soda req. for softening} = \frac{106}{100} \left[\begin{array}{l} \text{perm. Ca}^{++} \text{ Mg}^{+2} \text{ Al}^{+3} \text{ Fe}^{+2} + \text{H}^{+} \\ - UC_03 \end{array} \right]$$

$$\text{Eq. of } \text{CaCO}_3 + \text{Mg}(\text{C}\text{O}_3)_2 = \frac{7.5 \times 50}{7.3} = 5.14$$

$$\text{Ca}(\text{C}\text{O}_3)_2 = \frac{8.1 \times 50}{81} = 5$$

$$\text{MgCl}_2 = \frac{2 \times 50 \times 2}{95} = 2.11$$

$$\text{CaSO}_4 = \frac{13.6 \times 50 \times 2}{136} = 10$$

$$\text{mg NaOH} = \frac{12 \times 50 \times 2}{120} = 10$$

$$\text{lime seg.} = \frac{74}{100} [5 + 10.28 + 10 + 2.11]$$

$$= \frac{74}{100} [27.39]$$

$$= 20.26 \text{ mg/L} \times 50000 \text{ L} = 1013430 \text{ mg}$$

$$\text{soda seg.} = \frac{106}{100} [10 + 22.11] = 1.01 \text{ kg.}$$

$$= \frac{106 \times 22.11}{100}$$