shape

Date

Expt. No. _____ Page No. _____

temp. method ⇒ debye eq^n

$$P_M = P_i + P_o$$

$$= \frac{4}{3}\pi\alpha + \frac{4}{3}\pi N\left(\frac{u^2}{3KT}\right)$$

$$P_M = A + \frac{B}{T} \quad \text{— (1)}$$

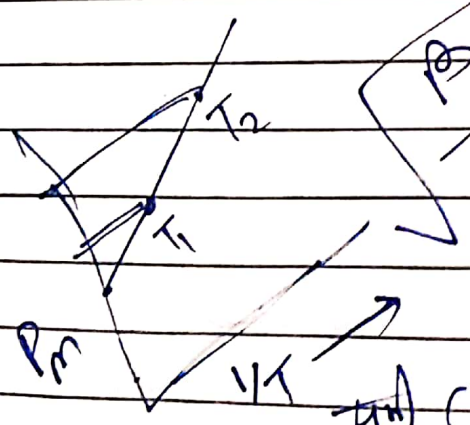
$$B = \frac{4}{3}\pi N\left(\frac{u^2}{3k}\right)$$

$$B = \frac{4\pi N}{9k}(u^2)$$

$u = ?$

$$\frac{B \times 9k}{4\pi N} = u^2$$

$$u = 0.0128\sqrt{B} + 10 \quad \text{— (2)}$$



(1) $P_{M_1} = A + \frac{B}{T_1}$ — (3)

(1) $P_{M_2} = A + \frac{B}{T_2}$ — (4)

(3) — (4)

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Expt. No. _____ Page No. _____

$$P_{m_1} - P_{m_2} = \left(A + \frac{B}{T_1}\right) - \left(A + \frac{B}{T_2}\right)$$

$$= A + \frac{B}{T_1} - A - \frac{B}{T_2}$$

$$= \frac{B}{T_1} - \frac{B}{T_2}$$

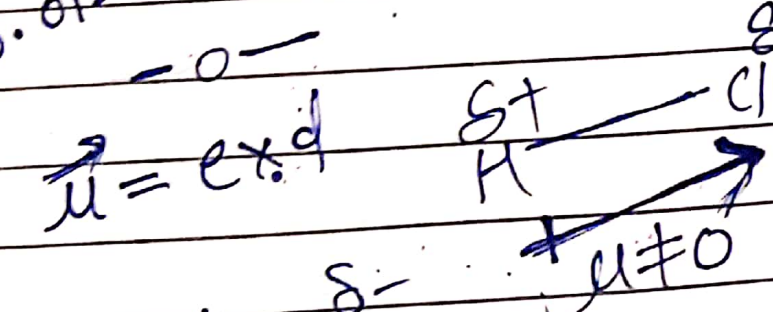
$$= \frac{B(T_2 - T_1)}{T_1 T_2}$$

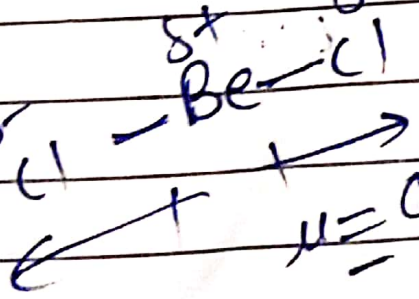
$$P_{m_1} - P_{m_2} = \frac{(P_{m_1} - P_{m_2}) \times (T_1 \times T_2)}{(T_2 - T_1)} = B \quad (5)$$

$$0.012 \sqrt{B} + 10^{-18} = \mu ?$$

—o—

$\vec{\mu} = e \times \vec{d}$



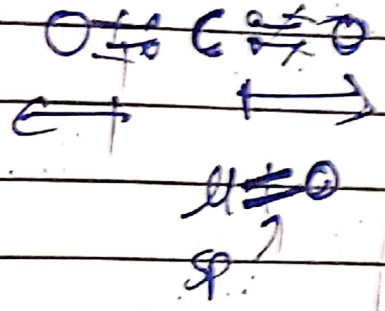


① Diatomic → H_2, N_2 — HF, HCl, ~~$BeCl_2$~~

② triatomic → $BeCl_2$, CO_2, SO_2 (jump)

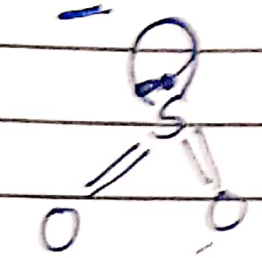
$\mu = 0$, $\mu \neq 0$

linear — non-linear



$\mu = 0$

sp

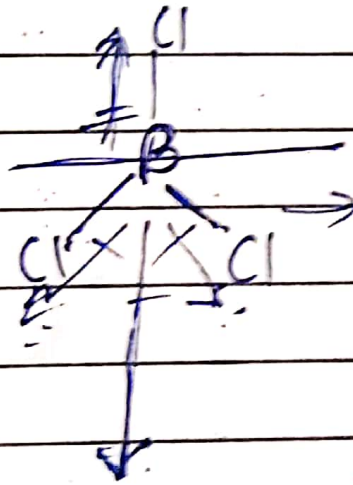


Geometry ← आकृति → $\mu = 0$

असममित → $\mu \neq 0$

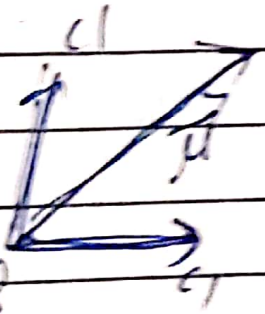
sp, असमान S. तल

③ tetratomic →



$\mu = 0$

sp^2



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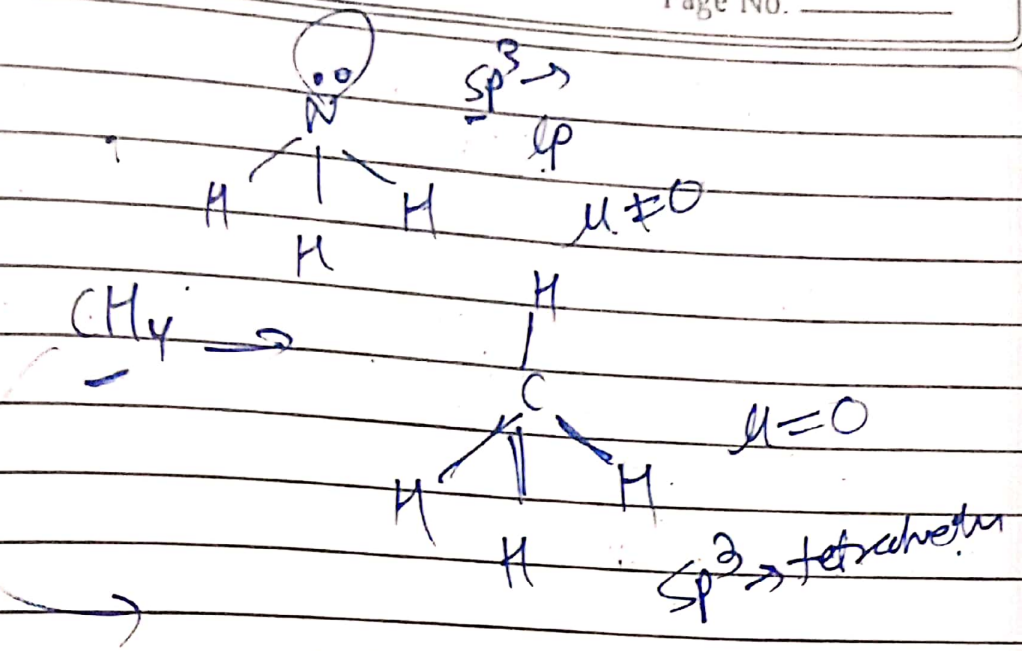
Expt. No. _____ Date _____

Page No. _____



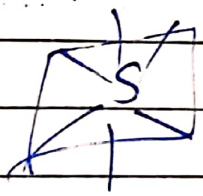
CH_4 →

CH_3F → distetrahedral

μ ≠ 0

PCl_5 → μ = 0 sym.

SF_6 → μ = 0



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Metal- Ligand Bonding in Transition metal Complexes

M — L
↳ bond

different theories –

① VBT ② CFT ③ MOT ④ LFT

I VBT

Pauling & Slater ने

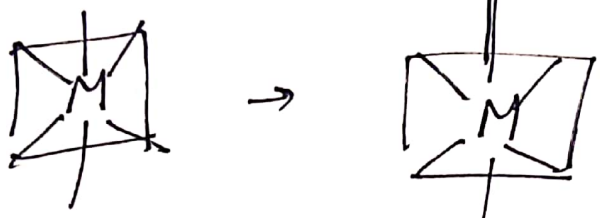
① M-L Bond purely covalent
② co-ordination no. के
③ low spin & high spin complexes
④ magnetic behaviour
⑤ geometry (structure, hybridizatn)

Limitatn of VBT

① Stability के बारे में नहीं
② excited state व splitting (×)

③ विकृति (disortion) ✗

④



octahedral

tetragonal
(disorted octa)

④ ligand के ओर में

⑤ Metal को ज्यादा महत्व

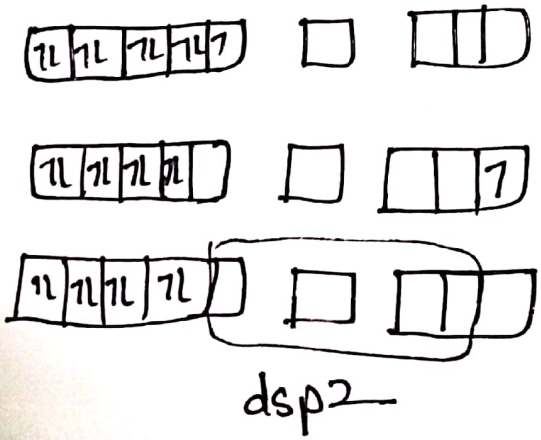
⑥ Rate और mechanism ✗

⑦ VBT के alc -4 co-ordinat वाले complex

$[Cu(NH_3)_4]^{2+}$

Cu^{2+} — $4s^2\ 3d^9 / 4s^1\ 3d^{10}$

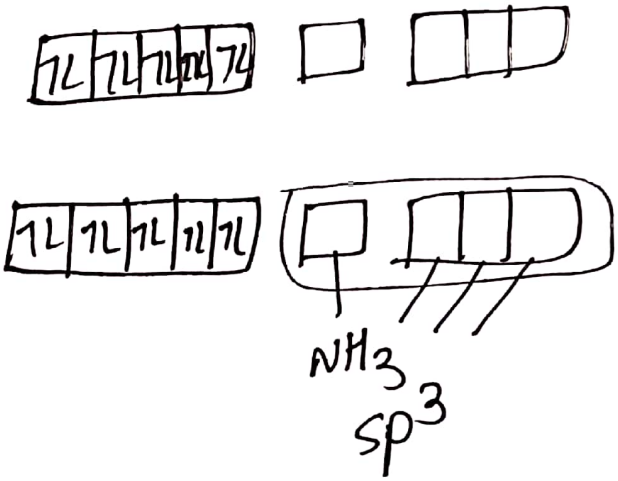
→ $3d^9\ 4s\ 4p$



dsp2

$[Zn(NH_3)_4]^{2+}$

$Zn^{2+} \Rightarrow 4s^2\ 3d^{10} / 4s\ 3d^{10}$



NH_3

sp^3

(8) $[Co(NH_3)_6]^{3+}$ $[CoF_6]^{3-}$

Same metal same oxidation state

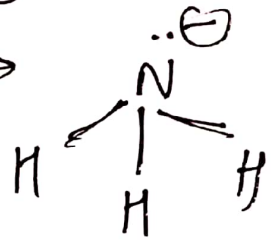
But diff geometry

Crystal feild Theory

(1) M–L purely ionic

(2) ligand को ऋणात्मक बिंदु आवेश

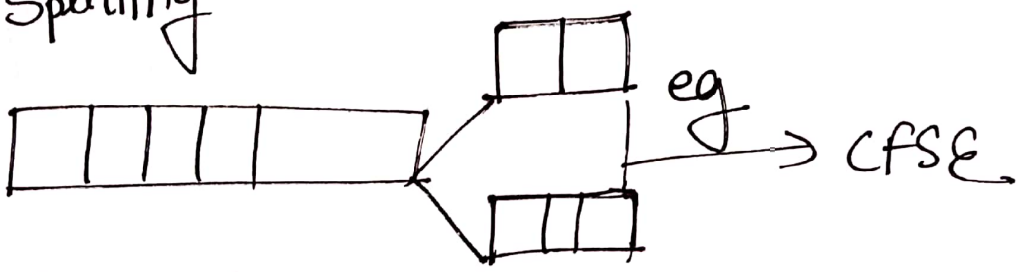
F^- Cl^- CN^- NH_3 →



(3) ये stability को explain → CFSE

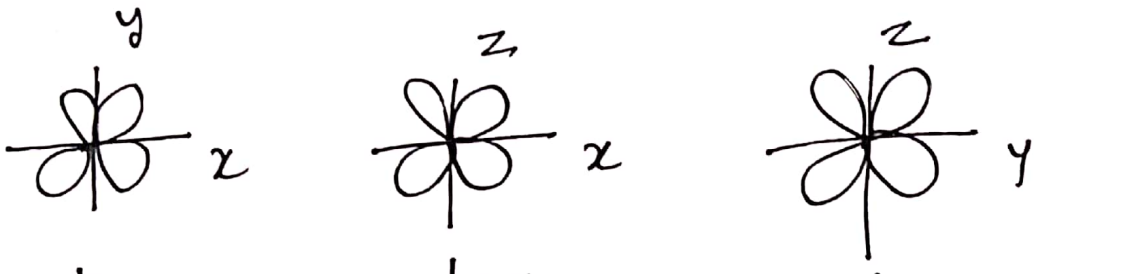
(4) M–L के बीच कोई interaction नहीं

(5) Splitting



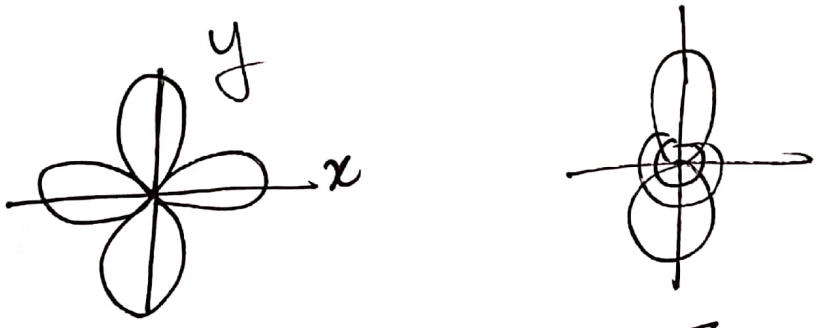
orbitals में overlapping (+) e⁻ sharing (+)

Crystal feild Splitting



dxy dzx dyz

t2g ~~orbits~~ lobe b/w the axes

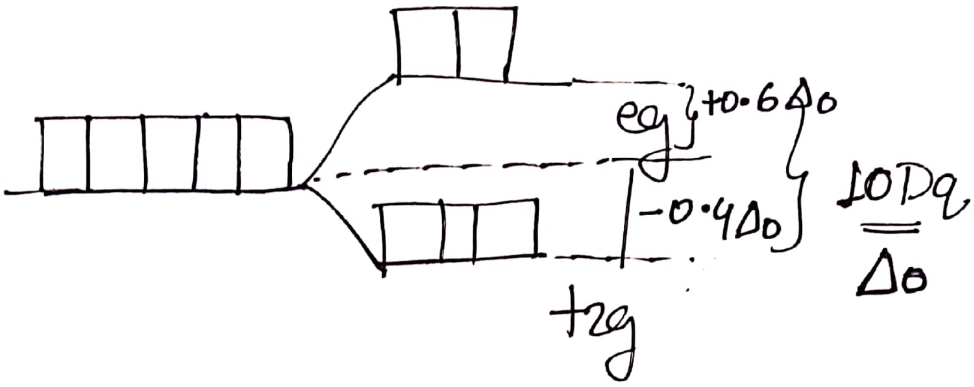


dx^2-y^2 dz^2

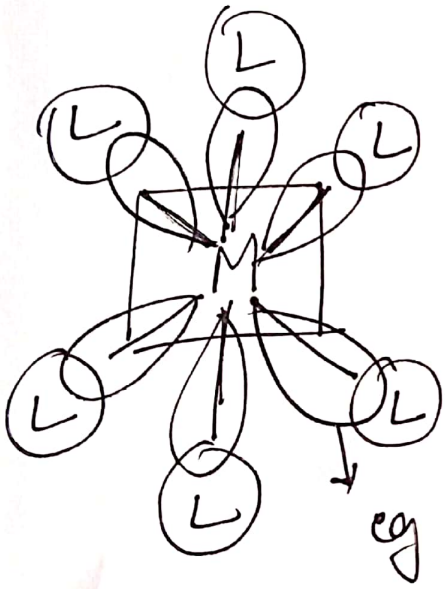
eg-orbital

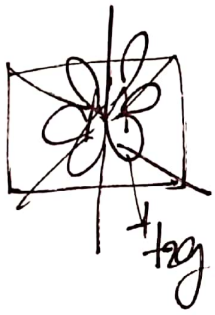
lobe along the axes

CFSE

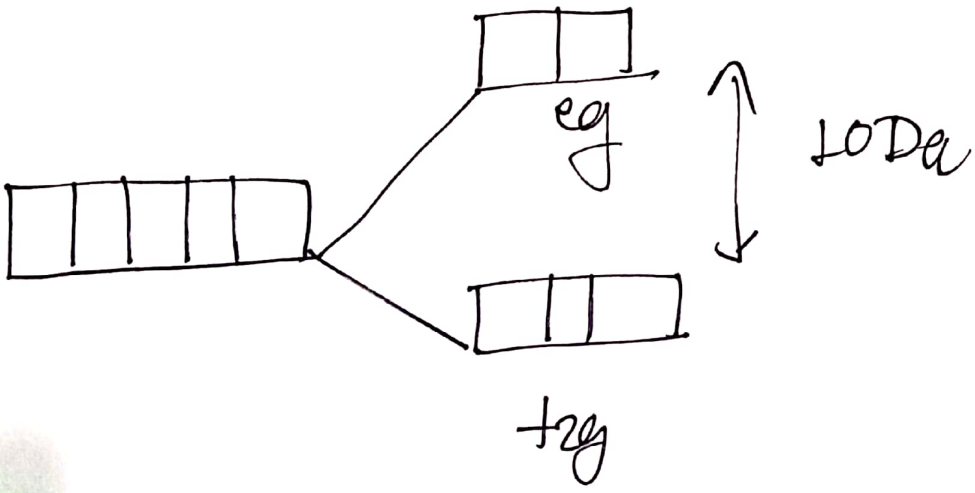


Splitting in Octahedral Complexes

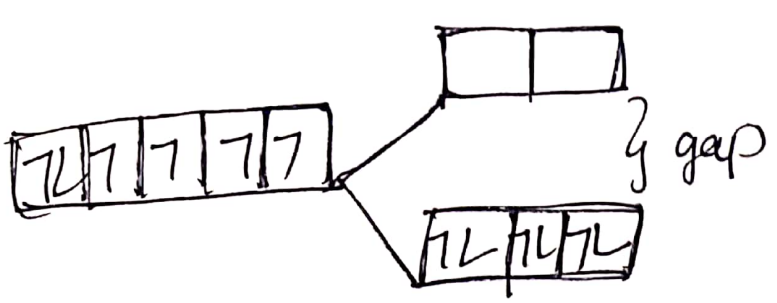


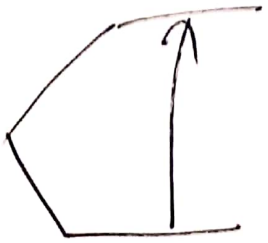


eg orbital L के direct contact में more repulsion तो eg की energy ↑



d^6 octahedral

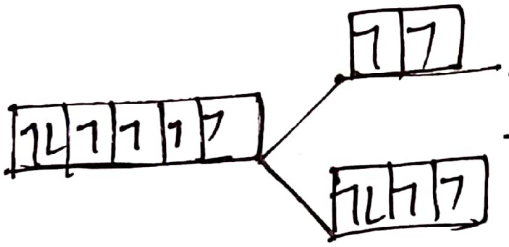




strong field ligand gap ↑ तो e⁻ का pairing

$\Delta_o > P$

P = Pairing energy / दो e⁻ को pair करने की आवश्यक ऊर्जा



gap ↓ e⁻ का pairing नहीं

$\Delta_o < P$

weak feild ligand

CFSE calculation ⇒ $4e^- \times -0.4 + 0.6 \times 2$

$= -1.6 + 1.2$

$= -0.4\,\Delta_o$

$[CoF_6]^{3-}$

Thermodynamic stable complex kinetically stable or unstable

Kinetic { labile → unstable
inert → stable

Relatn b/w stepwise Rate constn & overall equillibrum constant

K = eq. constant

$M + L \underset{}{\overset{K_1}{\rightleftharpoons}} [ML]$ $\quad K_1 = \frac{[ML]}{[M][L]}$

$[ML] + L \overset{K_2}{\rightleftharpoons} [ML_2]$ $\quad K_2 = \frac{[ML_2]}{[ML][L]}$

$[ML_2] + L \overset{K_3}{\rightleftharpoons} [ML_3]$ $\quad K_3 = \frac{[ML_3]}{[ML_2][L]}$

K_1, K_2, K_3 → stepwise eq. const.

$M + 2L \rightleftharpoons [ML_2]$ $\quad \beta = \frac{[ML_2]}{[M][L^2]}$

β – overall eq. const.

$$\beta_3 = \frac{[ML_3]}{[M][L]^3} \quad (1)$$

$([M] + 3L \rightarrow [ML_3])$ (2)

$\frac{[ML]}{[ML]}$ व $\frac{[ML_2]}{[ML_2]}$ को multiply

$$\beta_3 = \frac{[ML_3]}{[M][L]^3} \frac{[ML] \times [ML_2]}{[ML] \quad [ML_2]}$$

$$\beta_3 = \frac{[ML_3]\,[ML]\,[ML_2]}{[M][L][L][L][ML][ML_2]}$$

$$= \frac{[ML_3]}{[ML_2][L]} \frac{[ML_2]}{[ML][L]} \frac{[ML]}{[M][L]}$$

$$\beta_3 = K_3 \cdot K_2 \cdot K_1$$

$$\boxed{\beta_n = \sum_{n=1} K_n}$$

Stability const. $Ni^{2+} + NH_3 \rightleftharpoons [Ni(NH_3)]^{2+}$ $K_1 = 5 \times 10^2$

$[Ni(NH_3)]^{2+} + NH_3 \rightleftharpoons [Ni(NH_3)_2]^{2+}$ $K_2 = 1.3 \times 10^2$

$[Ni(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Ni(NH_3)_3]^{2+}$ $K_3 = 4.0 \times 10^1$

$[Ni(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Ni(NH_3)_4]^{2+}$ $K_4 = 1.2+$

L की संख्या ↑ Stability ↓

★ factor affecting thermd. stability of Complexes

(I) Metal — (i) size ⇒ size ↓ S ↑

(II) charge ⇒ charge ↑ S ↑

(III) electronegativity ⇒ Li > Na > Rb > Cs > Fr

e.n ↑ S ↑

(IV) Ionisation potential ⇒ IE ↑ S ↑

IE ↑ size small → M–L strong bond

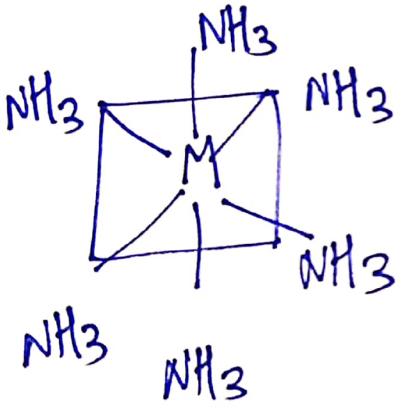
II Nature of ligand ⇒

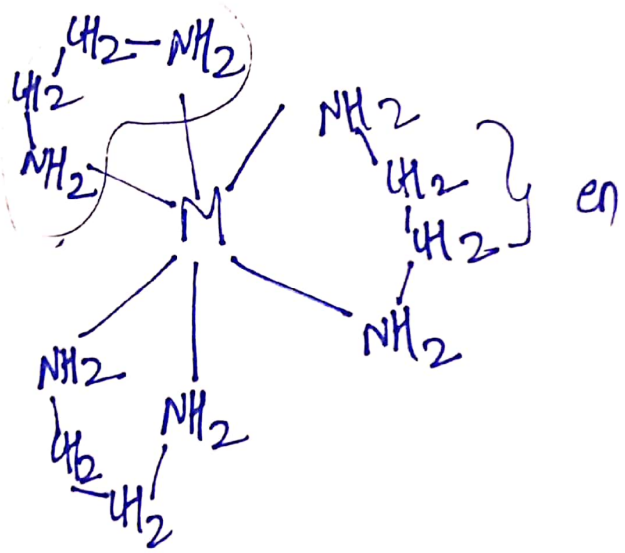
1) Basic character → e⁻ donatn ↑ S ↑

F > Cl > Br > I

2) charge → more (-ve) ↑ S ↑

~~3) Steric factor~~ →



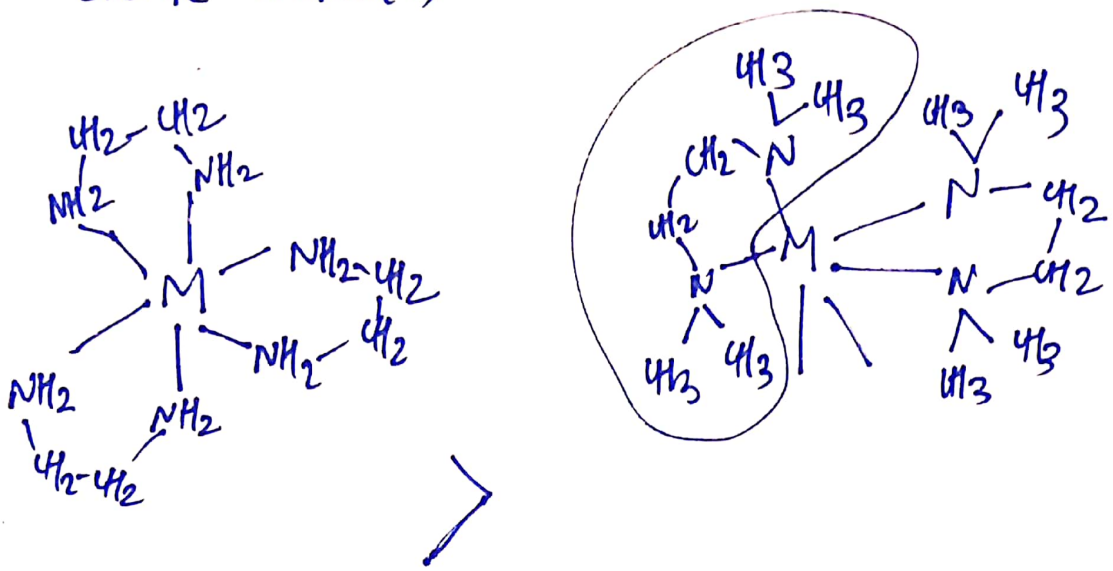


L size ↑ S ↓ M–L bond weak

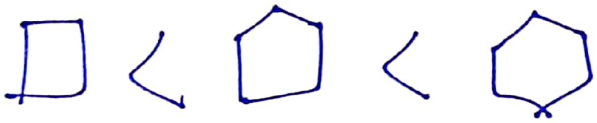
III Chelate effect ⇒

$[Ni(en)_3]^{2+}$ chelate

Steric factor ⇒

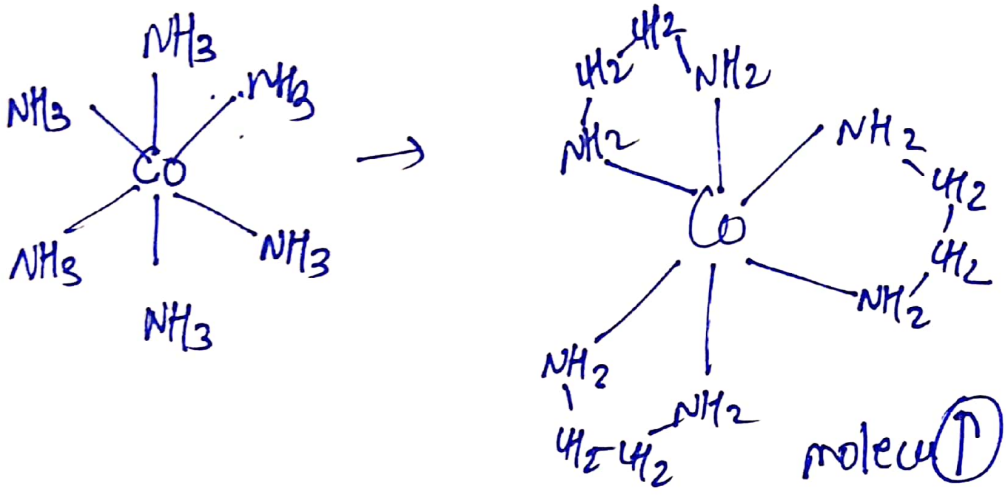


1) Size of ring ⇒ Δ ✗



II) entropy effect ⇒ ΔS ↑ Stab. ↑

$$[Co(NH_3)_6]^{3+} + 3en \rightarrow [Co(en)_3]^{3+} + 6NH_3$$

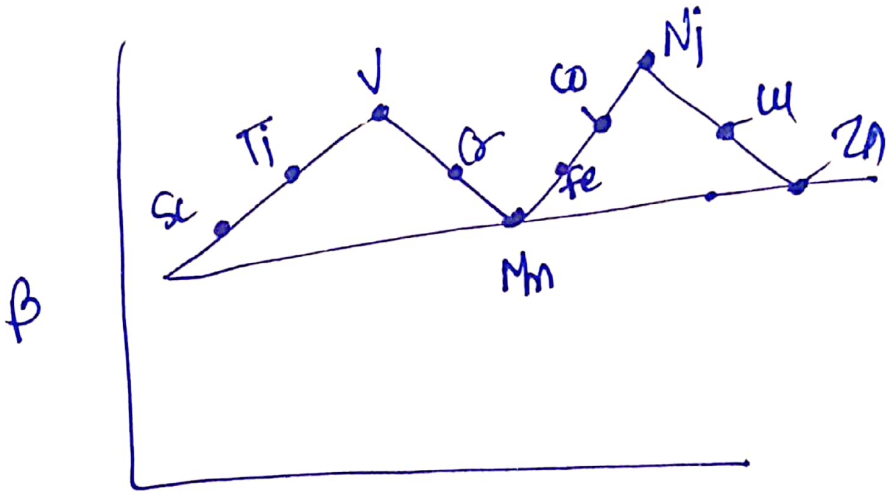


molecu ↑

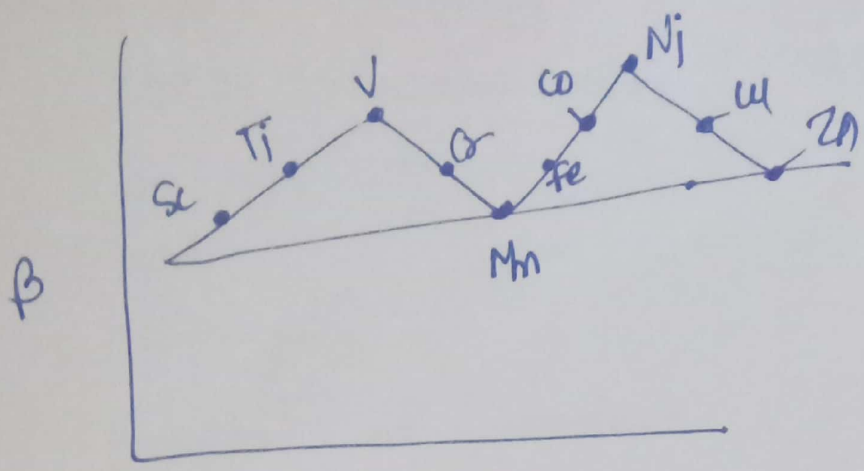
IV Crystal feild splitting effect ⇒

d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
-0.4	-0.8	-1.2	-0.6	00	-0.4	-0.8	-1.2	-0.6	0.0

oct. weak Ligand



Irving- williams order



Irving- william order

$d^1 < d^2 < d^3 > d^4 < d^5 < d^6 < d^7 < d^8 > d^9 > d^{10}$

kinetic stability को प्रभावित करने वाले कारक

(I) charge of Metal

$(NaCH_2O)_n^{+}$ $(Mg(H_2O)_n)^{2+}$ $(Al(H_2O)_n)^{3+}$

$+1 < +2 < +3$

(II) Raddii → $[Mg(H_2O)_6]^{2+} < [Ca(H_2O)_6]^{2+} < [Sr(H_2O)_4]^{2+}$

$0.65 < 0.99 < 1.13$

Radii (↓) S (↑)

(III) charge to Radius ratio

$\frac{+v}{\text{radii}}$ ↑ S ↑

(IV) geometry of complex-

4 C.N except 6 C.N.

Substitution Reaction in Complexes

⇒ समस्त अभिक्रिया मूलीय विभयन

⇒ $L^{\ominus}$ का subtn तो nucleophillic

⇒ $M^{\oplus}$ का sub तो electrophillic

⇒ $E_a = E_T - E_R$

⇒ Attacking reagent

M L

I. Substitution Reaction in octahedral

$S_N1 \rightarrow$

(a) $MX_5Y \xrightarrow{slow} MX_5 + Y$

(b) $MX_5 + Z \xrightarrow{fast} MX_5Z$

$$Rate = k_1[MX_5Y]$$

$$(MX_5Y) + Z \rightarrow (MX_5Z) + Y$$

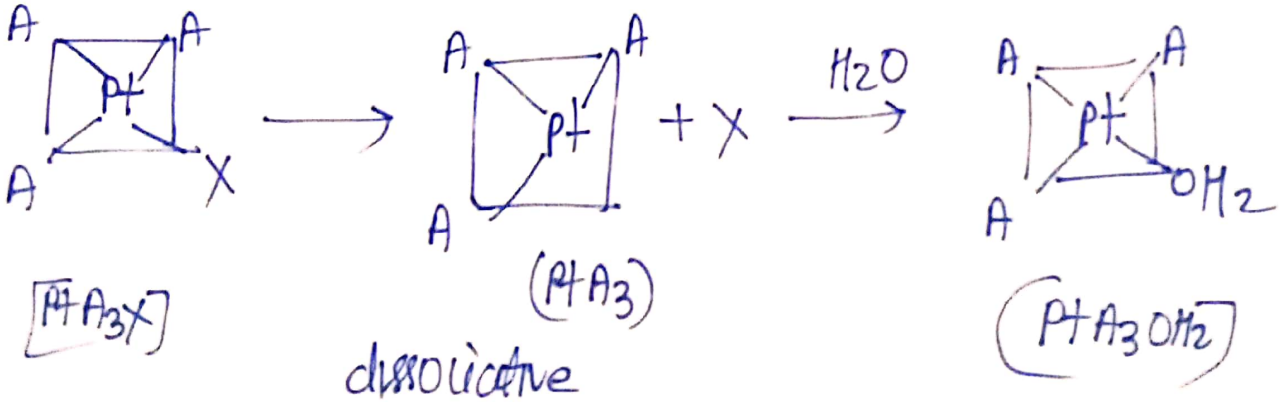
(2) S_N2 ⇒ $MX_5Y + Z \xrightarrow{slow} MX_5YZ$

$\xrightarrow{fast}$ $MX_5Z + Y$

$$Rate = k_2[MX_5Y][Z]$$

★ Substi^n Rea^n in square planner

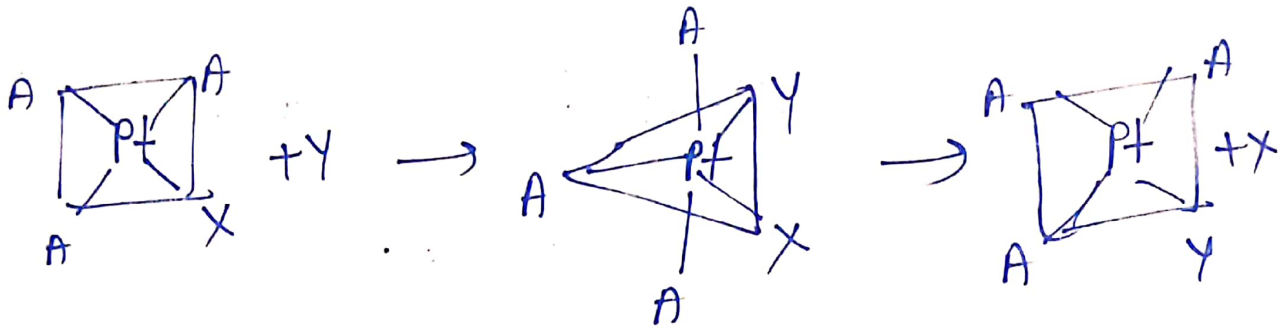
(I) Solvent as a Nucleophillic Reagent ⇒



$[PtA_3X]$ (PtA_3) (PtA_3OH_2)

dissociative

II L as a Nucleophillic reagent



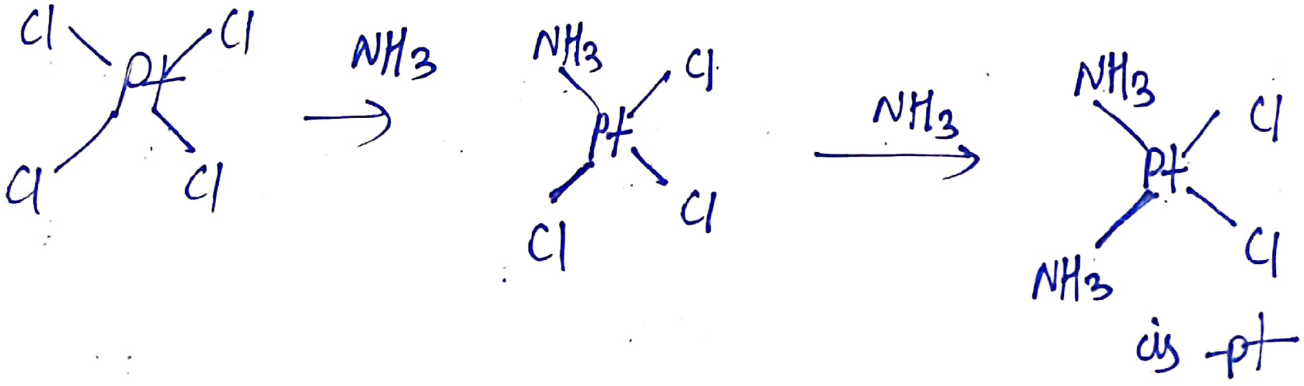
tri- bipy.

associative

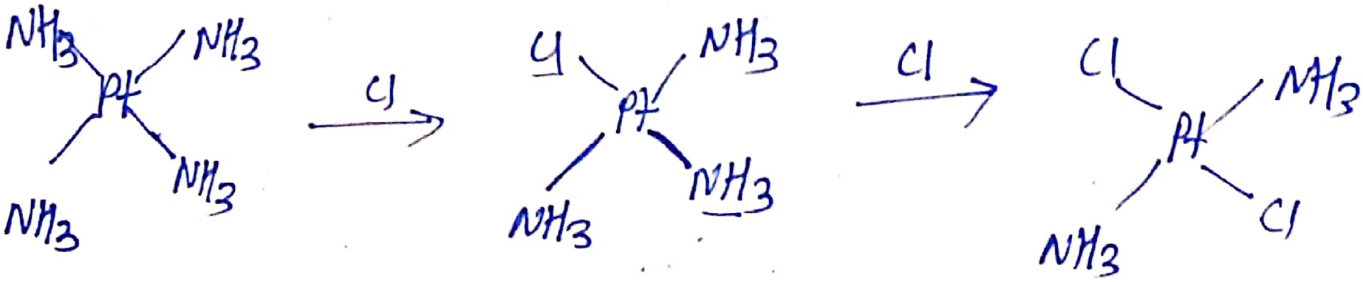
Trans effect

संकुल में उपस्थित L पर आने वाले L को अपने विपरीत स्थिति में आने के लिए निर्देशित करती है तो उसे trans effect कहते है।

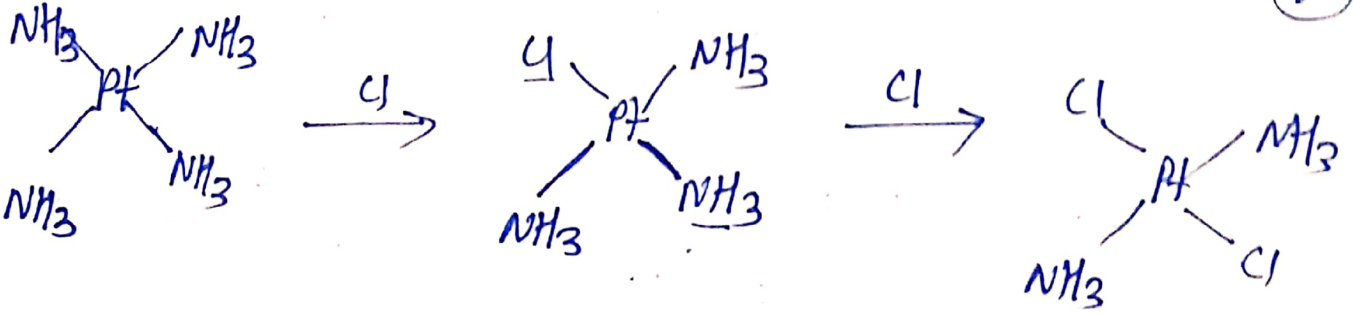
$CN > H_3 > NO_2 > Br > Cl > NH_3 > H_2O > F$



cis-pt



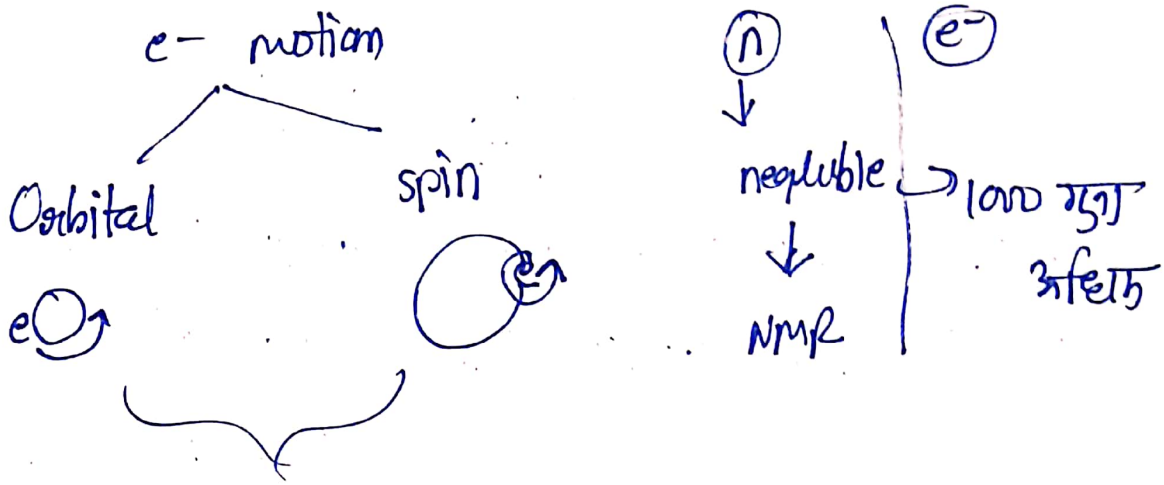
trans- Pt



trans- Pt

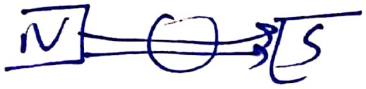
chap - 3. UNIT - II

Magnetic properties of metal complexes



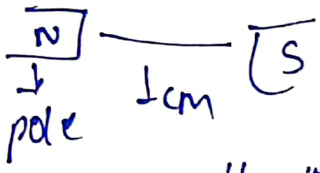
Some imp terms -

1) Magnetic induction ⇒ जब किसी चुं. पदार्थ को बाह्य चुंबकीय क्षेत्र में रखा जाता है तो उसमें जो चुंबकत्व उत्पन्न होता है उसे चुं. प्रेरण कहते हैं।



$B = H_0 + 4\pi I$

(2) ध्रुव प्रबलता ⇒ चुं की ध्रुव की शक्ति



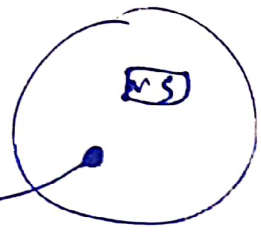
attraction force

N
Repulsion

(3) चुंबकीकरण की तीव्रता ⇒

$$I = \frac{M}{V} \quad \frac{\text{चुं आर्द्रण}}{\text{Volume}}$$

Material पर depend



material

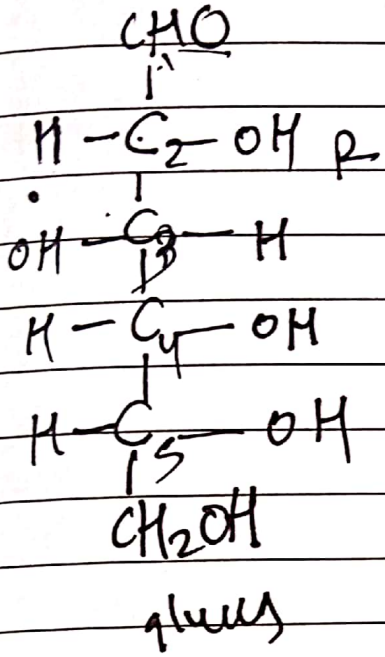
(4) चुं सुग्राहिता ⇒ $\chi = \frac{I}{H}$

Expt. No. _____ Page No. _____

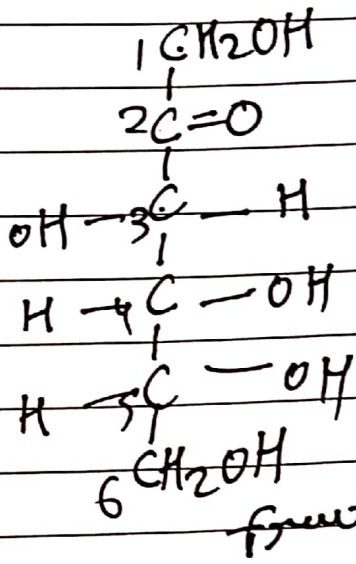
Fructose ⇒ fructosazone

$C_6H_{12}O_6$

$(CHOH)_4$

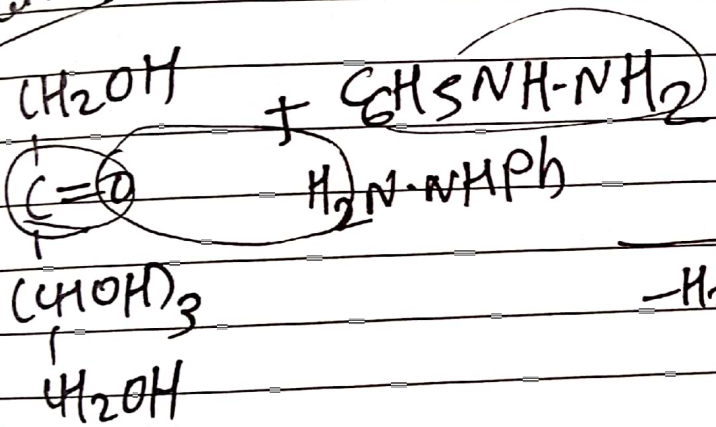


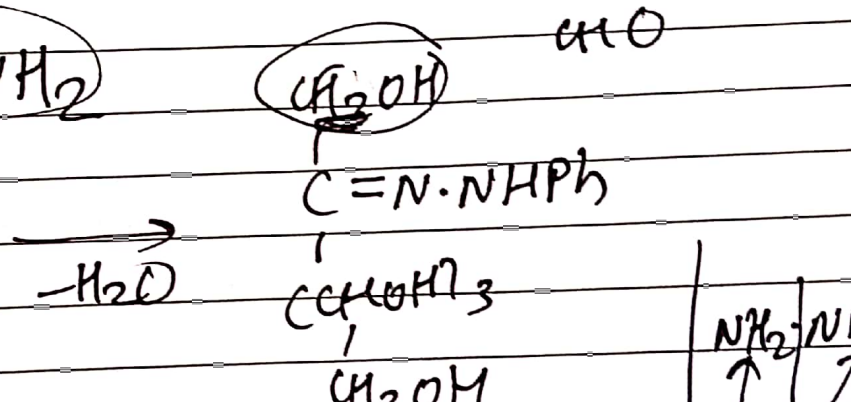
plus

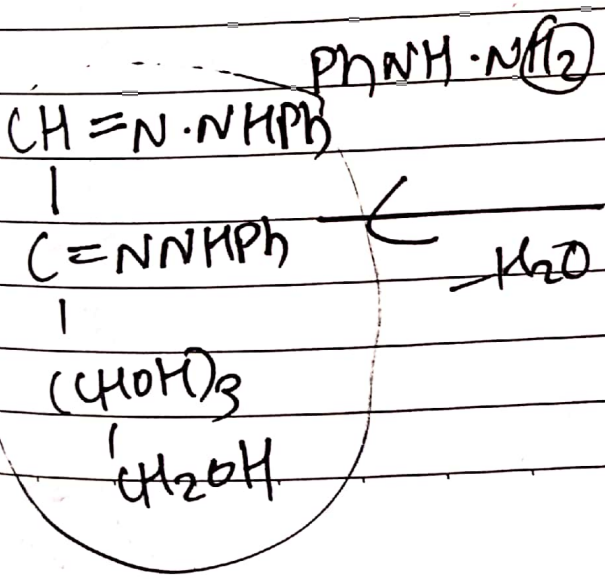


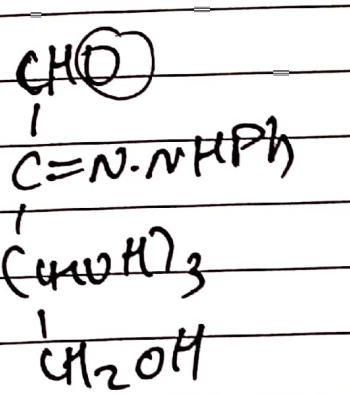
fructose

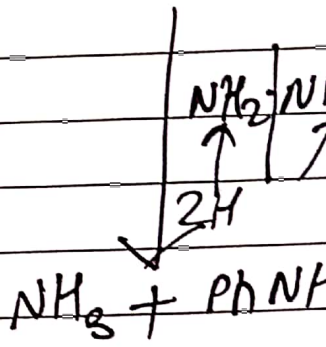
mech.











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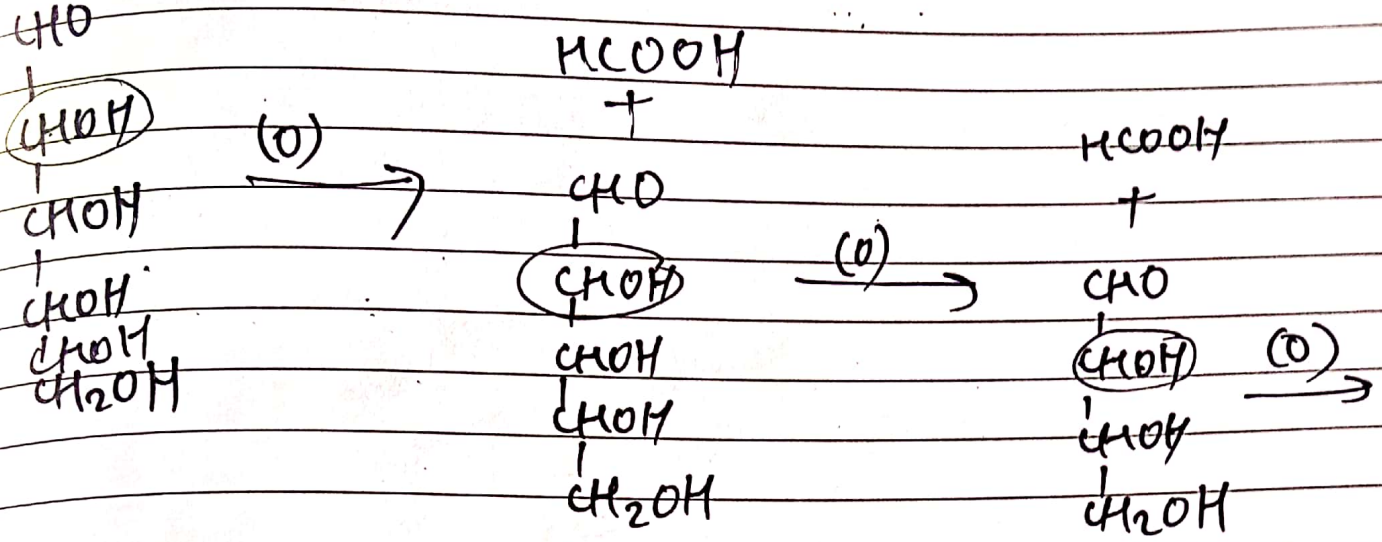
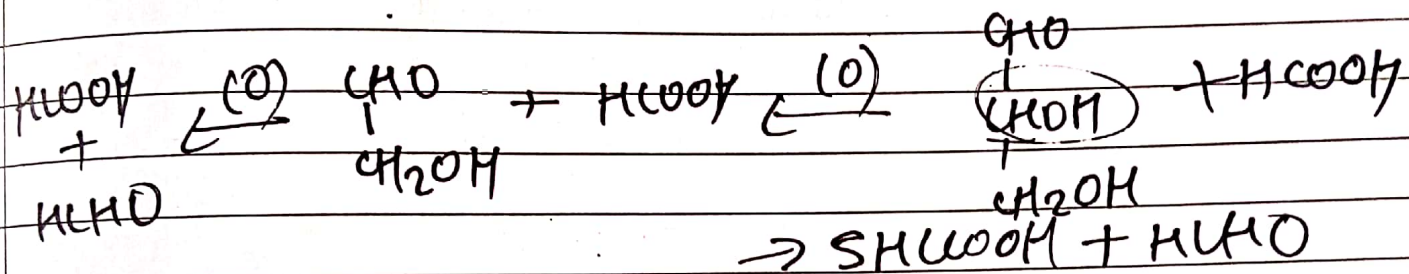
Expt. No. _____ Page No. _____

$Pb(OAc)_4 / HIO_4$

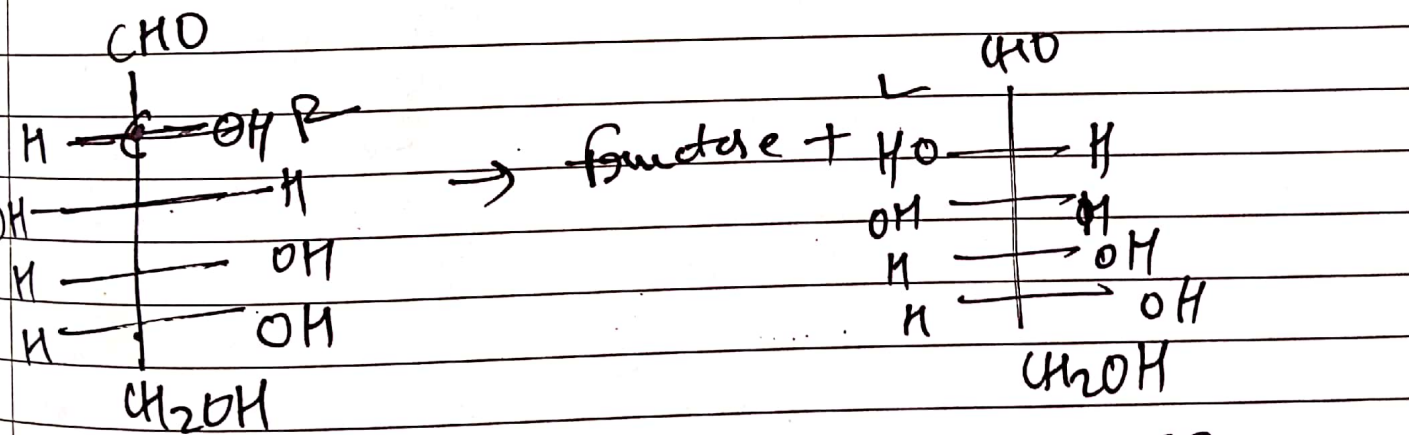




$\rightarrow 3HCOOH + HCHO$

Base $\rightarrow$ dil NaOH + Py + talulose $\rightarrow$ fructose + mannose

epimer — C-2 glucose



mechanism (X)

mannose

endiol (=) —OH / —OH

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Date

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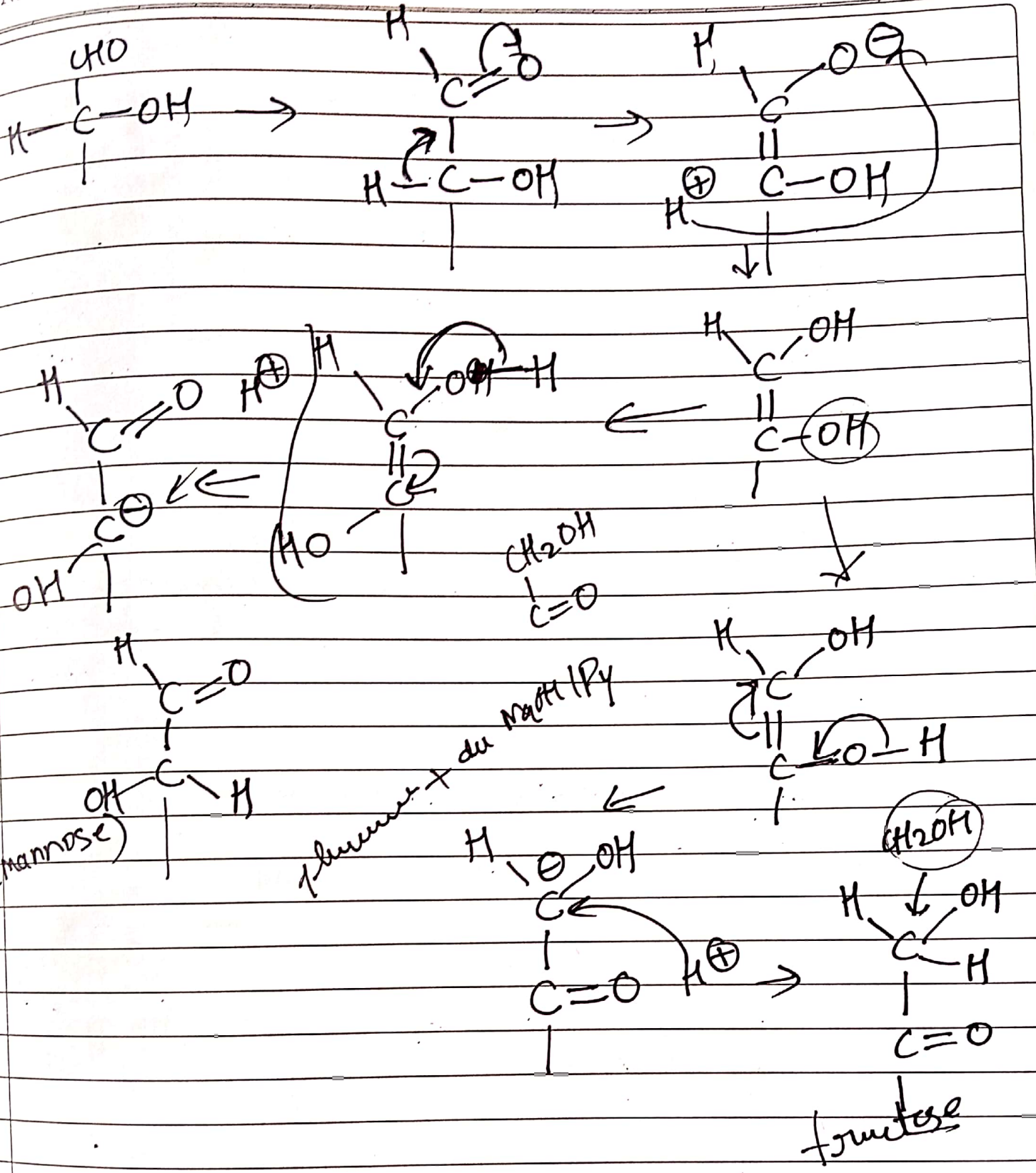

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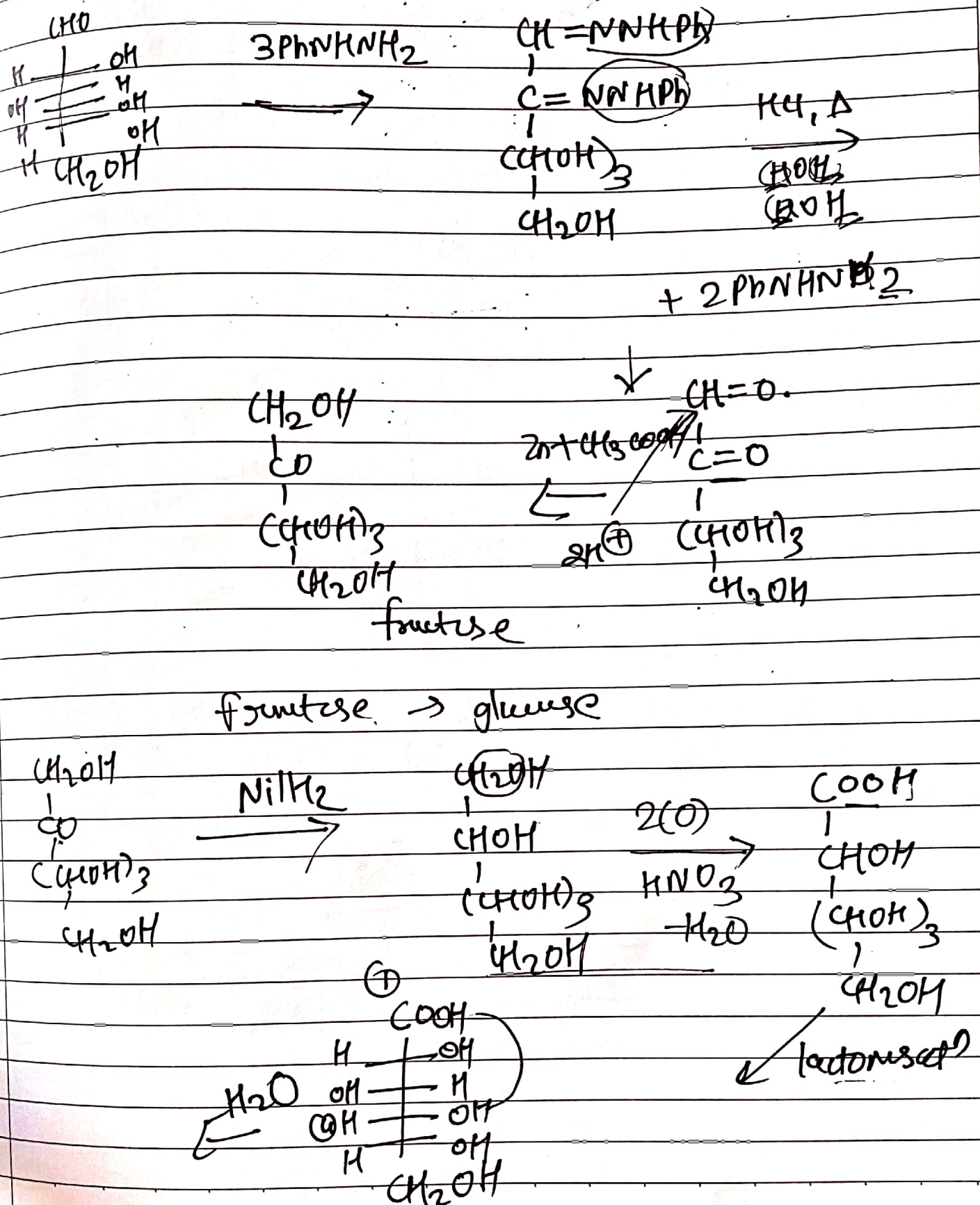
Date

Expt. No. glucose → fructose Page No.



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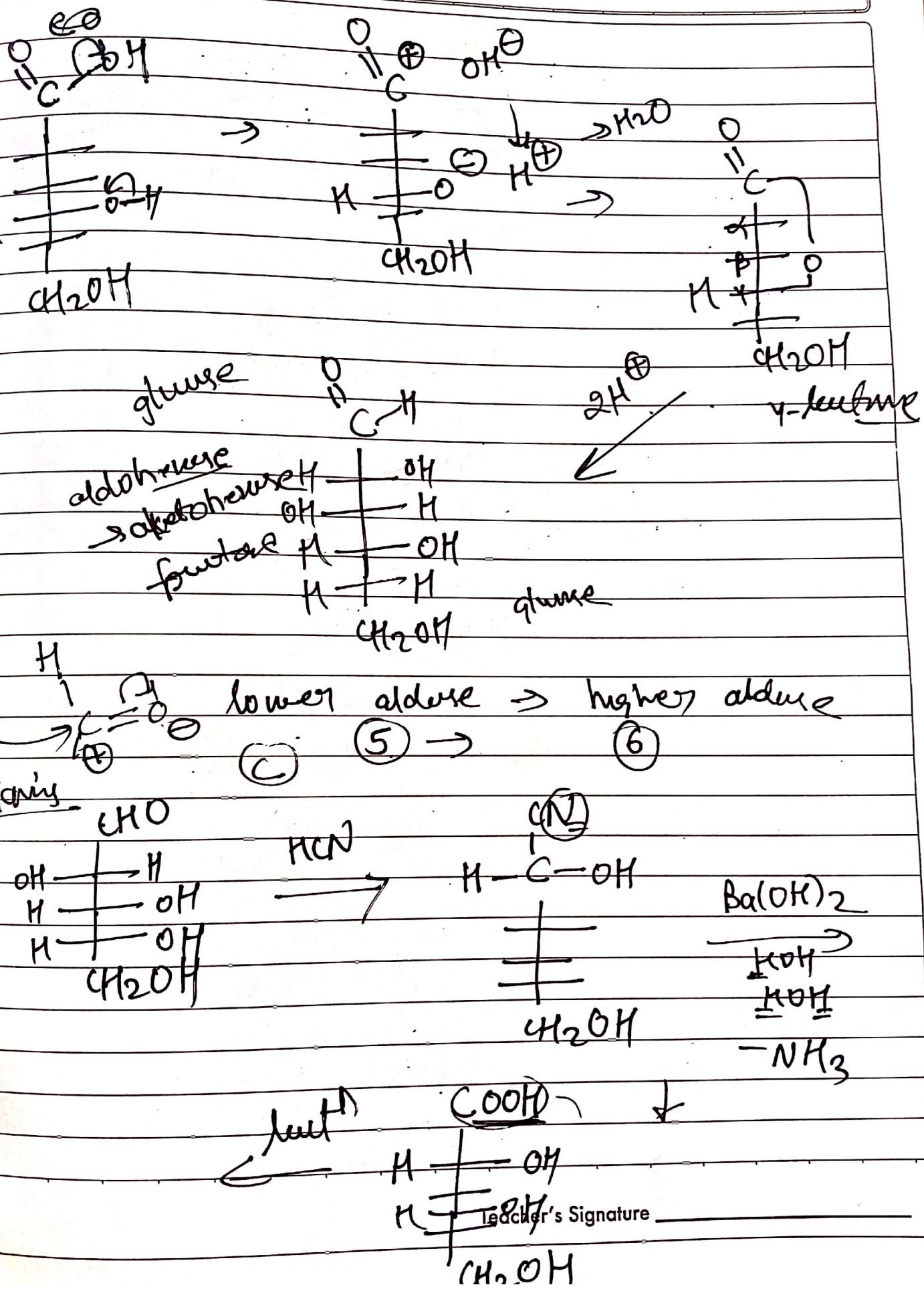
Expt. No. _____ Date _____

Page No. _____



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Date

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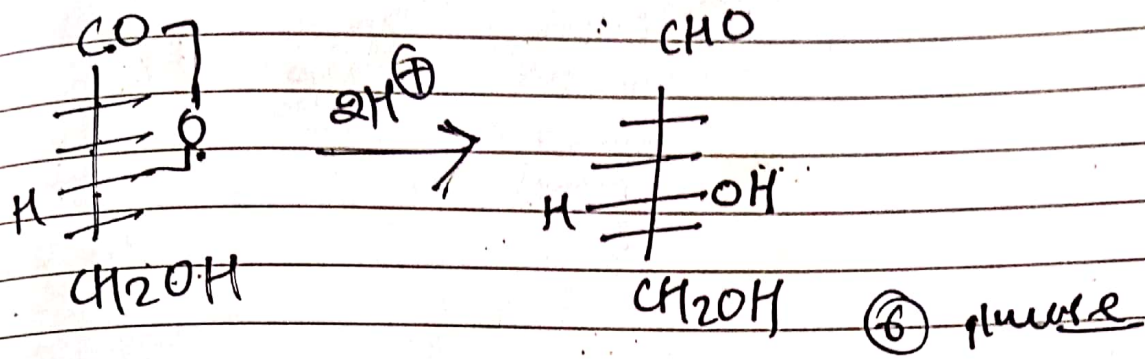
Expt. No.

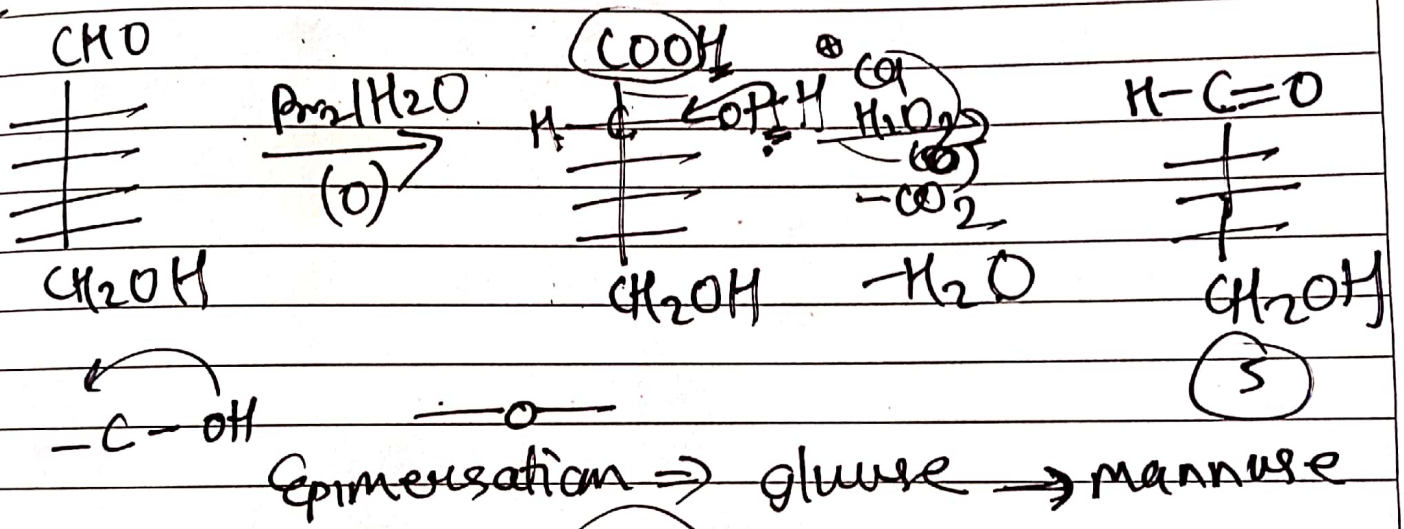


(6) glucose

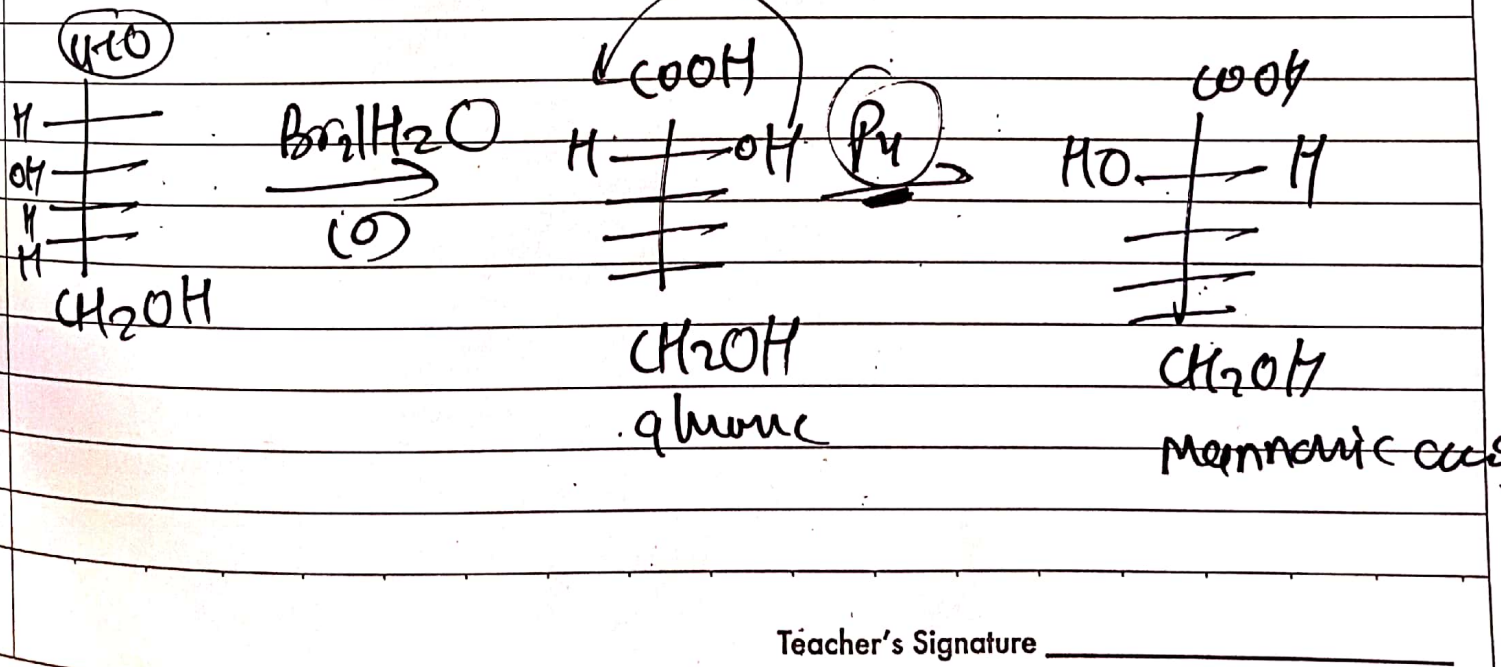
(4) 6 → 5

glucose → arabinose

Ruff's



Epimerisation ⇒ glucose → mannose



Date

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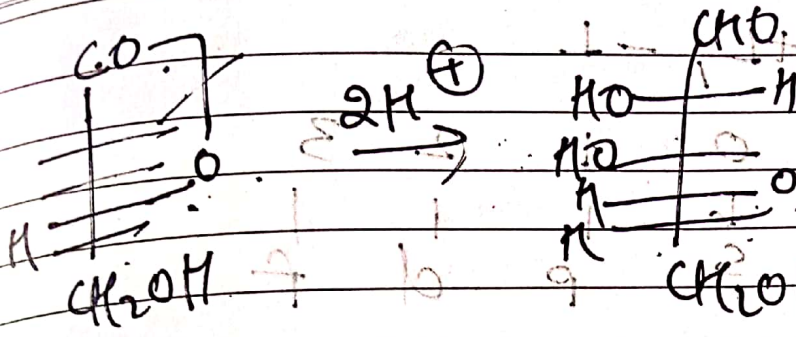
Page No.



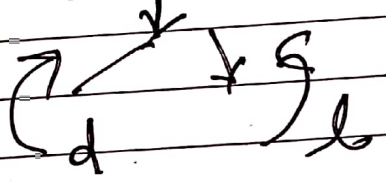
stereoisomers

atom diff

A | A — opt. inactive

B | B

↓ opti active



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Org. UNIT- II Biomolecules

Carbohydrates

* C, H, O से मिलकर
* H, O का समान अनुपात $C_x(H_2O)_y$
* चावल, आलू

$$6CO_2 + 6H_2O \xrightarrow{\text{sunlight}} C_6H_{12}O_6 + 6O_2 \uparrow$$

classification

- physical prop.
  - Sugar
    - ⇒ मीठा
    - ⇒ crystalline
    - ⇒ soluble in water
  - non-sugar
    - ⇒ tasteless
    - ⇒ insoluble in water
- chemical propert.
  - Mono
    - glucose
    - fructose
  - Oligo
    - Di
      - दो mono
      - eg- Maltose, sucrose, lactose
    - Tri
      - 3 mono
      - Raffinose
    - Poly

Poly $\xrightarrow{\text{hydrolysis}}$ many mono

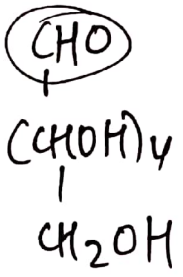
starch, amylose, cellulose

Monosaccharides

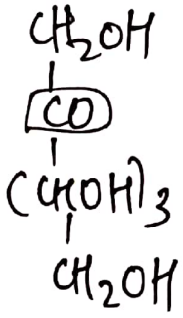
hydrolysis करने पर और अपघटित नहीं होते

total C		
3	$CH_2OH \cdot CHOH \cdot CHO$	aldotriose
4.	$CH_2OH \cdot (CHOH)_2 CHO$	aldotetrose
5	$CH_2OH (CHOH)_3 CHO$	aldopentose
6	$CH_2OH (CHOH)_4 CHO$	aldohexose (glucose)
	$CH_2OH (CHOH)_3 CO \cdot CH_2OH$	ketohexose (fructose)

glucose
Aldose, aldohexose
-CHO



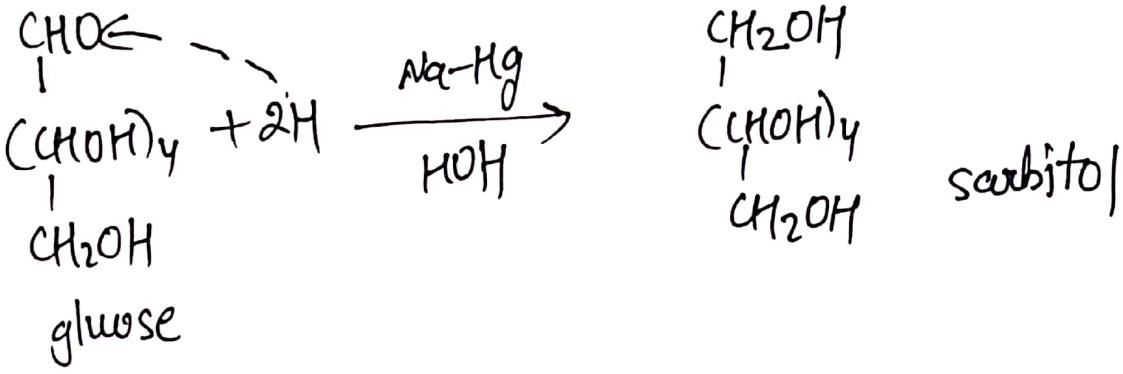
fructose
ketose, ketohexose
CO

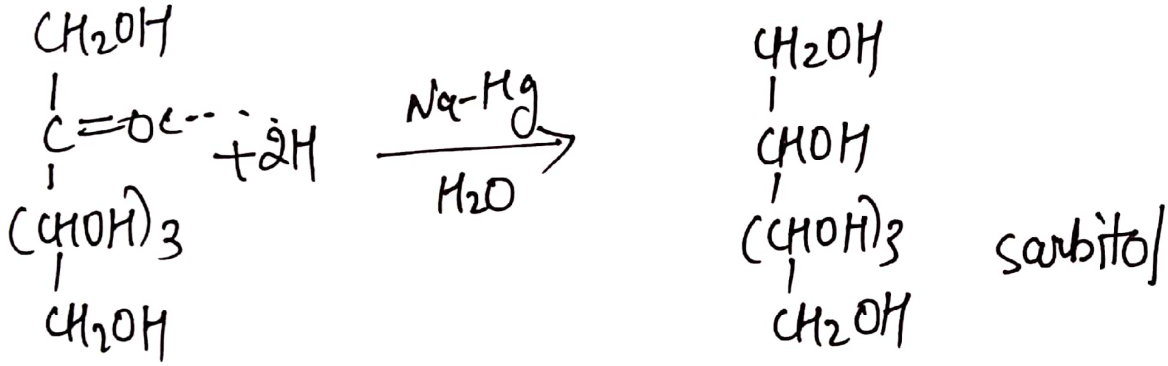


physical properties ⇒ (i) optically active (ii) colourless sweet, soluble in water, less soluble in alcohol

chemical properties ⇒

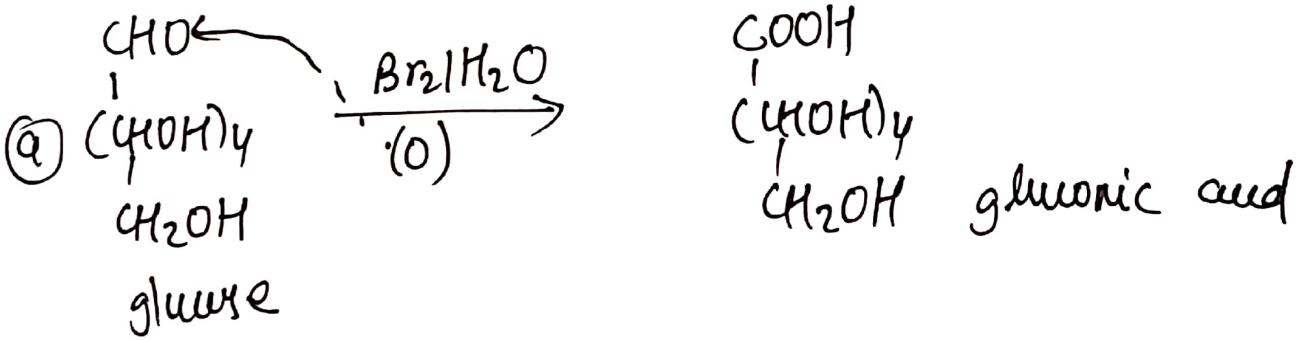
① Reduction ⇒ H का add



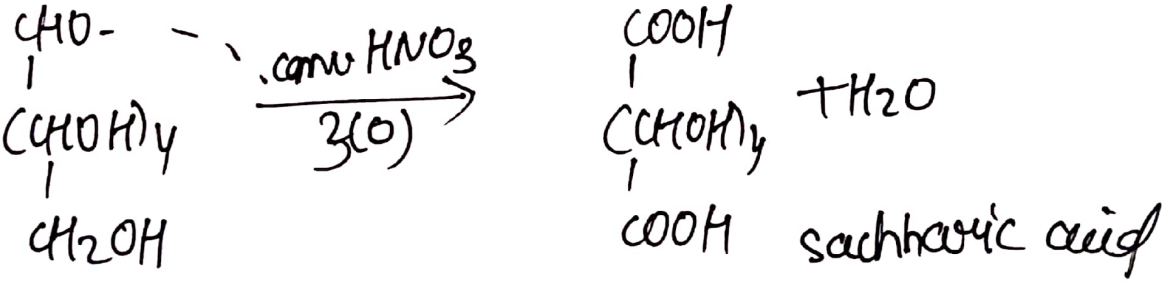


② Oxidation ⇒ O का add

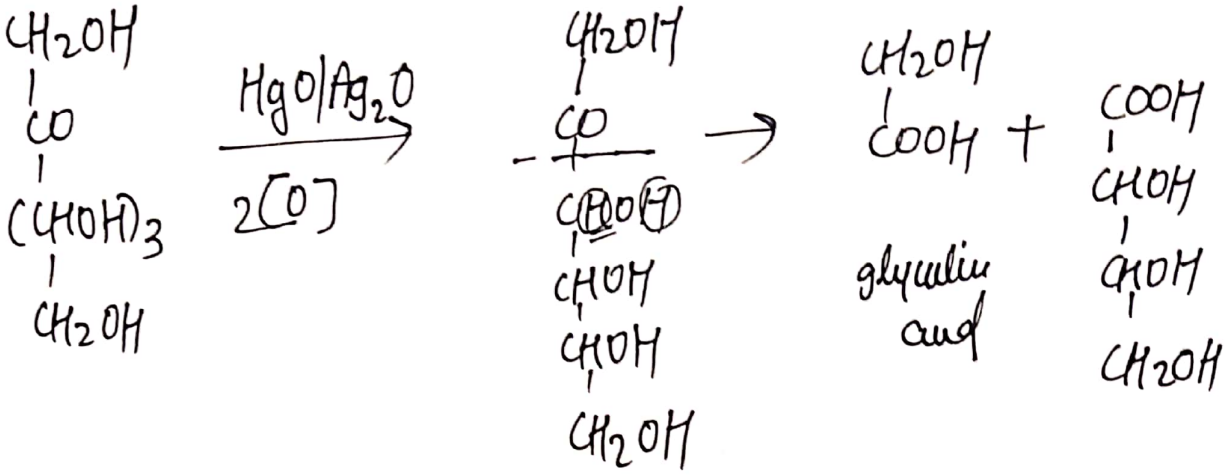
(a)

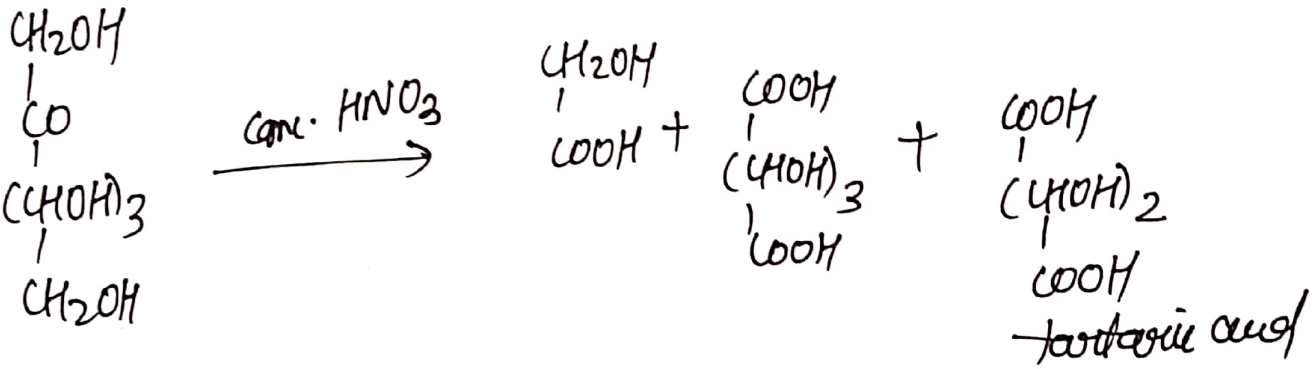


(b)



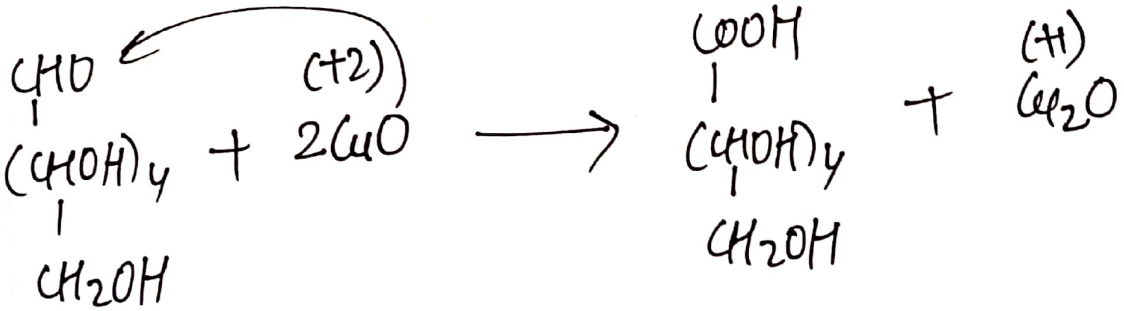
(b) fructose

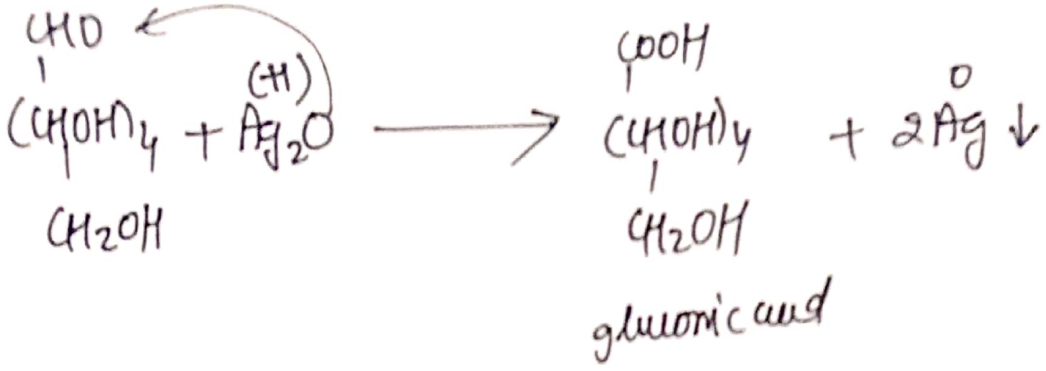




(3) Reducing nature :-

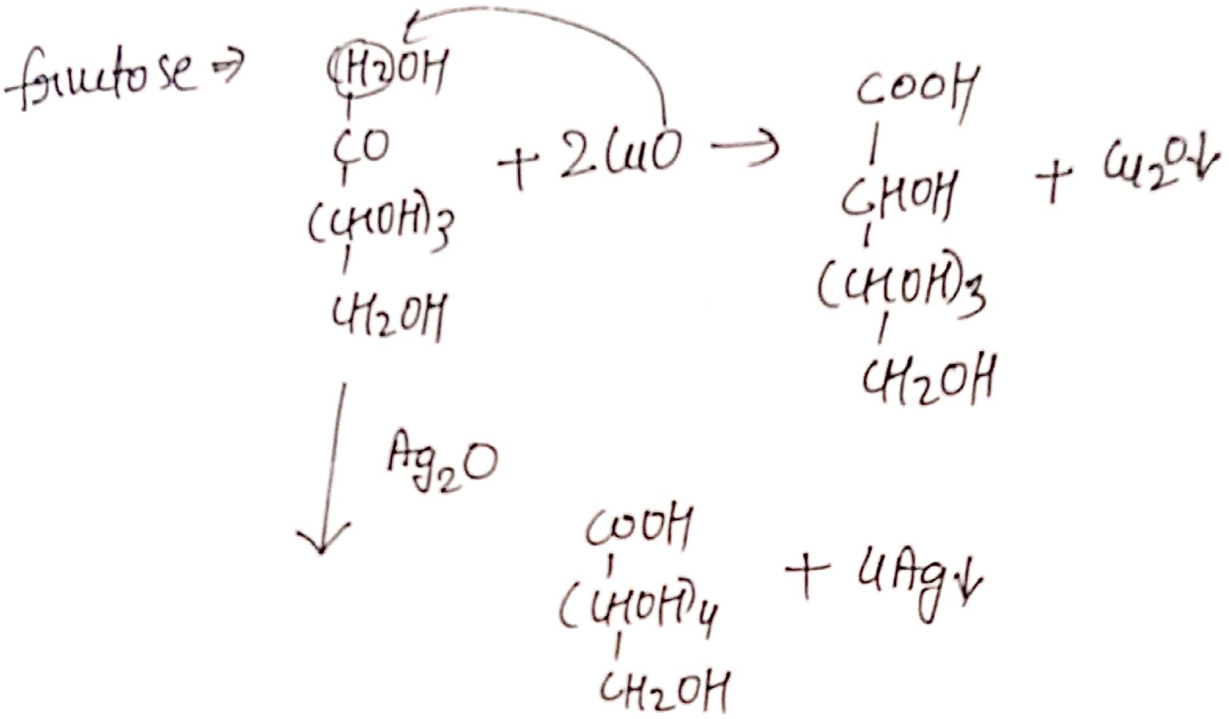
fehling soln



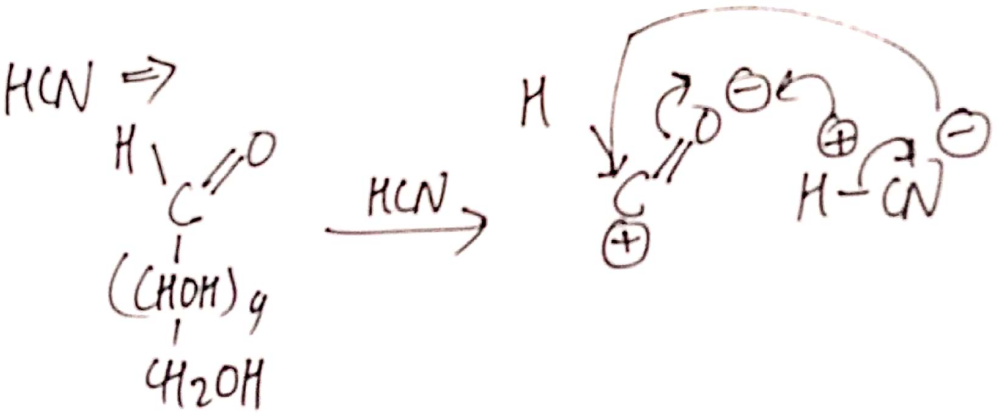


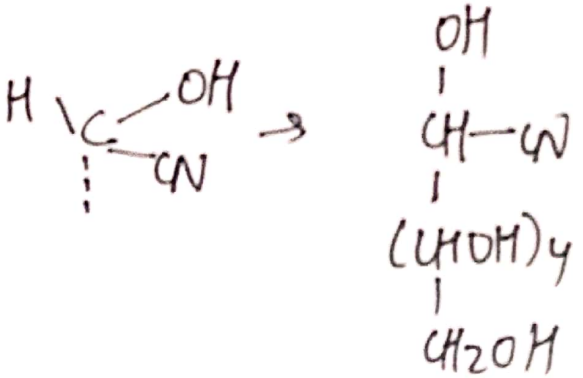
gluconic acid

fructose ⇒

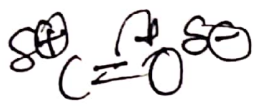


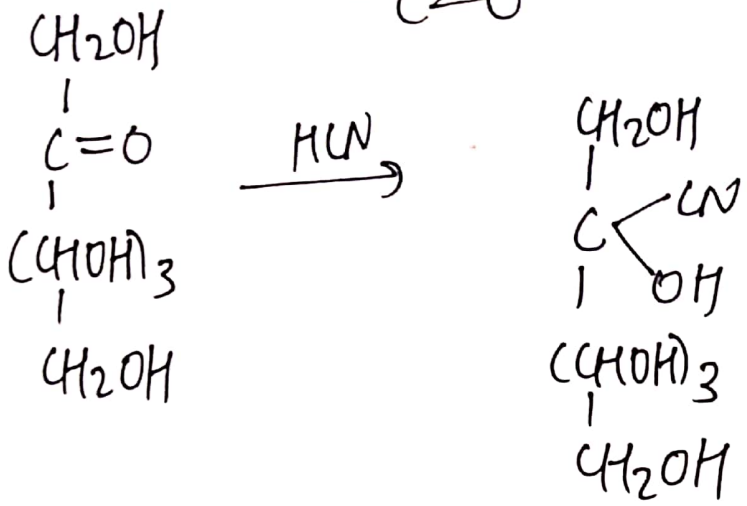
(4) HCN ⇒





glucocyanohydrin



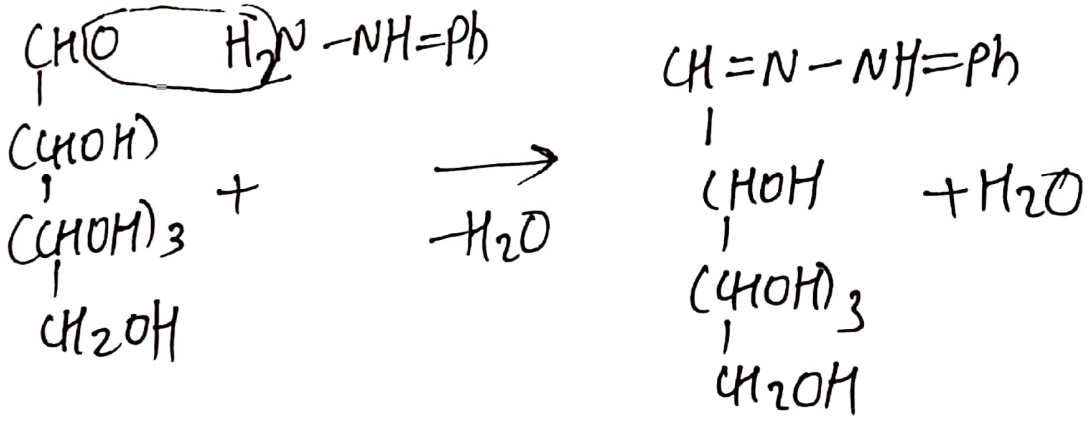


fructosecyanohydrin

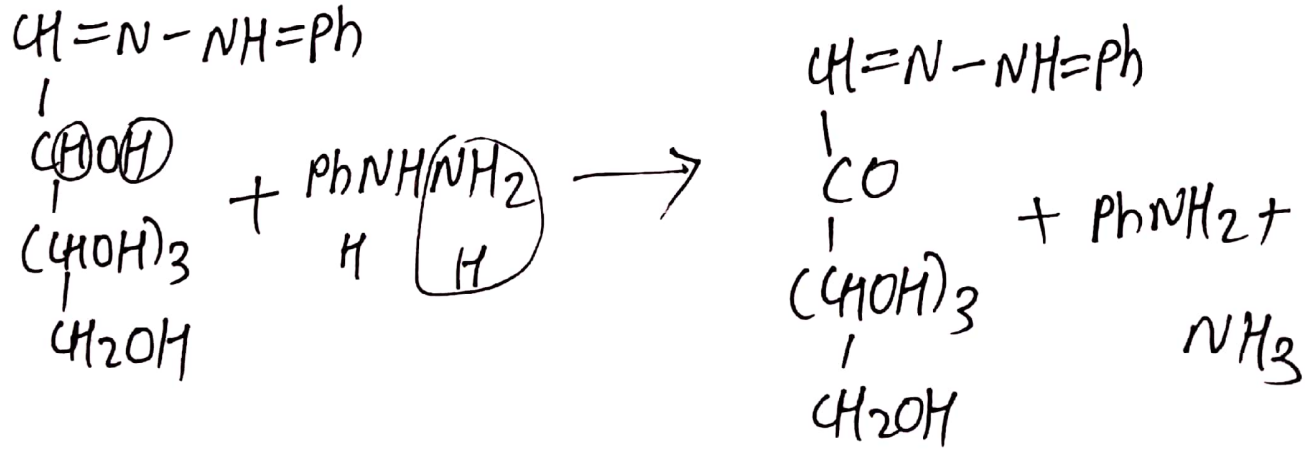
(5) hydroxyl amine ⇒

glucose + 3NH2NHPh → glucosazone + NH3 + H2O + PhNH2

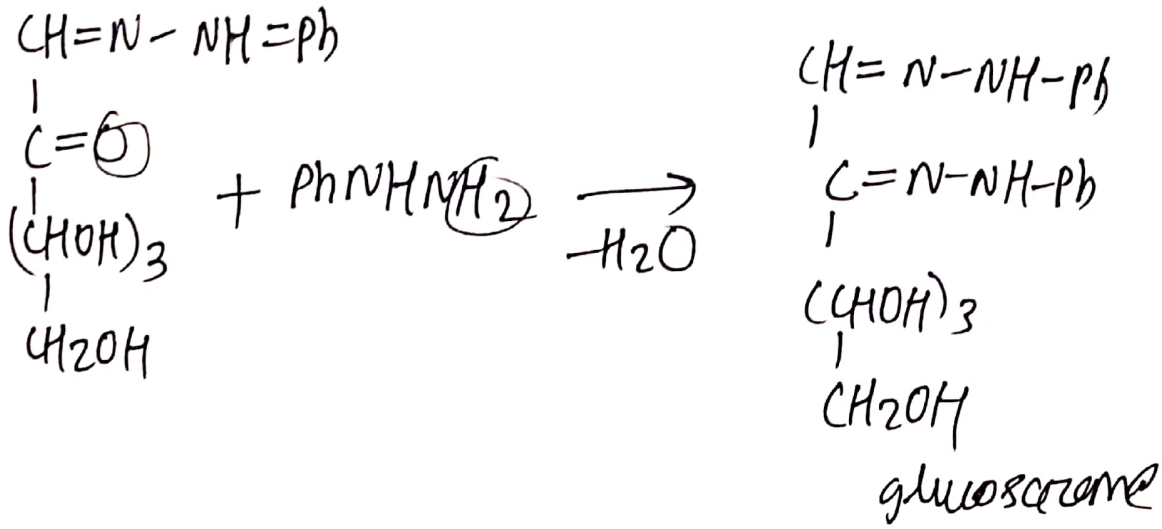
(I)



(II)



(11)



glucosazone

Jaisal

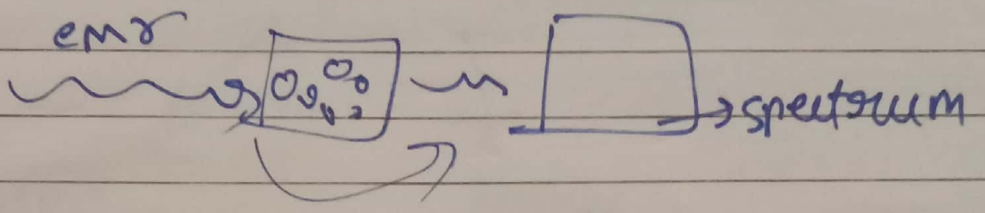
BSc III

Date

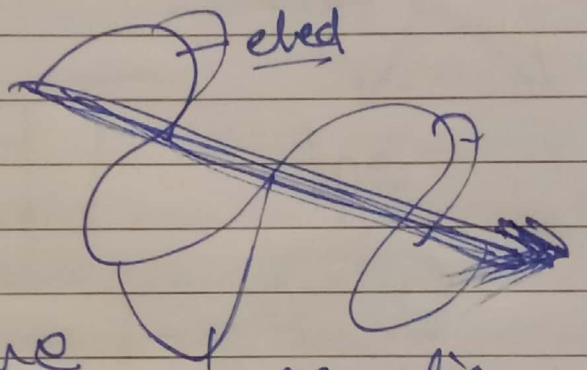
Expt. No. phy. chem. unit unit-3

Page No.

spectroscopy - I

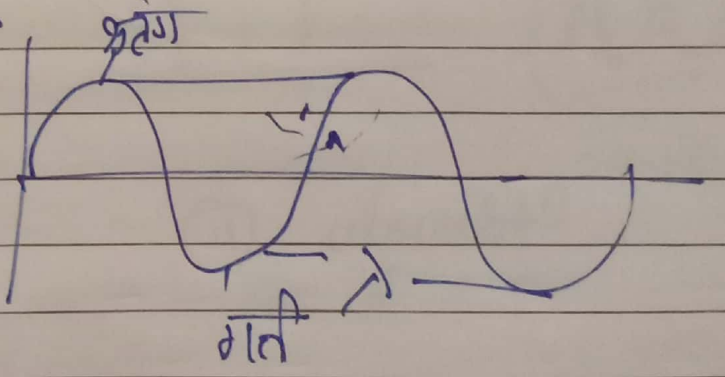


emr ⇒



particle wave

(I) λ →



(II) wave number ⇒ $\frac{1}{cm}$ →

$$\bar{\upsilon} = \frac{1}{\lambda}$$

(III) frequency ⇒ $\frac{1}{sec}$ Hz.

$\upsilon = c\bar{\upsilon}$ $\upsilon = \frac{c}{\lambda} = c \times \frac{1}{\lambda} = c\bar{\upsilon}$

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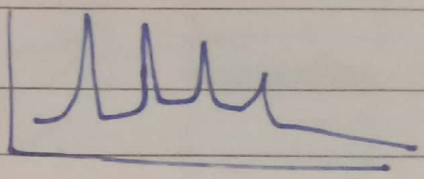
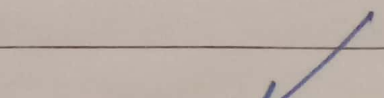
spectrum ⇒





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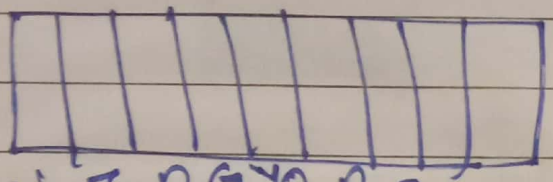
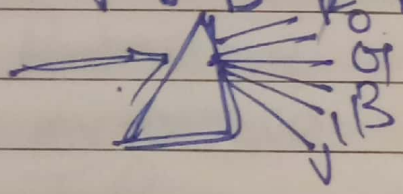
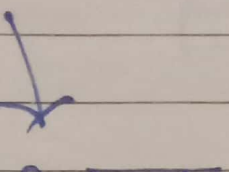


V I B G Y O R





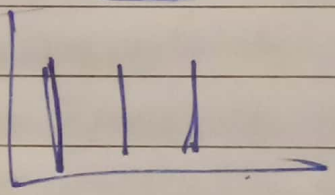
उत्सर्जन

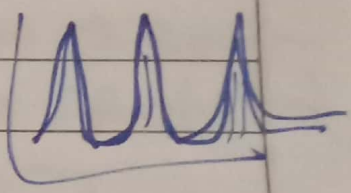
line

band

atom

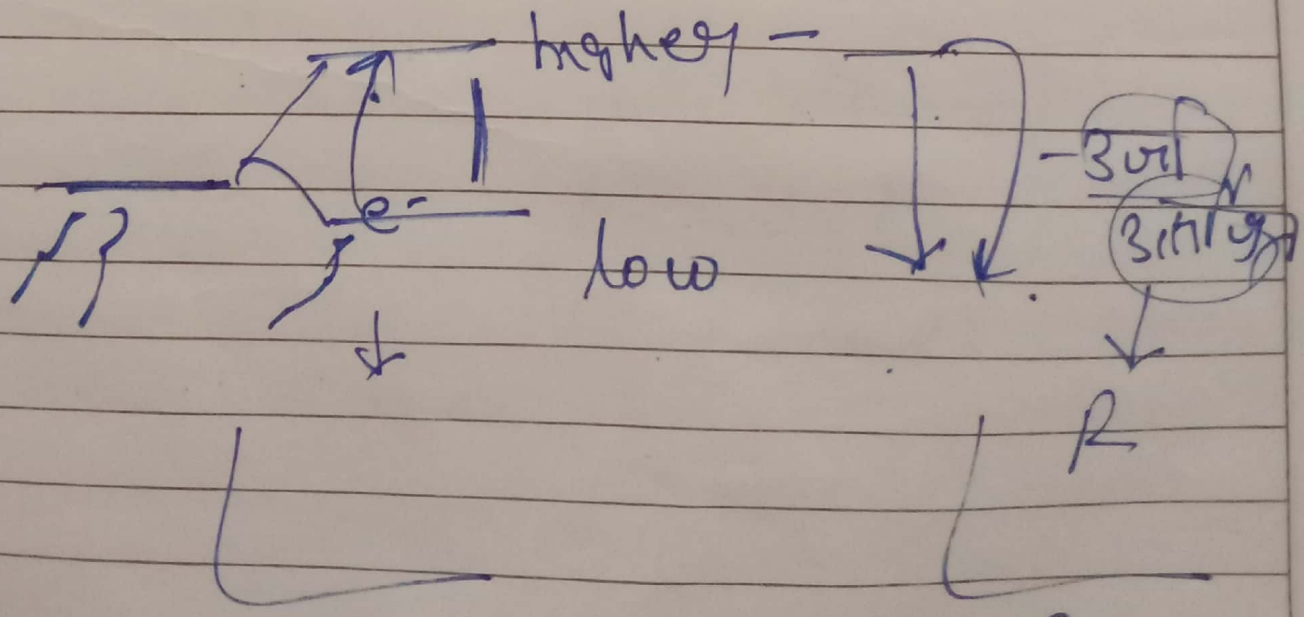
molecule





(i) emission

(ii) absorption



Teacher's Signature _____

Jaisri

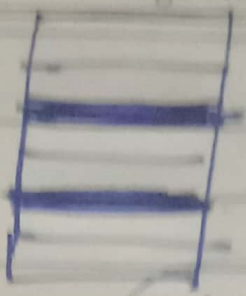
Date

Expt. No.

Page No.

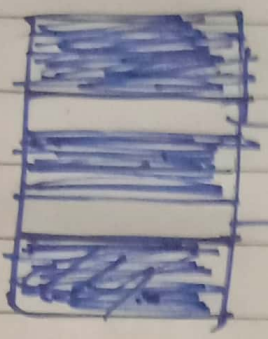
Pt (NaCl) → (Na → Na atom)

(2)



Double line

(absorption)



yellow

yellow

emission spectrum

visible (range)

λ (↓) & ν (↑)

Radiowave,	$3\times10^{13} - 3\times10^{9}$	nuclear → nmr
microwave	$3\times10^{9} - 3\times10^{6}$	→ rotation → spec
IR	$3\times10^{5} - 8000$	→ IR → IR sp(vib
visible	8000 – 4000	→ colour (e⁻)
UV	4000 – 150	→
X-ray	150 – 0.1	
γ-ray	0.1 – 0.01	
cosmic ray	0.01 – 0.0001	

λ (↓) ν (↑) E (↑)

$E = h\nu$

example

Date

Page No.

Born- Oppenheimer Approximation

☆ molecules

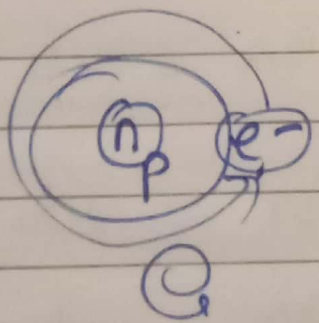
$$\varepsilon_{total} = \varepsilon_{vib} + \varepsilon_{rot.} + \varepsilon_{tr} + \varepsilon_{ele}$$

ε_{tr} → negligible

$$\varepsilon_{total} = \varepsilon_{vib} + \varepsilon_{rot} + \varepsilon_{ele.}$$

☆ atom → molecule

spectra → complex



e- mass >> n mass

e भार <<< n भार

नगण्य

negligible

Teacher's Signature

B.Sc. III

$CH_3-\overset{O}{\overset{\|}{C}}-O-H$

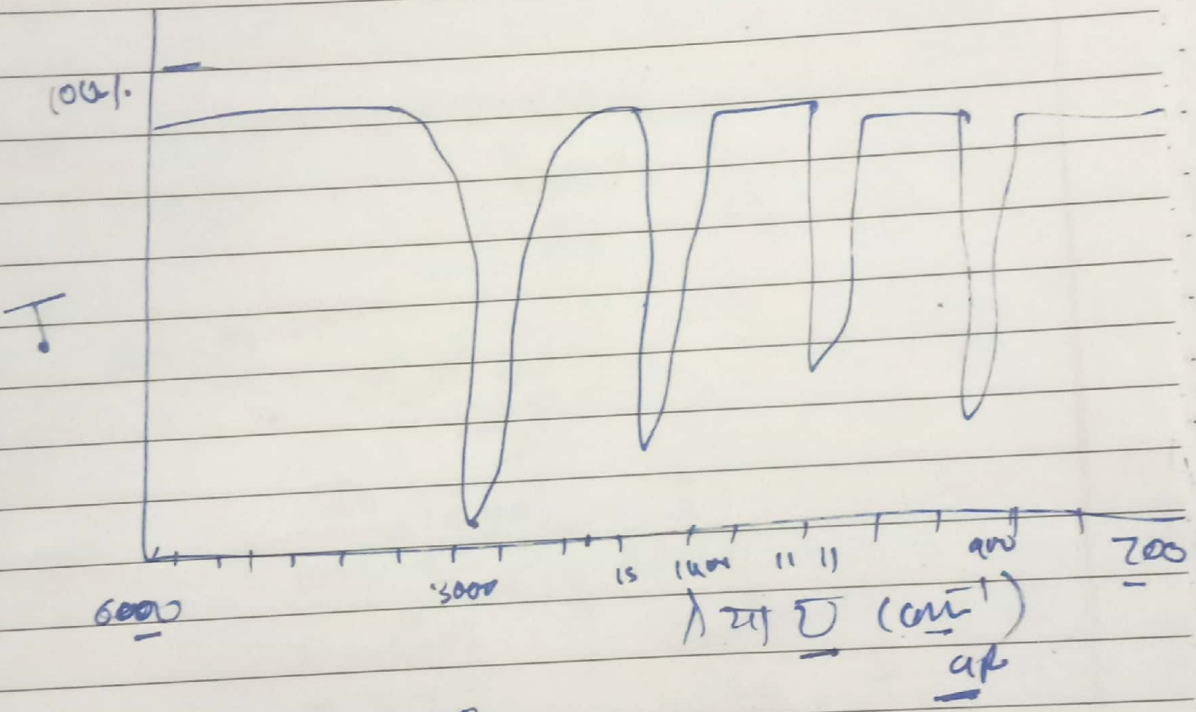
A

(I) O—H — 3030 cm^{-1}

(II) >C=O — C=O — 1710

(III) C—O → 1280

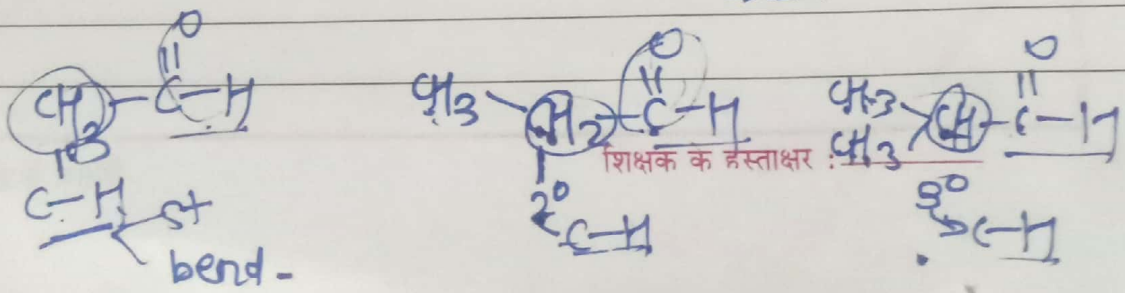
(IV) O—H (bending) → 945 cm^{-1}



qR

functional
1400 - 4000 cm^{-1}
—OH, —CHO, R—O—R, COOH
>C=O, RCOOR

fingerprint region
600 - 1400 cm^{-1}
— C—H st, bend
O—H
IMP.



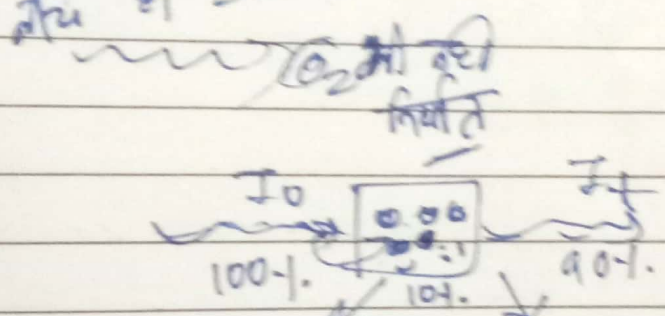
शिक्षक के हस्ताक्षर :

UV/visible spectroscopy

UV ——— Sp

UV
200 - 400 nm
10 - 200 nm
vacuum UV
200 - 400 nm
near UV

visible
400 - 800 nm
coloured compound



absorbed
$I_0 > I_t$

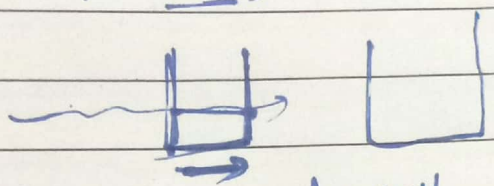
abs ⊗
$I_0 = I_t$

$$A = \frac{I_0}{I} \quad \text{or} \quad T = \frac{1}{A} = \frac{I}{I_0}$$

$$A = \log\left(\frac{1}{T}\right)$$

~~Theory~~ (=> Laws

Lambert's



sample cell

abs^n of hν ~~of~~ path length

$A \propto l$ — (I)

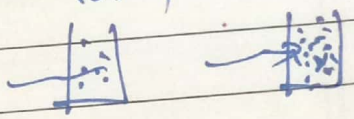
Beer's

$A \propto C$ — (II)

sample

1mg + 10ml

2mg + 10ml



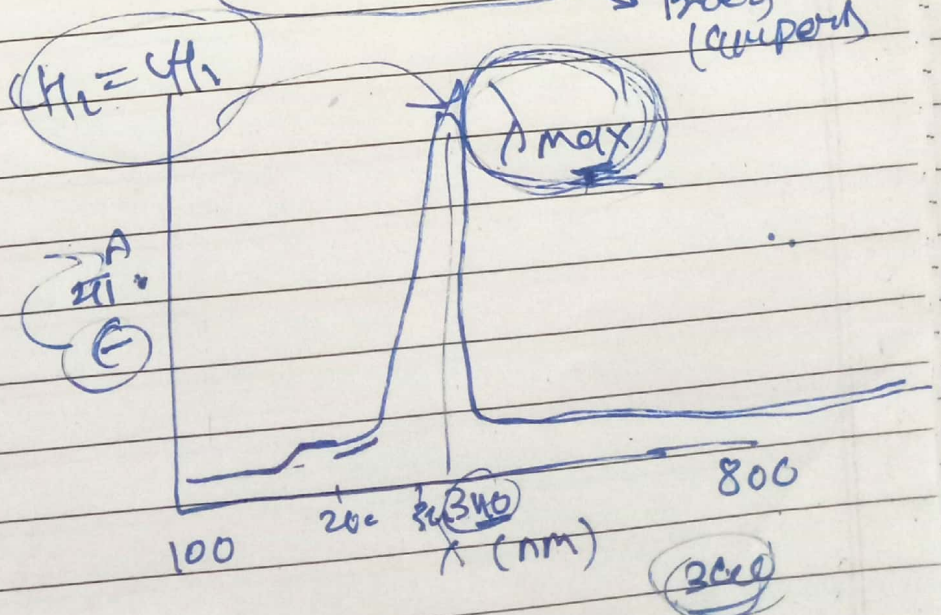
(I) & (II)

$A \propto C l$

$A = \epsilon C l$

(Molar absorbtivity coefficient)

$\log \frac{I_0}{I} = \epsilon C l$ → Beer's Lambert's

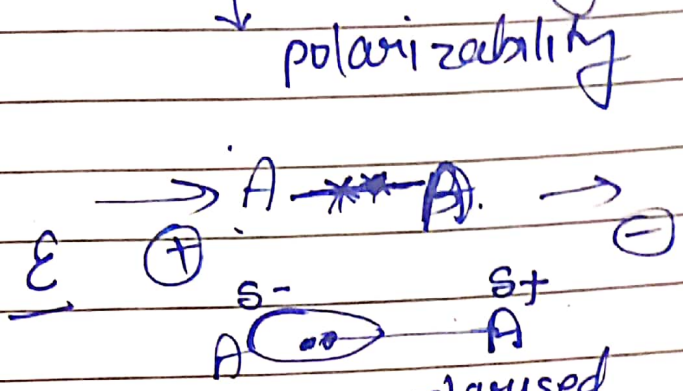


शिक्षक के हस्ताक्षर :

B.Sc. III

classical theory

polarizability

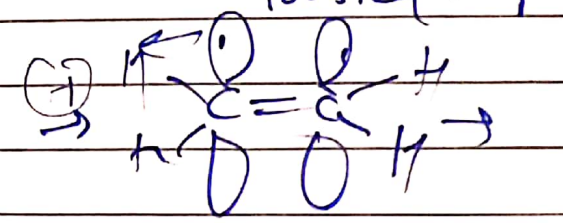


polarisation

polarizability — (I) applied E → ⊕ ⊖

(II) polarizability of molecule

- Hard
  - σ hard
  - H_2O, CH_4
  - ⊕ → pol^n not easily
  - ⊖
- Soft
  - pol^n easily
  - π bond
  - C_6H_6, C_2H_4
  - loosely held



$\mu \propto E$

induced dm — of applied

$\mu = \alpha E$

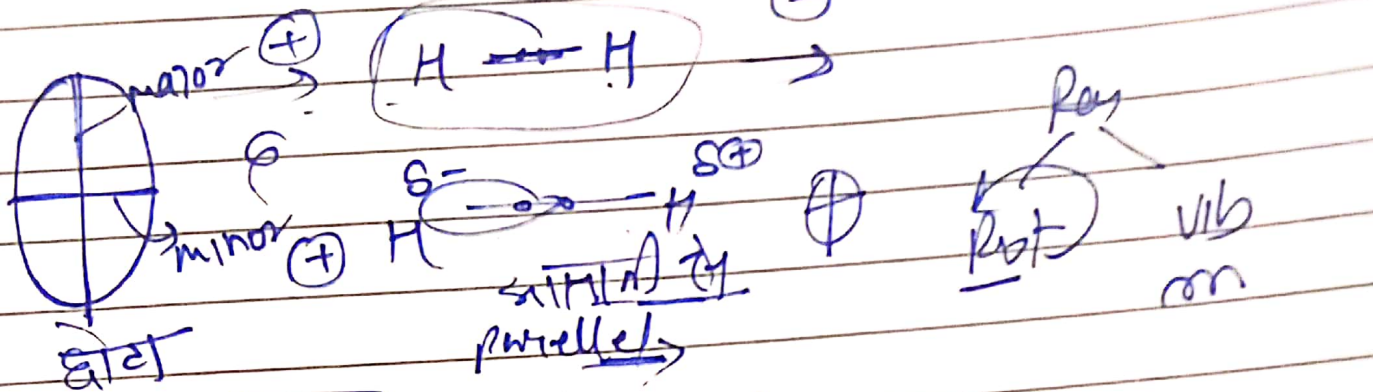
α → polarizability

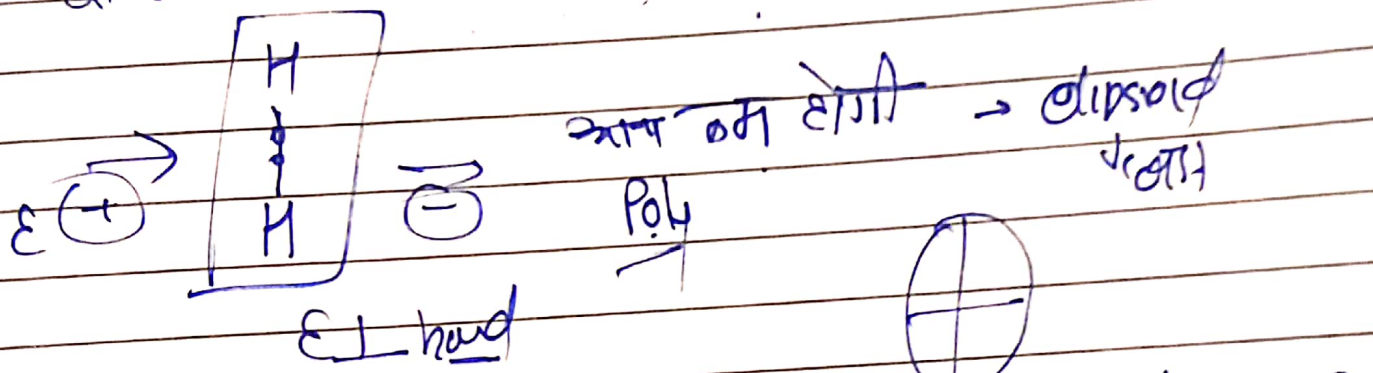
or Soft < Hard

Remark

Teacher's Sign.

polarizability ellipsoid





→ ellipsoid

change

Raman

$\mu \propto \alpha$, $\mu = \alpha E$

$F = f_0 \sin 2\pi\nu t$

$E \Rightarrow E_0$

ele. field

Static

Oscillating

ν → frequency

$$\alpha = \alpha_0 + \beta \sin 2\pi\nu_{vib} t$$

eq. polarizability

$\alpha = 0$

3 vib

$$\mu = (\alpha_0 + \beta \sin 2\pi\nu t) \cdot f_0 \sin 2\pi\nu t$$

α - molecules

electric field + emr

Remark

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Date
Page

$\beta = 0$ (change in polarizability during vib/Rot)

↓ Raman inactive

↓

Rayleigh

$\mu = (\alpha_0 + 0) \cdot E_0 \sin 2\pi\nu t$

$\mu = \alpha_0 \cdot E_0 \sin 2\pi\nu t$

↓

microwave → permanent μ

IR → μ changes during vib

Raman → polarizability change during vib or Rot

pure Rot. Raman

↓

anisotropy

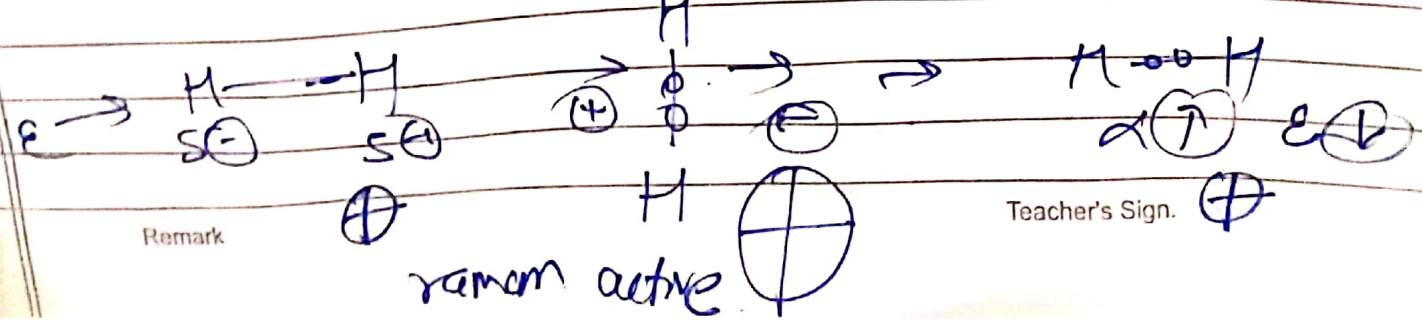
H_2 - Rot inactive

↓ Raman active

vib. Raman

↓

α change vib^n



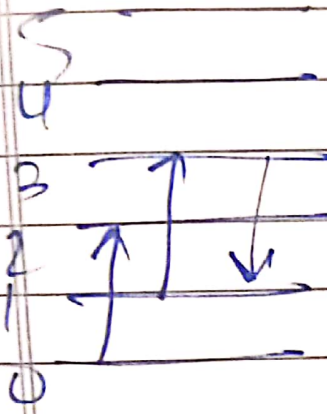
raman active

Remark

Teacher's Sign.

Rot Raman rule

$\Delta J = 0, \pm 2$



$J = J \rightarrow J = (J+2)$
ground excited

ΔE_J या $\bar{\upsilon}_J = E_{(J+2)} - E_J$

E_J या $\bar{\upsilon} = BJ(J+1)\ cm^{-1}$

$= B(J+2)(J+2+1) - BJ(J+1)$

$= B(J+2)(J+3) - BJ(J+1)$

$= B(J^2+3J+2J+6) - B(J^2+J)$

$= B(J^2+5J+6-J^2-J)$

$= B(6+4J)\ cm^{-1}$

$\Delta E_J = 2B(3+2J)\ cm^{-1}$ (Stokes)

$-2B(2J+3)$

$\Delta\bar{\upsilon} = B(4J+6)$

$J=0 \rightarrow B(4\times0+6) = 6B$

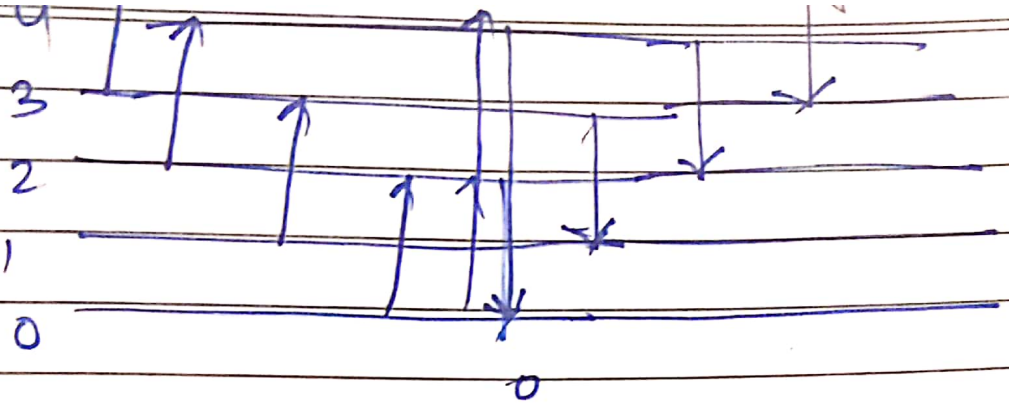
$J=1 \rightarrow B(4\times1+6) = 10B$

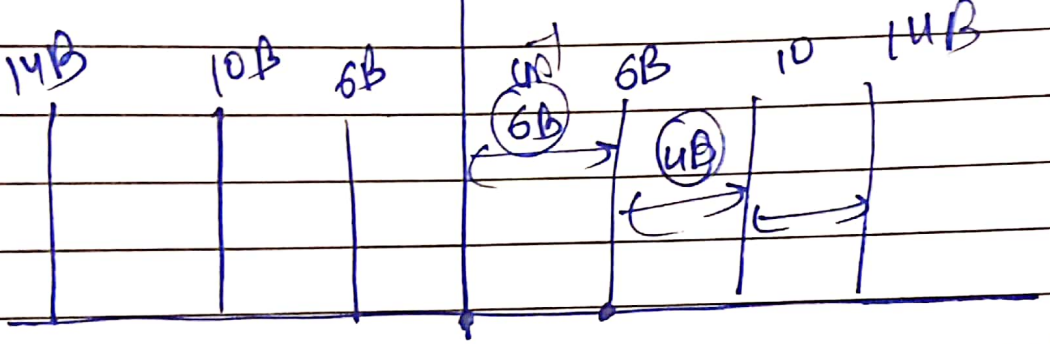
$J=2 \rightarrow B(4\times2+6) = 14B$ → $4B\ cm^{-1}$

=

Remark

Teacher's Sign.





Rayleigh

CO_2

Sym stret

⊕ घोटा

Asym St.

Remark

Raman active

same direction

same magnitude → Raman inactive

Teacher's Sign.

BSC III phys. chem.

UNIT - I

Elementary Quantum mechanics - I

mechanics

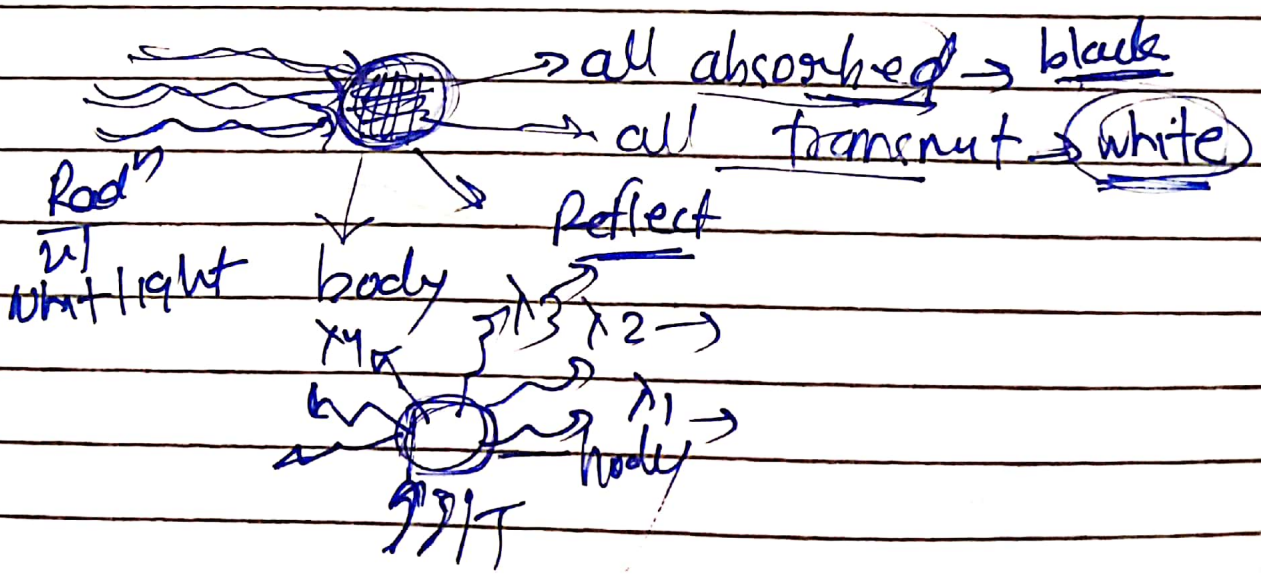
light

Quantum → practical → microscopic

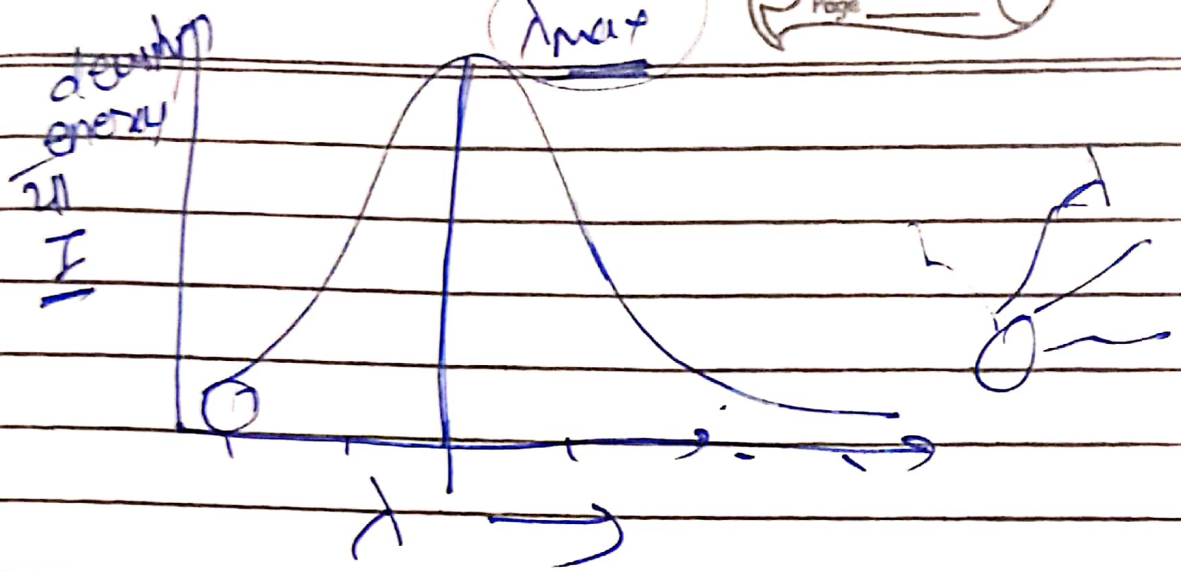
classical mechanics → wave

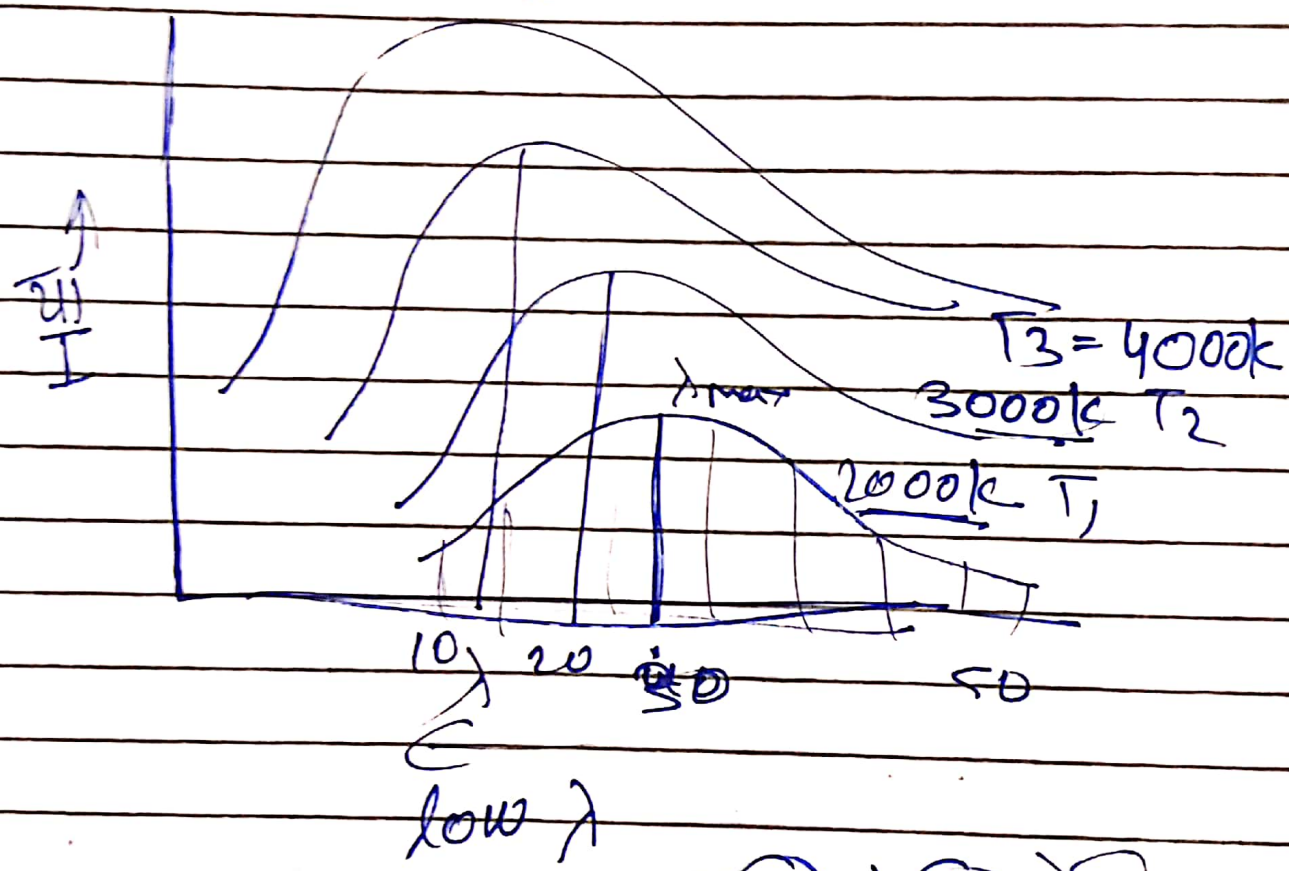
(P, N, e —

Black body Rad^n



Teacher's Signature .....





low λ

T ↑ λ ↓ छोटा

T ↑ λ ↓ ε ↑

$\varepsilon = h\nu$, $\varepsilon = \frac{hc}{\lambda}$

$\varepsilon \propto \frac{1}{\lambda}$

$\lambda \rightarrow T$

λ ↓ T ↑

λ ↑ T ↓

(i) Stephens - boltzmann law

$\rightsquigarrow \varepsilon \propto T^4$ $T \uparrow \varepsilon \uparrow$

$\varepsilon = \sigma T^4$

σ → const

(ii) wein - law $\Rightarrow$ $\lambda \propto \frac{1}{T}$

$\lambda = \frac{b}{T}$ wein const

$T \uparrow \lambda \downarrow \varepsilon \uparrow$

planks law

$\varepsilon = h\nu$

(i) ~~~~ wave

oooooooo → quanta / photon

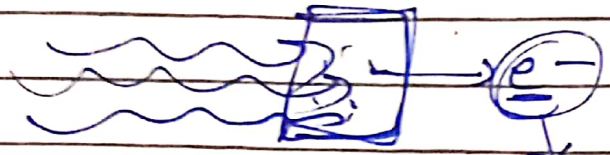
(ii) $\varepsilon = h\nu$ $h\nu$ $2h\nu$ $3h\nu$

$\varepsilon = h\nu$ fre

$\varepsilon \propto \nu$

Teacher's Signature .....

photoelectric effect



i) Threshold freq ν_0

ii) e^- – photo e^-

iii) Metal → Alkaline metal → s block ν_0 कम, s → e^- देती है, s → (+) charge

iv) ~ Radⁿ की उपस्थिति

e^- को बाहर निकलने के लिए → $E_0 = h\nu_0$

गतिज ऊर्जा देने के लिए → e^- → $\frac{1}{2}mv^2$ (KE)

कुल ऊर्जा = देहली ऊर्जा + गतिज ऊर्जा

$E = E_0 + KE$

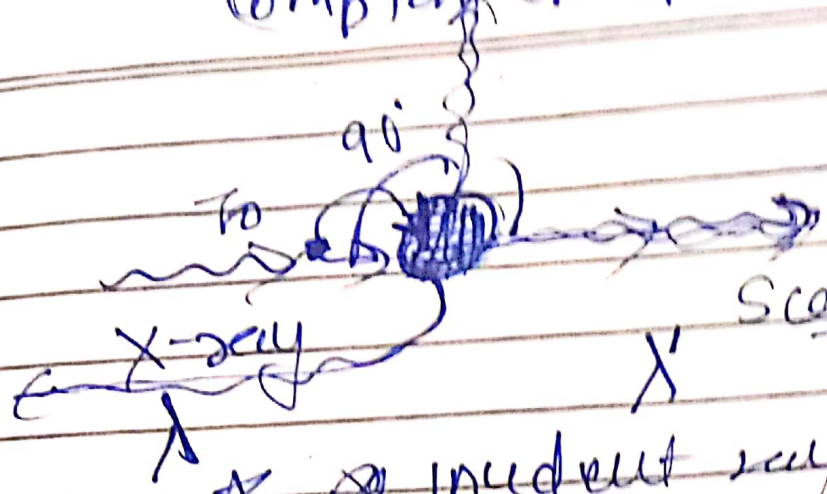
$h\nu = h\nu_0 + \frac{1}{2}mv^2$

$(h\nu - h\nu_0) = \frac{1}{2}mv^2$

$h(\nu - \nu_0) = \frac{1}{2}mv^2$

Teacher's Signature .....

Compton effect



* ~~*~~ Incident ray → ε hν
ε ↓ λ ↑

* θ depend

* $\Delta\lambda = \lambda - \lambda'$
↳ Compton displacement

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

(3) → (1) $\theta = 0°$

$$\Delta\lambda = \frac{h}{mc}(1-\cos 0°)$$

$(\cos 0° = 1)$

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

$$\boxed{\Delta\lambda = 0}$$

(II) $\theta = 90^\circ$

$$\Delta\lambda = \frac{h}{mc}(1 - \cos 90^\circ)$$

$(\cos 90 = 0)$

$$\Delta\lambda = \frac{h}{mc}(1 - \cos 90^\circ)$$

$$\Delta\lambda = \frac{h}{mc}(1 - 0)$$

$$\Delta\lambda = \frac{h}{mc} = \frac{6.625 \times 10^{-27}}{9.10 \times 10^{-28} \times 3 \times 10^{10}}$$

$$\Delta\lambda = 0.0242 \text{ Å}$$

(III) $\theta = 180^\circ$

$$\Delta\lambda = \frac{h}{mc}(1 - \cos 180^\circ)$$

$$= \frac{h}{mc}(1 - (-1)) \qquad (\cos 180^\circ = -1)$$

$$= \frac{h}{mc} \times 2$$

$$\Delta\lambda = 0.0242 \times 2$$

$$= 0.0484 \text{ Å}$$

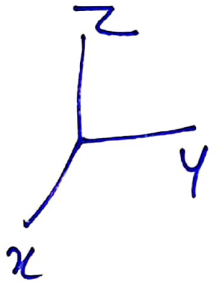
Teacher's Signature .....

Degrees of freedom

total degrees of fr = 3N → (no. of atom)

- Trans.
- vib.
- rot.

(1) Translational d of fredom ⇒



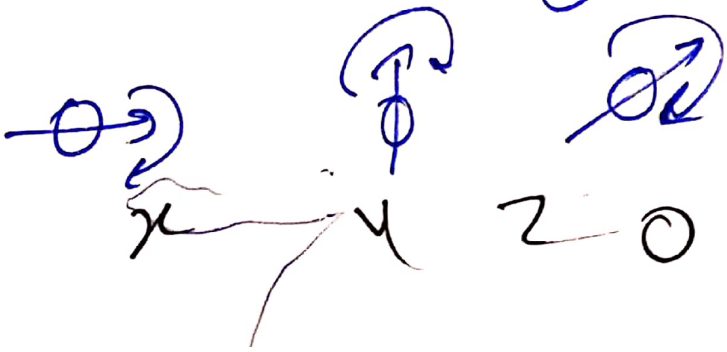
monoatomic → He, Ar, Ne, O

diatomic → H_2, N_2 OO

polyatomic → HCl, CO_2

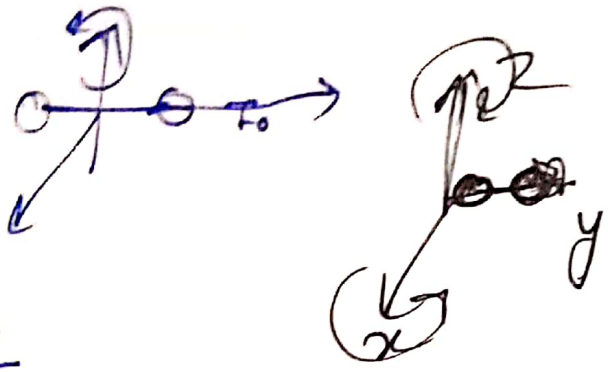
all के लिए = 3

Rotational d. of fr ⇒ (a) mono → He, Ne



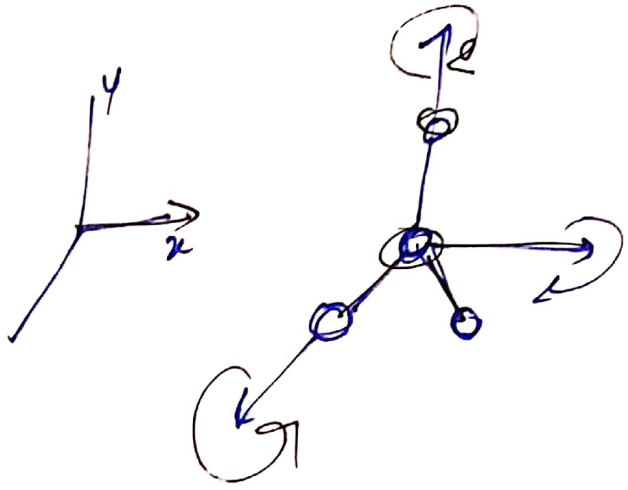
= 3

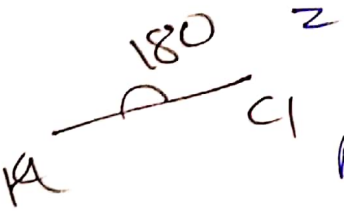
(b) diatomic → (linear)



R = 2

(c) polyatomic → (non-linear)





R dof = 3

(3) Vibrational d of fr ⇒

tra + vib + Rot = 3N

(linear) sp

CO_2, CO, H_2, HCl

tr. + Rot. + vib = 3N

3 + 2 + vib = 3N

(vib = 3N − 5)

dof

non-linear

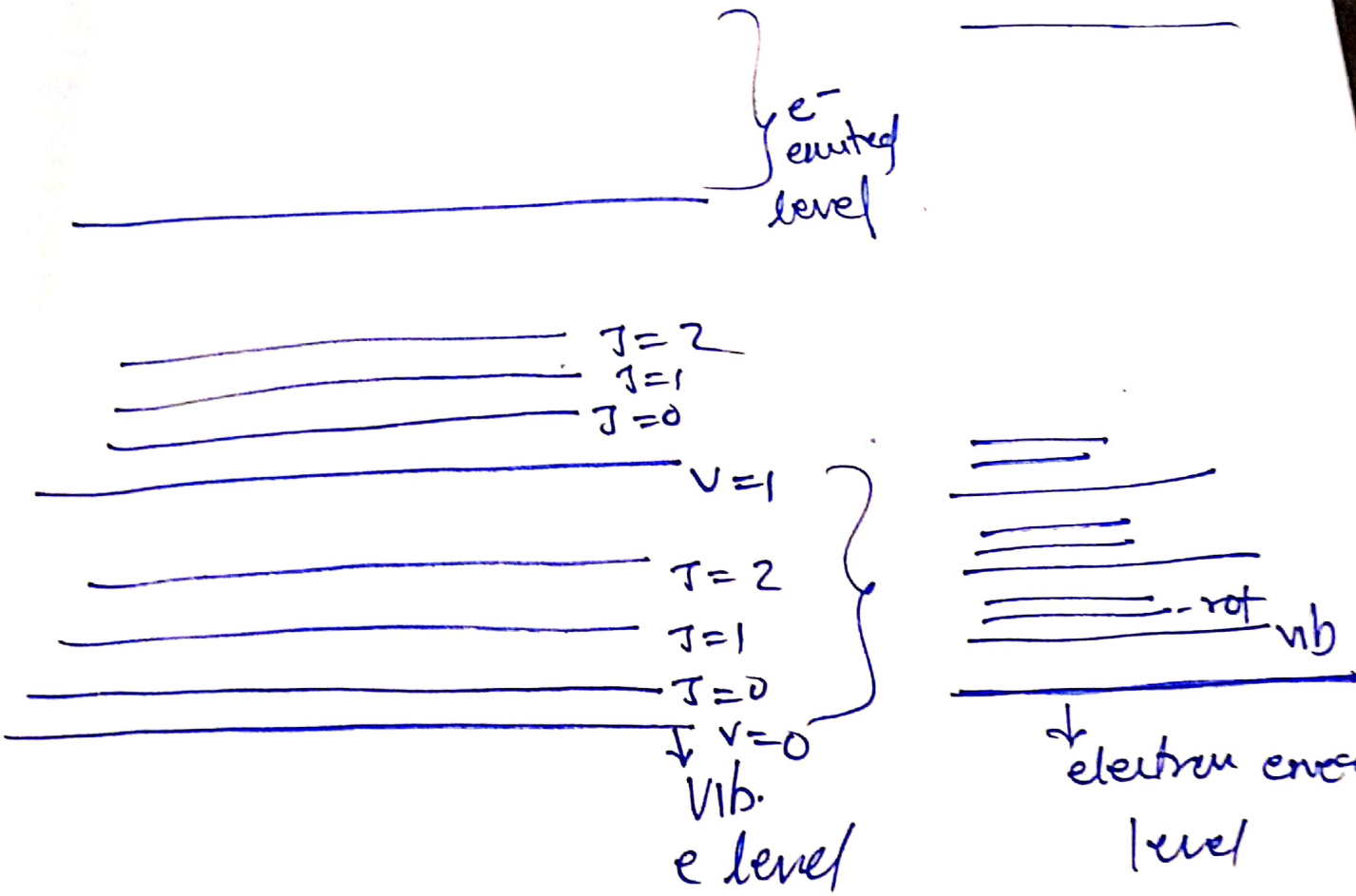
C_6H_6, H_2O, SO_2, CH_3Cl

tr + Rot. + vib. = 3N

3 + 3 + vib = 3N

(vib = 3N − 6)

Different energy levels



Rotational Spectrum

⇒ Microwave radⁿ → $3\times10^9 - 3\times10^6$ Å

⇒ Sample - gaseous

⇒ all molecules are not active

↙ ↘

Microwave active

↓

permanent dipole moment

HCl, CH_3Cl

Microwave inactive

↓

no dipole moment

↓

H_2, O_2, N_2

⇒

BSc III

CO, CO_2, C_6H_6, SO_2

CO

Sp $C \equiv O$

(3N-5)

$3\times2-5$

$6-5$

$=1$

Vib

CO_2

$O \overset{\pi}{\underset{\sigma}{\equiv}} C \overset{\pi}{\underset{\sigma}{=}} O$ $2\sigma = sp$

$x = x + 2(-2)$

$= x - 4$

$+4 = x$

CO_2

SO_2

$x + (-4) = 0$

$x = +4$

$6S - 4e^-$

$O \rightarrow 5$

lp+bp

$0 + 2 = 2$ sp

linear

3N-5

$3\times3-5$

$9-5$

$=4$

lp+bp = 1+2 = 3

sp^2

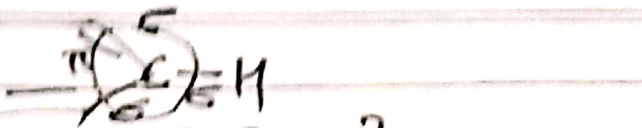
3N-6

$= 3\times3-6$

$= 9-6 = 3$

Teacher's Signature.....

Eg

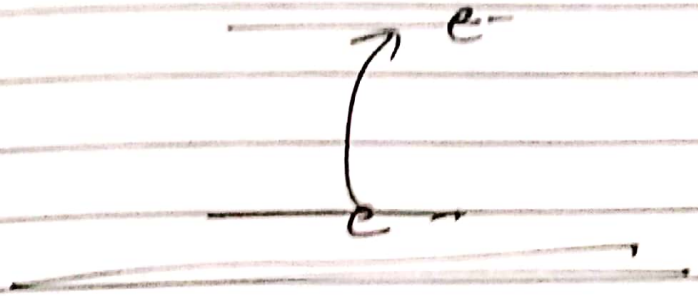


$3\sigma = sp^2$

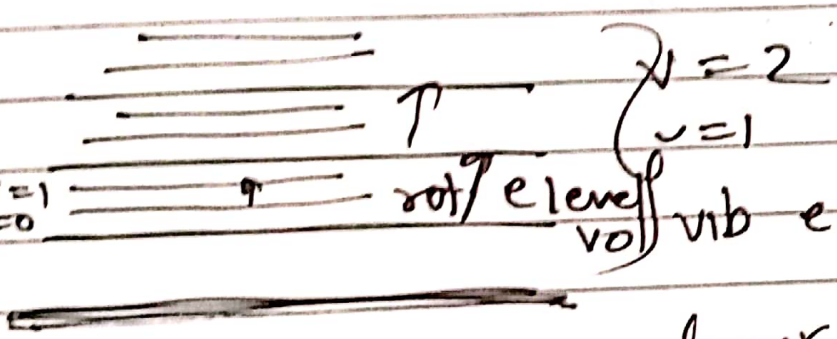
$3N - 6$

$= 3 \times 12 - 6$

$= 36 - 6 = 30$



Raman

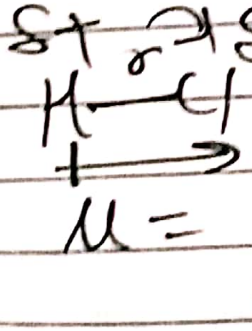


microwave

(9P)

lower e e level

→ UV/visible



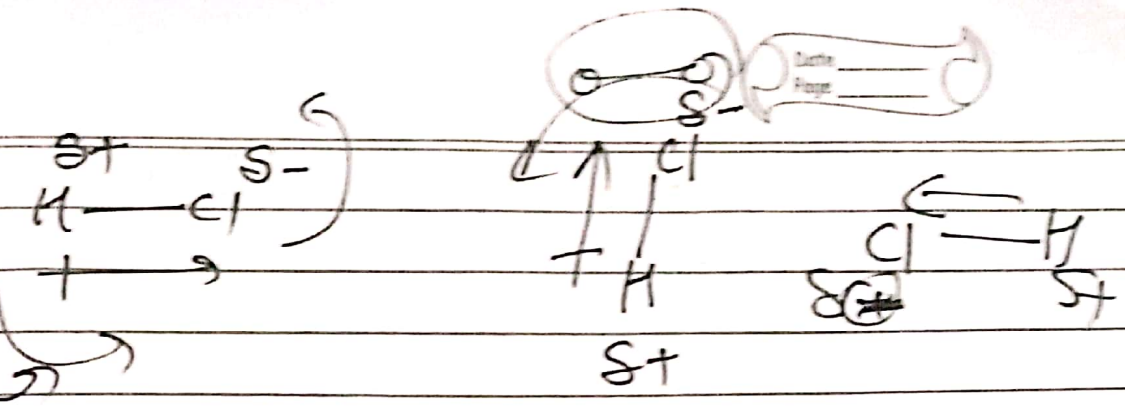
N_2 H_2O,

$N \equiv N$

$\mu = 0$

Inactive

Teacher's Signature.....



It change dm change

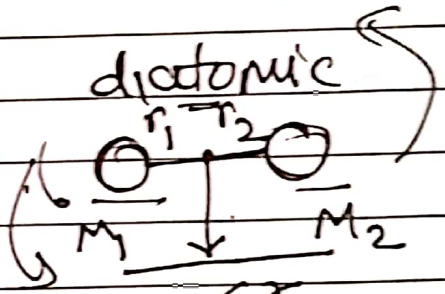
→ higher J = 1

→ lower J = 0

E_J

Rigid Rotor

bond length (x) change



$m_1 r_1 = m_2 r_2$ — (1)

$I = I_1 + I_2$

$= m_1 r_1^2 + m_2 r_2^2$ — (2)

$I = mr^2$

$r = r_1 + r_2$ — (3)

$r_2 = (r - r_1)$ — (4)

$m_1 r_1 = m_2 (r - r_1)$

$m_1 r_1 = m_2 r - m_2 r_1$

$m_1 r_1 + m_2 r_1 = m_2 r$

Teacher's Signature.....

$r_1 (M_1 + M_2) = M_2 r$

$r_1 = \frac{M_2 r}{(M_1 + M_2)}$

$r_2 = \frac{M_1 r}{(M_1 + M_2)}$

$I = M_1 \left(\frac{M_2 r}{M_1 + M_2}\right)^2 + M_2 \left(\frac{M_1 r}{M_1 + M_2}\right)^2$

$= \frac{M_1 M_2^2 r^2}{(M_1 + M_2)^2} + \frac{M_2 M_1^2 r^2}{(M_1 + M_2)^2}$

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

$= \frac{r^2 M_1 M_2 (M_2 + M_1)}{(M_1 + M_2)^2}$

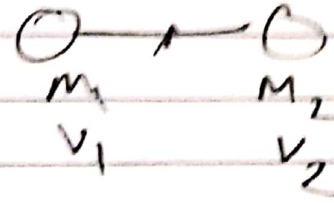
$I = r^2 \frac{M_1 M_2}{(M_1 + M_2)}$

μ = reduced mass

$I = \mu r^2$ — (2)

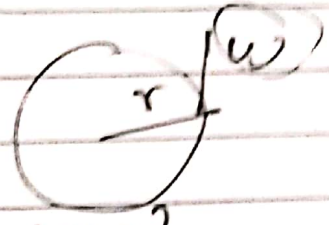
Teacher's Signature

$$\varepsilon = \frac{1}{2} m v^2$$



$$\varepsilon = \frac{1}{2} m_1 v_1^2 + \frac{1}{2} m_2 v_2^2$$

$$v = \omega \times r$$



$$\varepsilon = \frac{1}{2} m_1 (\omega r_1)^2 + \frac{1}{2} m_2 (\omega r_2)^2$$

$$= \frac{1}{2} m_1 \omega^2 r_1^2 + \frac{1}{2} m_2 \omega^2 r_2^2$$

$$= \frac{1}{2} \omega^2 (m_1 r_1^2 + m_2 r_2^2)$$

$$\varepsilon = \frac{1}{2} \omega^2 I$$

$$I = \frac{2\varepsilon}{\omega^2} \quad (8) \qquad \omega^2 = \frac{2\varepsilon}{I}$$

and we $L = I\omega$

$$L^2 = I^2 \omega^2 \quad (9)$$

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

$$L^2 = J(J+1) \frac{h^2}{4\pi^2} \quad (10)$$

Teacher's Signature

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

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

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

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

$$\frac{\varepsilon}{hc} = \frac{h}{8\pi^2 I hc} J(J+1) \quad \frac{cm^{-1}}{\upsilon}$$

$\varepsilon = h\nu$

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

$\varepsilon = hc\bar{\nu}$

$\frac{\varepsilon}{hc} = \bar{\nu}$

$$\varepsilon \rightarrow \bar{\upsilon} = \frac{h}{8\pi^2 Ic} J(J+1) \quad cm^{-1}$$

wave no.

$\varepsilon_J \propto \bar{\upsilon}$

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

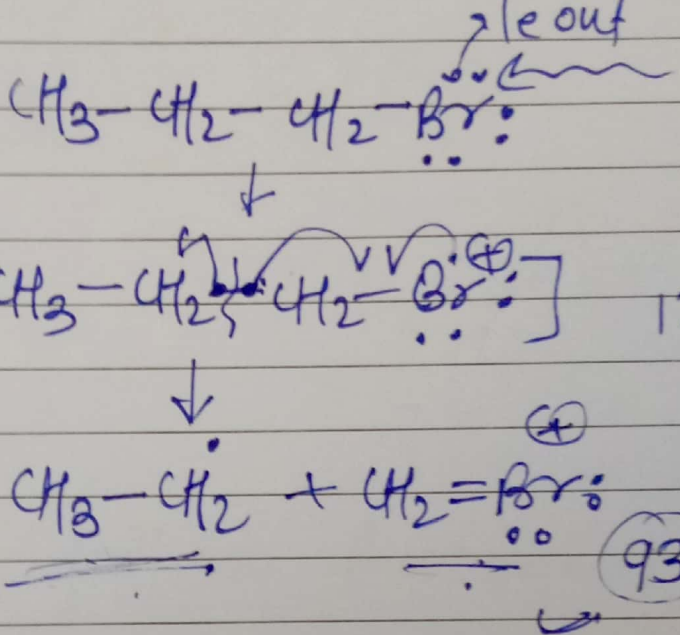
$$\bar{\upsilon} = BJ(J+1)\ cm^{-1}$$

Teacher's Signature.....

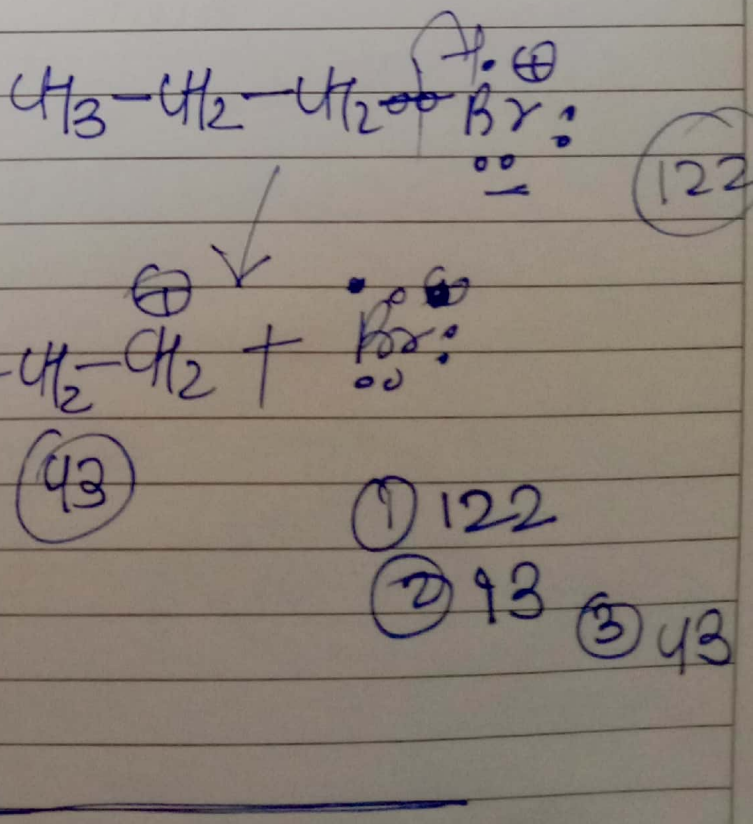
Mass spectrometry

(II) Homolytic cleavage (α-cleavage)

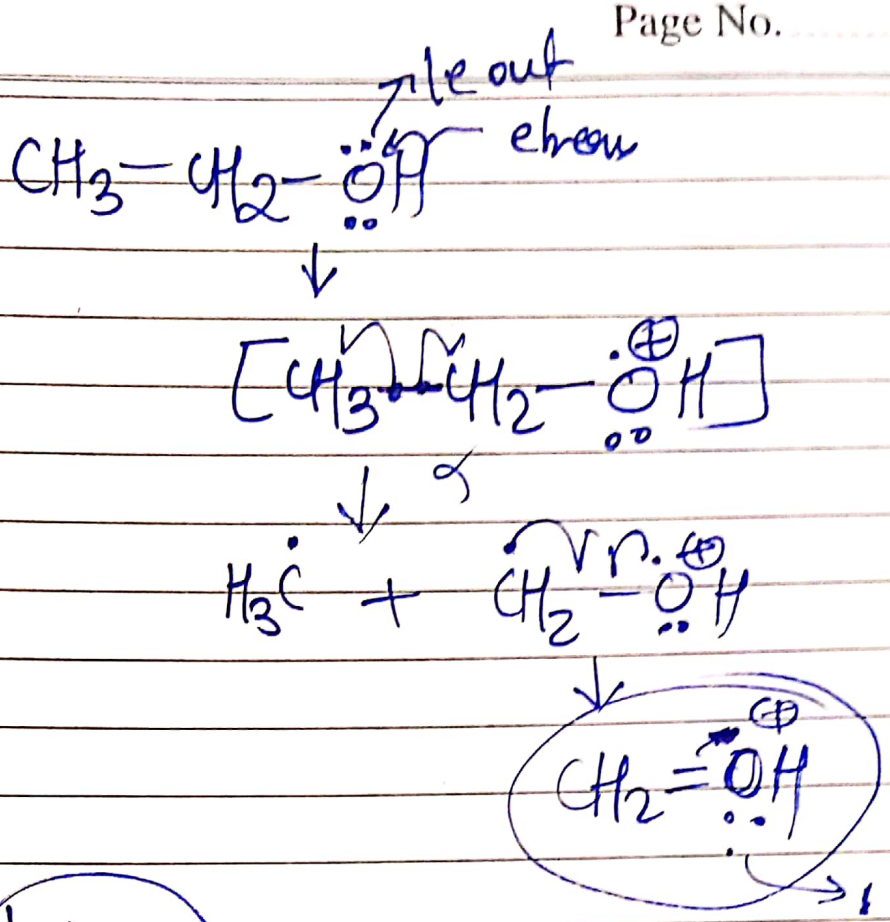
1) alkyl halide ⇒



Heterod



Teacher's Signature : _____



Ketone

MC Lattonty Rearrangement

→ ketone, -CHO aldy

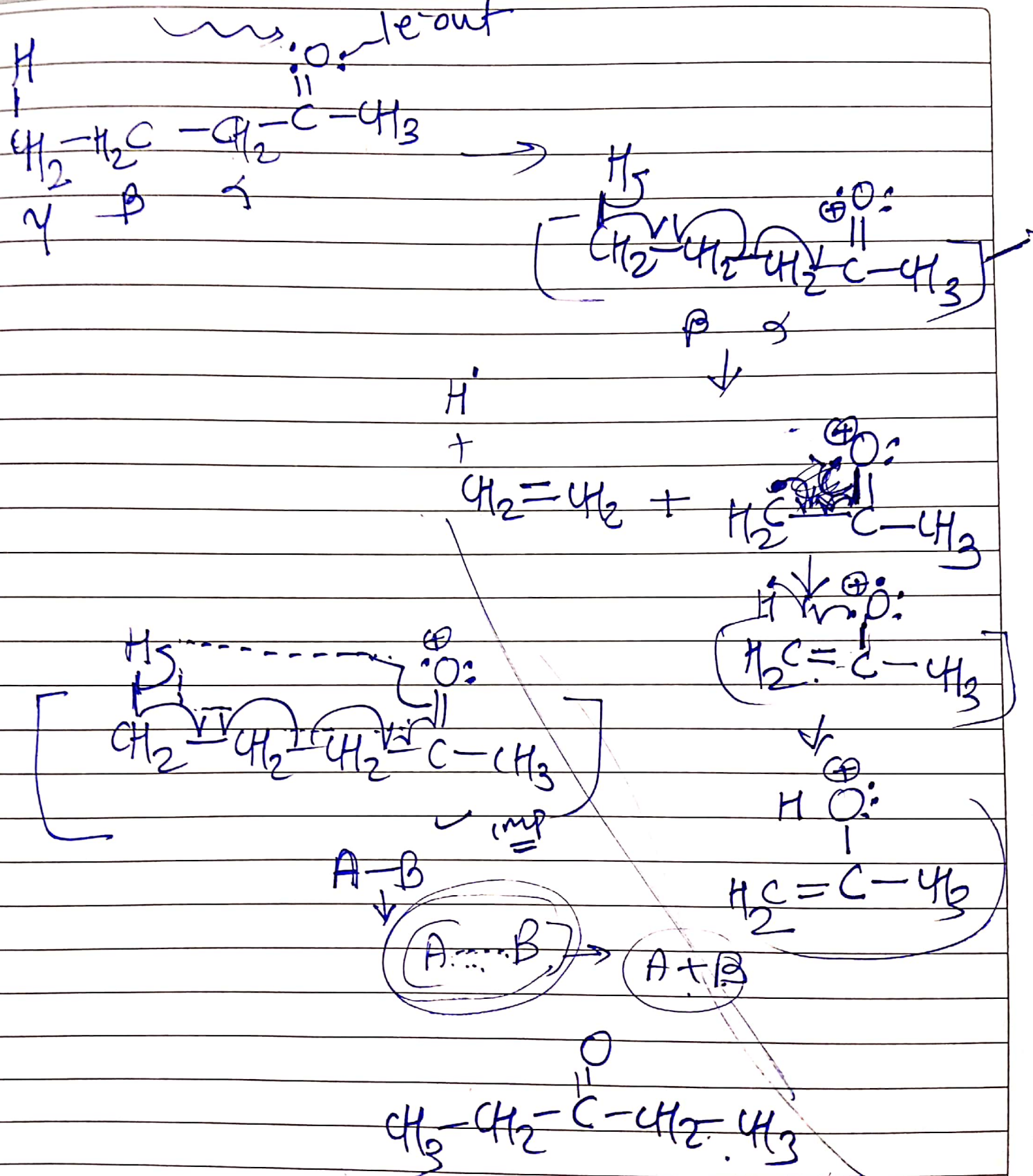
→ migrat[n] H/ carbonyl group के O की तरफ

→ γ-C उपर होना

→ antiand ester geom.

→ 6 member T.S

A → [A---P] ---P

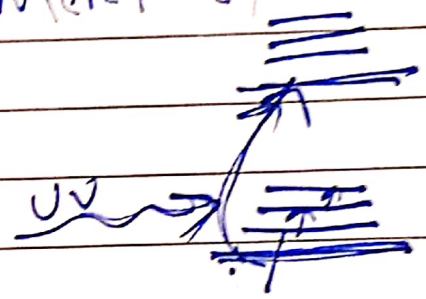


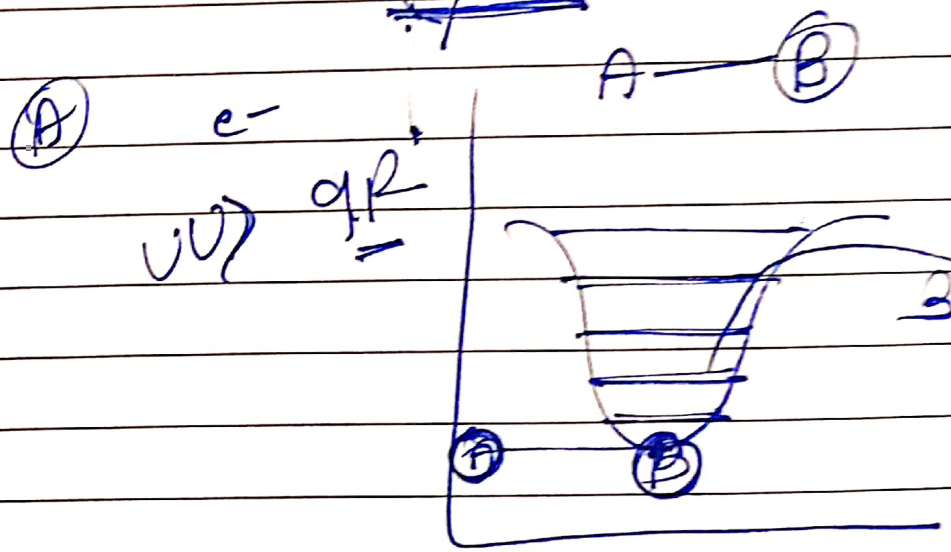
phys. chem. unit IV

franck condon principle

UV-visible

(काफी अणु में e- transition होता जाते 10^{-15} sec में होता है कि nucleus को गति में परिवर्तन नहीं मिलता है।





$\psi = c_1\psi_A + c_2\psi_B$

① sp — ② (s + p_x)

$\psi_1 = a_1\psi_s + b_1\psi_{p_x}$

$\psi_2 = a_2\psi_s + b_2\psi_{p_x}$

a_1, a_2, b_1, b_2 ~ calculate

① Individual orbital normalized

$\int \psi_1^2 d\tau = 1, \quad \int \psi_2^2 d\tau = 1$

② orthogonal $\int \psi_1 \psi_2 d\tau = 0$

③ ⇒ one equivalent (sp) (sp)

मोलिक ⇒ S (·) non-directional, (sp²)

① → ② sp $\frac{1}{2}$ $\frac{1}{2}$ $sp^2, p^2 sp^2$

S − $a_1^2 = a_2^2 = \frac{1}{2}$ (·) $\frac{1}{3}$

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

① $\int \psi_1^2 d\tau = 1$

$\int (a_1\psi_s + b_1\psi_{p_x})^2 d\tau = 1$

$\int a_1^2\psi_s^2 d\tau + \int b_1^2\psi_{p_x}^2 d\tau + \int 2a_1\psi_s b_1\psi_{p_x} d\tau = 1$

$\psi_1\psi_1$ $\psi_2\psi_2$ $2a_1b_1 \int \psi_s\psi_{p_x} d\tau$ (= 0)

शिक्षक के हस्ताक्षर

Scanned with CamScanner

$$a_1^2 + b_1^2 + 0 = 1$$

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

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

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

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

(ii) $\int \psi_1 \psi_2 \, d\tau = 0$

$$\int (a_1\psi_S + b_1\psi_{P_x}) \cdot (a_2\psi_S + b_2\psi_{P_x}) \, d\tau = 0$$

$$\int (a_1 a_2 \psi_S^2 + a_1 b_2 \psi_S \psi_{P_x} + b_1 a_2 \psi_{P_x} \psi_S + b_1 b_2 \psi_{P_x}^2) \, d\tau = 0$$

$$\int a_1 a_2 \underline{\psi_S^2} \, d\tau + \int a_1 b_2 \underline{\psi_S \psi_{P_x}} \, d\tau + \int b_1 a_2 \underline{\psi_{P_x} \psi_S} \, d\tau + \int b_1 b_2 \psi_{P_x}^2 \, d\tau = 0$$

(1) (0) (0) (1)

$$\Rightarrow a_1 a_2 + b_1 b_2 = 0$$

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

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

शिक्षक के हस्ताक्षर :

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

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

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

$$\therefore -\frac{1 \times \sqrt{2}}{\sqrt{2}\sqrt{2}}$$

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

$$\psi_1 = \frac{1}{\sqrt{2}} \psi_S + \frac{1}{\sqrt{2}} \psi_{P_x}$$

$$\psi_2 = \frac{1}{\sqrt{2}} \psi_S - \frac{1}{\sqrt{2}} \psi_{P_x}$$

Imp

BSc III $\psi_1 \psi_2$

Navbodh
PAGE NO.
DATE / /

sp^2 hybridization

$s + p_x + p_y =$

$\psi_1 = a_1\psi_s + b_1\psi_{p_x} + c_1\psi_{p_y}$

$\psi_2 = a_2\psi_s + b_2\psi_{p_x} + c_2\psi_{p_y}$

$\psi_3 = a_3\psi_s + b_3\psi_{p_x} + c_3\psi_{p_y}$

$s \rightarrow \frac{1}{\sqrt{n}}$ $\quad a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}$

sp & $n=2$ $\quad \frac{1}{\sqrt{2}}$

sp^2 $\quad n=3 = \frac{1}{\sqrt{3}}$

sp^3 $\quad n=4 = \frac{1}{\sqrt{4}}$

$\star \quad c_1 = 0$ (p_y) $\quad s + p_x \rightarrow$

(i) $\int \psi_1^2 d\tau$ (ii) $\int \psi_1\psi_2 d\tau = 0$ $\quad \int \psi_1\psi_2 d\tau = 0$

(iii) $\int \psi_1\psi_3 d\tau = 0$ (iv) $\int \psi_2^2 d\tau = 1$ (v) $\int \psi_3^2 d\tau = 1$

(i) $\int \psi_1^2 d\tau = 1 \Rightarrow \int (a_1\psi_s + b_1\psi_{p_x} + c_1\psi_{p_y})^2 d\tau = 1$

$(a+b)^2 = a^2 + b^2 + 2ab$

$\int a_1^2\psi_s^2 d\tau + \int b_1^2\psi_{p_x}^2 d\tau + \int 2a_1\psi_s b_1\psi_{p_x} d\tau = 1$

$a_1^2 + b_1^2 + 0 = 1 \quad \left(a_1 = \frac{1}{\sqrt{3}}\right)$

$\left(\frac{1}{\sqrt{3}}\right)^2 + b_1^2 = 1$

$b_1^2 = 1 - \frac{1}{\sqrt{2}}$ या $1 - \frac{1}{3}$

शिक्षक के हस्ताक्षर :

$b_1^2 = 1 - \frac{1}{3} \Rightarrow \frac{3-1}{3} = \frac{2}{3}$

$b_1^2 = \frac{2}{3} \Rightarrow b_1 = \sqrt{\frac{2}{3}}$ — (1)

(ii) $\int \psi_1 \psi_2 \, d\tau = 0$

$\Rightarrow \int (a_1\psi_S + b_1\psi_{P_x})(a_2\psi_S + b_2\psi_{P_x} + c_2\psi_{P_y}) d\tau = 0$

$\Rightarrow \int a_1\psi_S a_2\psi_S \, d\tau + \int a_1\psi_S b_2\psi_{P_x} d\tau + \int a_1\psi_S c_2\psi_{P_y} +$

$\int b_1\psi_{P_x} a_2\psi_S + \int b_1\psi_{P_x} b_2\psi_{P_x} + \int b_1\psi_{P_x} c_2\psi_{P_y} d\tau = 0$

$\Rightarrow \int a_1 a_2 \psi_S^2 d\tau + \int b_1 b_2 \psi_{P_x}^2 d\tau = 0$

$\Rightarrow a_1 a_2 + b_1 b_2 = 0$

$\frac{1}{\sqrt{3}} \frac{1}{\sqrt{3}} + \sqrt{\frac{2}{3}} b_2 = 0$

$\sqrt{\frac{2}{3}} b_2 = -\frac{1}{\sqrt{3}} \frac{1}{\sqrt{3}}$

$b_2 = -\frac{1}{\sqrt{3}} \frac{1}{\sqrt{3}} \times \frac{\sqrt{3}}{\sqrt{2}}$

$b_1 = -\frac{1}{\sqrt{6}}$ — (2)

शिक्षक के हस्ताक्षर :

(iii) $\int \psi_1 \psi_3 \, d\tau = 0$

(iv) $\int \psi_2^2 \, d\tau = 1$

$$\Rightarrow \int (a_2\psi_S + b_2\psi_{Px} + c_2\psi_{Py})^2 \, d\tau = 1$$

(a) (b) (c)

$$(a+b+c)^2 = a^2+b^2+c^2+2ab+2ac+2bc$$

$$\Rightarrow \int a_2^2\psi_S^2 \, d\tau + \int b_2^2\psi_{Px}^2 \, d\tau + \int c_2^2\psi_{Py}^2 \, d\tau + \int 2\, a_2\psi_S b_2\psi_{Px} \, d\tau + \int a_2\psi_S c_2\psi_{Py} \, d\tau + \int b_2\psi_{Px} c_2\psi_{Py} \, d\tau = 1$$

(1) (0) (0) (0)

$$\Rightarrow a_2^2 + b_2^2 + c_2^2 = 1$$

$$\left(\frac{1}{\sqrt{3}}\right)^2 + \left(-\frac{1}{\sqrt{6}}\right)^2 + c_2^2 = 1$$

$$\frac{1}{3} + \frac{1}{6} + c_2^2 = 1$$

$$c_2^2 = 1 - \frac{1}{3} - \frac{1}{6}$$

$$= \frac{6-2-1}{6} = \frac{6-3}{6} = \frac{3}{6}$$

$$c_2^2 = \frac{1}{2}$$

$$\boxed{c_2 = \frac{1}{\sqrt{2}}}$$

$$b_3 = -\frac{1}{\sqrt{6}}$$

$$c_3 = \frac{1}{\sqrt{2}}$$

शिक्षक के हस्ताक्षर :

$$\psi_1 = \frac{1}{\sqrt{3}}\psi_S + \sqrt{\frac{2}{3}} + 0$$

$$\psi_2 = \frac{1}{\sqrt{3}}\psi_S + \frac{1}{\sqrt{6}}\psi_{P_x} + \frac{1}{\sqrt{2}}\psi_{P_y}$$

$$\psi_3 = \frac{1}{\sqrt{3}}\psi_S - \frac{1}{\sqrt{6}}\psi_{P_x} - \frac{1}{\sqrt{2}}\psi_{P_y}$$

$$c_2 = c_3 = \pm\frac{1}{\sqrt{2}}$$

sp^3

$\psi_1 \quad \psi_2 \quad \psi_3 \quad \psi_4$

$$a_1\psi_S + b_1\psi_{P_x} + c_1\psi_{P_y} + d_1\psi_{P_z}$$

$S + P_x + P_y + P_z$

$\downarrow$

$4sp^3$

$c_1 = d_1 = 0$

$\psi_{P_y} \quad \psi_{P_z}$

$$a_1 = a_2 = a_3 = a_4 = \frac{1}{\sqrt{4}}$$

$S \rightarrow$

$$\frac{1}{\sqrt{4}} = \frac{1}{\sqrt{n}}$$

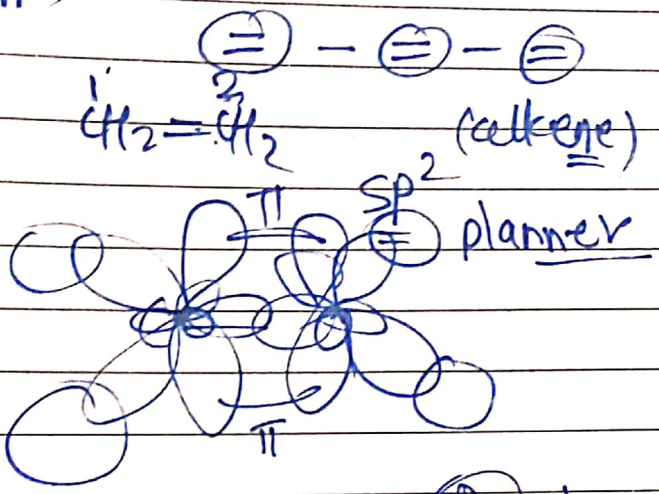
शिक्षक के हस्ताक्षर :

Huckel MOT

$(4n+2)\pi e^-$

* cyclic → cyclic and conjugated

यदि π apply



* energy calculated (P π bond ⊥ plane)

Saular determinant

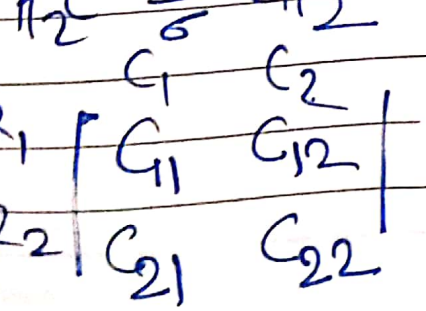
$$\begin{vmatrix} 1 & 2 \\ 3 & 4 \end{vmatrix}$$

R → 1 2

R → 3 4

order = (R×C) या (M×N)

(2×2)



① πe^- no. of = 2

order (2×2)

शिक्षक के हस्ताक्षर : _____

energy

$C = (H - ES)$

Integral

$$= \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix}$$

3 types Integral ⇒ ① α जब $H_{11} = H_{22} = H_{33} = \alpha$

(11) overlap integral S

S_{ij} $\begin{cases} S_{i=j} & S = 1 \\ S_{i \neq j} & S = 0 \end{cases}$

$$= \begin{bmatrix} \alpha - \varepsilon \times 1 & H_{12} - \varepsilon \times 0 \\ H_{21} - \varepsilon \times 0 & \alpha - \varepsilon \times 1 \end{bmatrix}$$

$$= \begin{vmatrix} \alpha - \varepsilon & H_{12} \\ H_{21} & \alpha - \varepsilon \end{vmatrix} \quad \begin{matrix} C_1 - C_2 \\ C_2 - C_1 \end{matrix}$$

③ Resonance integral H_{ij} $\begin{cases} C_1 - C_2 \text{ bond} \rightarrow \beta \\ C_1 - C_2 \text{ bond नहीं} \rightarrow 0 \end{cases}$

शिक्षक के हस्ताक्षर :

(X)

$\Rightarrow$ $\begin{vmatrix} \beta & \alpha-\varepsilon & \beta \\ & \beta & \alpha-\varepsilon \end{vmatrix}$

β से divide

$\Rightarrow$ $\begin{vmatrix} \frac{\alpha-\varepsilon}{\beta} & 1 \\ 1 & \frac{\alpha-\varepsilon}{\beta} \end{vmatrix} \Rightarrow \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix}$

माना $\Rightarrow \boxed{\frac{\alpha-\varepsilon}{\beta} = x}$ ①

$\Rightarrow \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$

$\boxed{x^2 - 1^2 = 0}$

$\boxed{x^2 - 1 = 0}$

$(a^2-b^2) = (a+b)(a-b)$

$(x+1)=0 \qquad (x-1)=0$

$x=-1 \qquad x=+1$

① $(x=-1)$ $\frac{\alpha-\varepsilon}{\beta} = x$ | we know $\beta = -75$

$\frac{\alpha-\varepsilon}{\beta} = -1$ | $\alpha - 75 = \varepsilon$

$\alpha - \varepsilon = -\beta$ | $-75 = \varepsilon$

$\alpha + \beta = \varepsilon$

शिक्षक के हस्ताक्षर :

(11) $x-1=0$

$x=+1$

$\frac{\alpha-\varepsilon}{\beta}=+1$

$\alpha-\varepsilon=\beta$

$\alpha-\beta=\varepsilon$

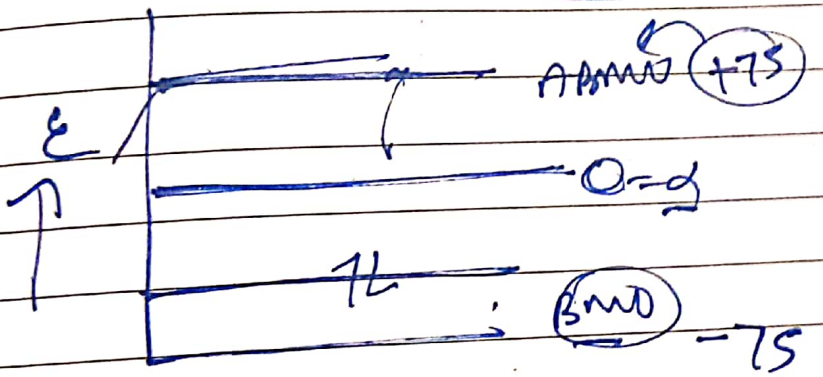
$\alpha-(-75)=\varepsilon$

$\alpha+75=\varepsilon$

$+75=\varepsilon$

$\varepsilon=-75$

$\Rightarrow$ BMO



$2\pi e-(\alpha-\beta)=\varepsilon$

$(\alpha+\beta)=\varepsilon$

BMO $(\psi_1) = c_1\phi_1 + c_2\phi_2$

ABMO $\psi_2 = c_1\phi_1 - c_2\phi_2$

$$\begin{vmatrix} c_1 & c_2 \\ x & 1 \\ 1 & x \end{vmatrix} = 0 \Rightarrow c_1x + c_2x1 = 0$$

$x=-1$

$c_1(-1)+c_2=0$

$-c_1+c_2=0$

$c_1=c_2$ — (11)

शिक्षक के हस्ताक्षर : _____

Navbodh
PAGE NO :
DATE : / /

$$\int \psi_1^2 \, d\tau = 1$$

$$\int (c_1\phi_1 + c_2\phi_2)^2 \, d\tau = 1$$

$$\int c_1^2\phi_1^2 \, d\tau + \int c_2^2\phi_2^2 \, d\tau + \int 2c_1\phi_1 c_2\phi_2 \, d\tau = 1$$

$$\Rightarrow \quad c_1^2 + c_2^2 + 0 = 1$$

$$c_1 = c_2$$

$$c_1^2 + c_1^2 = 1$$

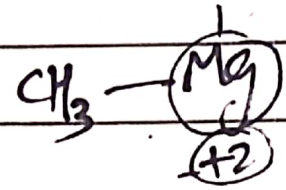
$$2c_1^2 = 1$$

$$c_1^2 = \frac{1}{2}$$

$$\boxed{c_1 = \frac{1}{\sqrt{2}} = c_2}$$

Nature of C—M bond in OMC

CH_3MgBr



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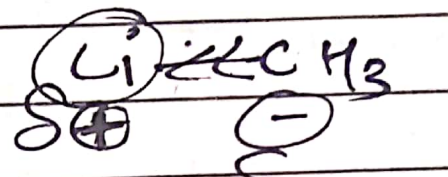
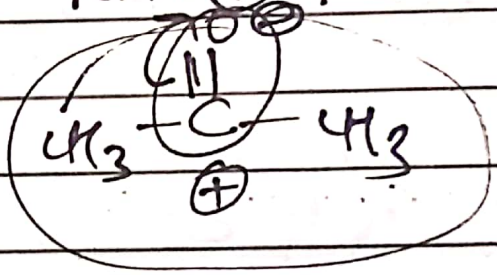


ionic 43%

ionic ↑ React ↑



organo-Sulphur-OMC

O = S

R—OH

R—SH

thio alcohol

R—O—R

R—S—R

thio-ether

R—CHO , R—CHS

Thio-alcohol / Mercaptan / Thiole

$R-OH \xrightarrow{+S} R-SH \xrightarrow{H} H-SH$

$R-SH$ → Sulphydril

H_2S

Aromatic ⇒

(1) $C_2H_5I + KSH \rightarrow C_2H_5SH + KI$

(2) CH_3MgBr (Grignard reagent) $+S \rightarrow CH_3-S-MgBr \xrightarrow{H-OH}$

$CH_3SH + Mg(OH)Br$

(3) $5\,C_2H_5OH + P_2S_5 \xrightarrow{P_2O_5} 5\,C_2H_5SH + P_2O_5$

(4) $CH_3-CH=CH_2 + H-SH \rightarrow$

$CH_2=CH_2$

$CH_3-\underset{\underset{SH}{|}}{CH}-CH_3$

Phy. properties ⇒ gas, colourless, liquid

MP bp – alcohol से कम

R–SH कम H-bond (X) water insoluble | R–OH + H-bond

Chemical Reaⁿ ⇒ R–SH → $H^{\oplus}$ + $RS^{\ominus}$ (acidic)

(1) Na ⇒ $2RSH + Na \rightarrow H_2 + 2RSNa$ / RONa

(II) $HgO + 2RSH \rightarrow H_2O + (RS)_2Hg$

(3) $R-COOH + HSR \rightarrow R-COSR + H_2O$ (ester)

R–COOR Thio-ester

$CH_3COCl + HSR \rightarrow HCl + CH_3COSR$

CH_3

C_2H_5

Date
Page

4) oxidatn ⇒ mild oxidants

H_2O_2

$2R-SH + H_2O_2 \longrightarrow R-S-S-R$

diallyl di sulphide

$2H_2O$

$KMnO_4 / K_2Cr_2O_7$

$C_2H_5SH + 3[O] \longrightarrow C_2H_5-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-OH$

Sulphonic acid

SO_3H

5) base ⇒ $CH_3-SH + NaOH \longrightarrow CH_3SNa + H_2O$

6) $R-CH=O + \begin{matrix} HSCH_3 \\ HSCH_3 \end{matrix} \rightarrow R-\underset{H}{C}(SCH_3)_2$

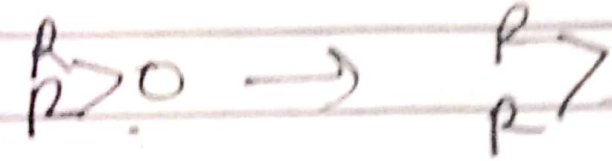
mercaptal

Sulphonal

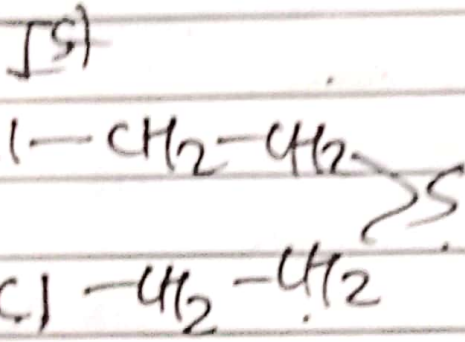
$(CH_3)_2C(SO_2C_2H_5)_2$

Remark 3 Teacher's Sign.

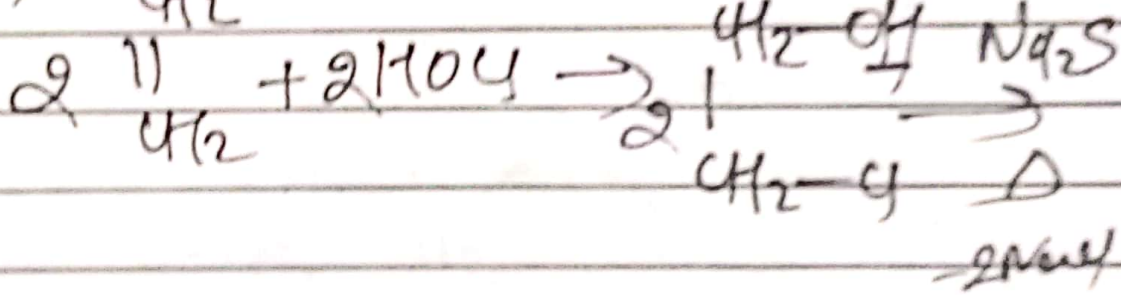
Thio-ether

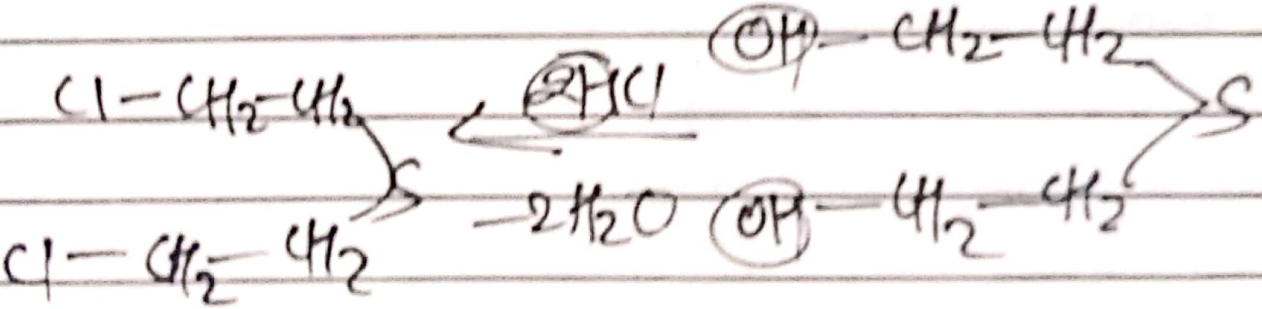


Mustard gas



formation ⇒





217°C

Date
Page

chemical proper →

(1) mix gas $\xrightarrow{Cl_2}$ $Cl-CH_2-CH_2$ $>S\rightarrow Cl$ $Cl-CH_2-CH_2$

pure

(II) oxid^n →

$Cl-CH_2-CH_2$ $>S$ $\xrightarrow{(O)}$ $>S\rightarrow O$

$Cl-CH_2-CH_2$

$\xrightarrow{(O)}$

$Cl-CH_2-CH_2$ $>S\rightarrow O$ $Cl-CH_2-CH_2$ $\rightarrow O$

Sulphone

(III) $\xrightarrow{2NaOH}$ $-2NaCl$

$OH-CH_2-CH_2$ $>S$ $OH-CH_2-CH_2$

Remark

Teacher's Sign.

alkyl / acyl

Sulphonic acid

CH_3-SO_3H

$C_6H_5-SO_3H$ (imp)

$CH_3-C_6H_5-SO_3H$

aro sulf acid

$C_6H_5-SO_3H$

Preparation →

$C_6H_6 \xrightarrow[\text{(conc. } H_2SO_4)]{\text{(सांद्र)}\ SO_3} C_6H_5-SO_3H$

$\overset{\ominus}{OH}-\overset{\oplus}{SO_2H}$

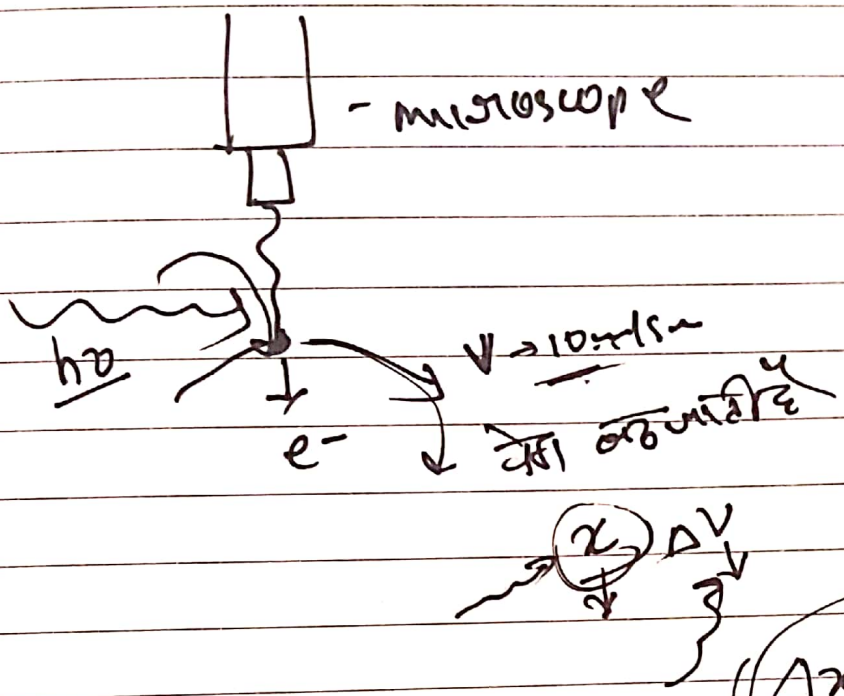
C_6H_5-H

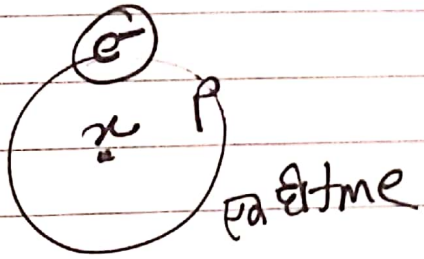
$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$

oleum

(I) (II) (III)

heisenberg's uncertainty principle



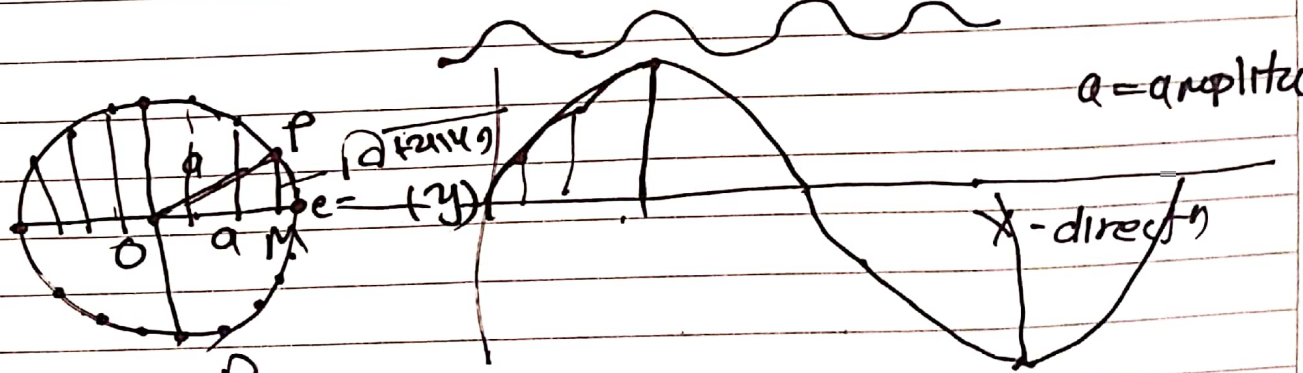


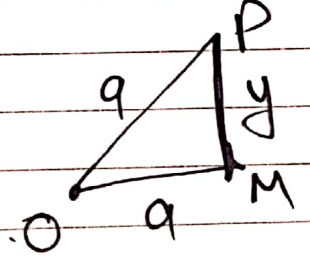
$$\Delta x \times \Delta \hat{p}_{(m \times v)} \geq \frac{h}{4\pi}$$

wave

em ~~~ matter wave

λ, υ, v





$$\sin\theta = \frac{\text{लं}}{\text{क}\cdot} = \frac{PM}{OP} = \frac{y}{a}$$

$$\sin\theta = \frac{y}{a}$$

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$\frac{y}{a} = \sin\theta$

$y = a\sin\theta$ — (1)

ω = ang. velocity

v = linear v

$360^\circ = 2\pi$

180×2

$\omega = \frac{2\pi}{t}$ — (2) $= \pi$ $\omega = \frac{\theta}{t}$ — (3)

t समय में $\theta = \omega t$ — (4)

θ का मान (1) में

$y = a\sin\omega t$ — (5)

$\omega = \frac{2\pi}{t}$

1 sec में 1 चक्कर लगाता है तो

$\nu = \frac{1}{t}$ — (6)

1 sec में

$\omega = 2\pi \times \frac{1}{t}$

$\omega = 2\pi\nu$ — (7)

$y = A\sin 2\pi\nu t$

$c = \frac{dx}{t} = \frac{x}{t}$

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

$y = A\sin 2\pi\nu\frac{x}{c}$

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

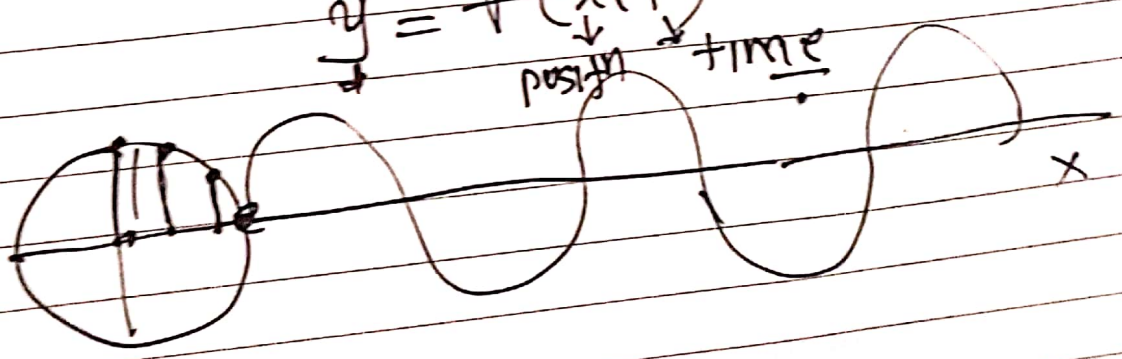
$$y = A \sin 2\pi \frac{c}{\lambda} \times \frac{x}{c}$$

$$\boxed{\psi = A \sin 2\pi \frac{x}{\lambda}}$$ wave eqn

Schrodinger wave eqn
↳ atom e⁻ की problem of finding
e, p, n (atom)

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

ψ = wave funct^{n}
E = total energy (KE + PE)
V = PE of e⁻
h = , m = e⁻ mass



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$$\psi = A \sin \frac{2\pi x}{\lambda} \quad -(1)$$

x च्या सापेक्ष double diff करून घेऊ

$$\frac{d^2\psi}{dx^2} = \frac{d^2}{dx^2}\left(A \sin \frac{2\pi}{\lambda} x\right)$$

$$= \frac{d}{dx}\left[\frac{d}{dx}\left(A \sin \frac{2\pi}{\lambda} x\right)\right]$$

$$= \frac{d}{dx}\left[A \cos \frac{2\pi}{\lambda} x \cdot \frac{2\pi}{\lambda}\right]$$

$$= -A \sin \frac{2\pi}{\lambda} x \cdot \frac{2\pi}{\lambda} \cdot \frac{2\pi}{\lambda}$$

$$\frac{d^2\psi}{dx^2} = -\left(A \sin \frac{2\pi}{\lambda} x\right) \frac{4\pi^2}{\lambda^2}$$

$$\frac{d^2\psi}{dx^2} = -\psi \frac{4\pi^2}{\lambda^2} \quad -(2)$$

$$\therefore \lambda = \frac{h}{mv} \Rightarrow \lambda^2 = \frac{h^2}{m^2v^2} \quad -(3)$$

$$\frac{d^2\psi}{dx^2} = -\psi \frac{4\pi^2 m^2 v^2}{h^2} \quad -(4)$$

$$T.E. = KE + PE$$

$$\mathcal{E} = \frac{1}{2}mv^2 + V$$

$$(\mathcal{E} - V) = \frac{1}{2}mv^2$$

$$2(\mathcal{E} - V) = mv^2 \quad \text{— (5)}$$

$$\frac{d^2\psi}{dx^2} = -\psi \frac{4\pi^2 m(v^2 m)}{h^2}$$

$$\frac{d^2\psi}{dx^2} = -\psi \frac{4\pi^2 m \times 2(\mathcal{E} - V)}{h^2}$$

$$\frac{d^2\psi}{dx^2} = -\frac{8\pi^2 m(\mathcal{E} - V)\psi}{h^2}$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m(\mathcal{E} - V)\psi}{h^2} = 0$$

(x) dx (y, z)

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2 m(\mathcal{E} - V)\psi}{h^2} = 0$$

laplacian operator ∇^2

$$\nabla^2 = \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)$$

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dz^2} + \frac{d^2\psi}{dy^2} + \frac{8\pi^2 m(E-V)\psi}{h^2} = 0$$

$$\left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)\psi +$$

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

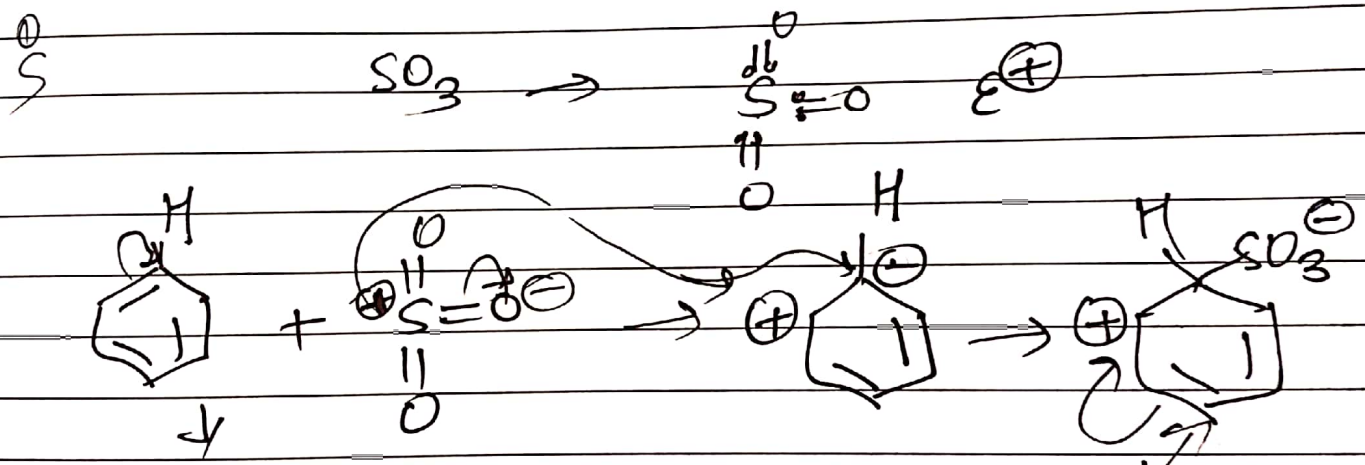
Aromatic Sulphonic acid

$C_6H_5-SO_3H$ $\quad$ $C_6H_5-SO_3H$ $\quad$ $C_6H_5-CH_3$ $\quad$ $C_6H_5-SO_2Cl$

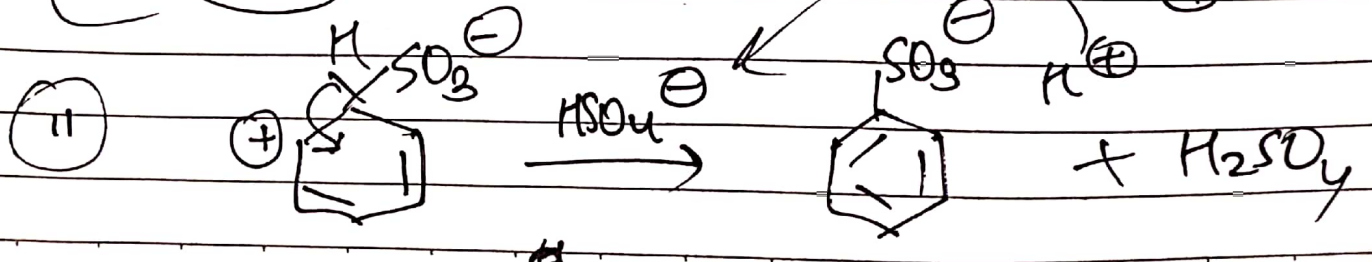
$C_6H_5 + \cancel{HNO_3} \xrightarrow[\text{con } H_2SO_4]{} \underset{\ominus \quad \oplus}{OH-SO_3H}$ $\quad$  $+ H_2O$

mech ⇒ (I) $2H_2SO_4 \rightleftharpoons SO_3 + HSO_4^- + H_3O^+$

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ (oleum)



(II)



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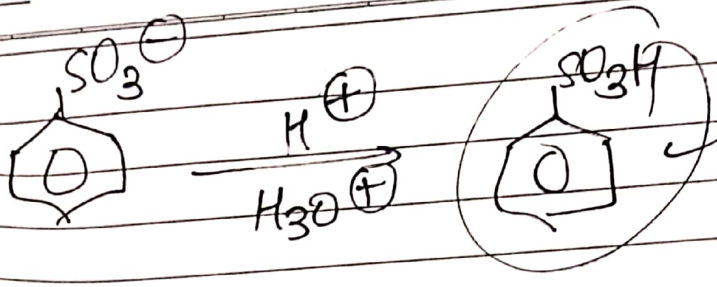
Date

Page No.



formation ⇒ (1) $H_2SO_4 \rightarrow OH-SO_3H$

$C_6H_6 + Cl-SO_3H \xrightarrow[-HCl]{} C_6H_5SO_3H$

(II) $C_6H_5SH \xrightarrow{3(O)} C_6H_5SO_3H$

Reaⁿ ⇒ (1) BSA → phenol

$C_6H_5SO_3H + NaOH \text{ (or } KOH) \rightarrow C_6H_5SO_3Na$ (or $C_6H_5SO_3K$)

$C_6H_5SO_3K + KOH \rightarrow K_2SO_3 + C_6H_5OH$

(2) → phenyl cyanide

$C_6H_5SO_3K + KCN \rightarrow C_6H_5CN$

(3) → C_6H_6

$C_6H_5SO_3H + HOH \rightarrow C_6H_6 +$

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Date

Page No.

④ BSA → benzoic acid

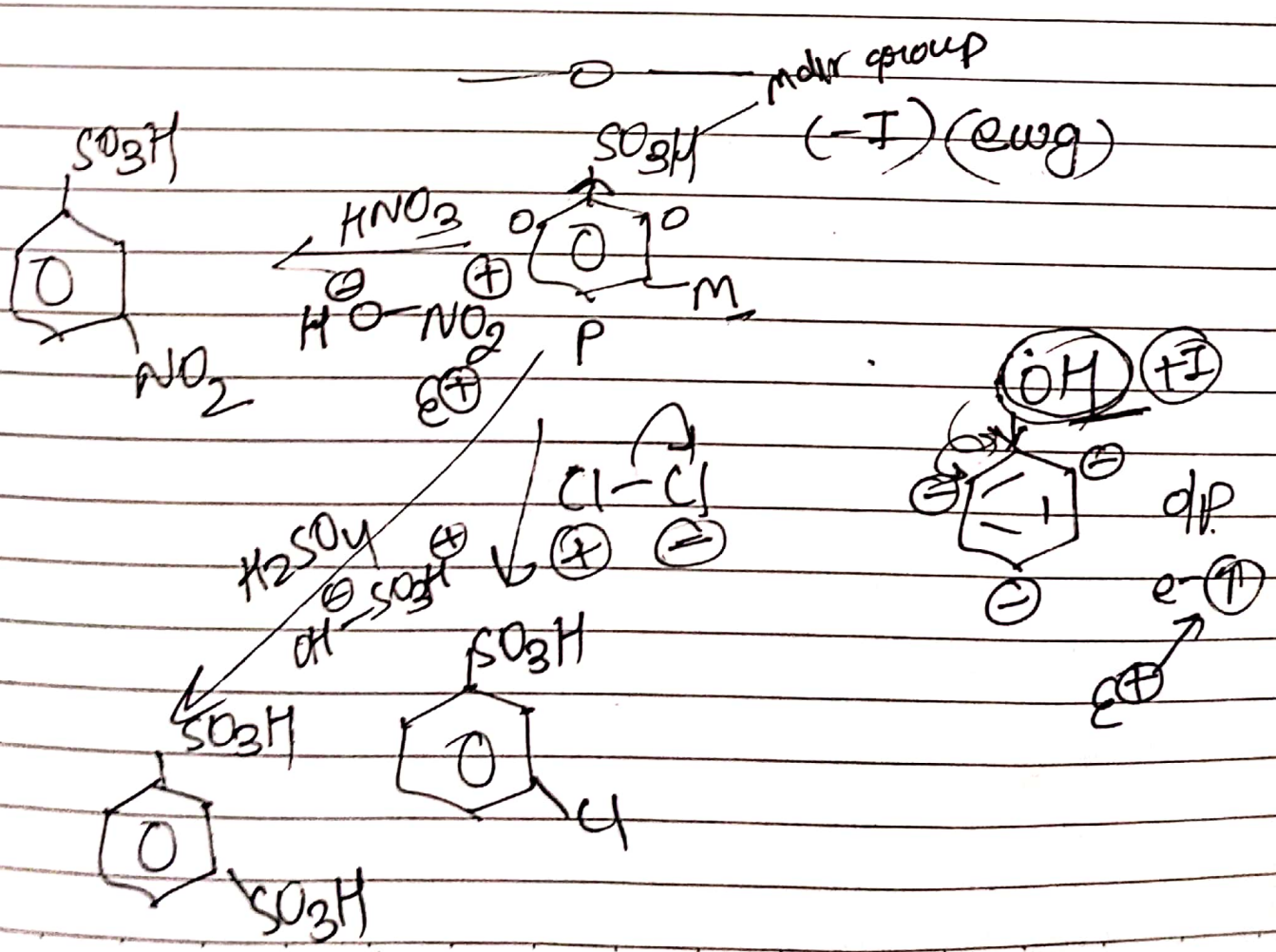
$C_6H_5SO_3K + HCOOK \longrightarrow C_6H_5COOK$

⑤ BSA → aniline

$C_6H_5SO_3Na + NaNH_2 \rightarrow Na_2SO_3 + C_6H_5NH_2$

⑥ BSA → trinitrobenzene

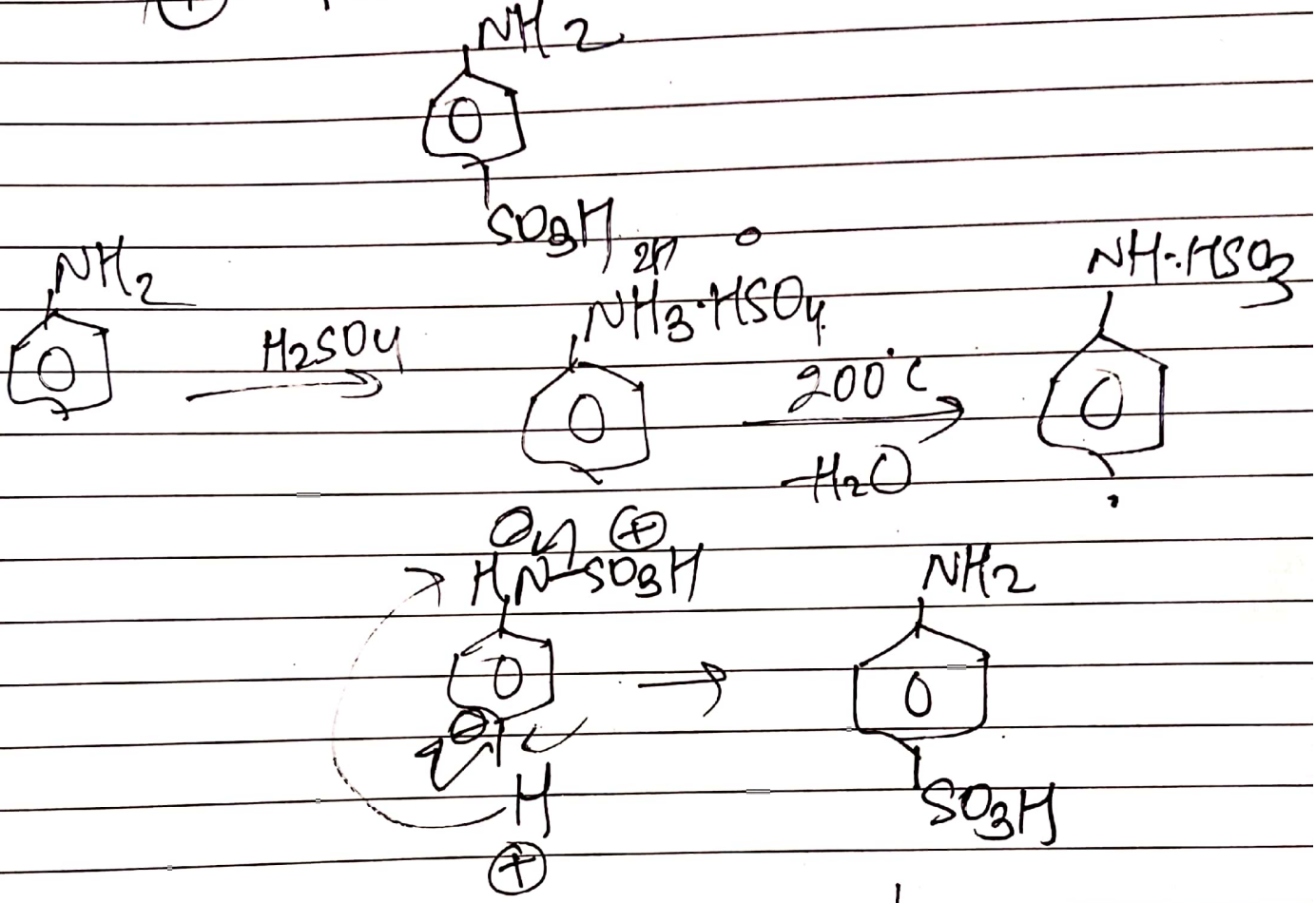
$C_6H_5SO_3H \xrightarrow[-H_2O]{2H} C_6H_5SO_2H \xrightarrow[-2H_2O]{4H} C_6H_5S$



Date

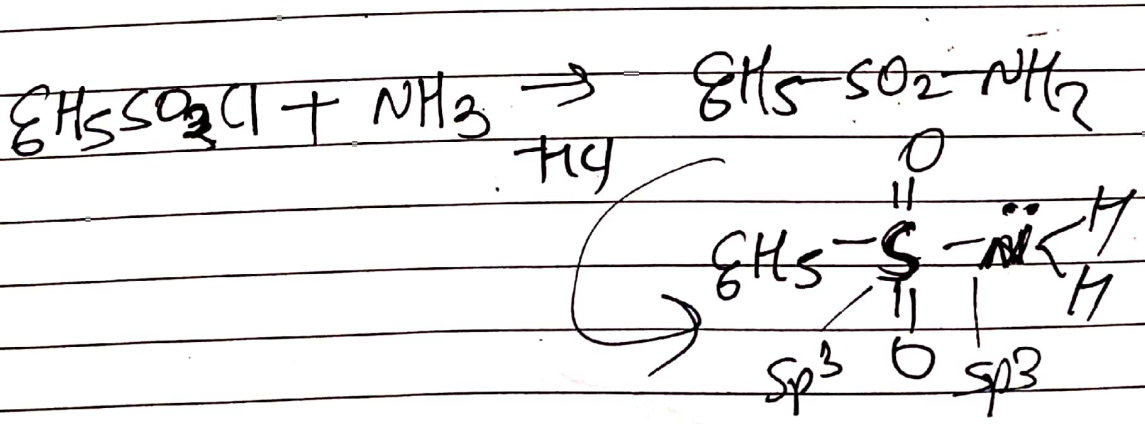
Page No.

① Sulphanilic Acid



Dyes / drugs

② Sulphanamide



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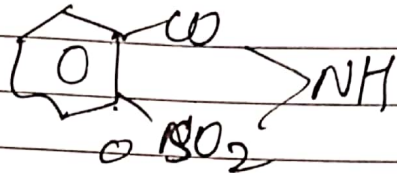
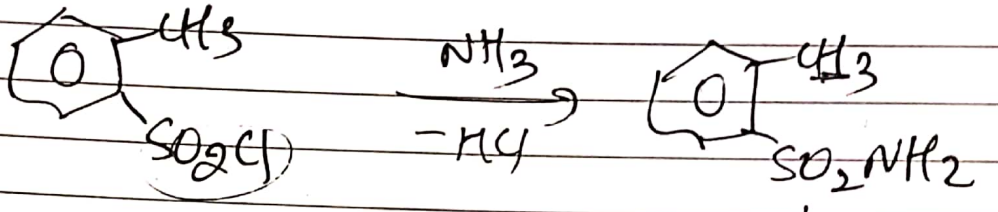
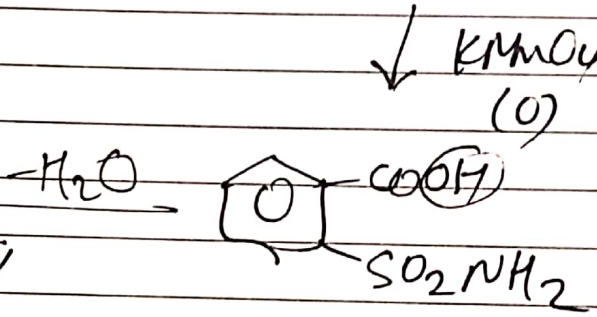
(3) Saccharine

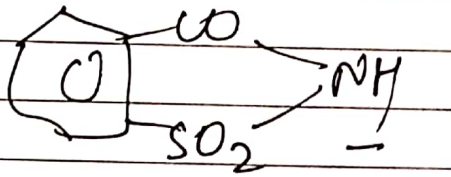


- O-sulpho be

methods ⇒

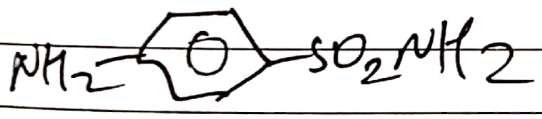


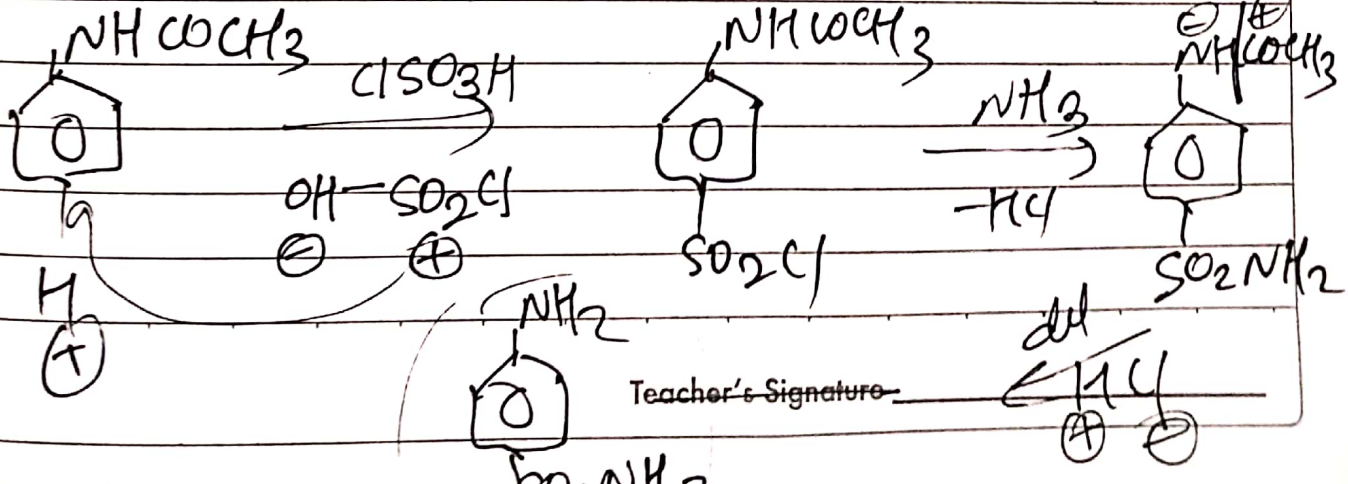




Soln

Sulphanilamide





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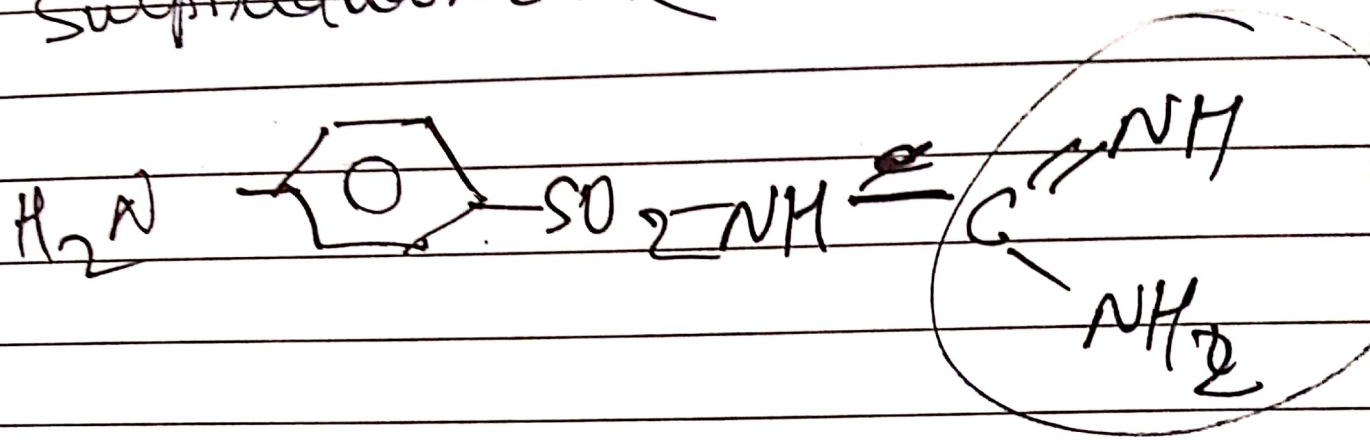
Page No. _____

Sulphaguanidine

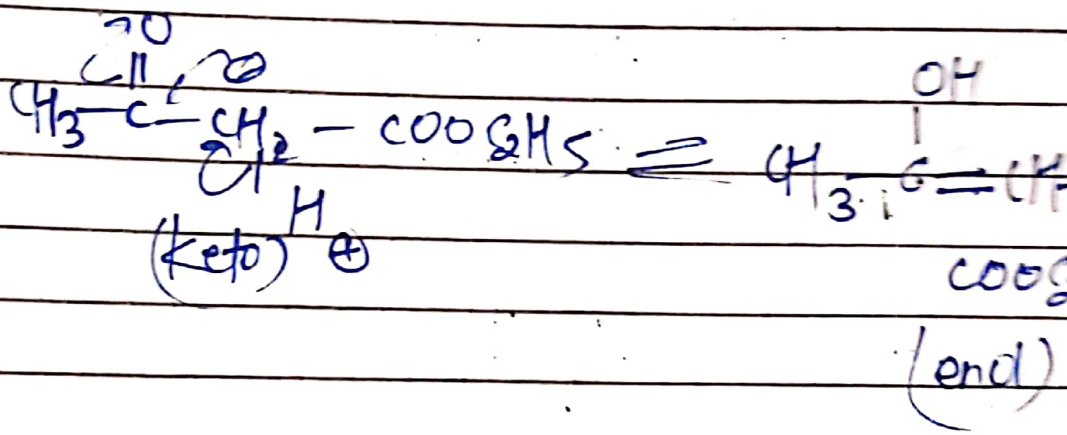


AAE

(Aceto Acetic Ester)

$CH_3COOC_2H_5$

$CH_3CO-CH_2-COOC_2H_5$



(keto) (end)

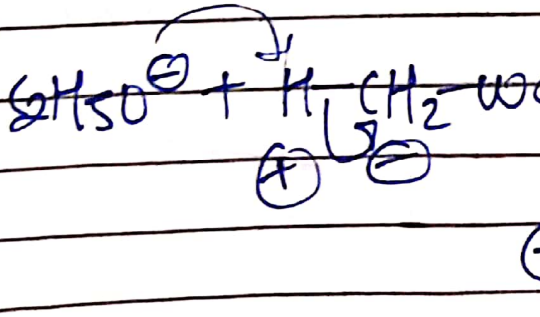
(1) Claisens condensation ⇒

$CH_3-COOC_2H_5 + H-CH_2-COOC_2H_5 \xrightarrow{C_2H_5ONa}$

$C_2H_5OH + CH_3-CO-CH_2-COOC_2H_5$

(AAE)

mech — (I) $C_2H_5ONa \rightleftharpoons C_2H_5O^{\ominus} + Na^{\oplus}$

(II) 

Remark

Teacher's Sign.

(III) $CH_3-\overset{\overset{O}{\|}}{C}(+)-OC_2H_5 + CH_2(-)-COOC_2H_5 \rightarrow$

$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-COOC_2H_5$

OC_2H_5

(IV) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-COOC_2H_5$ (AAE)

(keto) (imp)

Rean ⇒ (lecture) (I) $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-COOC_2H_5 + 2H$

$\xrightarrow{Na\text{-}Hg}$ $CH_3-\underset{OH}{CH}-CH_2-$

AAE $+HCN \rightarrow$

$CH_3-\underset{OH}{\overset{|}{C}}-CH_2-COOC_2H_5$

CN

Teacher's Sign.

Remark

Synthetic applicatn of AAE

(1) AAE → acetic acid

$CH_3-CO-CH_2-COOC_2H_5 \xrightarrow{alc\,KOH}$

$CH_3COOH + CH_3COOH + C_2H_5OH$

(2) AAE → Valeric acid

$CH_3-CO-\overset{\ominus}{C}H_2-COOC_2H_5$

$\xrightarrow[(ii)\,C_2H_5I]{(i)\,C_2H_5ONa}$

$-HI$

$CH_3-CO-\overset{\ominus}{C}H-COOC_2H_5 \xrightarrow{CH_3I} \xrightarrow{HI}$

(3)

(4) $CH_3-\underset{C_2H_5}{\underset{|}{C}}H-COOH \xrightleftharpoons{2HOH}$ (d) $CH_3COOH + C_2H_5OH$

$CH_3CO-\underset{C_2H_5}{\underset{|}{C}}H-COOC_2H_5$

Remark

Teacher's Sign.

op cultures

Structure of AAE

keto ⇌ enol

OH

(i) ester ← keto enol

(ii) dynamic equilibrium keto ⇌ enol

(iii) keto 92.5%. enol - 7.5%.

(iv) tautomerism

↓

H atom दो जगह से शिफ्ट

$H-C\equiv N \rightleftharpoons H-N=C$

isocyanide

$R-N(=O)\rightarrow O \rightleftharpoons H-O-N=O$

(RNO_2)

HNO_2

NO_2 ONO

Remark

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BSc III

Hamiltonian operator

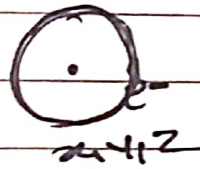
$$H = KE + PE$$

$$= \frac{1}{2}mv^2 + V$$

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

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

$(p = m \times v)$



$$H = \frac{p^2}{2m} + V \quad \text{— (1)}$$

$$\hat{p} = \hat{p}_x + \hat{p}_y + \hat{p}_z$$

$$\hat{p}_x = \frac{h}{2\pi i}\frac{\partial}{\partial x}, \quad \hat{p}_y = \frac{h}{2\pi i}\frac{\partial}{\partial y}$$

$$\hat{p}_z = \frac{h}{2\pi i}\frac{\partial}{\partial z}$$

$$\hat{p}^2 = (\hat{p}_x + \hat{p}_y + \hat{p}_z)^2$$

$$= \left(\frac{h}{2\pi i}\frac{\partial}{\partial x}\right)^2 + \left(\frac{h}{2\pi i}\frac{\partial}{\partial y}\right)^2 + \left(\frac{h}{2\pi i}\frac{\partial}{\partial z}\right)^2$$

=

Teacher's Signature.....

$$= \frac{h^2}{4\pi^2 i^2}\frac{\partial^2}{\partial x^2} + \frac{h^2}{4\pi^2 i}\frac{\partial^2}{\partial y^2} + \frac{h^2}{4\pi^2 i^2}\frac{\partial^2}{\partial z^2}$$

$$= \frac{h^2}{4\pi^2 i^2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$$

$$\nabla^2$$

$$p^2 = \frac{h^2}{4\pi^2 i^2}\nabla^2$$

$$i = \sqrt{-1}$$

$$i^2 = -1$$

$$p^2 = -\frac{h^2}{4\pi^2}\nabla^2 \quad -(2)$$

$$H = \frac{-h^2}{4\pi^2 \times 2m}\nabla^2 + V_{(x,y,z)}$$

$$H = \frac{-h^2}{8\pi^2 m}\nabla^2 + V$$

we know

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

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

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

$$= E\psi - V\psi$$

Teacher's Signature.....

$$-\nabla^2\psi\frac{h^2}{8\pi^2 m} = \varepsilon\psi - V\psi$$

$$-\nabla^2\frac{h^2}{8\pi^2 m}\psi + V\psi = \varepsilon\psi$$

$$\left(-\nabla^2\frac{h^2}{8\pi^2 m} + V\right)\psi = \varepsilon\psi$$

$$H = -\nabla^2\frac{h^2}{8\pi^2 m} + V$$

$$\boxed{H\psi = \varepsilon\psi}$$

physical significance ψ & ψ^2

$\psi \Rightarrow$ wave funct^n of e-

$\psi \Rightarrow$ probability of finding e-

-ve (x) +ve (o)

$\psi^2 \Rightarrow$ probability density

high low

o ↓ e⁻ (x)

1 2 3

$$P = \int_0^\infty \psi^2 4\pi r^2 dr = 1$$

3D space

Teacher's Signature.....

Postulates of quantum mechanics

Operator ⇒ ⊕ ⊖ ⊗

4 + 10 ⇒ 14

operator → funct^n = funct^n f''

$\frac{d}{dx}$, $\int dx$, फलन

$\frac{d}{dx}\, x^3 \Rightarrow f = f'$

$= 3x^2$

(i) addit^n of ⇒

$(\hat{A}+\hat{B})f = \hat{A}f + \hat{B}f$

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

$= 2x + 2x$

$= 4x$

(ii) Subst^n ⇒ $(\hat{A}-\hat{B})f = \hat{A}f - \hat{B}f$

(iii) multiplicat^n ⇒ $\hat{A}\hat{B}f \Rightarrow \hat{B}f \Rightarrow f'$

$\hat{A}f \Rightarrow f''$

$\frac{d}{dx}\int 3x^2\, dx$

$\hat{A}\ \hat{B}: f$

$\Rightarrow \frac{d}{dx}\left(\frac{3x^{2+1}}{2+1}\right) \Rightarrow \frac{d}{dx}\cdot\frac{3x^3}{3} \Rightarrow \frac{d}{dx}x^3$

$\Rightarrow 3x^2$

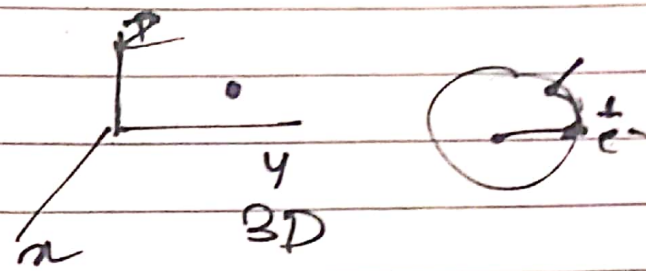
Teacher's Signature.....

(II) किसी भी system की physical state को defined ——— as a ψ

$\psi(x,t)$

↓ ↓

posⁿ time



(III) ψ का I, II derivative

$\left(\frac{d}{dx}\right)\left(\frac{d^2}{dx^2}\right)$ → well behaved

ψ का soln → अनुत finite values

finite value → value

→ single valued

→ continuous

follows → ψ normalised

$$\int_{-\infty}^{+\infty} \psi\psi^* \, d\tau = 1$$

↓

Teacher's Signature.....

(IV) observable quan की वही value allowed value है जो eigen value

~~होगा~~

$\hat{H}\psi = a\psi$

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

same value

eg - $\frac{d}{dx}(e^{2x}) = 2e^{2x}$

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

eigen operator, same value = eigen value

eigen value equation

$\frac{d}{dx}(x^2) = 2x$

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

(V) e- x p

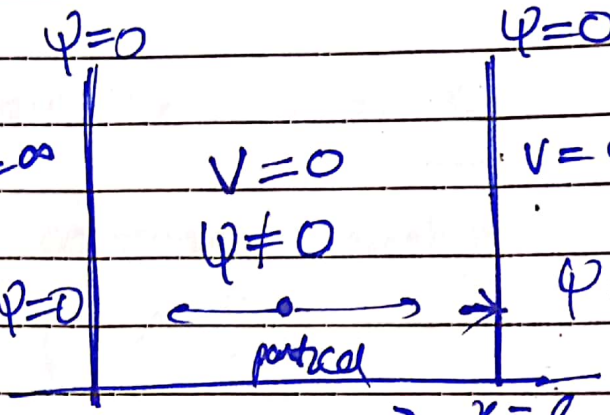
$\bar{A} = \frac{\int \psi \hat{A} \psi^* d\tau}{\int \psi \psi^* d\tau}$

average value calculate

BSc III

Date
Page

partical in 1-D box



shown eqn

$$\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}+\frac{d^2\psi}{dz^2}+\frac{8\pi^2M}{h^2}(E-V)\psi=0$$

eqn → x → 0 to 2π → $x=0$ to $x=l$

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2M}{h^2}(E-V)\psi=0$$

box

E, ψ

outside the box $V=\infty$

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2M}{h^2}(E-\infty)\psi=0$$

inside the box $V=0$

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2M}{h^2}(E-0)\psi=0$$

$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2M}{h^2}E\psi=0$$

$$\frac{8\pi^2mE}{h^2} \quad \text{Remark} \quad \frac{2mE\times4\pi^2}{h^2} \quad \Leftarrow \quad k^2\pi^2a^2=\frac{2mE}{h^2} \quad \Leftarrow \quad k=\frac{h}{2\pi}$$

Teacher's Sign.

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad \text{— (I)}$$

$$\Downarrow$$

$$\psi_x = A \sin kx + B \cos x \quad \text{— (II)}$$

A, B- arbitrary const

apply boundary condn

$\Rightarrow x = 0$, $\psi_0 = 0$

$$\psi_{(0)} = A \sin k0 + B \cos 0$$

$(\cos 0 = 1)$

$$0 = 0 + B \times 1$$

$$\boxed{0 = B} \quad \text{— (III)}$$

B ki value eqn (II) me

$$\psi_{(x)} = A \sin kx + B \cos x$$

$$\psi_{(x)} = A \sin kx \quad \text{— (IV)}$$

$\Rightarrow x = L$, $\psi_{(L)} = 0$

$$\psi_{(L)} = A \sin kL + B \cos L$$

$$0 = A \sin kL + 0$$

Remark

Teacher's Sign.

$A \sin KL = 0$

$A \neq 0$, $\sin KL = 0$

$B = 0$ घटेगा

KL angle

we know $\sin n\pi = 0$

$\sin 180 = 0$, $\sin 360 = 0$

$\sin KL = 0$ / $\sin n\pi = 0$

$\sin KL = \sin n\pi$

$KL = n\pi$

$$K = \frac{n\pi}{L}$$

$$K^2 = \frac{n^2\pi^2}{L^2} \quad \text{(V)}$$

$$K^2 = \frac{8mE\pi^2}{h^2} \quad \text{(VI)}$$

$$\frac{8\pi^2 mE}{h^2} = \frac{n^2\pi^2}{L^2}$$

$$\boxed{E = \frac{n^2 h^2}{8mL^2}}$$

Remark

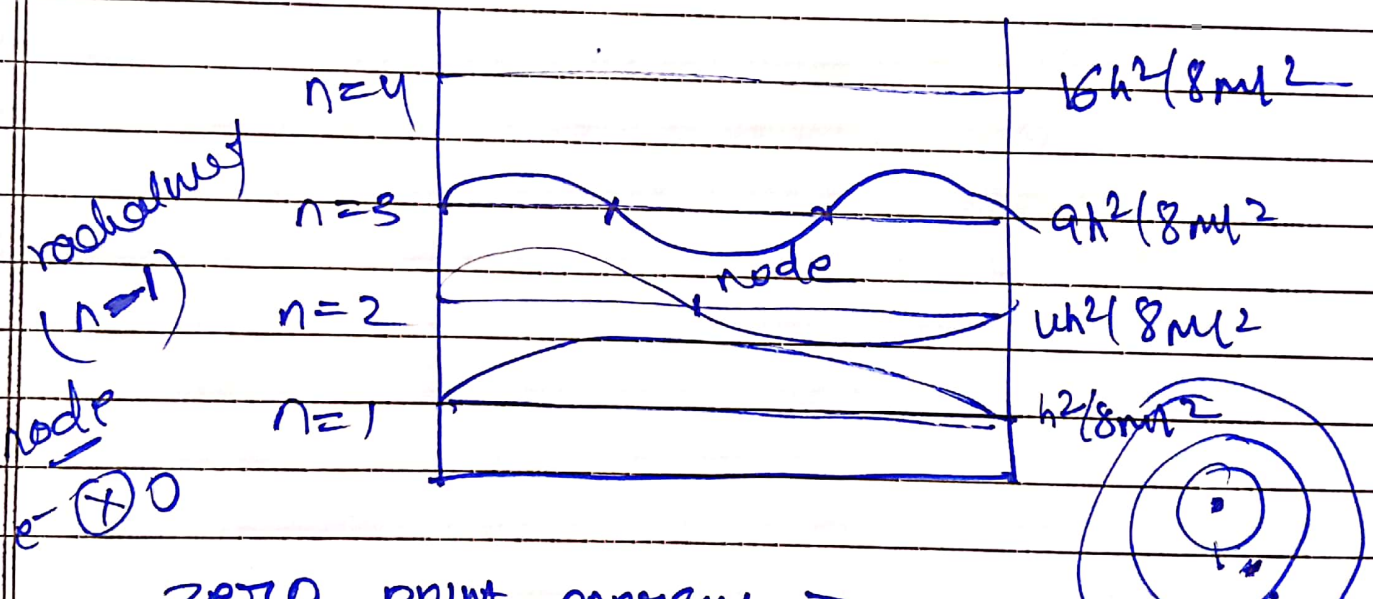
Teacher's Sign.

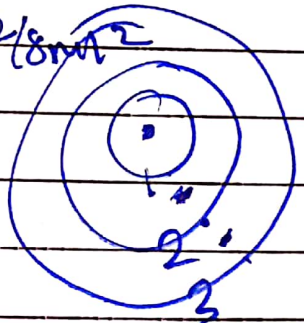
$n=1 \quad \varepsilon_1 = \frac{1^2h^2}{8ml^2}$

$n=2 \quad \varepsilon_2 = \frac{4h^2}{8ml^2}$

$n=3 \quad \varepsilon_3 = \frac{9h^2}{8ml^2}$

$\varepsilon = n^2h^2$





zero point energy $\Rightarrow n=0$

$\varepsilon = \frac{0^2h^2}{8ml^2}$

$\boxed{\varepsilon = 0}$

$n=0$ possible

$\psi = 0$

Remark

Teacher's Sign.

Date
Page

$E_{min} = n=1, \frac{h^2 h^2}{8ml^2}$

zero point energy $n=1 \Rightarrow \frac{h^2}{8ml^2}$

$E_1 \rightarrow E_2$

$\Delta E = E_2 - E_1$

$= \frac{4h^2}{8ml^2} - \frac{h^2}{8ml^2}$

$= \frac{3h^2}{8ml^2}$

$\psi(x) = A \sin kx$

$k = \frac{n\pi}{L}$

$kL = n\pi$

$k = \frac{n\pi}{L}$

$\psi(x) = A \sin\left(\frac{n\pi}{L}\right) x$ — (VII)

$$\int \psi \psi^* \, d\tau = 1$$

$$\int_{x=0}^{x=L} A \sin\left(\frac{n\pi}{L}\right) x \cdot A \sin\left(\frac{n\pi}{L}\right) x \, dx = 1$$

$$\int_0^L A^2 \sin^2\left(\frac{n\pi}{L}\right) x \cdot dx = 1$$

x, y, z

$$A^2 \int_0^L \sin^2\left(\frac{n\pi}{L}\right) x \cdot dx = 1$$

$$\left[\sin^2 = \frac{1 - \cos 2x}{2}\right]$$

$$A^2 \int_0^L \frac{1 - \cos\left(\frac{2n\pi}{L}\right) x}{2} \cdot dx = 1$$

$\frac{1-x}{2} \to \frac{1}{2} - \frac{x}{2}$

$$A^2 \int_0^L \frac{1}{2} dx - \int_0^L \frac{\cos\left(\frac{2n\pi}{L}\right) x \, dx}{2} = 1$$

Remark

Teacher's Sign.

$$A^2 \times \frac{1}{2}\left[\int_0^l dx - \int_0^l \cos\left(\frac{2n\pi}{l}\right)x\,dx\right] = 1$$

$$\int 1\,dx = x$$

$$A^2 \times \frac{1}{2}\left[(x)_0^l - \int_0^l \frac{\sin\frac{2n\pi}{l}x}{\frac{2n\pi}{l}}\,dx\right] = 1$$

$$\frac{A^2}{2}\left[(l-0) - \frac{l}{2n\pi} \times \int_0^l \sin\frac{2n\pi}{l}x\,dx\right] = 1$$

$$\frac{A^2}{2}\left[l - \frac{l}{2n\pi}\left[\sin\frac{2n\pi}{l} \times l - \sin\left(\frac{2n\pi}{l}\right)\times 0\right]\right] = 1$$

$$\frac{A^2}{2}\left[l - \frac{l}{2n\pi}\left[\sin 2n\pi - 0\right]\right] = 1$$

$$\left(\sin n\pi = 0\right)$$

$$\frac{A^2}{2}\left[l - \frac{l}{2n\pi} \times 0\right] = 1$$

$$\frac{A^2}{2} \times l = 1 \Rightarrow A^2 = \frac{2}{l} \Rightarrow \boxed{A = \sqrt{\frac{2}{l}}}$$

Remark

Teacher's Sign.

$$\psi(x) = \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi}{l}\right)x$$

$$\underline{E} \;/\; \underline{\psi}$$

Expt. No. _____ Date _____

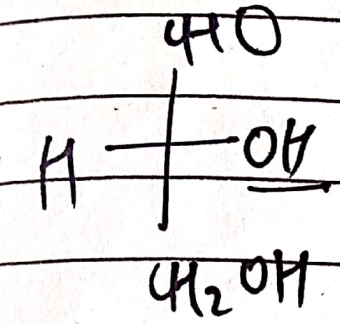
Page No. _____

Stereochemistry

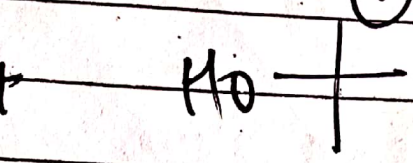
D L In Monosac.

(d l)

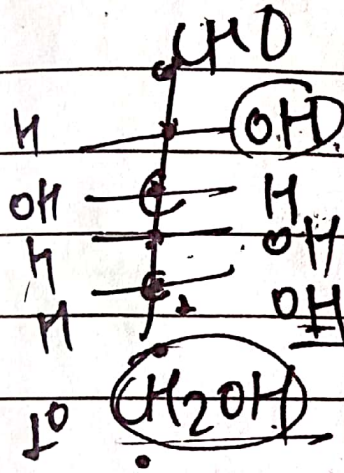
(+)



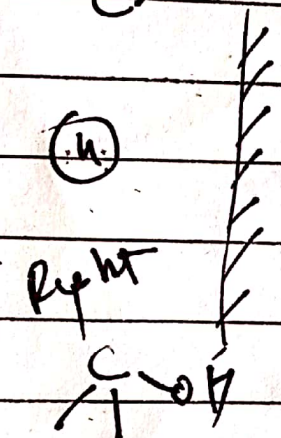
Right

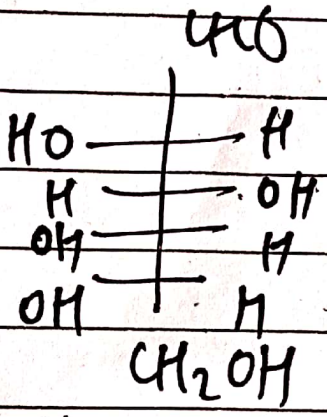


L-glycer



(n)





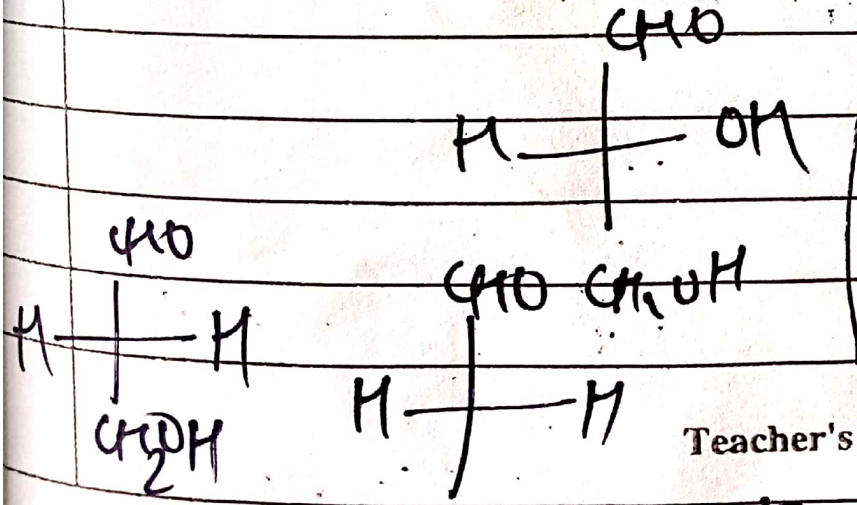
D-

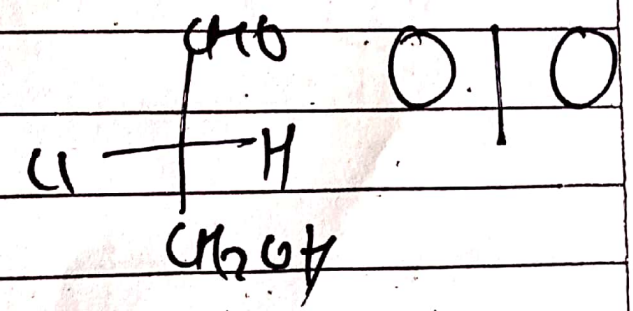
Right

nonsuperimposible-opt actm

enantiomer ⇒ Mirror image →

Diastereomer ⇒ Non-Mirror image





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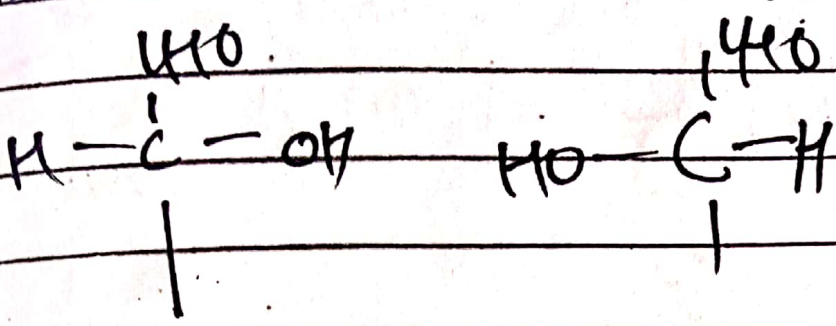
opt Inq (X)

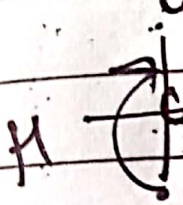
Expt. No.

epimer → C-1 config. change



2^n , n = asy C no. of

$2^4 = 2 \times 2 \times 2 \times 2 = 16$

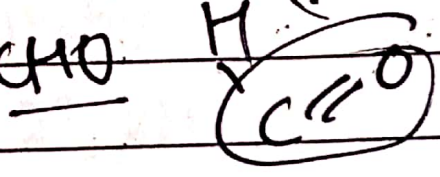


$2^1 = 2$

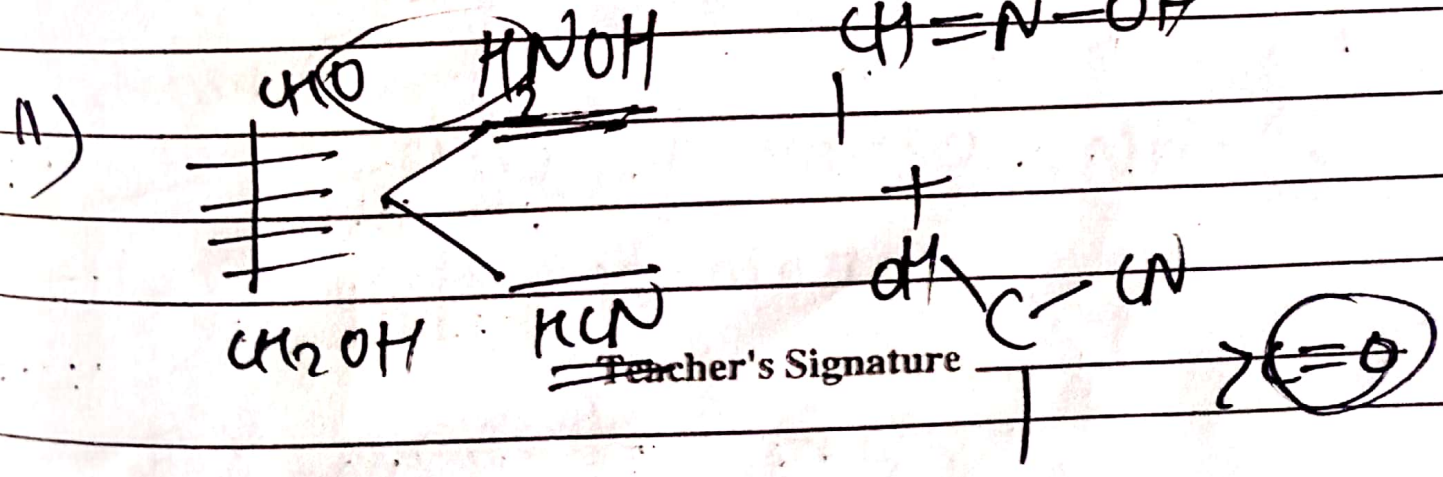
d l

glucose structure (open chain)

1) $C_6H_{12}O_6$



A)



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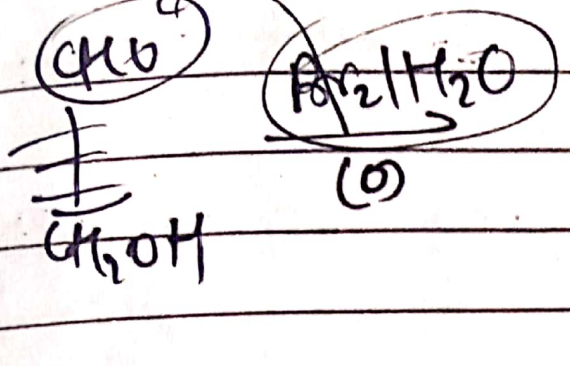
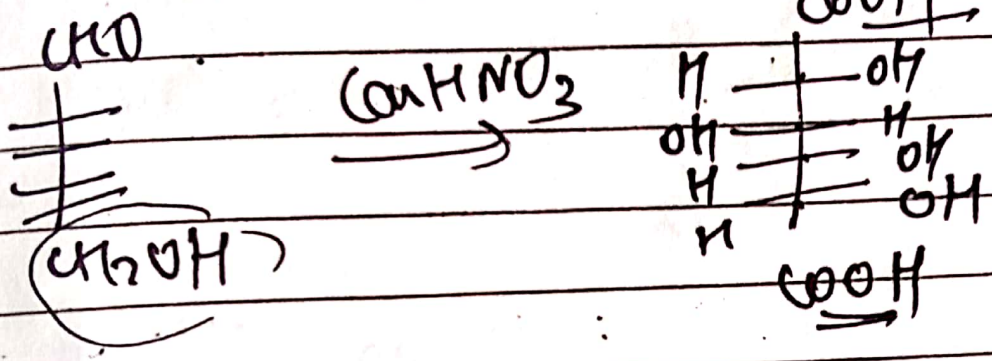
Expt. No. _____ Page No. _____

$-CHO$ $-C=O$ (1)

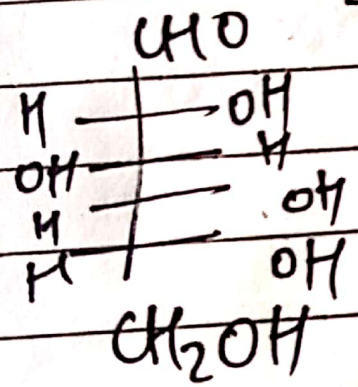
ii) 

$-CHO$ ✓

iii) 

1^0 $-OH$ ✓ easily

2^0 $-OH$ → (4)



$-CHO$

$1 - 1^0 - OH$

$4 - 2^0 - OH$

define (X)

i) $-CHO$ / $NaHSO_3$, NH_3 (X)

ii) α, β - isomer (X)

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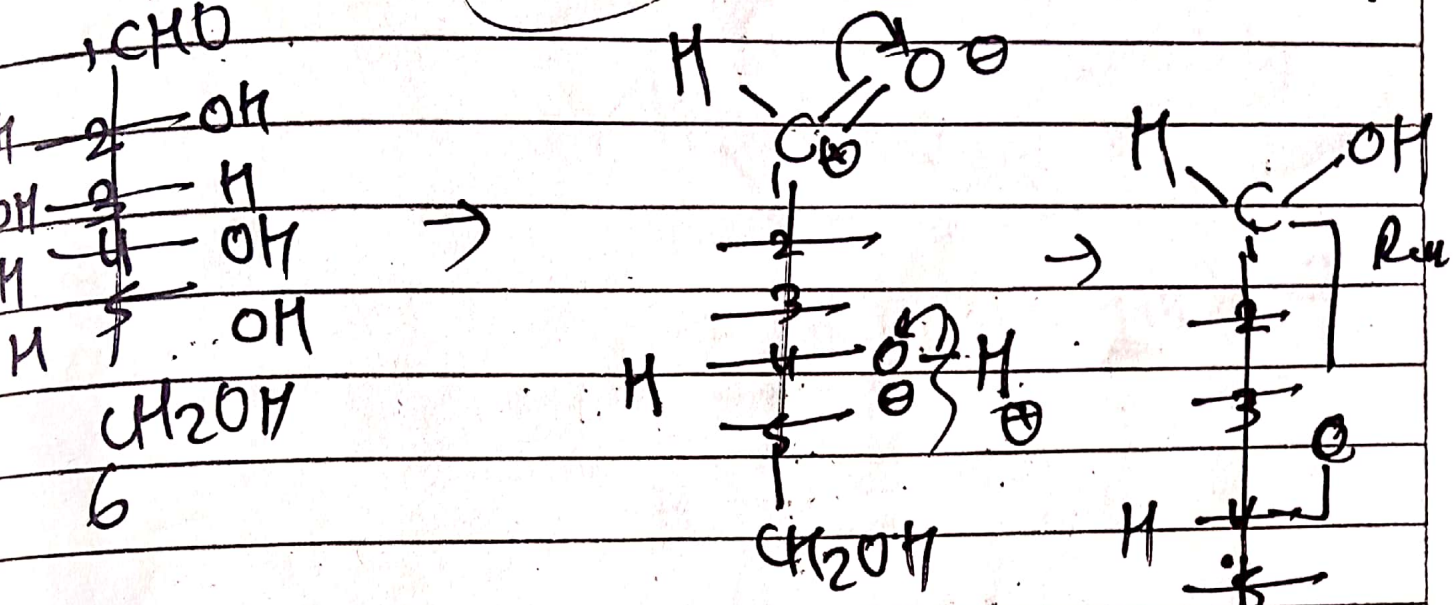
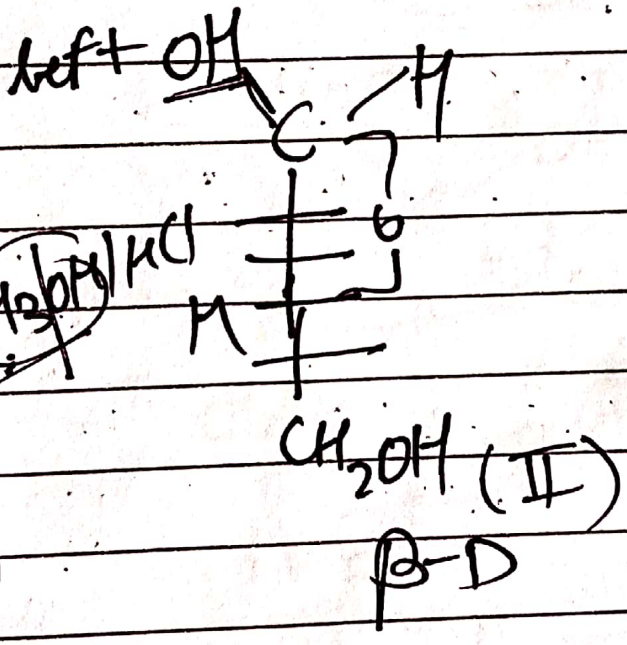
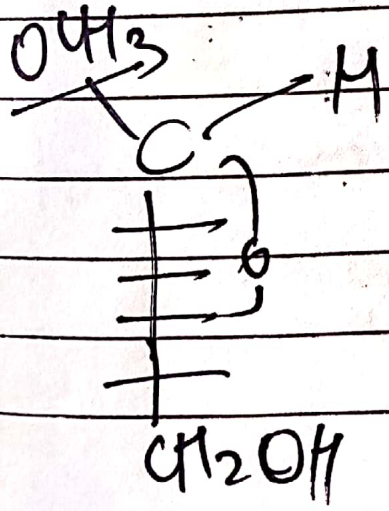
iii) ~~mutarotation~~ (X)

Expt. No. _____ Page No. _____

ring structure 1893, fischer Tollen
5 mem. (4C + 1O) C_1-C_4







(II) β-D..

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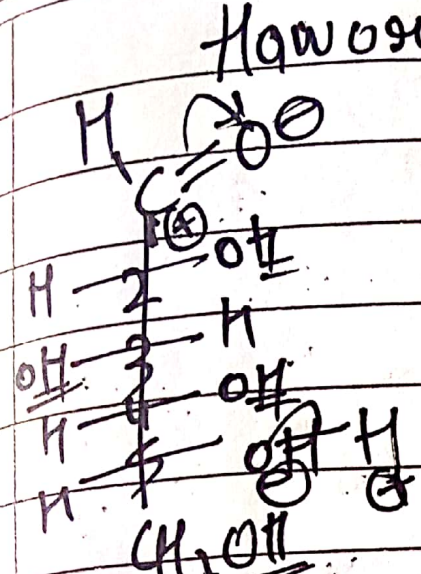
Date

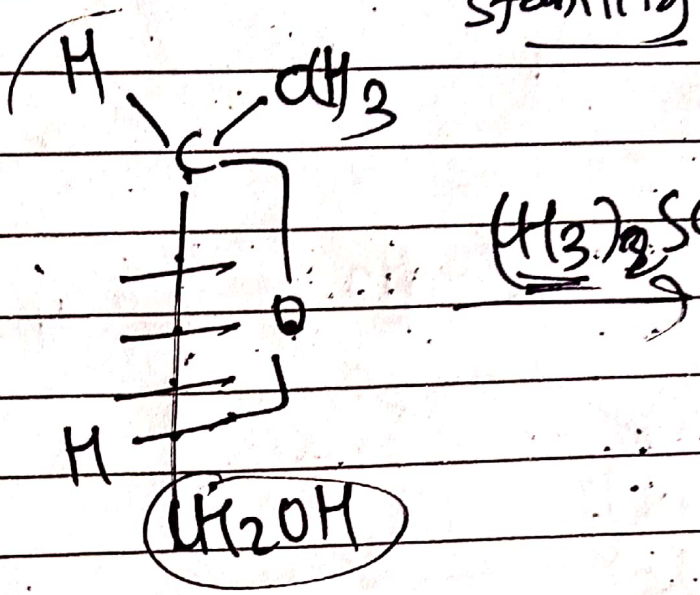
Expt. No. Page No.

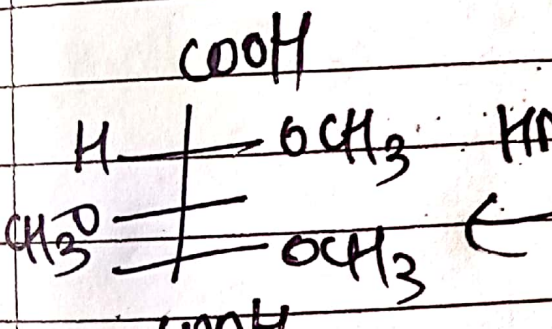
Haworth 1926 — (6) mem

$C_1 - C_5$ (5C + 1O)

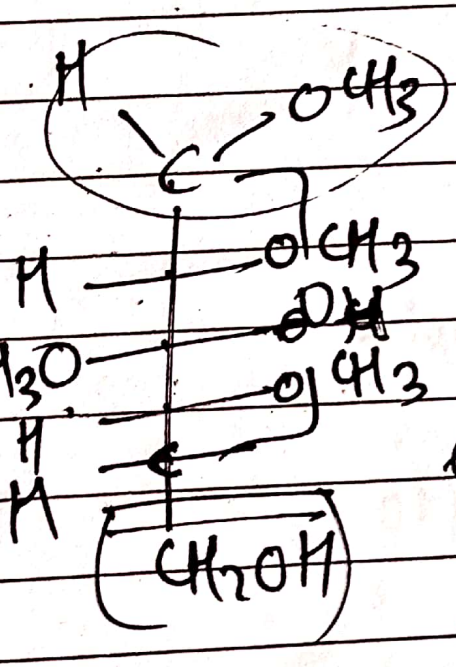


stability

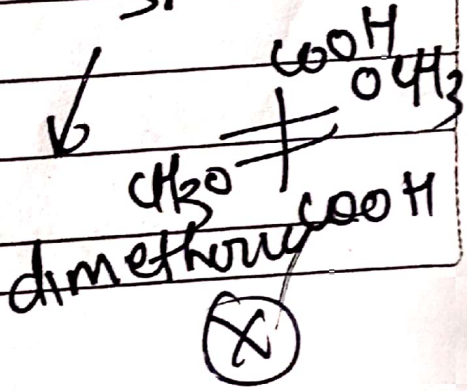




trimethoxy



6 mer



dimethoxy

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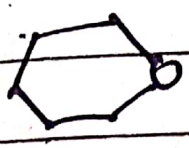
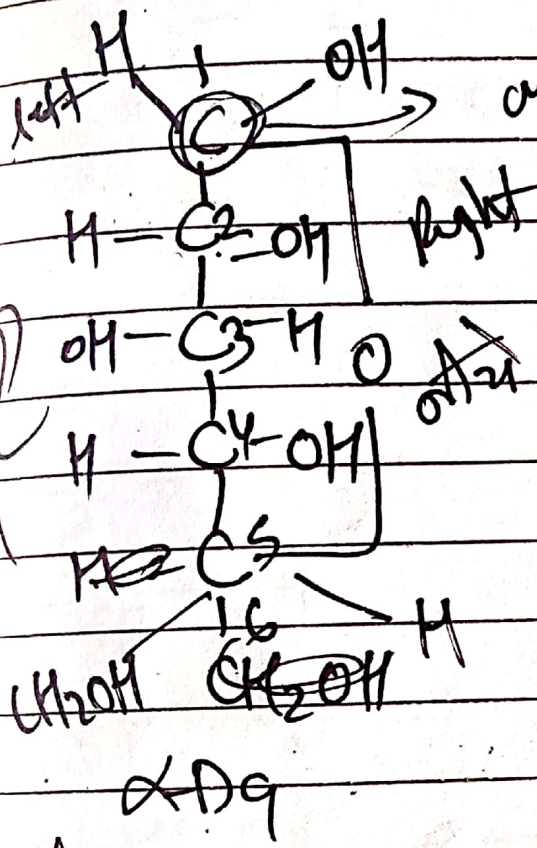
Expt. No. _____ Page No. _____

cyclic glucose ← α & β

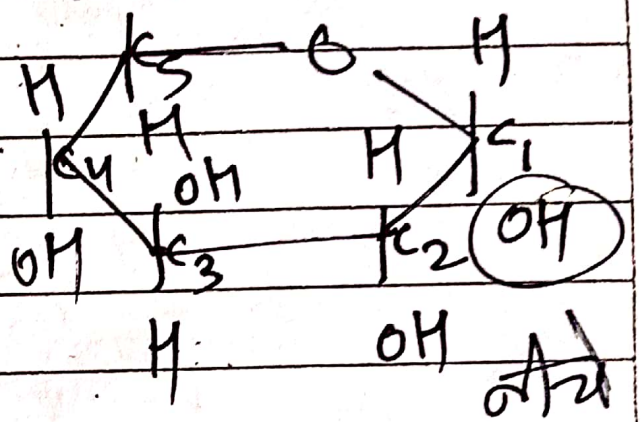


glucopyranose



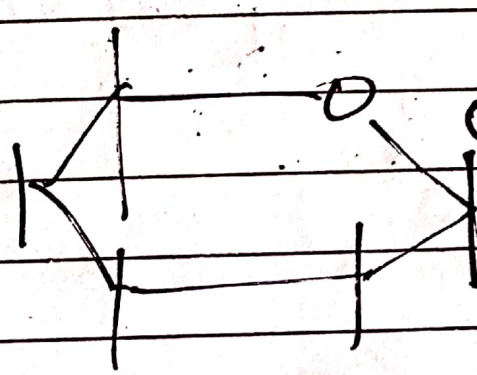
α-D-glu

fischer



α-D-glu

Haworth



β-glucose

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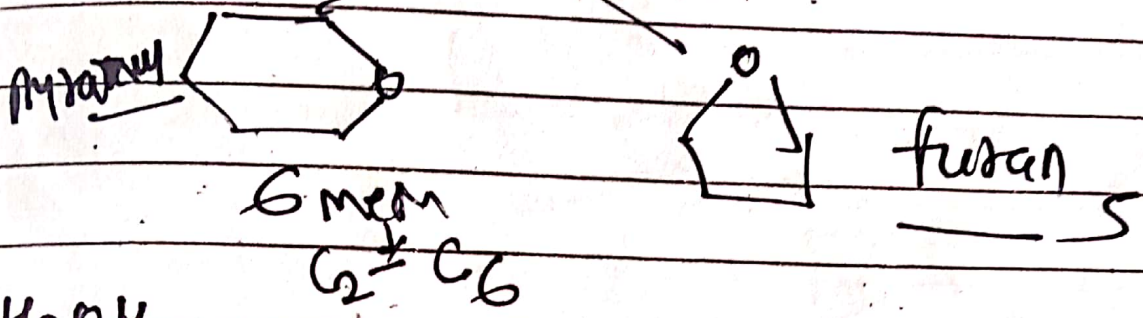
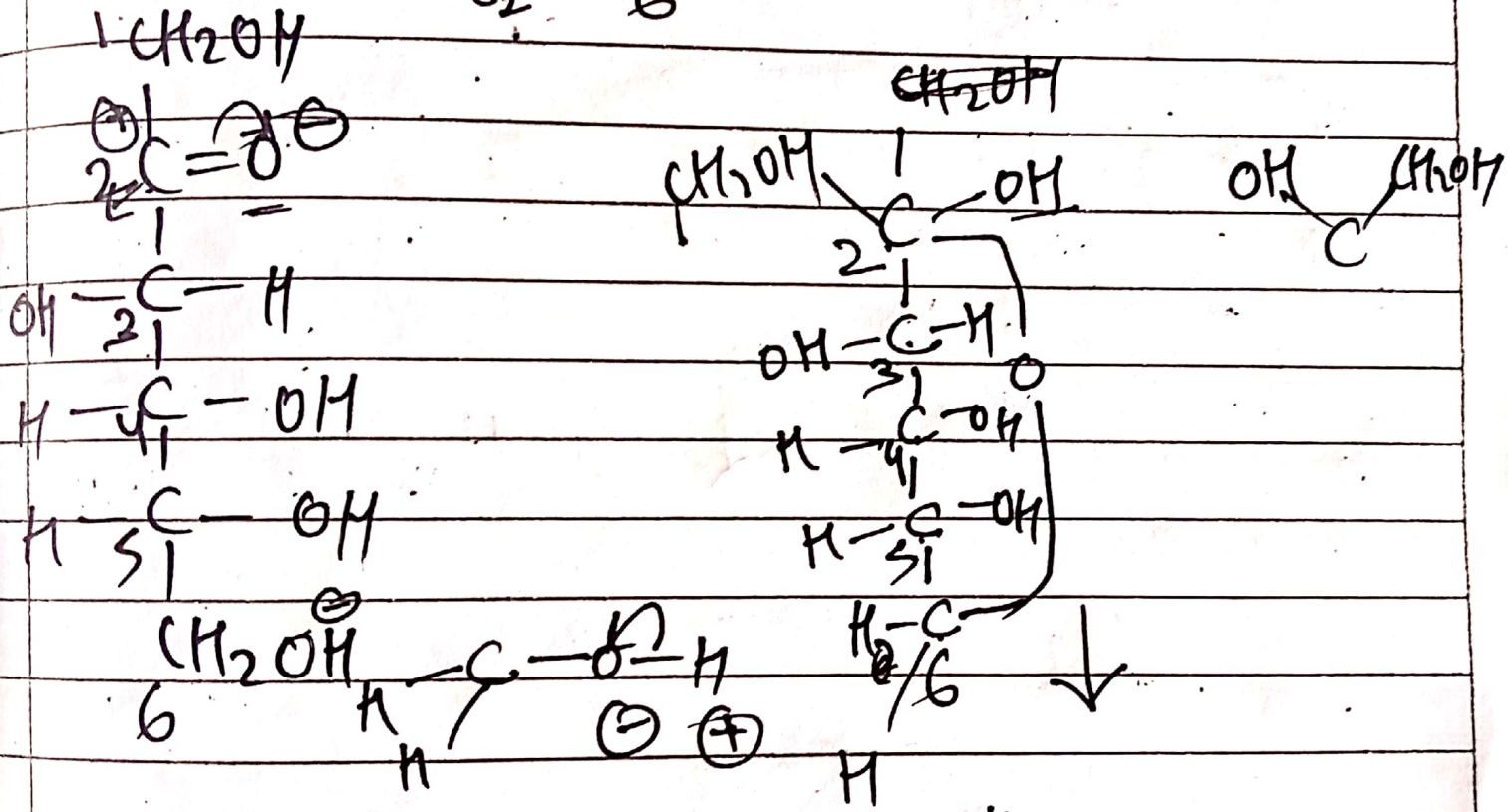
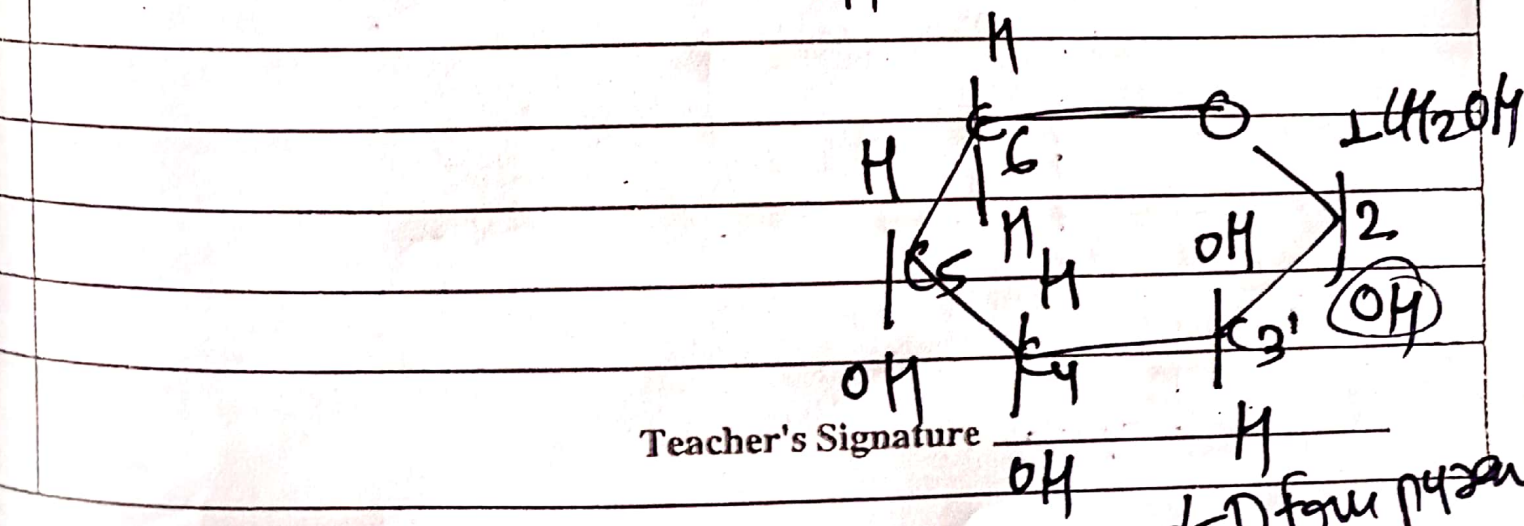
Date

Expt. No. Page No.

fructose → levulose, fruit sugar







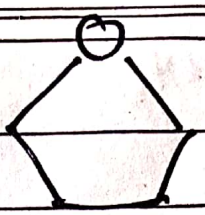
Teacher's Signature

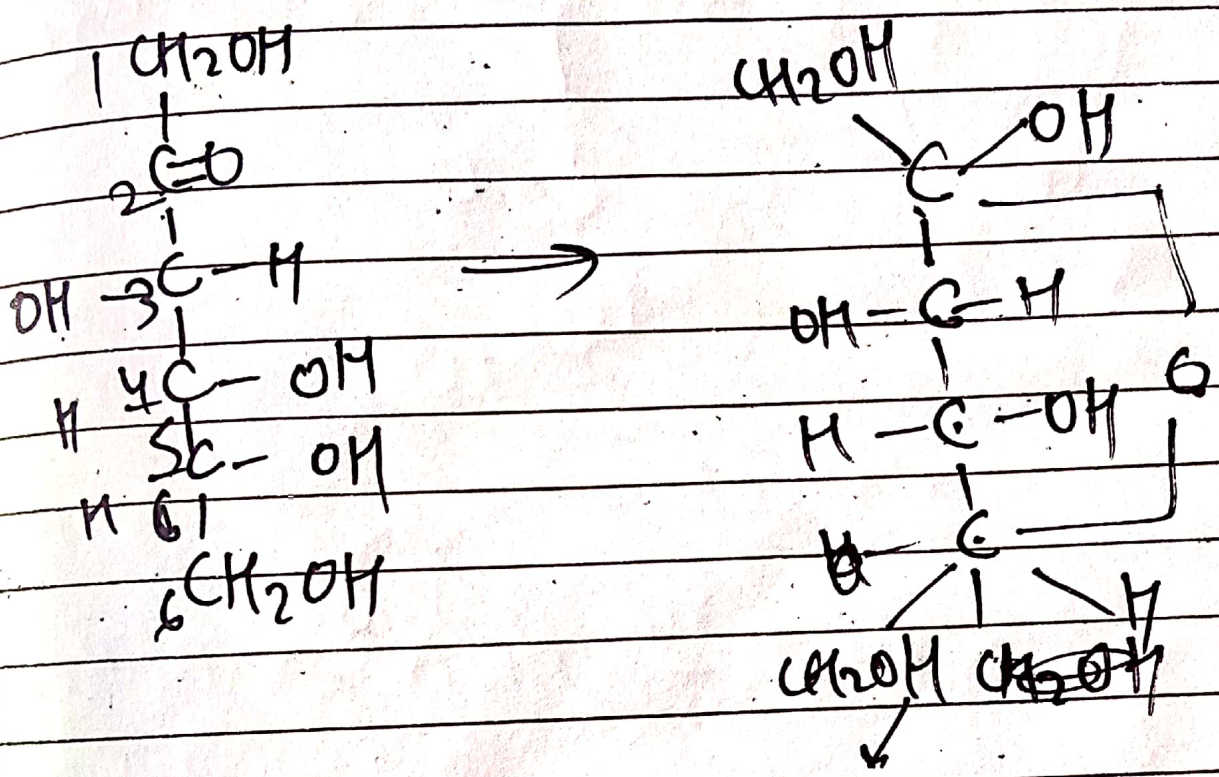
α-D fructopyranose

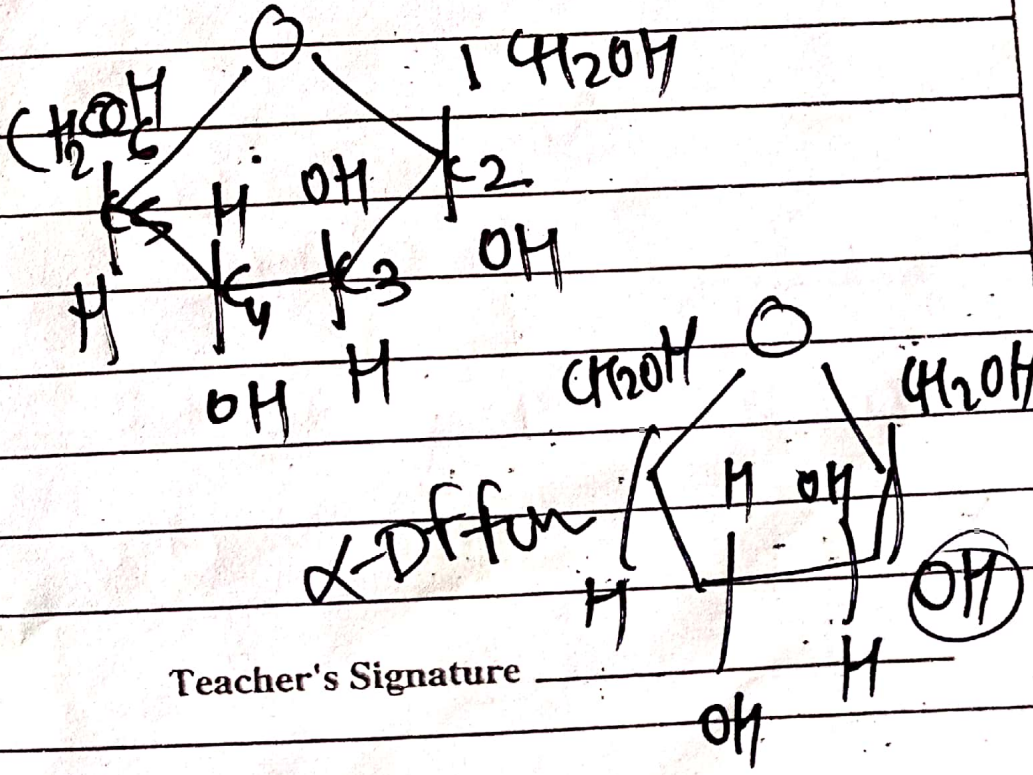
Date

Expt. No. Page No.

5 mem
C_2-C_5





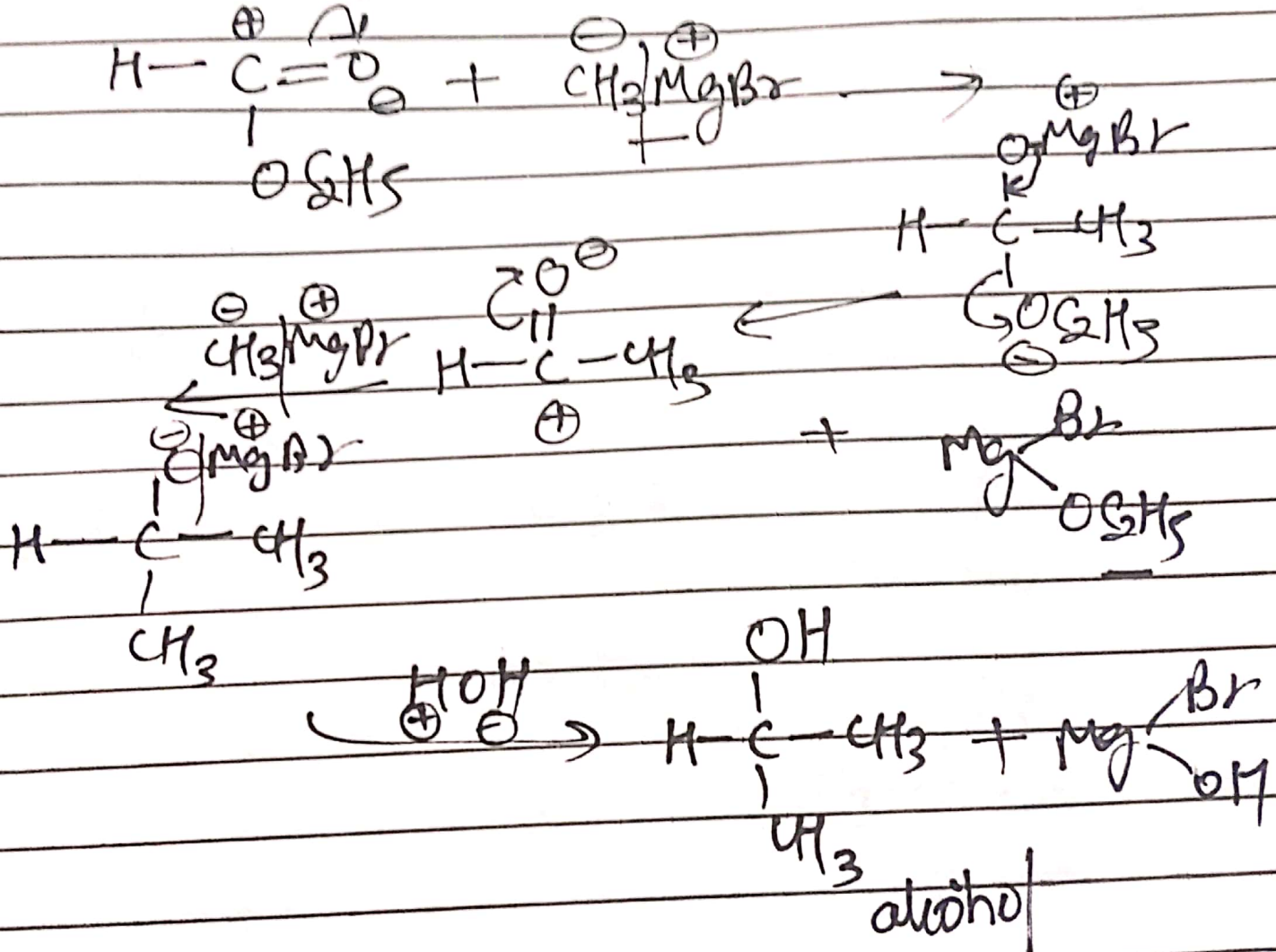


Teacher's Signature

(C) Double decomposition & addition

2 mol of CH_3MgBr

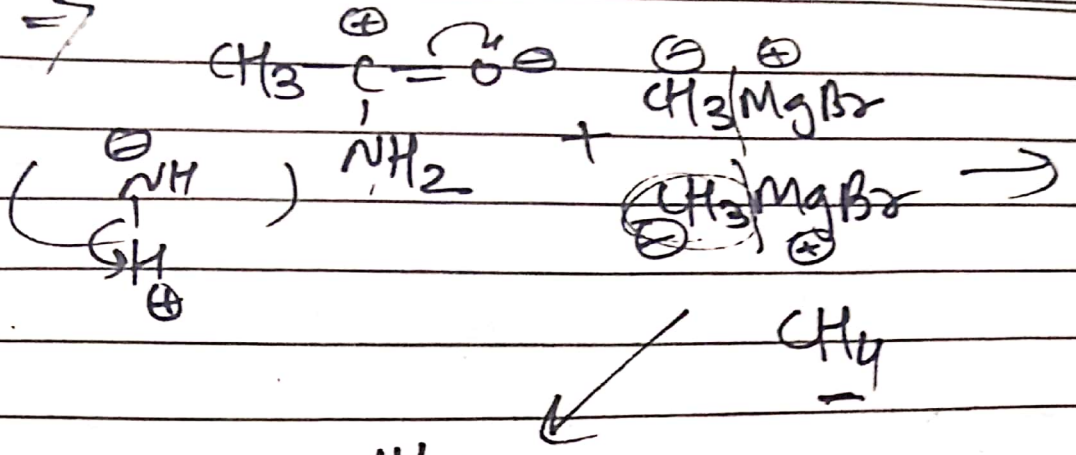
(1) Ester ⇒



alcohol

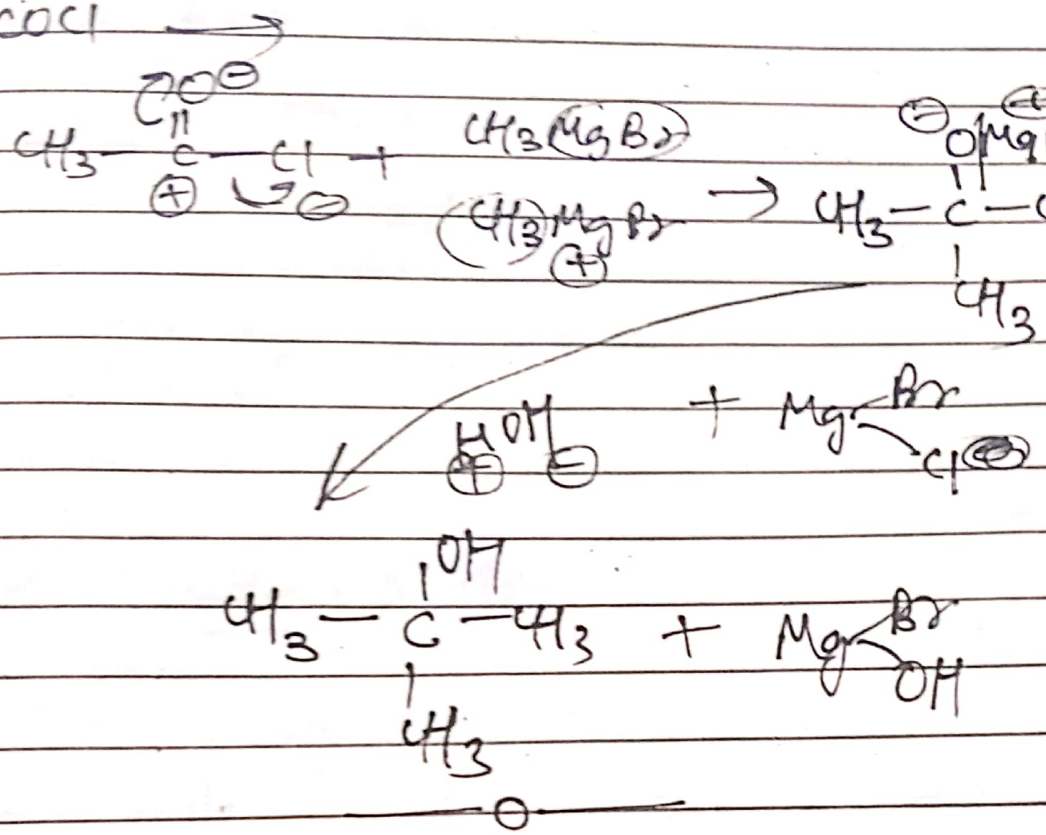
$CH_3-C(=O)-C_2H_5 \longrightarrow$

(2) Amide →



(3)

Scanned with CamScanner



Organo-zinc compound $(CH_3)_2Zn$

dialkyl zinc $(C_2H_5)_2Zn$

formation ⇒ (I) $C_2H_5I + Zn \rightarrow C_2H_5ZnI$

$C_2H_5ZnI + C_2H_5ZnI \rightarrow (C_2H_5)_2Zn + ZnI_2$

(II) $2C_2H_5-I + Zn-Cu \rightarrow$

$(C_2H_5)_2Zn + CuI_2$

Remark

Teacher's Sign.

colourless, 118°C, flammable liquid

Chemical Reaⁿ ⇒ ① alkane ←

water, alcohol, alkyl halide

$C_2H_5-Zn-C_2H_5 + 2HOH \rightarrow 2C_2H_6 + Zn(OH)_2$

$C_2H_5-Zn-C_2H_5 + 2C_2H_5\overset{\ominus}{O}\overset{\oplus}{H} \rightarrow 2C_2H_6 + Zn(OC_2H_5)_2$

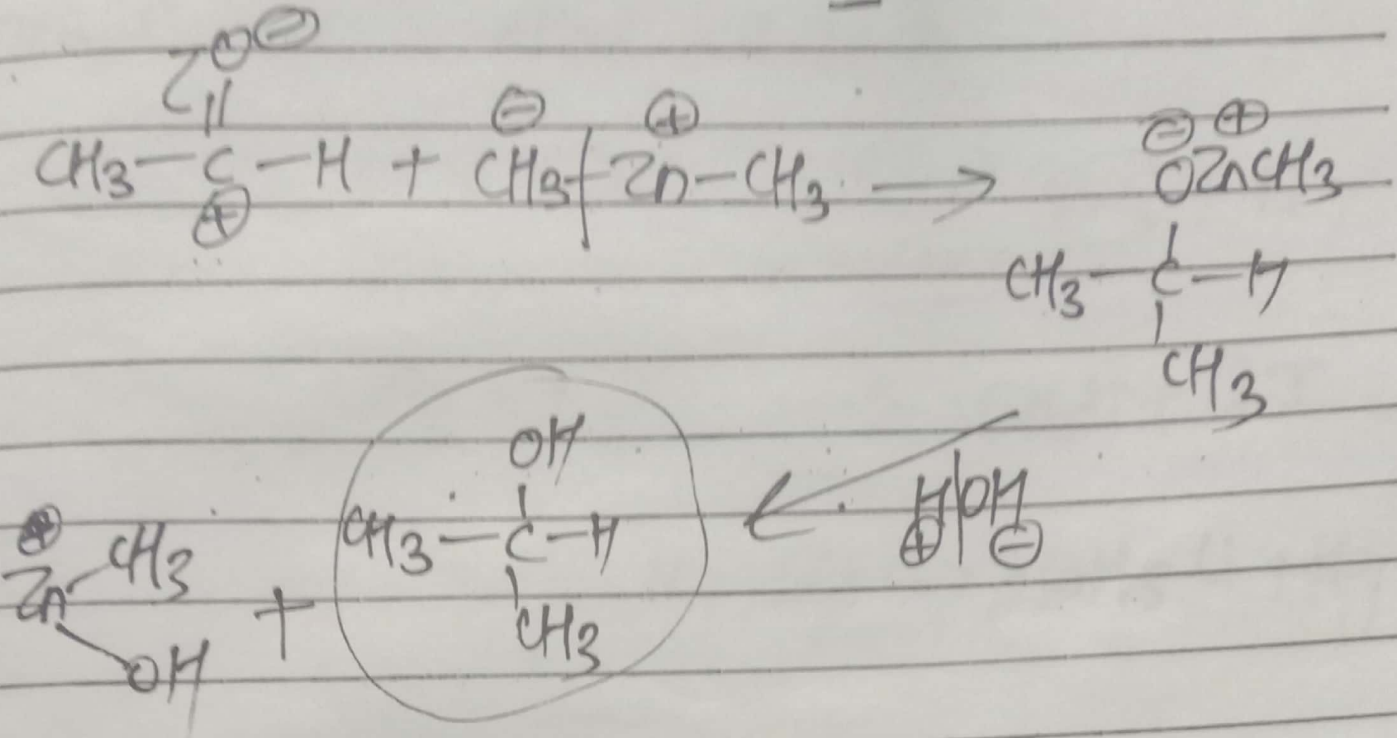
$C_2H_5-Zn-C_2H_5 + 2CH_3I \rightarrow 2C_2H_5-CH_3 + ZnI_2$

(11)

$CH_3-\overset{\overset{O}{\|}}{\underset{\oplus}{C}}-Cl + C_2H_5-\overset{\ominus}{|}\overset{\oplus}{Zn}-C_2H_5 \rightarrow$

$CH_3-\overset{\overset{O-Zn-C_2H_5}{|}}{\underset{C_2H_5}{C}}-Cl \xrightarrow{HOH} CH_3-\overset{\overset{O}{\|}}{C}-C_2H_5 + Zn(C_2H_5)Cl^{\ominus} \rightarrow C_2H_6 + Zn(OH)Cl$

(3) ether → alcohol



(4)

$$C_2H_5-Zn-C_2H_5 + 2I_2 \rightarrow 2C_2H_5I + ZnI_2$$

—o—

Organo-li-comp.

Li—OMC

(I) CH_3-Li (II) C_2H_5Li (III) $CH_3-CH_2-CH_2-CH_2-Li$

C_6H_5-Li

Remark

Teacher's Sign

Date
Page

formation ⇒ (I) alkyl halide

$$R-X + 2Li \xrightarrow[n\text{-hexane}]{-10^\circ C} R-Li + LiX$$

$$C_2H_5I + 2Li \longrightarrow C_2H_5Li + LiI$$

(II)

$$(C_2H_5)_2Hg + 2Li \longrightarrow 2C_2H_5Li + Hg$$

Chemical Reaction ⇒

(I)

$$R^{\ominus}-Li^{\oplus} + H^{\oplus}-OH^{\ominus} \longrightarrow LiOH + RH$$

$$CH_3^{\ominus}-Li^{\oplus} + C_2H_5O^{\ominus}-H^{\oplus} \longrightarrow CH_4\uparrow$$

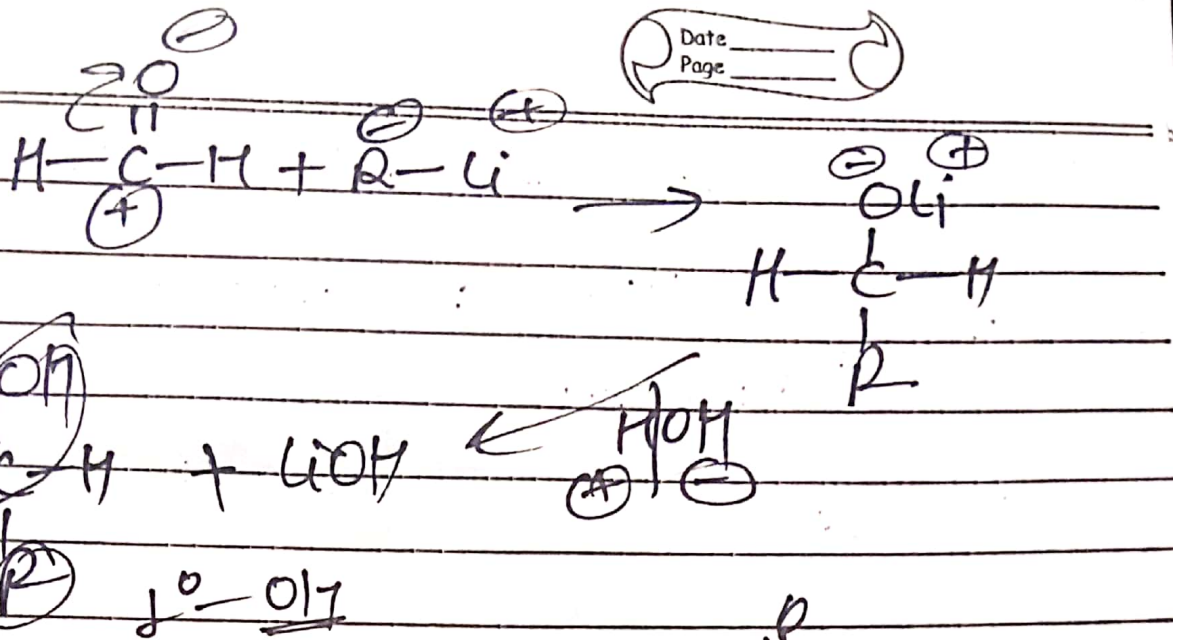
$$R-OH \quad R^{\ominus}O-H^{\oplus}$$

$$LiOC_2H_5$$

(II) ~~$C_2H_5Li + S \longrightarrow$~~ $C_2H_5S^{\ominus}Li^{\oplus} \xrightarrow{H^{\oplus}OH^{\ominus}}$

$$C_2H_5SH + LiOH$$

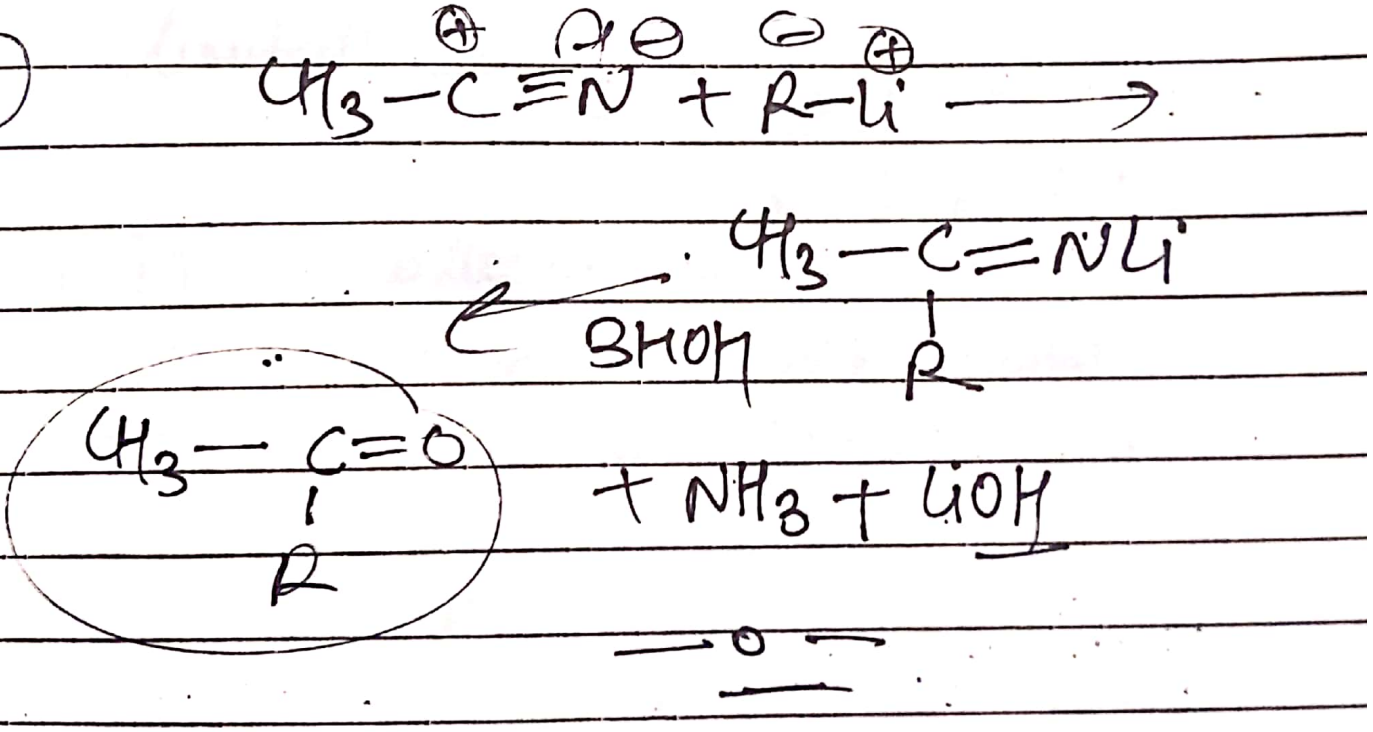
(III)



(II) $CH_3-\overset{R}{\overset{|}{C}}=H$

(III) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

(IV)



$+ NH_3 + LiOH$

—o—

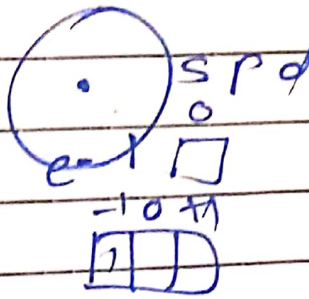
BSc III

ψ

Schrodinger wave eqn for H-atom

single e⁻ system, He^+, Li^{2+}

(n l) (m)

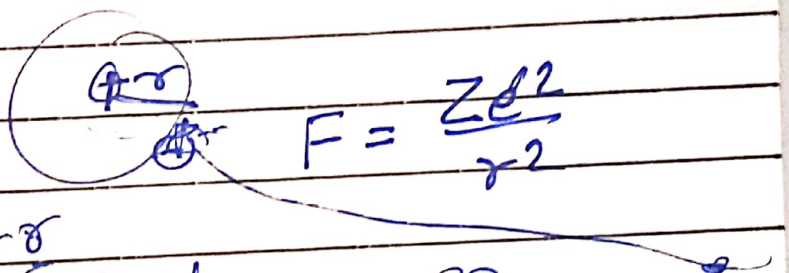


$$H\psi = E\psi$$

$$H = \frac{-h^2}{8\pi^2 m}\nabla^2 + V$$

$$\frac{-h^2}{8\pi^2 m}\nabla^2\psi + V\psi = E\psi \quad \text{---(1)}$$

A/c Coulombs



$$F = \frac{Ze^2}{r^2}$$

$$V = \int_{\infty}^{r} f \times dr \qquad 3D$$

$$\int r^n dr = \frac{r^{n+1}}{n+1}$$

$$V = \int_{\infty}^{r} \frac{Ze^2}{r^2} dr \Rightarrow Ze^2 \int \frac{1}{r^2} dr$$

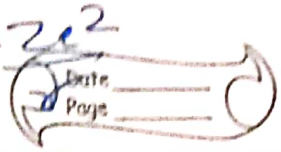
$$\Rightarrow Ze^2 \int \frac{r^{-2+1}}{-2+1} \Rightarrow Ze^2 \int \frac{r^{-1}}{-1}$$

$$\Rightarrow 2e^2 \int -\frac{1}{r} \Rightarrow -\frac{Ze^2}{r}$$

Remark

Teacher's Sign.

(1)



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

Cartesian coordinate

$x = r\sin\theta\cos\phi$ $\quad r = 0 \text{ to } \infty$

$y = r\sin\theta\sin\phi$ $\quad \theta = 0 \text{ to } \pi$

$z = r\cos\theta$ $\quad \phi = 0 \text{ to } 360$

→ Spherical motion ⇒ Car coordinate → polar coordinate

$x, y, z \rightarrow r\theta\phi$

$$\frac{d^2\psi}{dx^2}=\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right), \quad \left(\frac{d^2\psi}{dy^2}\right)=\frac{1}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right)$$

$$\frac{d^2\psi}{dz^2}=\frac{1}{r^2\sin^2\theta}\frac{d^2\psi}{d\phi^2}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right)+\frac{1}{r^2\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\psi}{d\theta}\right)+\frac{1}{r^2\sin^2\theta}\left(\frac{d^2\psi}{d\phi^2}\right)+\frac{8\pi^2m}{h^2}\left(E+\frac{2e^2}{r}\right)\psi=0$$

r^2 ~~cm~~ ~~Tsin~~

Remark

Teacher's Sign.

$$\frac{d}{dr}\left(\frac{r^2 d\psi}{dr}\right) + \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\psi}{d\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{d^2\psi}{d\phi^2}\right)$$

$$+ \frac{8\pi^2 m}{h^2}\left(\epsilon + \frac{2e^2}{r}\right) r^2 = 0 \quad (3)$$

$$\psi(r,\theta,\phi) = \underbrace{\psi(r) \times \psi(\theta) \times \psi(\phi)}_{n\ l\ \ m}$$

Radial angular

$$\psi = R\Theta\Phi$$

$$\left(r^2 \frac{d R\Theta\Phi}{dr}\right) + \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d R\Theta\Phi}{d\theta}\right) + \frac{1}{\sin^2\theta}$$

$$\left(\frac{d^2 R\Theta\Phi}{d\phi^2}\right) + 8 \text{ ——— } = 0$$

$$\frac{R\Theta\Phi}{R\Theta\Phi}\frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) + \frac{R\Phi}{R\Theta\Phi}\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) + \frac{1}{\sin^2\theta}$$

$$\frac{R\Theta}{R\Theta\Phi}\left(\frac{d^2\Phi}{d\phi^2}\right) + 8 \text{ ~~~~ } = 0$$

$R\Theta\Phi$ से divide

Remark Teacher's Sign.

$$\Rightarrow \frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)$$

$$+\frac{1}{\Phi}\frac{1}{\sin^2\theta}\left(\frac{d^2\Phi}{d\phi^2}\right)+\frac{8\pi^2m}{h^2}\left(E+\frac{2e^2}{r}\right)=0$$

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{8\pi^2m}{h^2}\left(E+\frac{2e^2}{r}\right)\psi=\beta$$

$$\frac{1}{\Phi}\left(\frac{d^2\Phi}{d\phi^2}\right)=-m^2 \quad \text{— constant}$$

$$\Rightarrow \beta+\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)-\frac{m^2}{\sin^2\theta}=0$$

$$\frac{1}{\Theta}\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)+\left(\beta-\frac{m^2}{\sin^2\theta}\right)=0$$

Radial wave

Date
Page

ψ → Radial wave fn → radius
→ orbital
→ angular → axis ~~to~~ ~~angle~~
w.r. angle

$\psi_{total} = \psi_{(r)} \times \psi_{(\theta)(\phi)}$ → 0–360
↓
0 to 180

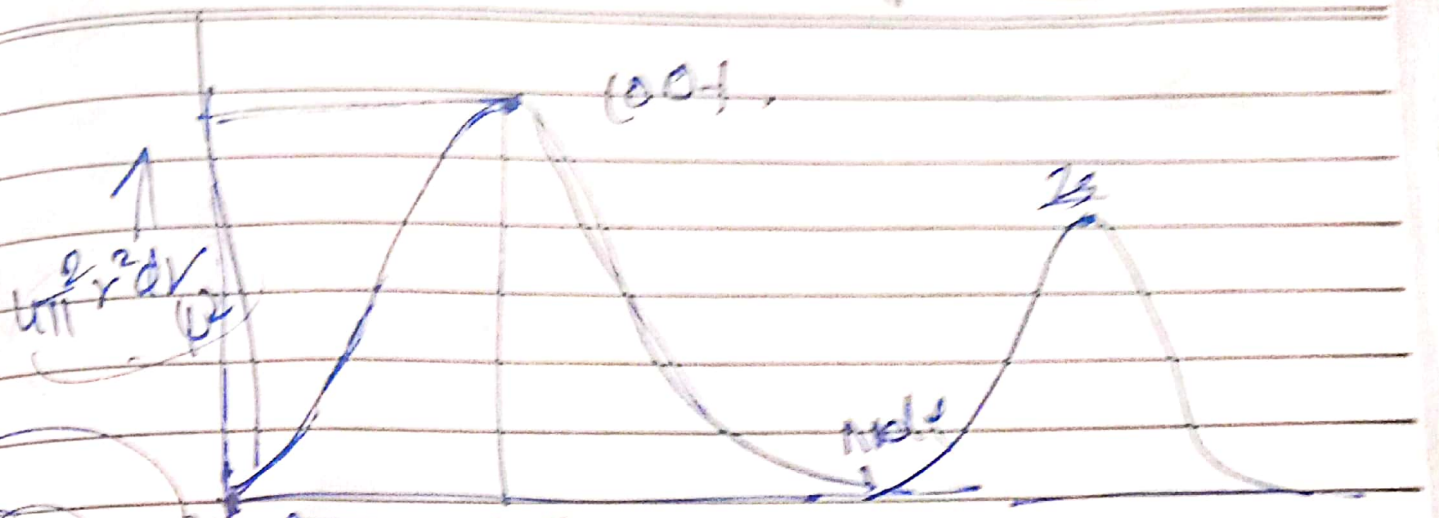
ψ → +ve
→ -ve
γ
produce ⊣ (X)

ψ^2 = probability density ⇒ e ~~on~~ ~~surface~~

total probability = Vol of shell $\times \psi^2$

RPD

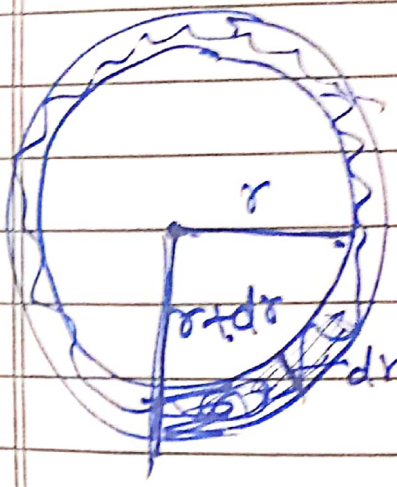
$$P = 4\pi r^2 dr \cdot \psi^2$$



nodal

$4\pi^2 r^2 dr$

* Shell volume



$\frac{4\pi r^3}{3}$

Shell vol. = vol. of sphere $(r+dr)$ − vol. of sph (r)

$$= \frac{4}{3}\pi(r+dr)^3 - \frac{4}{3}\pi r^3$$

$$(a+b)^3 = a^3 + b^3 + 3ab(a+b)$$

$$= \frac{4}{3}\pi\left(r^3 + dr^3 + 3r\,dr(r+dr)\right) - \frac{4}{3}\pi r^3$$

Remark

Teacher's Sign.

$$= \frac{4}{3}\pi\left(r^3 + dr^3 + 3r^2dr + 3rdr^2\right) - \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\pi\left(r^3 + dr^3 + 3r^2dr + 3rdr^2 - r^3\right)$$

$$= \frac{4}{3}\pi\left(dr^3 + 3r^2dr + 3rdr^2\right)$$

dr^3 & dr^2 → negligible

$$= \frac{4}{3}\pi \times 3r^2dr$$

vol. of shell $\Rightarrow 4\pi r^2 dr$

$$\therefore P = 4\pi r^2 dr \times \psi^2$$

BSc III

PH - Unit - II

Elementary quantum mechanics - II

उदा. ⇒ HCl HBr

H — Cl

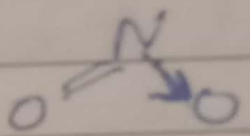
↓ bond

↙ ↓ ↘ co-ordinate

ionic bond ⑦ ⑥ covalent bond C↔C

N⁺→O⁻

NO_2



VBT ⇒ 1) H H → H_2

overlapping

2) orbital - half-filled ⇒ H ↕ H

3) ⑦ ⑦ ⑦

electron density ⑦ bond strong ⑦

4) overlap ← सममिति अक्ष

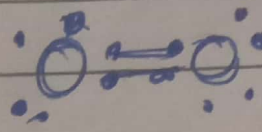
सममिति symmetry

Remark

Teacher's Sign.

limitation ⇒ (I) covalent bond नहीं

(II) co-ordinate bond (X) IP

(III) O_2 3 तरीके  ⇒ यौगिक

para → unpaired e⁻ ✓

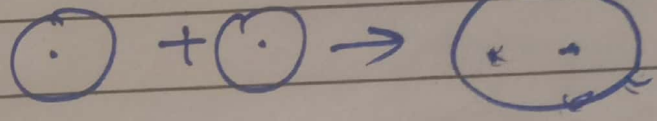
dia → unp e⁻ (X)

अनुचुम्बकीय → O_2 paramag.

(IV) $H_2^{\oplus}$ $O_2^{\ominus}$ O_2^{2-} नहीं (X)

(V) resonance

MOT

I) overlapping 

AO AO MO

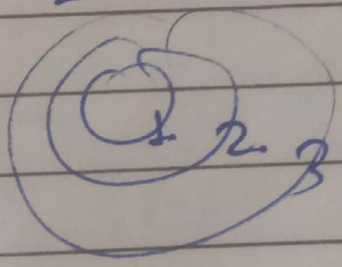
II) MOT → MO → polycentric

III) over ← (समान ऊ – D समान)

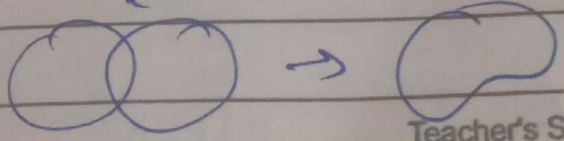
समान sym

1s – 2s

& over (X)

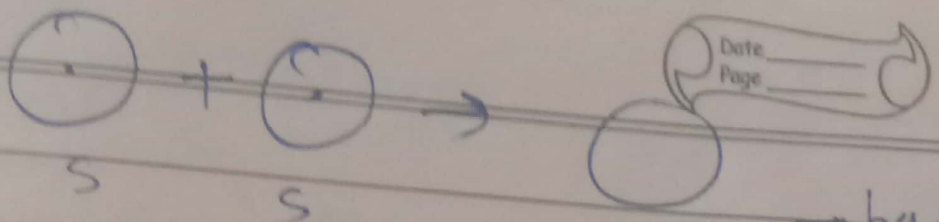


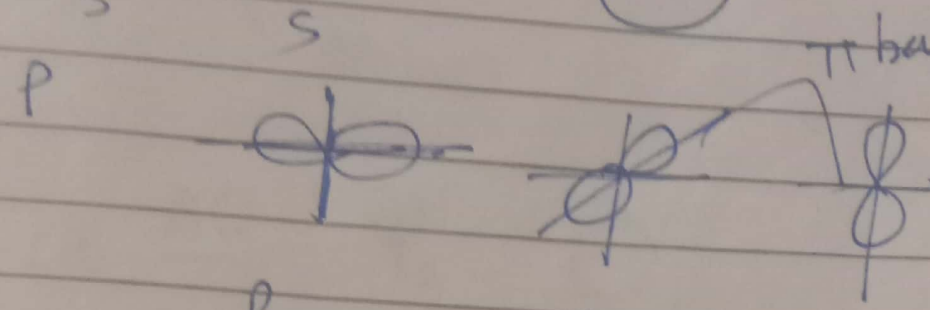
1s – 1s



Remark

Teacher's Sign.





σ_{1s} σ_{1s}^* σ_{2s} σ_{2s}^* $(\pi_{2p_x} = \pi_{2p_y})$ σ_{2p_z}

π — σ_{2p_z}

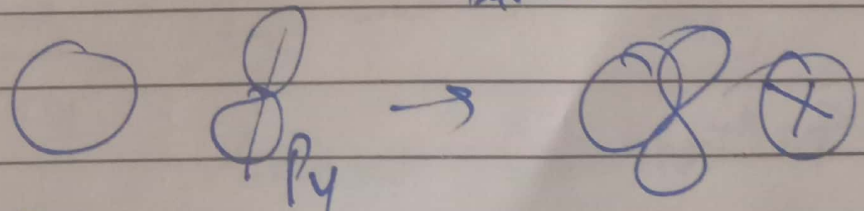
σ —

Symmetry → orbital shape

σ^*

2s - 2p$_y$ (*)

n = Sigma



(2) $2p_z - 2p_z$ / $3p_z - 2p_z$

Remark $4p_x - 3p_x$ / $3s - 4s$ Teacher's Sign. $3p_x - 3p_x$

(iv) MO ⟨ ABMO
BBMO

2

(v) (A) AO — ψ_A
B → ψ_B

(vi) B.O → Bond order

$\frac{N_b - N_a}{2}$ = No. of bond

b-o + (-)

O_2 3 ≡ O=O

N_2 3 ≡ N≡N

MO

$N_2 > O_2$

$N_2 < O_2$

LCAO

shrd' way ⊥ e⁻ system with

eqn → linear Combnat" of AO

Remark

Teacher's Sign.

LCAO

Date
Page

(A) (B)

ψ_A ψ_B

(1) addit^n → same sign ka fi phase

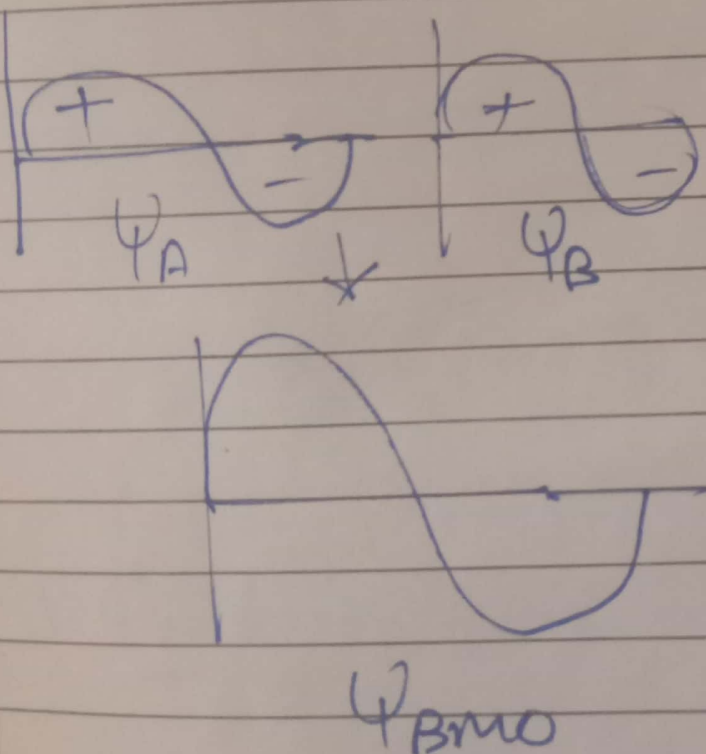
$\psi_{MO} = \psi_A + \psi_B$

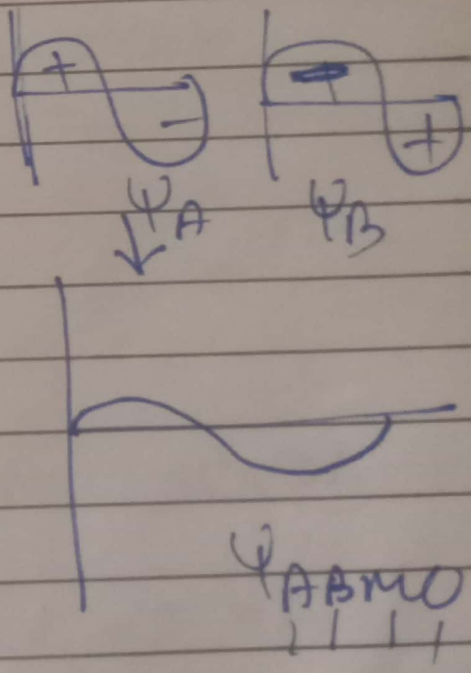
→ ~~constructive interference~~

(II) substract^n

$\psi_{MO} = \psi_A - \psi_B$

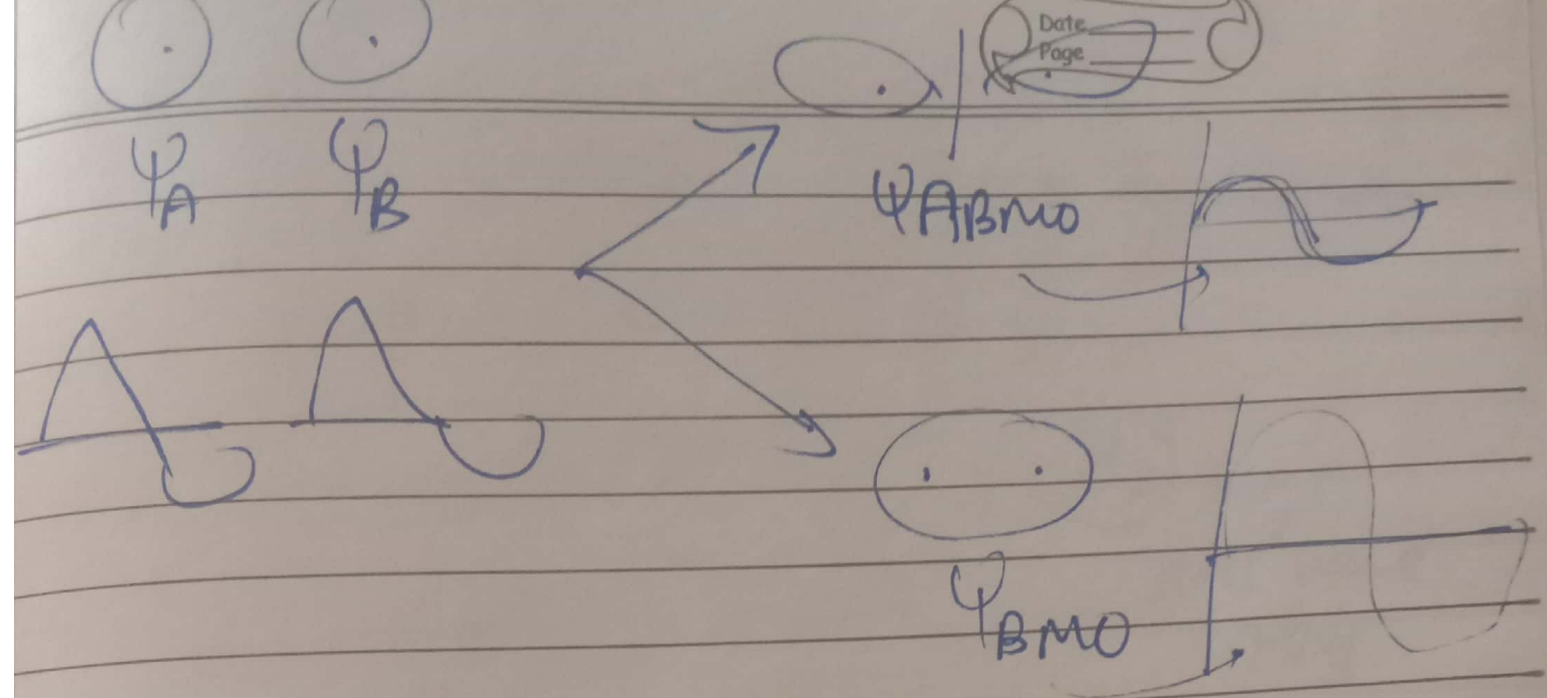
destructive





Remark

Teacher's Sign.



$$\phi_{MO} \text{ or } \psi_{MO} = c_1\psi_A + c_2\psi_B$$

c_1: probability of finding of e

c_2: probability of finding of e

$$\int \psi_{MO}\psi'_{MO}\, d\tau = 1$$

or

$$\int \psi_{MO}^2\, d\tau = 1$$

$$\int (c_1\psi_A + c_2\psi_B)^2\, d\tau = 1$$

$$(a+b)^2 = a^2 + b^2 + 2ab$$

$$\int c_1^2\psi_A^2\, d\tau + \int c_2^2\psi_B^2\, d\tau + \int 2c_1c_2\psi_A\psi_B\, d\tau = 1$$

$\psi_A^2\, d\tau = 1$ normalized

$\psi_A\psi_B\, d\tau = 0$ orthogonal

$\psi_B\psi_B\, d\tau = 1$

$\psi_1\psi_2\, d\tau = 0$

Remark

Teacher's Sign.

$\Rightarrow C_1^2 \times 1 + C_2^2 \times 1 + 2C_1C_2 \times 0$

$\Rightarrow C_1^2 + C_2^2 = 1$

$C_1 = C_2$ (H_2^+ same H–H bond)

$\Rightarrow C_1^2 + C_1^2 = 1$

$2C_1^2 = 1$

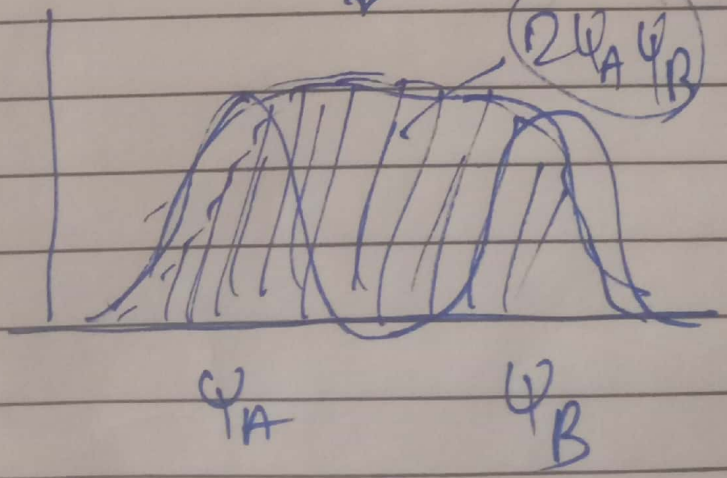
$C_1^2 = \frac{1}{2}$

$C_1 = \frac{1}{\sqrt{2}}$

$C_2 = C_1 = \frac{1}{\sqrt{2}}$

$\psi_{BMO}^2 = C(\psi_A + C_2\psi_B)^2$

$= \frac{1}{\sqrt{2}}(\psi_A^2 + \psi_B^2 + 2\psi_A\psi_B)$

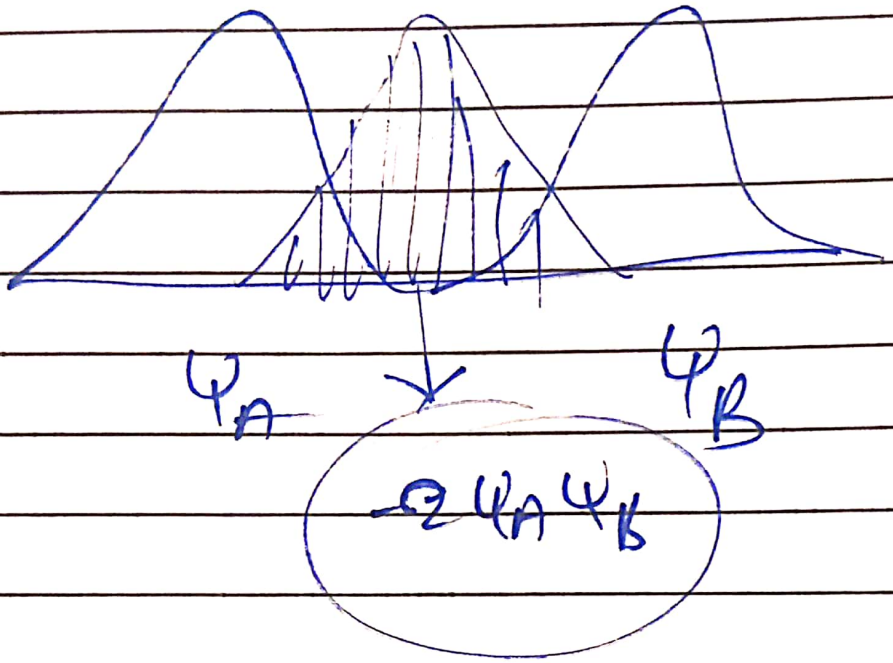


Remark

Teacher's Sign.

Page

$$\psi^2_{ABMO} = \frac{1}{\sqrt{2}}\left(\psi_A^2 + \psi_B^2 - 2\psi_A\psi_B\right)$$



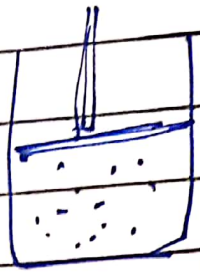
Page No.

pt. No.

Phys. chem. Unit- V

Thermodynamics—

E, H, S, G, A



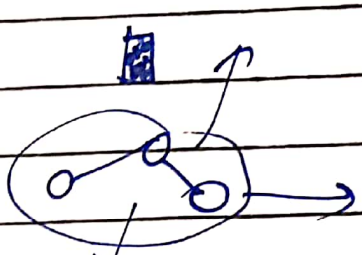
PdV

I II ⇒ (S)

स्वतः प्रवर्तित → ⁘ S(↑)

—o—

gas > liq > solid



T(↓) गति(↓) S(↓)

3rd law thermod.

(1) plemks statement ⇒

solid / liquid ~~OK / -27~~

10°C →

273

~~2731~~

0°C → 273K

-273°C ⇒ 0K

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Date

Page No.

absolute temp → 0K | -273°C

T ① → 0 S

$\lim_{T \to 0} \Delta G_p = \lim_{T \to 0} \Delta S$

2 lewis & Randalls ⇒ $S \neq 0$

Pure solid abs. entropy ≠ 0

Applicatn of 3rd law

① S ⇒ ② ΔG ③ K

① entropy ⇒ ΔS, ΔU, ΔH, ΔG, ΔA

State fn

I → II

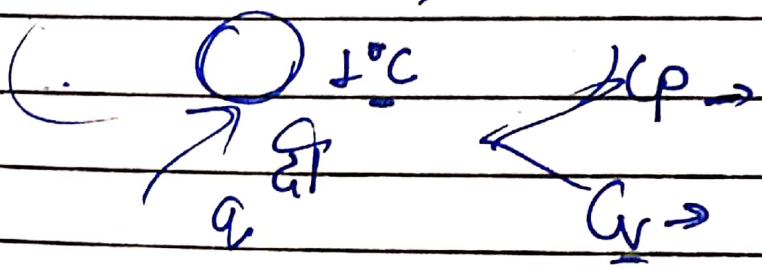
S_1 S_2

$\Delta S = S_2 - S_1$

No.

$$\Delta S = \frac{q}{T} \Rightarrow \frac{q_p}{T}$$ at constant P

heat capacity $C_p = \left(\frac{\Delta H}{\Delta T}\right)$



$$\Delta S = \frac{C_p}{T}$$ limit से integrate

$$\int \Rightarrow S_T - S_0$$

S_T → at temp T

S_0 → at temp

$$\int_0^T \Delta S = \int_0^T \frac{C_p}{T} dT$$

$$(S_T - S_0) = C_p \int_0^T \frac{1}{T} dT$$

$$= C_p [\ln T]_0^T \quad \left(\int \frac{1}{x} dx = \ln x\right)$$

Date

Page No.

Expt. No.

$S_T - S_0 = C_p \ln T$

OK $\rightarrow S_0 = 0$

$S_T = C_p \ln T$, imp

(2) $\Delta G \Rightarrow \Delta S , \Delta H$

$\Delta G = \Delta H - T\Delta S$

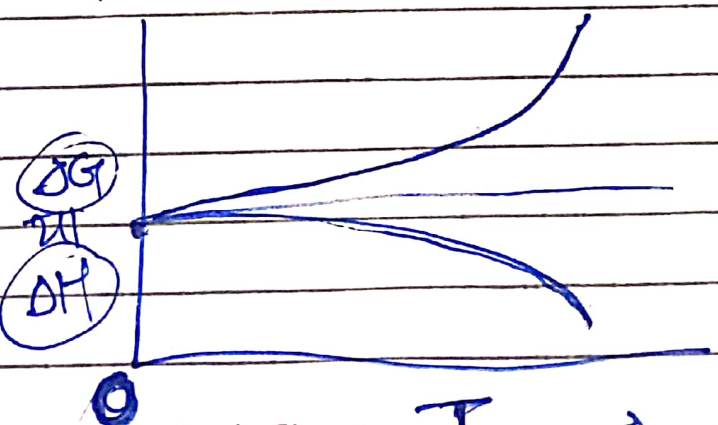
(3) $K \Rightarrow \Delta G = -RT \ln K$

—o—

Nernst heat theorem

W Nernst ΔH व ΔG & T

के साथ



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Date

Page No.

Expt. No.

$\lim_{T \to 0} \Delta S$

$G = H - TS$

$G = E + PV - TS$

$dG = dE + PdV + VdP - TdS - SdT$

$= TdS - PdV + PdV + VdP - TdS - SdT$

$dG = VdP - SdT \quad \text{---(1)}$

at const P, $dP = 0$

$dG = -SdT$

$dG_1 = -S_1 dT \quad , dG_2 = -S_2 dT$

$\Delta G = dG_2 - dG_1 = -S_2 dT - (-S_1 dT)$

$= -S_2 dT + S_1 dT$

$d(\Delta G) = -(S_2 - S_1) dT$

$-\Delta S dT$

$-\frac{d(\Delta G)}{dT} = \Delta S$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = \Delta H + T\left(-\frac{d(\Delta G)}{dT}\right)$

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0 — 2 0

$T = 0$

$$\Delta G = \Delta H \neq 0$$

$$\Delta S = \left[\frac{d(\Delta G)}{dT}\right]_{\to 0} \neq 0$$

$\to 0$

Heat theorem mathematical expressed as

$$\lim_{T \to 0} \Delta S$$

$$C_p = \left[\frac{\partial(\Delta H)}{\partial T}\right]_p$$

Kirchhoff's eqn

$$\lim_{T \to 0} C_p = \lim_{T \to 0} \Delta S \to 0$$

at 0K temp

Diff - gas / liq → (x)

Date

Expt. No.

Page No.

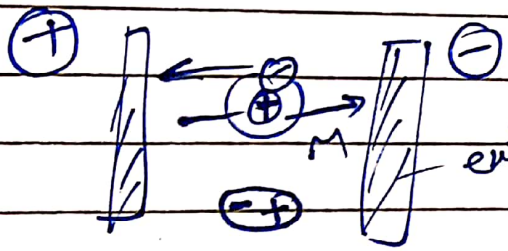
Unit - 5 (B)

Physical Prop. & Molecular structure

Molecule

polar — $\mu \neq 0$ — HCl, HF — $H^{\delta+}-Cl^{\delta-}$

non-polar — $\mu = 0$ — natural N_2, O_2, H_2 — $Cl-Cl$



polarisation

$\mu_i \propto F$ या ε

$\mu_i = \alpha F$ — (1)

Clausius - Mosotti eqn

↳ molar polarisation ज्ञात calculate

↳ Relation α, F और D

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$D = \frac{\varepsilon_0}{\varepsilon}$ — (2) applied Effect

material Effect

⊕ ⊕ ⊖ molecule

$\varepsilon_0 = D\varepsilon$ — (3)

dielectricity ⇒ $\varepsilon_0 = \varepsilon + 4\pi I$ — (4)

I = dipole moment per unit volume

$D\varepsilon = \varepsilon + 4\pi I$

$D\varepsilon - \varepsilon = 4\pi I$

$\frac{D\varepsilon - \varepsilon}{4\pi} = I$

$\frac{\varepsilon(D+1)}{4\pi} = I$ — (5)

$I = (\mu_i) N$ — (6)

N = no. of molecule present in unit

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$$F = \varepsilon_0 + \frac{4}{3}\pi I - 4\pi I$$

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

$$F = \varepsilon + \frac{4}{3}\pi I \quad \text{— (7)}$$

I की value को रखने पर

$$F = \varepsilon + \frac{4}{3}\pi \frac{(D-1)}{4\pi}\varepsilon$$

$$= \varepsilon + \frac{(D-1)\varepsilon}{3}$$

$$= \varepsilon + \frac{D\varepsilon - \varepsilon}{3}$$

$$= \frac{\varepsilon + D\varepsilon}{1} - \frac{\varepsilon}{3}$$

$$= \frac{3\varepsilon + D\varepsilon - \varepsilon}{3}$$

$$F = \frac{2\varepsilon + D\varepsilon}{3} \Rightarrow \frac{(D+2)\varepsilon}{3} \quad \text{— (8)}$$

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$$M = \alpha \times F$$

$$M = \alpha \times \frac{(D+2)\varepsilon}{3}$$

$$I = M \times n$$

$$= \alpha \times \frac{(D+2)\varepsilon}{3} \times n$$

where $n = \frac{NP}{M}$ = [illegible]

$$I = \frac{(D+2)\alpha\varepsilon}{3} \times \frac{NP}{M} \quad \text{— (9)}$$

[illegible] (5) & (9)

$$\frac{\varepsilon'(D-1)}{4\pi} = \frac{(D+2)\alpha\varepsilon}{3} \times \frac{NP}{M}$$

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

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

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but polar अणु के लिए

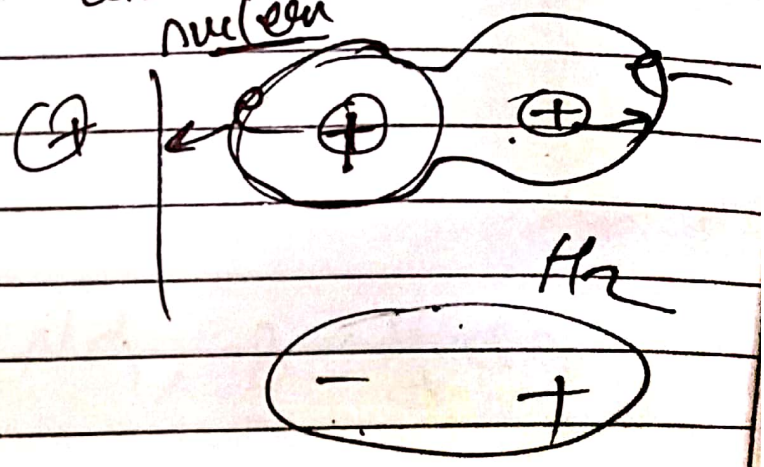
$\mu_i = P_m = P_a + P_e$

for nonpolar Molecule →

P_a → atomic

P_e → electronic

μ_i



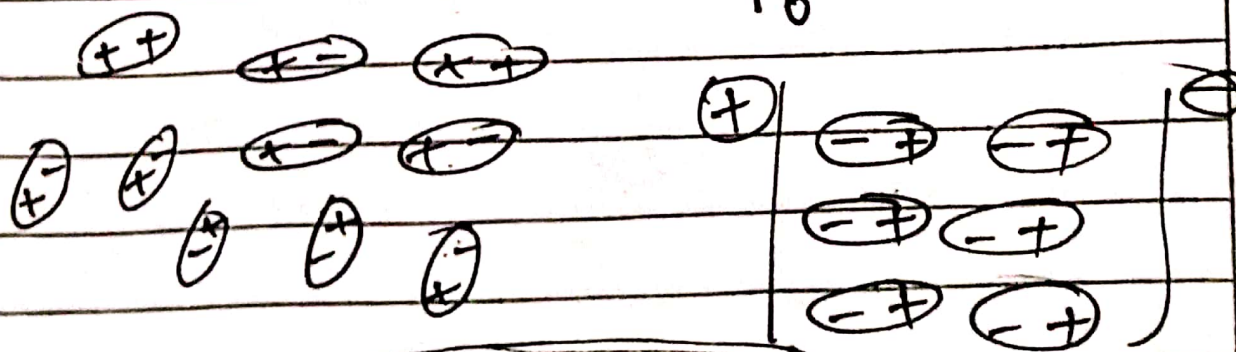
dipole moment (μ)

$\mu = e \times d$

$\delta+$ $\delta-$

निष्कर्ष polar molecules → $\mu \neq 0$

P_0



$P = P_i + P_o$

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Date

Page No.

$$P_m = P_i + P_o \rightarrow$$

$$P_i = \frac{4}{3}\pi N\alpha$$

$$P_o = \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right)$$

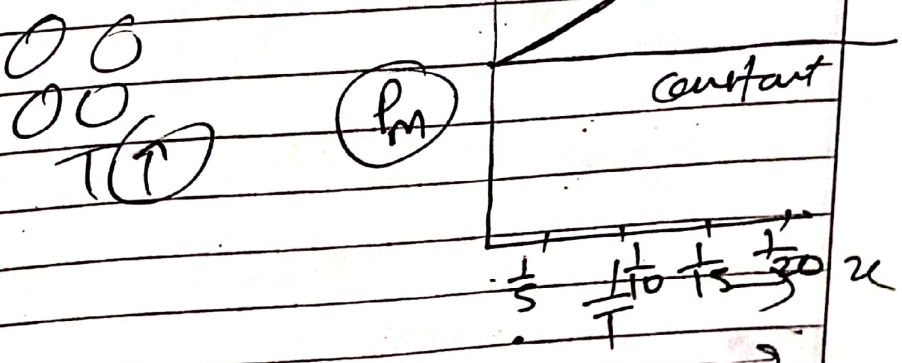
$$P_M = \left(\frac{4}{3}\pi N\alpha\right) + \frac{4}{3}\pi N\left(\frac{\mu^2}{3kT}\right)$$

$$A = \frac{4}{3}\pi N\alpha, \quad B = \frac{4}{3}\pi N\left(\frac{\mu^2}{3k}\right)$$

$$P_M = A + \frac{B}{T}$$

debye-eqn

$P_m \propto \frac{1}{T}$ ↑



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Date

Expt. No. Page No.

(h=3)

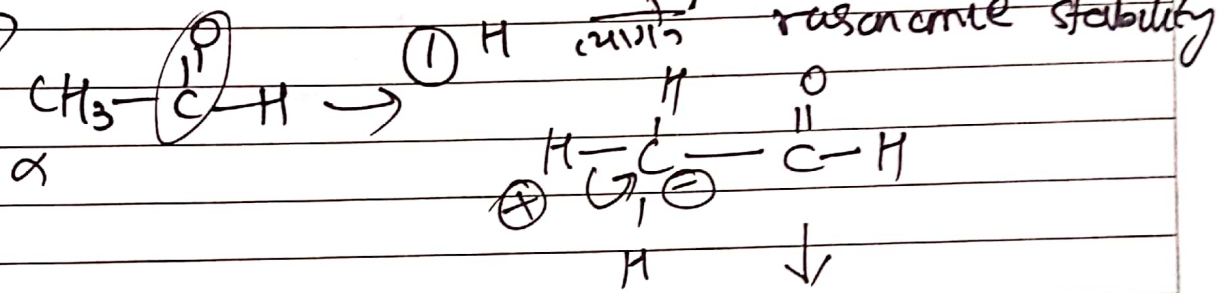
enolates via Organic synthesis via enolates

* carbonyl compounds जैसे $-\overset{O}{\overset{\|}{C}}-$

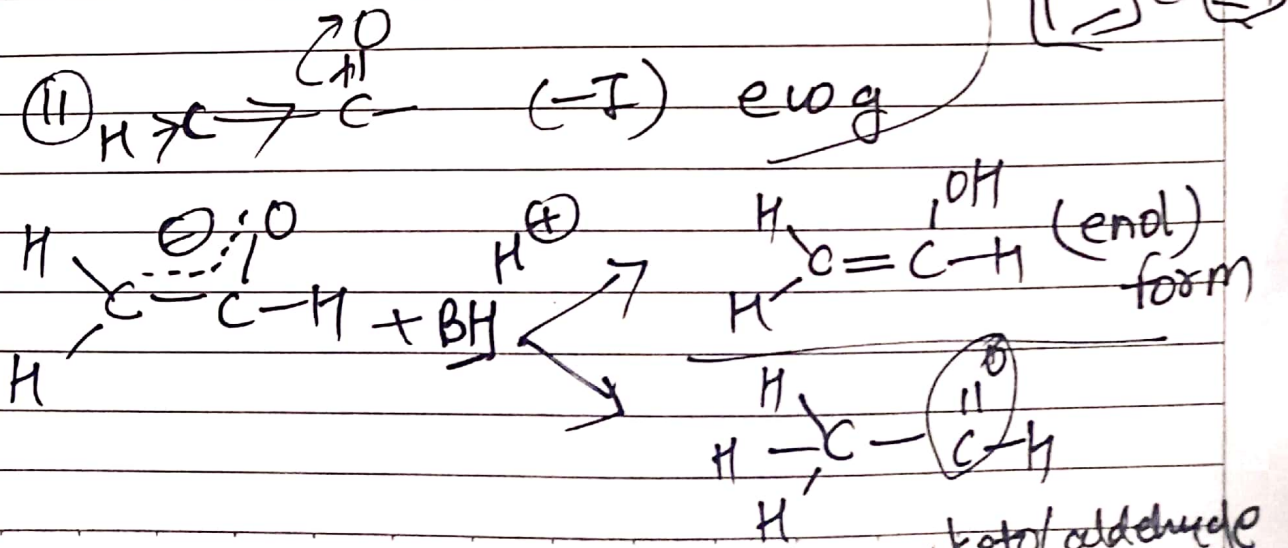
CH_3CHO, $R-\overset{O}{\overset{\|}{C}}-R$, $R-\overset{O}{\overset{\|}{C}}-OR$

enolate ion formation ⇒ α-H की acidity

कारण ⇒



(II) $H_3C \rightarrow C-$ (−I) effect



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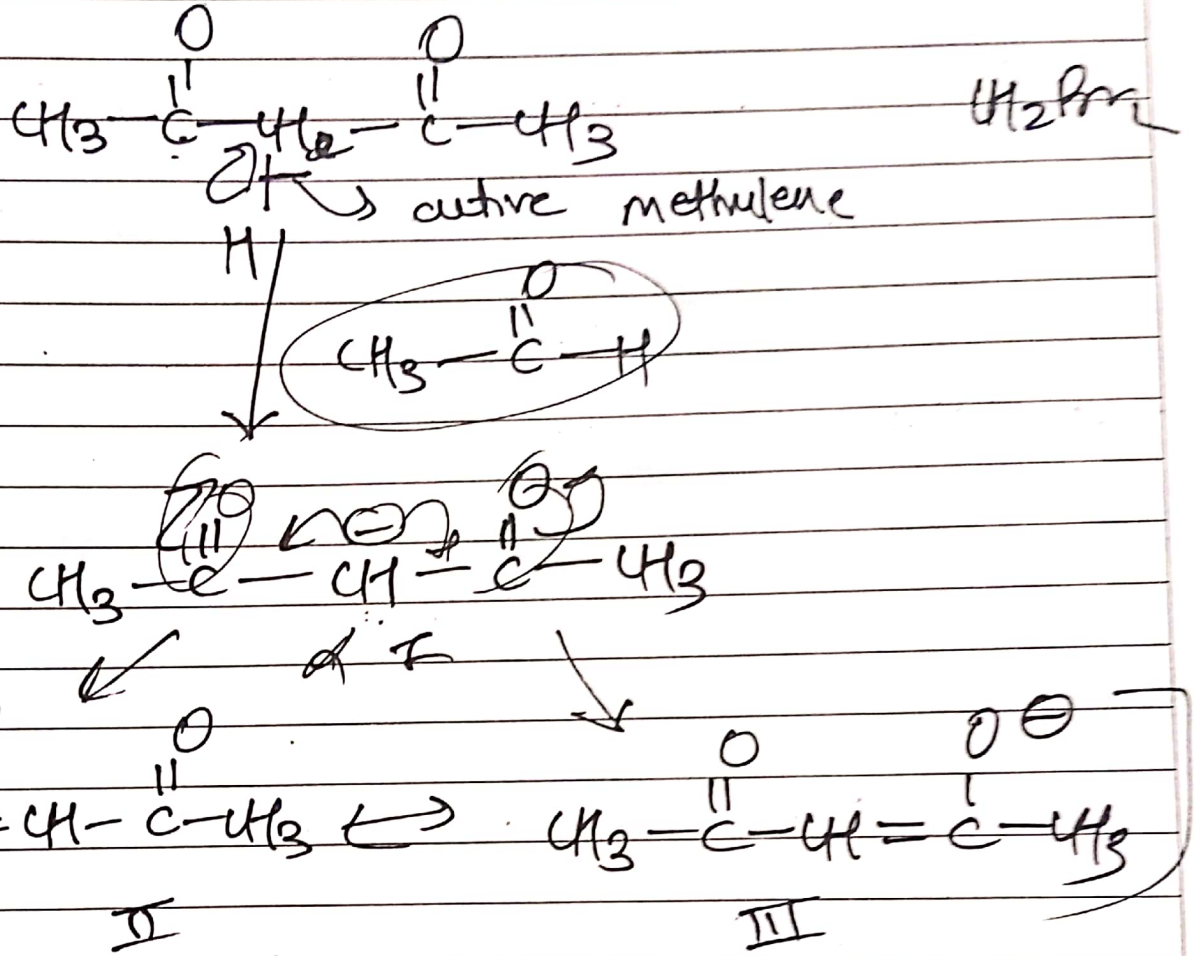
(enolizat^n)

active methylene condⁿ



- ☆ polycarbonyl
- ☆ more RS show
- ∧ stability (T)
- ☆ $-CH_2$ group
- ☆ $-\alpha H$ acidity (T)

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(I) Malonic ester

diethyl malonate $CH_2(COOC_2H_5)_2$

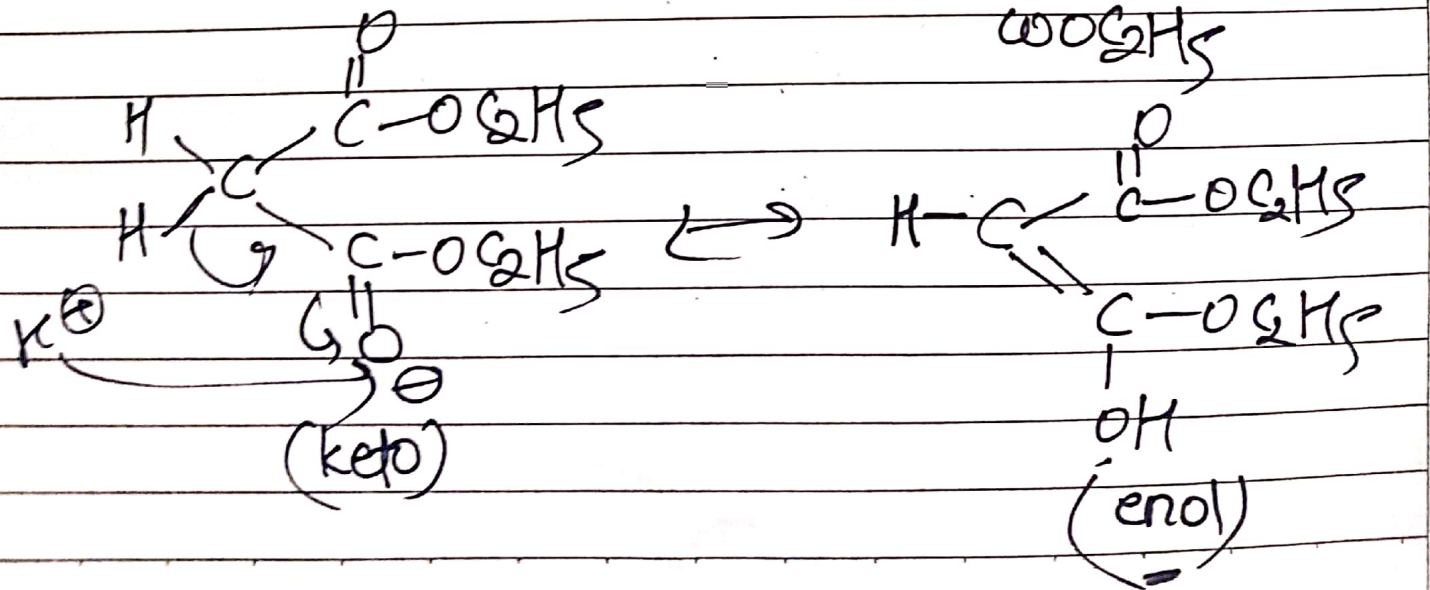
formation ⇒

$CH_3-COOH \xrightarrow{Cl_2,\ -HCl} Cl-CH_2-COOH \xrightarrow[\Delta]{K_2CO_3} Cl-CH_2-COOK + KOH + CO_2$

$Cl-CH_2-COOK \xrightarrow[-KCl]{KCN} CN-CH_2-COOK$

$CH_2(CN)(COOK) \xrightarrow[2HCl]{2HOH} KCl + NH_4Cl + CH_2(COOH)_2$

$CH_2(COOH)_2 \xrightarrow{2C_2H_5OH} CH_2(COOC_2H_5)_2$



Date

Dept. No. Page No.

Applicat^n . R R-R

(I) M·C· → Mono / dialkyl

$CH_2(COOC_2H_5)_2 \xrightarrow[HX]{R-X} R-CH(COOC_2H_5)_2$

$\xrightarrow[HX]{R-X}$

$(CH_3)\,R\,R\,C(COOC_2H_5)_2$

(II) M·E → Acetic acid

$CH_2(COOC_2H_5)_2 \xrightarrow[2C_2H_5OH]{2H_2O} CH_2(COOH)_2 \xrightarrow[-CO_2]{\Delta} CH_3-COOH$

(III) M·E· → Propanoic acid

$CH_2(COOC_2H_5)_2 \xrightarrow[HI]{CH_3I} CH_3-CH(COOC_2H_5)_2$

$\xrightarrow[-2C_2H_5OH]{2H_2O} CH_3-CH(COOH)_2 \xrightarrow[-CO_2]{\Delta} CH_3-CH_2-COOH$

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Expt. No. _____ Date _____ Page No. _____

$NaCH(COOC_2H_5)_2 \xrightarrow{NaOH} CH_2(COOC_2H_5)_2 \xrightarrow{-H_2O}$

(I) M.E. → succinic acid $CH_2(COOH)_2$

$CH_2(COOH)_2$

$NaCH(COOC_2H_5)_2$

I_2 +

$NaCH(COOC_2H_5)_2$ $\rightarrow$ $CH(COOC_2H_5)_2$ $-NaI$ $CH(COOC_2H_5)_2$

$CH(COOC_2H_5)_2$

$\xrightarrow{C_2H_5OH}$ $-2C_2H_5OH$

$CH(COOH)_2$

$\xrightarrow{\Delta}$ $CH(COOH)_2$

$-2CO_2$

$CH_2(COOH)_2$

(II) M.E → glutaric

(III) M.E → adipic acid

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Date

Expt. No. Page No.

Org. chem.

UNIT-3 Polymers

Natural poly →
synthetic poly → → imp
Semi synthetic

Poly ⇒ many mers ⇒ parts

Polymers → Homo ⇒ same monomer polythene
→ Hetero ⇒ diff monomers

$n(CH_2=CH_2)$ nylon-66
adipic +

Classification

(I) Structure of polymer

(i) linear poly.

$-(CH_2-CH_2)-$

(ii) branched

(iii) cross-linked poly

strong

bakelite

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Expt. No. _____ Page No. _____

(B) On the bases method of preparation

↙ ↓

Addition → by product (X) PVC

Condensation → by product H_2O, CO_2, NH_2 Nylon 66 (H_2O)

(C) On the bases of thermal behaviour

↓ ↓

thermoplastic → heat → fusion → with hard → Resuable

thermosetting → heat → non-resuable

(D) physical properties

↙ ↘

(I) Elastomer → Rubber → for intermolecular forces

(II) fibres → for strong

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Date

Page No.

Expt. No.

2 Addit^n Polymer^n → (I) initiation

(II) propagation (III) termination

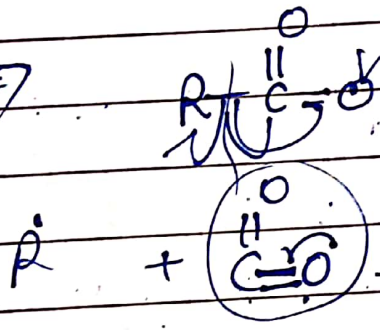
$H-O-O-H$ H_2O_2 H_2O

free radical ↓ • | Cation ⊕ | Anion ⊖

(I) free Rad. Polym^n ⇒ polythene

Peroxide ($R-C(=O)-O-O-C(=O)-R$)

(I) Init^n ⇒



(II) propag^n ⇒ $\dot{R} + CH_2=CH_2 \longrightarrow R-CH_2-\dot{C}H_2$

$R-CH_2-\dot{C}H_2 + CH_2=CH_2 \rightarrow R-CH_2-CH_2-CH_2-\dot{C}H_2$

$+ CH_2=CH_2$

⟶

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Date

Expt. No. Page No.

(iii) termination ⇒

$$R-CH_2-CH_2-CH_2-\overset{\bullet}{C}H_2 + \overset{\bullet}{C}H_2-CH_2-CH_2-R$$

$$\downarrow$$

$$R-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-R$$

2. Cationic poly

$H_2SO_4 / HF / BF_3$

(i) initiation ⇒ $H_2SO_4 \rightarrow H^+ + HSO_4^-$

$$H^+ + CH_2=CH_2 \rightarrow CH_3-\overset{+}{C}H_2$$

carbocation

(ii) Propagation ⇒ $CH_3-\overset{+}{C}H_2 + CH_2=CH_2 \rightarrow$

$$CH_3-CH_2-CH_2-\overset{+}{C}H-CH_2-CH_2$$

(iii) termination ⇒

$$CH_3-CH_2-CH_2-CH_2 + HSO_4^- \rightarrow CH_3-CH_2-CH=CH_2 + H_2SO_4$$

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$CH_3-CH_2-CH=CH_2 + H_2SO_4$

(III) Anionic addition Polymerisation ⇒

$KNH_2 \rightarrow K^{\oplus} + NH_2^{\ominus}$

(i) Initiation ⇒ $NH_2^{\ominus} + CH_2=\overset{\ominus}{C}H-C_6H_5 \longrightarrow NH_2-CH_2-\underset{C_6H_5}{\overset{\ominus}{C}H}$

Styrene

(ii) Propagation ⇒ $NH_2-CH_2-\underset{C_6H_5}{\overset{\ominus}{C}H} + CH_2=CH-C_6H_5$

$\downarrow$

$NH_2-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{\overset{\ominus}{C}H}$

(iii) Termination ⇒ $NH_2-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{\overset{\ominus}{C}H} + NH_3 \rightarrow$

$\downarrow$

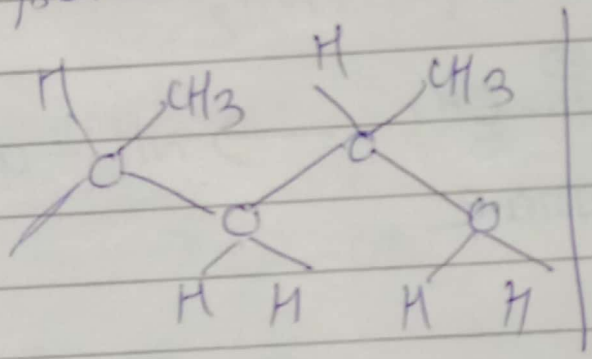
$NH_2^{\ominus}$

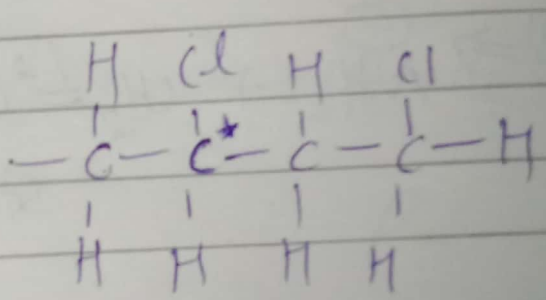
tactacity ⇒ Greek taktikos = arrangement of order

order से होता physical properties का पता चलता है।

जिग्लर-नाटा से बना Polymer stereochemical control बना हो सकता है। जैसे propelene Polymer 3 types के बनाए जाते है।

(I) isotactic ⇒ PVC (vinyl chloride) $-CH_2-\underset{H}{C}-Cl$





एक ही order में रहता है

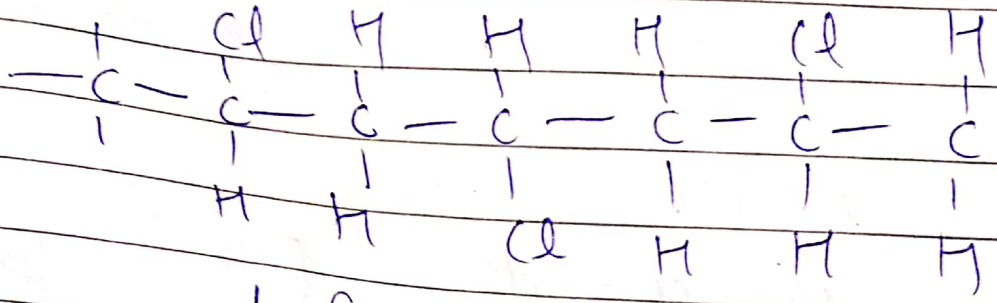
tactacity से जुड़े होने वाली physical properties—

(I) ruged - flexible (II) crystalline - non crystalline

(III) on which temp they melts

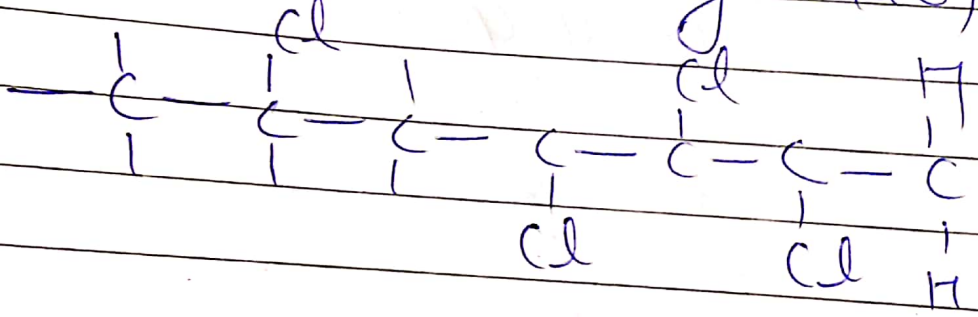
(IV) solvent में solubility का पता चलता है।

(2) Syndiotactic ⇒



d for l, d, l-d

(iii) Atactic :→ randomly ordered



Ziegler-Natta catalyst

Imp Polymers

Vinyl Polymers

monomer

① PVC — vinyl chloride $CH_2=CH-Cl$ — $[CH_2-\underset{Cl}{CH}-CH_2-]$

② Dralon — vinyl cyanide $CH_2=CH-CN$

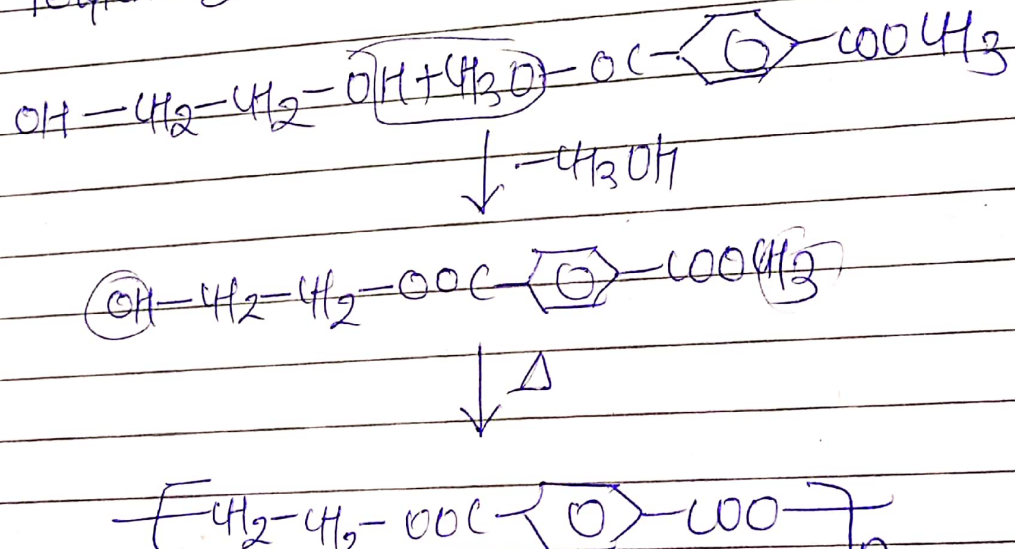
③ Teflon — $CF_2=CF_2$

④ Polystyrene — $C_6H_5-CH=CH_2$

Polyesters

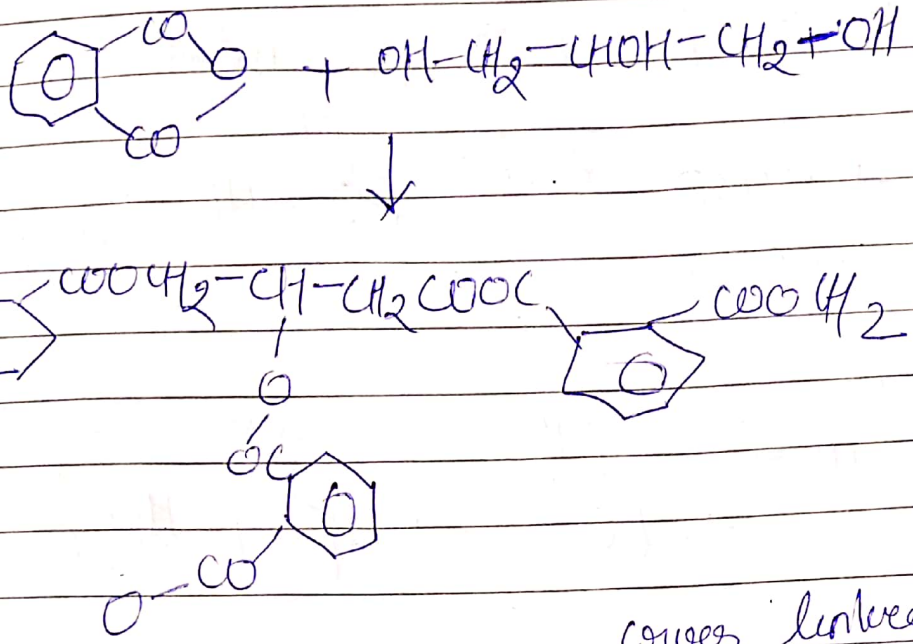
monomer

① Terylene-Dacron — ethylene glycol + dimethyte



terelen / dacron

(2) Glyptal → thalic anhydride + glycerol



cross linked polymer

Polyamides

(1) Nylon 6-6 → Adepic acid + hexamethylene diamine

$$HOOC-(CH_2)_4-COOH + H-NH-(CH_2)_6-NH_2$$

$$\downarrow \text{heat} - H_2O$$

$$HOOC-(CH_2)_4-CO-NH-(CH_2)_6-NH_2$$

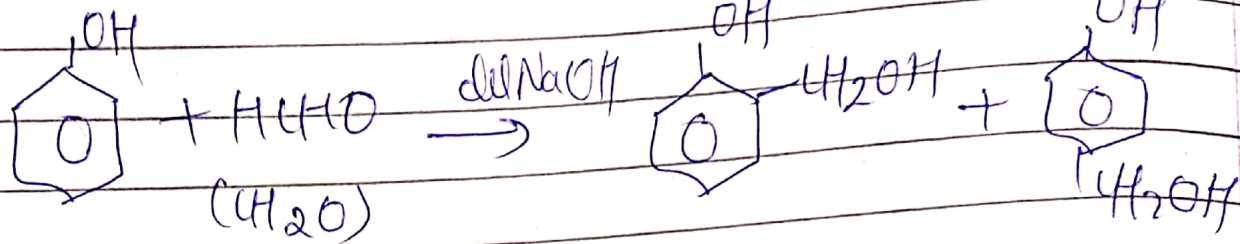
$$\downarrow -H_2O$$

$$-\left[-OC-(CH_2)_4-CO-NH-(CH_2)_6-NH-\right]_n$$

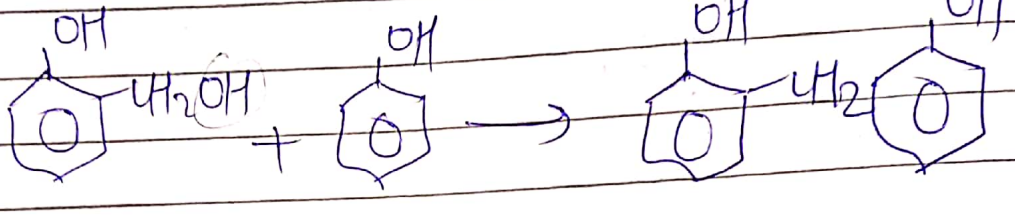
Phenolic Resins

(1) Phenol - HCHO Resins ⇒ ~~Bakelite~~

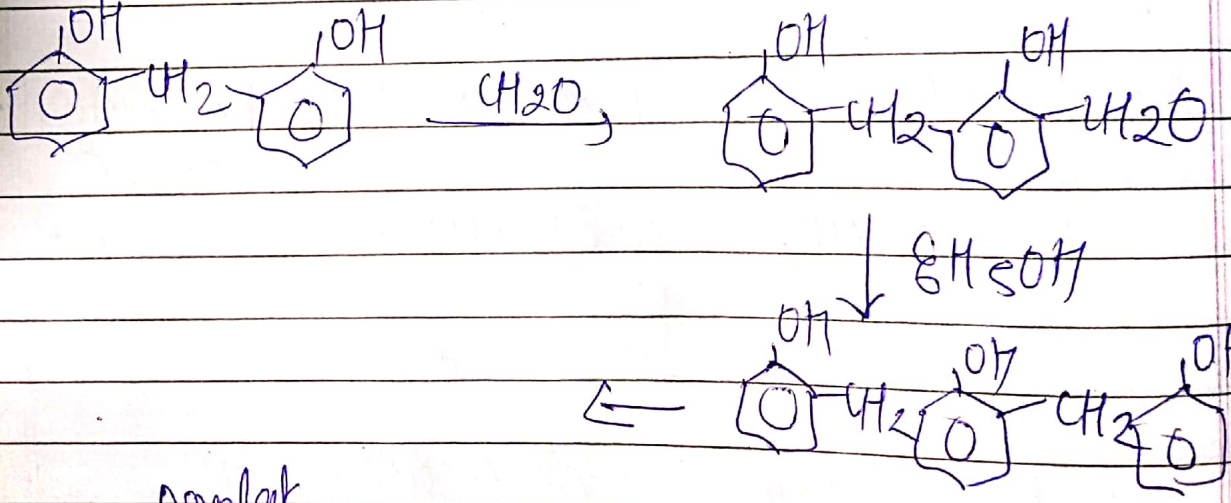
(I)



(II)

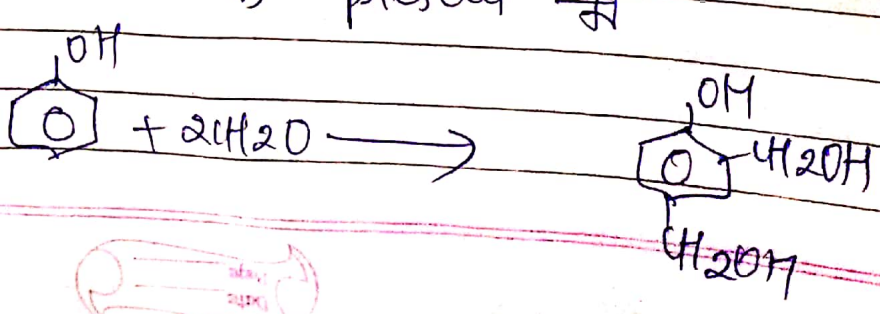


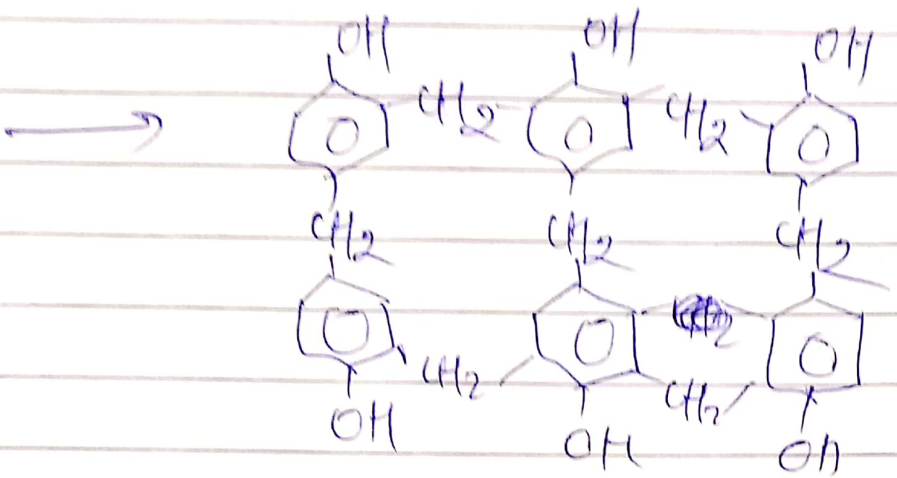
(2) यदि phenol - formaldehyde 1:1 ratio में हो तो Novolak resines बनता है



Novolak

(2) यदि HCHO excess amount में हो तो, strong base के present में





(Bakelite)

Rubber

(1) Natural Rubber ⇒ 500 Rubber plant से प्राप्त

↓

पौधो की छाल से Fluffy पदार्थ → latex

↓

latex में 25-40% hydrocarbon

↓

But इसमे fatty acid, protein, resins भी

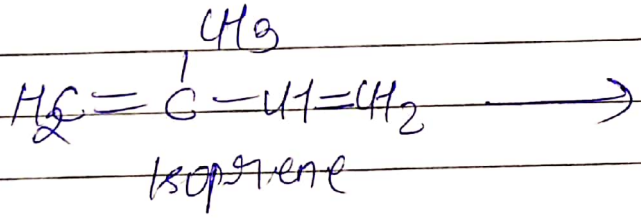
↓

Rubber में acetic acid dissolve करके या कच्चा Rubber

↓

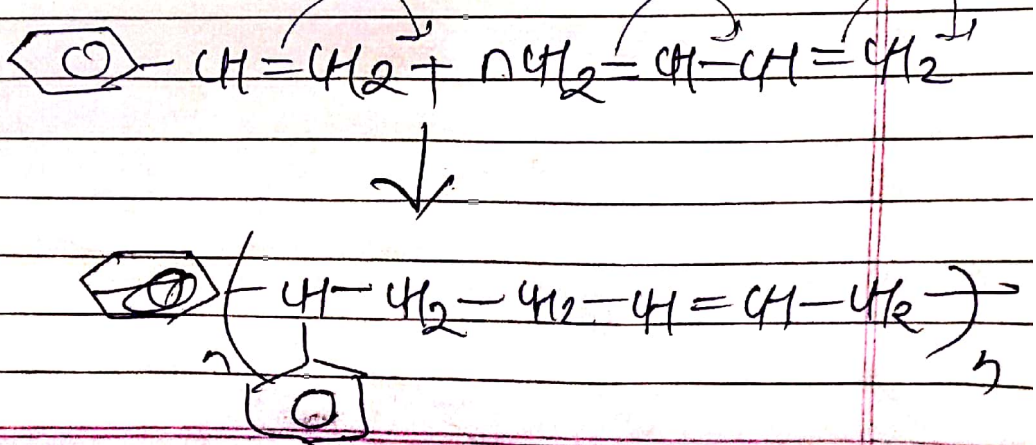
elasticity के लिए S के साथ heat → vulcanisation

monomer



(2) Synthetic Rubber ⇒

(1) Styrene - Butadiene



potential)

D_e = dissociation ...

BSc III

t. No.

Date

Page No.

H — Cl

SHO → k

hooke's law

$f \propto x$

$f = kx$

↓ force cont

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{m \text{ or } \mu}} \quad (1)$$

$$E_v = \left(v + \tfrac{1}{2}\right) h\omega$$

2 ↑

1 ~~ono~~

0

$\left(v_1 + \frac{1}{2}\right)h\omega$ ↓ → 2 → $\left(v_2 + \frac{1}{2}\right)h\omega$

$q\omega$ $e\omega$

$$\Delta E = E_2 - E_1$$

$$= \left(v_2 + \tfrac{1}{2}\right)h\omega - \left(v_1 + \tfrac{1}{2}\right)h\omega$$

$$\Delta E = \left(v_2 + \tfrac{1}{2} - v_1 - \tfrac{1}{2}\right) h\omega$$

$T_2 - T_1$

$E_2 - E_1$

$\Delta v = \pm 1$

$$\Delta E = (v_2 - v_1)\, h\omega$$

$$\Delta E = \Delta v \; h\omega$$

$(1 \to 2$

$\Delta v = +1)$

$$\frac{\Delta E}{h} = \frac{h\omega}{h}$$

h से divide

$$\upsilon = \omega \quad (2)$$

$E = h\upsilon$

$\frac{E}{h} = \upsilon$

Teacher's Signature

intensity of

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

$$c\omega = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

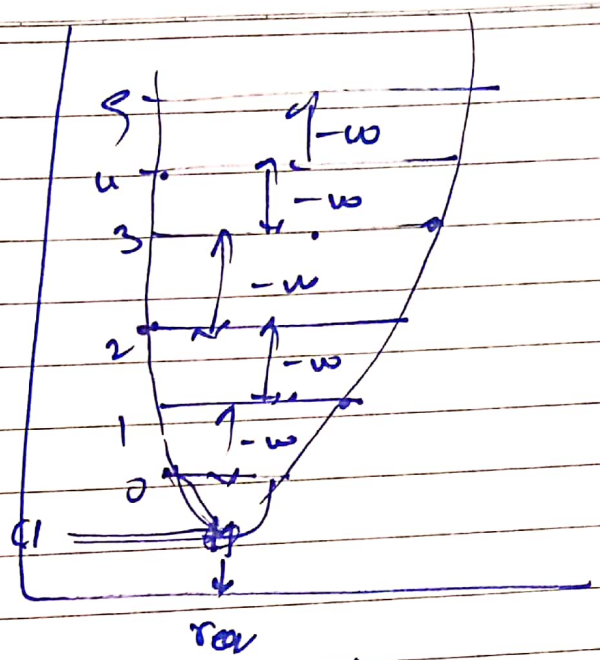
$$\omega_{osc} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

$$2\pi c\omega = \sqrt{\frac{k}{\mu}}$$

$$(2\pi c\omega)^2 = \frac{k}{\mu}$$

$$4\pi^2 c^2 \omega^2 = \frac{k}{\mu}$$

$$\boxed{4\pi^2 c^2 \omega^2 \mu = k}$$



H — Cl

$$\varepsilon_v = \left(v+\frac{1}{2}\right)\omega \ cm^{-1}$$

$0 \to 1 \to \omega$

$1 \to 2 \to \omega$

$2 \to 3 \to \omega$

SHO

zero point energy

$v = 0 \to \varepsilon_v = \left(0+\frac{1}{2}\right)\omega$

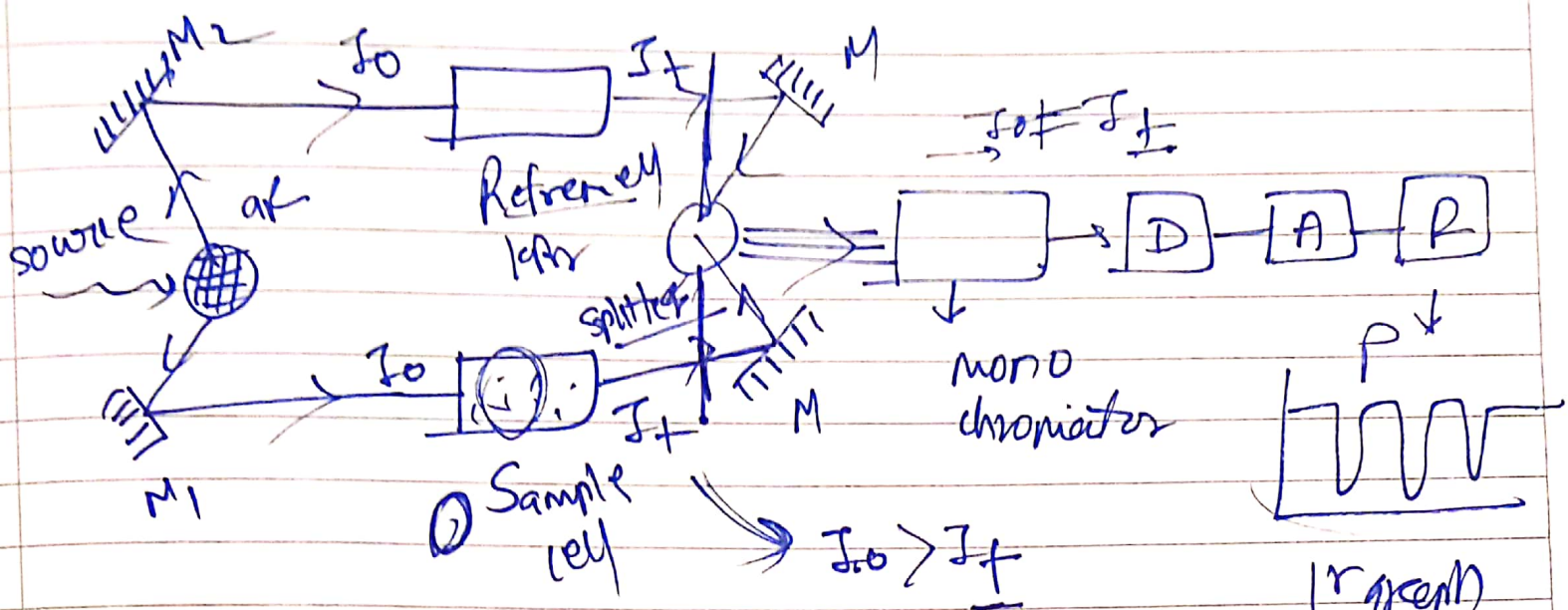
$= 0+\frac{1}{2}\omega$

$$\boxed{\varepsilon_0 = \frac{1}{2}\omega \ cm^{-1}}$$

Teacher's Signature

Page No.

IR Instrument



① Source ⇒ MIR — UV → tungsten filament 2mm

MIR — or — Globber SiC 2-5mm

FIR — 1300-1700°C

— nernst globber

1000-1800°C Cr, Y, Cr wires

2mm - 10mm (wire)

② Sample/Sampling ⇒ Sample → gas / liq / solid → IR

FTIR → gaseous

Solvent ⇒ H_2O (X) → IR active

CS_2 CCl_4

Sampling ⇒ ① 1 mg sample + nujol (3-4 drop) + (paraffin hydrocarbon)

→ paste

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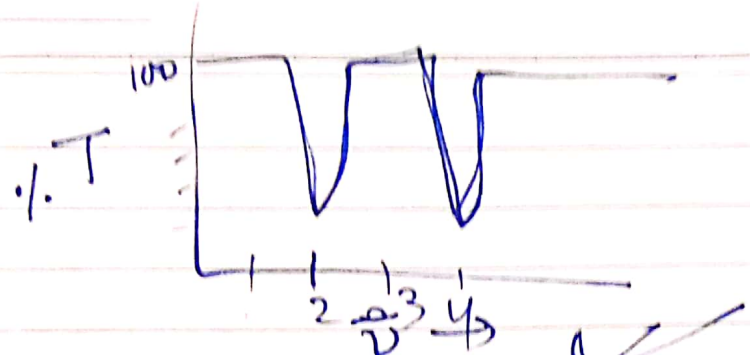
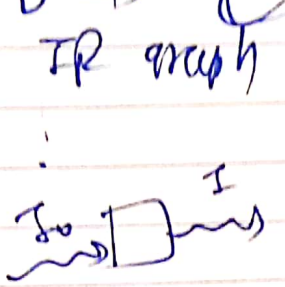
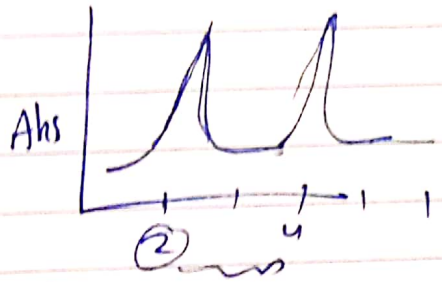
Expt. No. Page No.

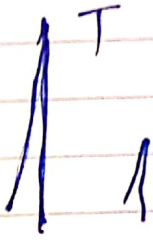


IR graph



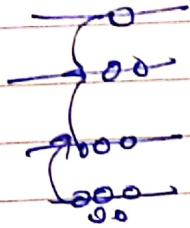


$Ab = \frac{1}{T}$



Intensity of spectral line

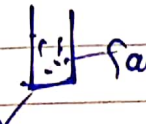
(i) population density ⇒



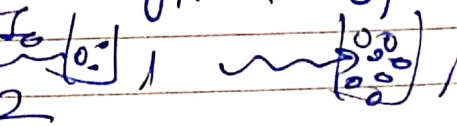
(↑) in (↓)

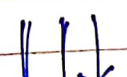
low e level – intense

high e – low intense

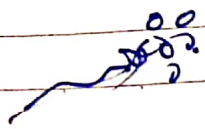
(ii) Sample concentⁿ ⇒  sample g/ml

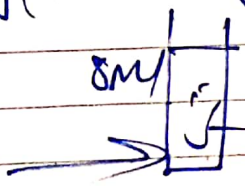
cell 1g/50ml 3g/10ml



(iii) Sample cell ⇒ 

1g/1ml 1g/10ml





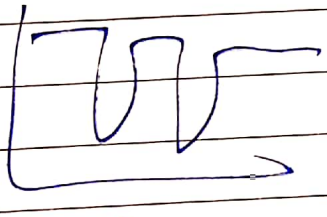
Teacher's Signature

(2) 1 mg sample + 300 mg KBr NaBr KCl NaCl
↓
mixed → ○ pellet

(3) – mono

(4) detector → Bolometer, thermo couple

(5) Recorder →

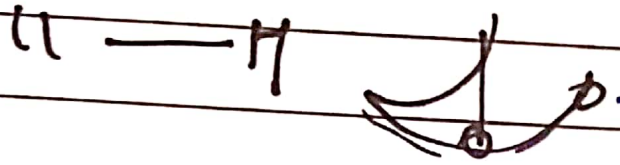


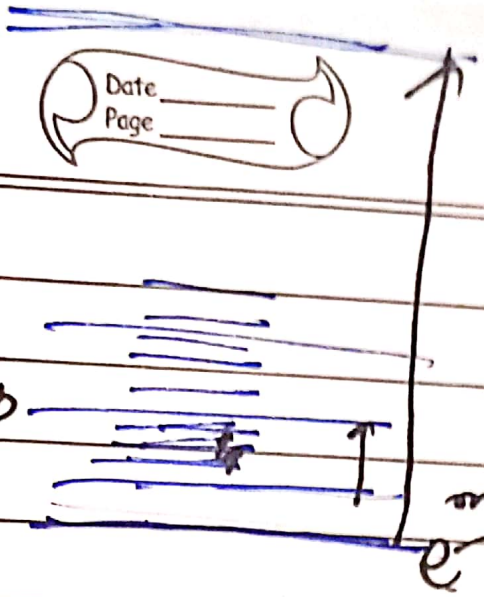
IR graph

Name class
Sub Date

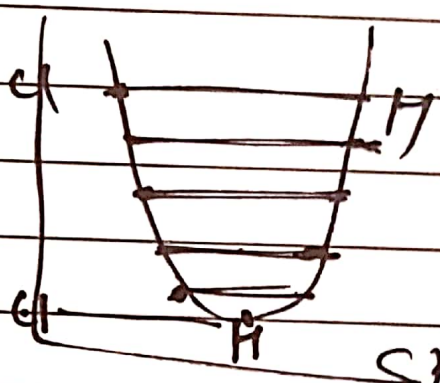
BSc III

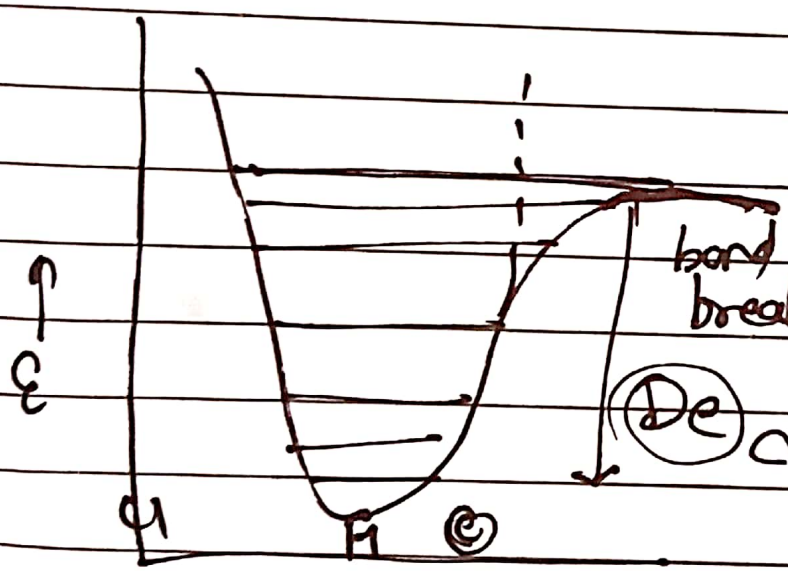
SHO





Harmonicity ⇒





Morse potential

D_e = dissociation energy

$De = \frac{\omega}{4\chi}$ → anharmonicity constant

$\Delta v = \pm 1$ ⇒ (i) fundamental band

another vibrations

$\Delta V = \pm 1, \pm 2, \pm 3, \pm 4$

(1) ΔV = $v=0 \rightarrow v=1$ (first fundamental band)

(2) $\Delta V \Rightarrow v=0 \rightarrow v=2$ (± 2)
(first overtone band)

(3) $\Delta V \Rightarrow v=0 \rightarrow v=3$ (± 3).
(Second overtone band)

overtone → non-fundamental band

energy level — SHO $\leftarrow G_v = (v+\frac{1}{2})\bar{\omega}_{osc}$ cm^{-1}

$$\varepsilon_v = (v+\tfrac{1}{2})\omega - (v+\tfrac{1}{2})^2 \omega.x$$

AHO

(1) $0 \rightarrow 1$ (e)

$\Delta\varepsilon = \varepsilon_1 - \varepsilon_0$

$$\Delta\varepsilon = \left[(1+\tfrac{1}{2})\omega - (1+\tfrac{1}{2})^2 \omega.x\right] - \left[(0+\tfrac{1}{2})\omega - (0+\tfrac{1}{2})^2 \omega.x\right]$$

Remark

Teacher's Sign.

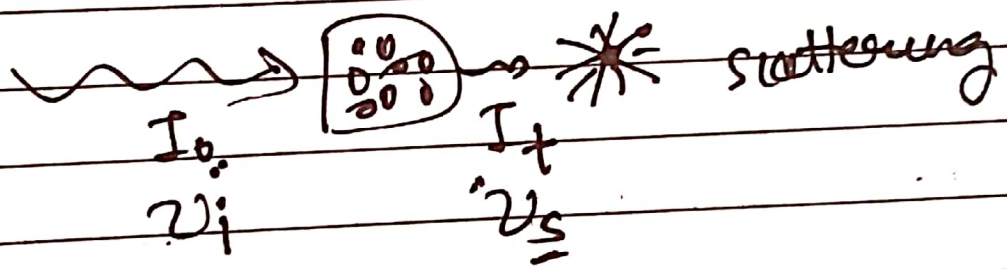
$$\Delta E = \frac{3}{2}w - \frac{9}{4}wx - \left(\frac{1}{2}w - \frac{1}{4}wx\right)$$

$$\Delta E = \frac{3}{2}w - \frac{9}{4}wx - \frac{1}{2}w + \frac{1}{4}wx$$

$$= \frac{2}{2}w - \frac{8}{4}wx$$

Raman Spectra

monochromatic light



3 types

(I) $\nu_i = \nu_s$

Rayleigh

(II) $\nu_i > \nu_s$

stokes lines

(III) $\nu_i < \nu_s$

Anti stokes lines

Raman lines

Remark

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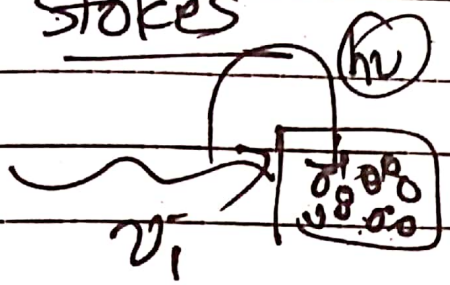
Date
Page

Stokes

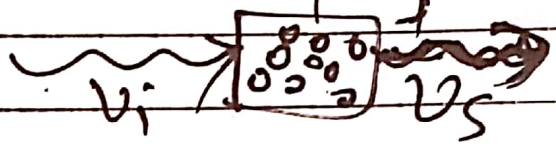


$\Delta\nu = \nu_i - \nu_s$

$= \nu_i > \nu_s$

$\Delta\nu = +ve$

Anti stokes



$\nu_s > \nu_i$

$\Delta\nu = \nu_i - \nu_s$

$= -ve$

Quantum

light → matter

- elastic collision
  - Rayleigh
- inelastic
  - Stokes
  - Anti

Remark

Teacher's Sign.

Date
Page

emr

wave

classical

macro

partical

Quantum mechanics

micro

pure

photon quanty

hv

Raman spectra

classical theory

polarizability

quantum theory

Ray

SO Anti