Inorganic UNIT-I

Metal- Ligand Bonding in Transition metal Complexes

$M - L$
↳ bond

different theories -

① VBT ② CFT ③ MOT ④ LFT

I VBT

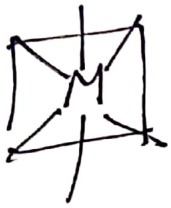
Paulling & Slater ने

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

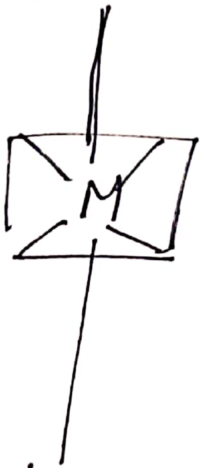
Limitatn of VBT

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

③ विकृति (disortion) ⊗

④ 

octahedral



tetragonal
(distorted octa)

④ ligand के बारे में

⑤ Metal को ज्यादा महत्व

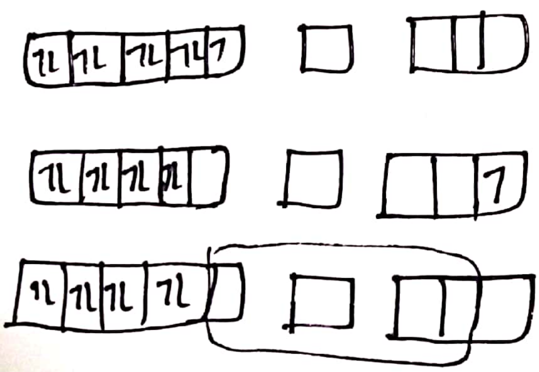
⑥ Rate और mechanism ⊗

⑦ VBT के a/c -4 co-ordinate वाले complex

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

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

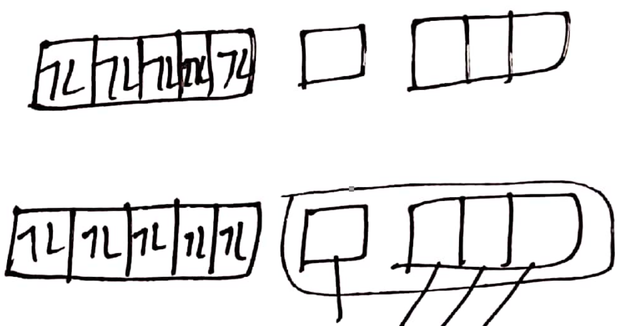
→ $3d^9$ 4s 4p



dsp2

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

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



sp^3

Scanned with CamScanner

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

same metal same oxidatⁿ state

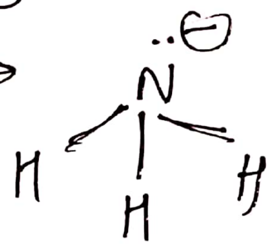
But diff geomatory

Crystal feild Theory

(1) M–L purely ionic

(2) legand को ऋणात्मक बिंदु आवेश

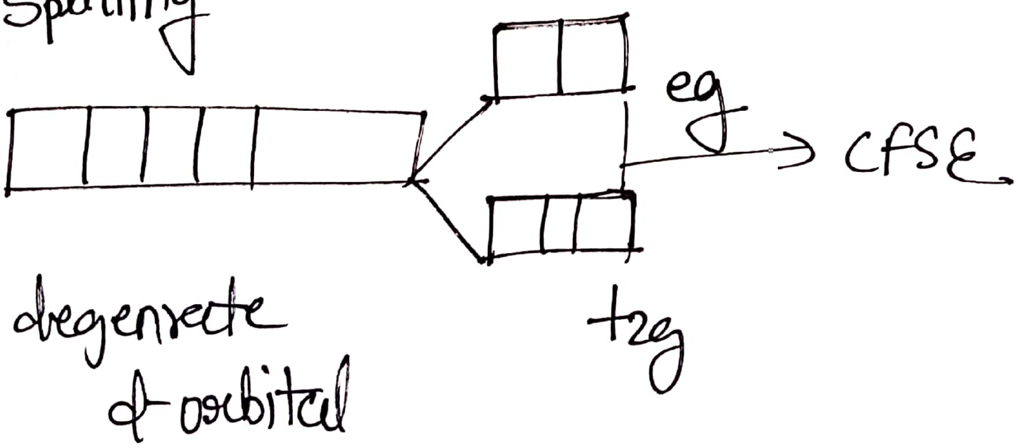
F^- Cl^- CN^- NH_3 →



(3) ये stability को explain → CFSE

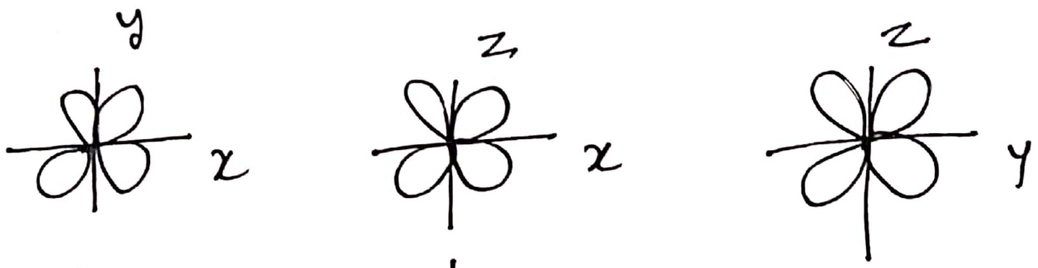
(4) M–L के बीच कोई interaction नहीं

(5) Splitting



6 orbitals में overlapping ⊗ e- sharing ⊗

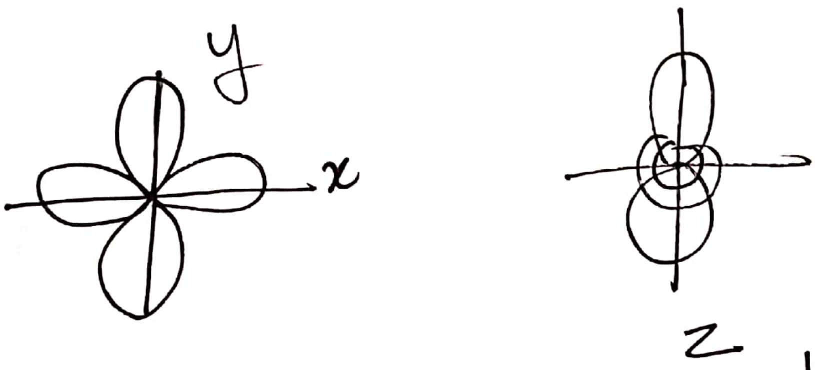
Crystal feild Splitting 



dxy dzx dyz

$\underbrace{\qquad\qquad\qquad}$

t_{2g} ~~axis~~ lobe b/w the axes



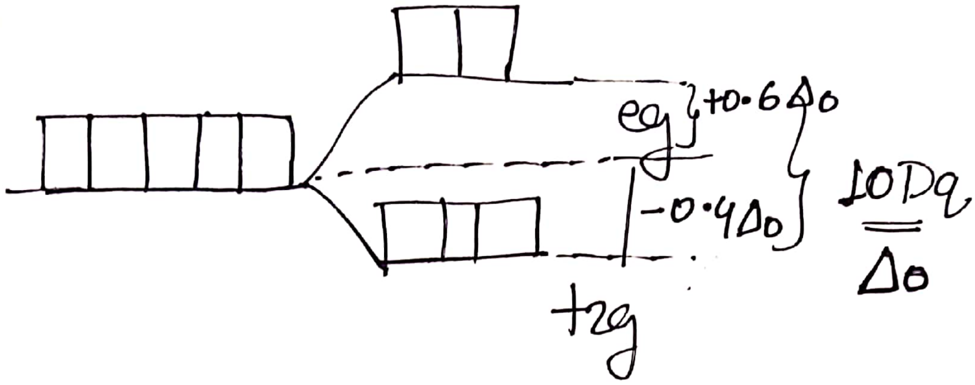
dx^2-y^2 dz^2

$\underbrace{\qquad\qquad\qquad}$

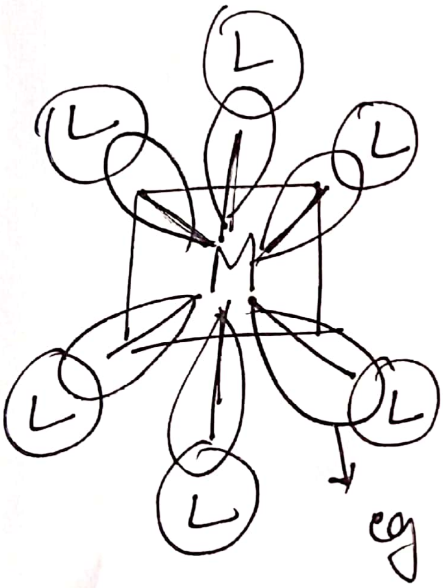
eg-orbital

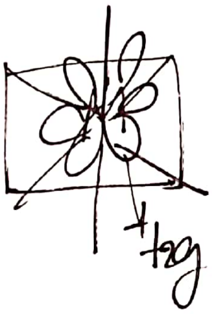
lobe along the axes

CFSE



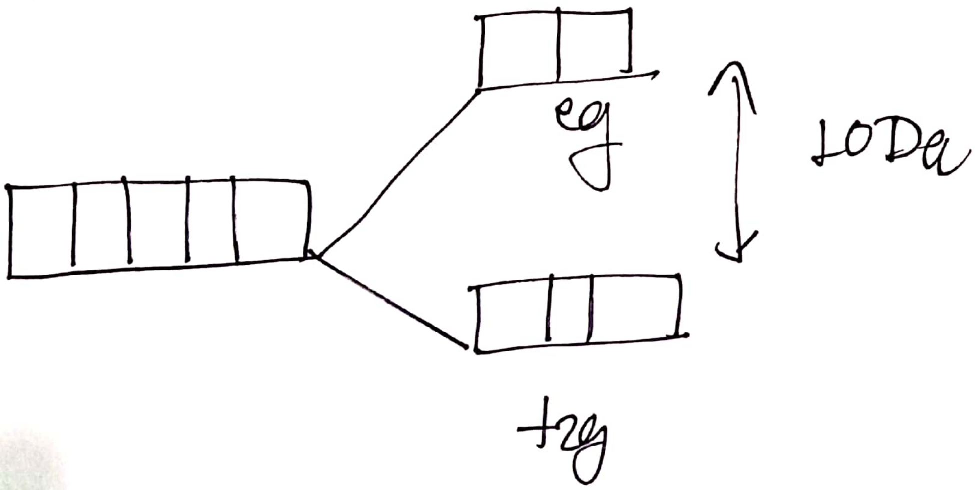
Splitting in Octahedral Complexes



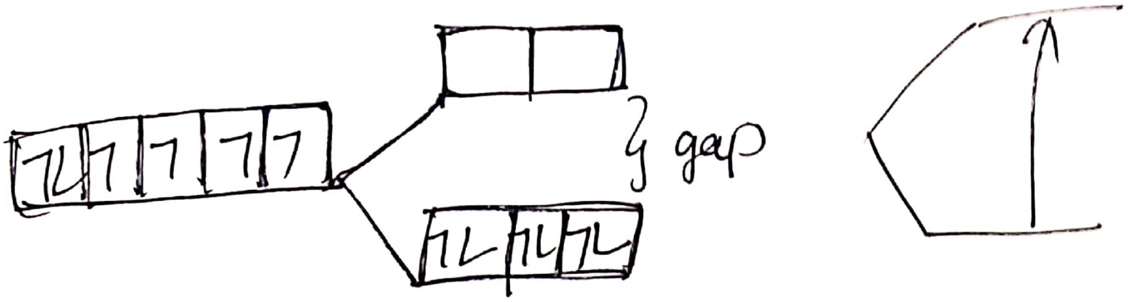


eg orbital L के direct contact में

more repulsion तो eg की energy ↑



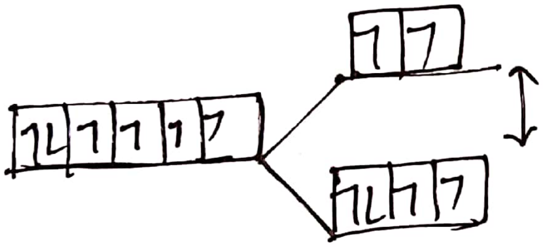
d^6 octahedral



strong field L gap (↑) तो e^- का pairing

$\Delta_o > P$

P = Pairing energy | दो e^- को pair कराने की आवश्यक ऊर्जा



gap (↓) e^- का pairing नहीं

$\Delta_o < P$

weak feild ligand

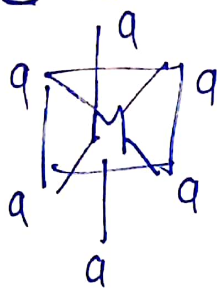
CFSE calculation $\Rightarrow 4e^- \times -0.4 + 0.6 \times 2$

$= -1.6 + 1.2$

$= -0.4\,\Delta_o$

$[CoF_6]^{3-}$

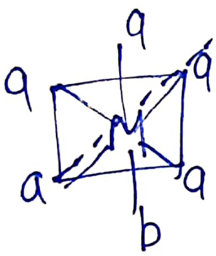
1 $[Ma_6]$



(aa) (aa) (aa) GI ✗

opt. ✗

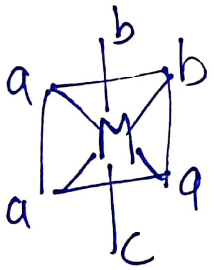
2 $[Ma_5b]$

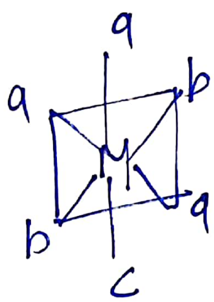


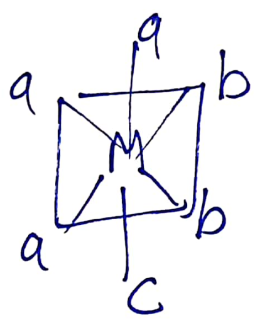
(aa) (aa) (ab) — GI ✗

opt. inactive POS present

3 $[Ma_3b_2c]$







(aa, ab, bc) (aa) (bb) (ac) (ab) (ab) (ac)

same ligand — POS ✓ opt. inactive

same arrangem

POS ✗ opt. inacti

GI = 3 OP. I = ✗

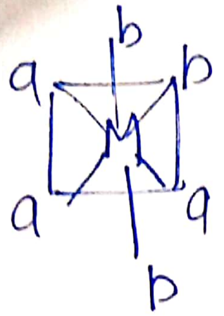
4 $[Ma_3b_3]$

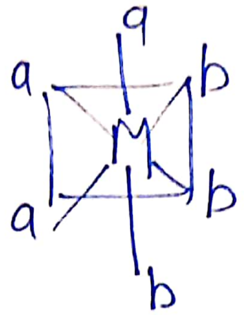
(aa) (ab) (bb)

(ab) (ab) (ab)

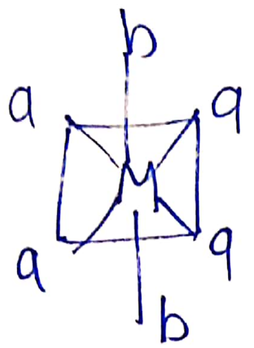
GI — 2

OI — ✗

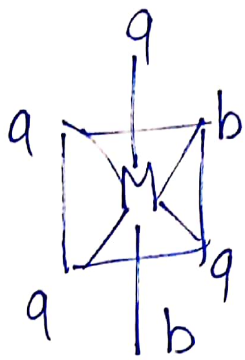




(5) $[Ma_4b_2]$



(aa) (aa) (bb)



GI – 2

(aa) (ab) (ab)

OI – X

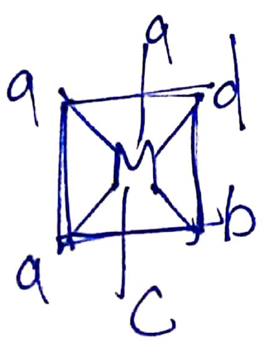
(6) $[Ma_3bcd]$ GI – 4

(aa) (ab) (cd) — op. inactive

(aa) (ac) (bd) → op. inac.

(aa) (bc) (ad) → op. inac.

(ab) (ac) (ad) → op. active → POS X



7 $[Ma_2b_2c_2]$

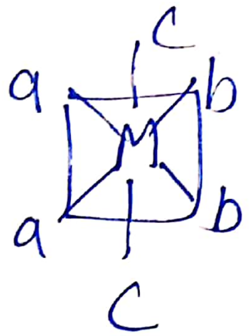
(aa) (bb) (cc) → opt. ina.

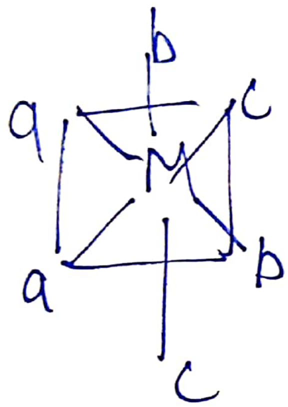
(ab) (ab) (cc) → opt. ina

(aa) (bc) (bc) - opt. inac.

(ac) (ac) (bb) - opt. inac.

(ab) (ac) (bc) - opt. active → POS (x)





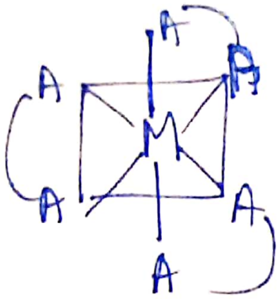
POS (x)

8 Bidentate ligand

↓ sym (AA) → C_2O_4

↓ asymm. (AB) → Gly

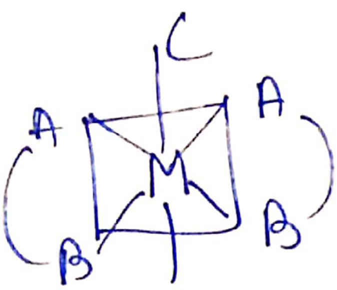
1 $[M(AA)_3]$



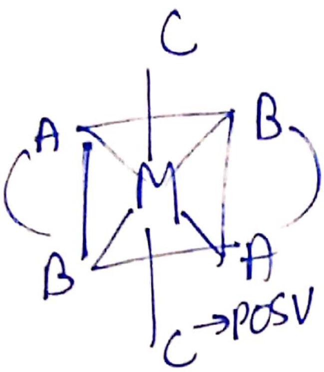
GI ⊗

OP ✓ POS ⊗

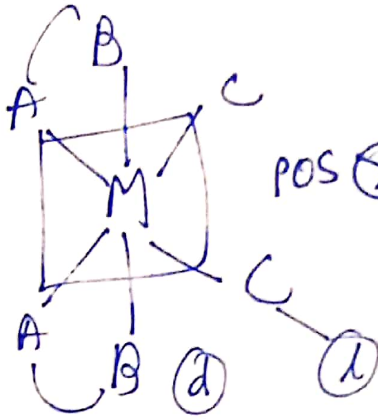
10 $[M(AB)_2C_2]$ GI - 5



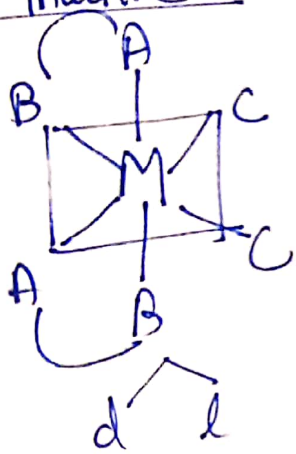
POS ✓
opt- inactive

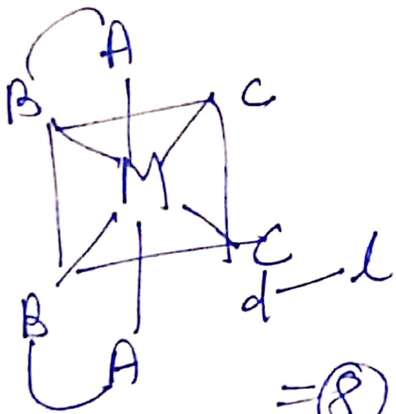


→ POS ✓



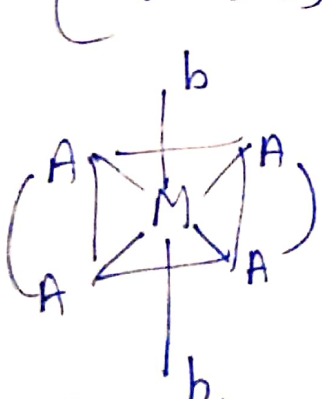
POS ⊗



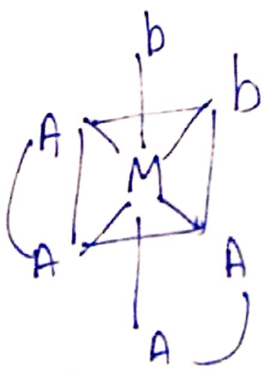


= 8

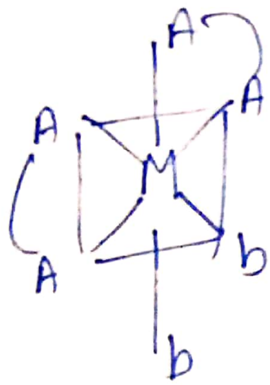
11 $[M(AA)_2b_2]$ - GI = 2 OI



POS present
= opt inactive



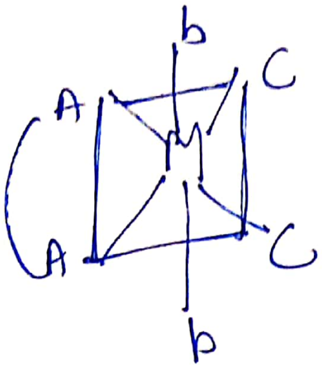
(AA) (Ab)(Ab)

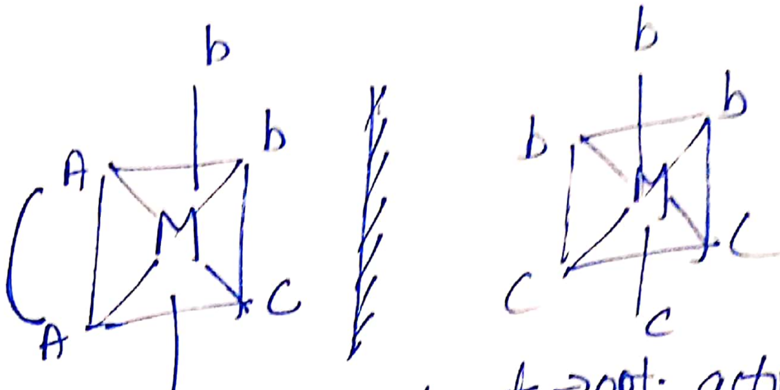


(Ab)(Ab)(AA)

same

12. $[M(AA)b_2c_2]$





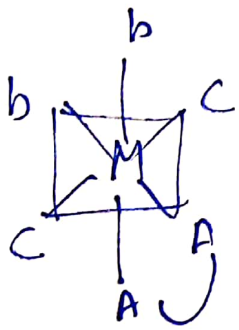
POS absent → opt. active

POS present
↓
opt. inactive

= 8

(AC) (AC) (bb)

(AC) (Ab) (bC)
→ POS absent → opt. active



= 4

(Ab) (cc) (Ab)
opt. inactive

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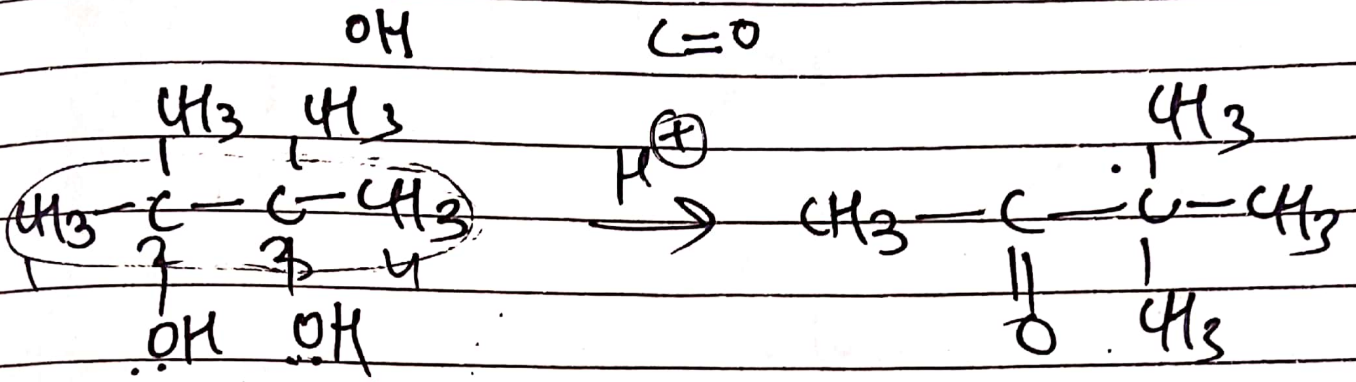
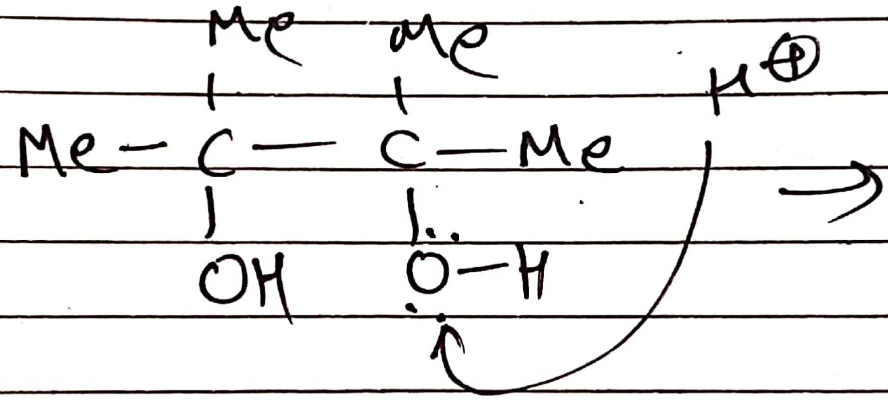
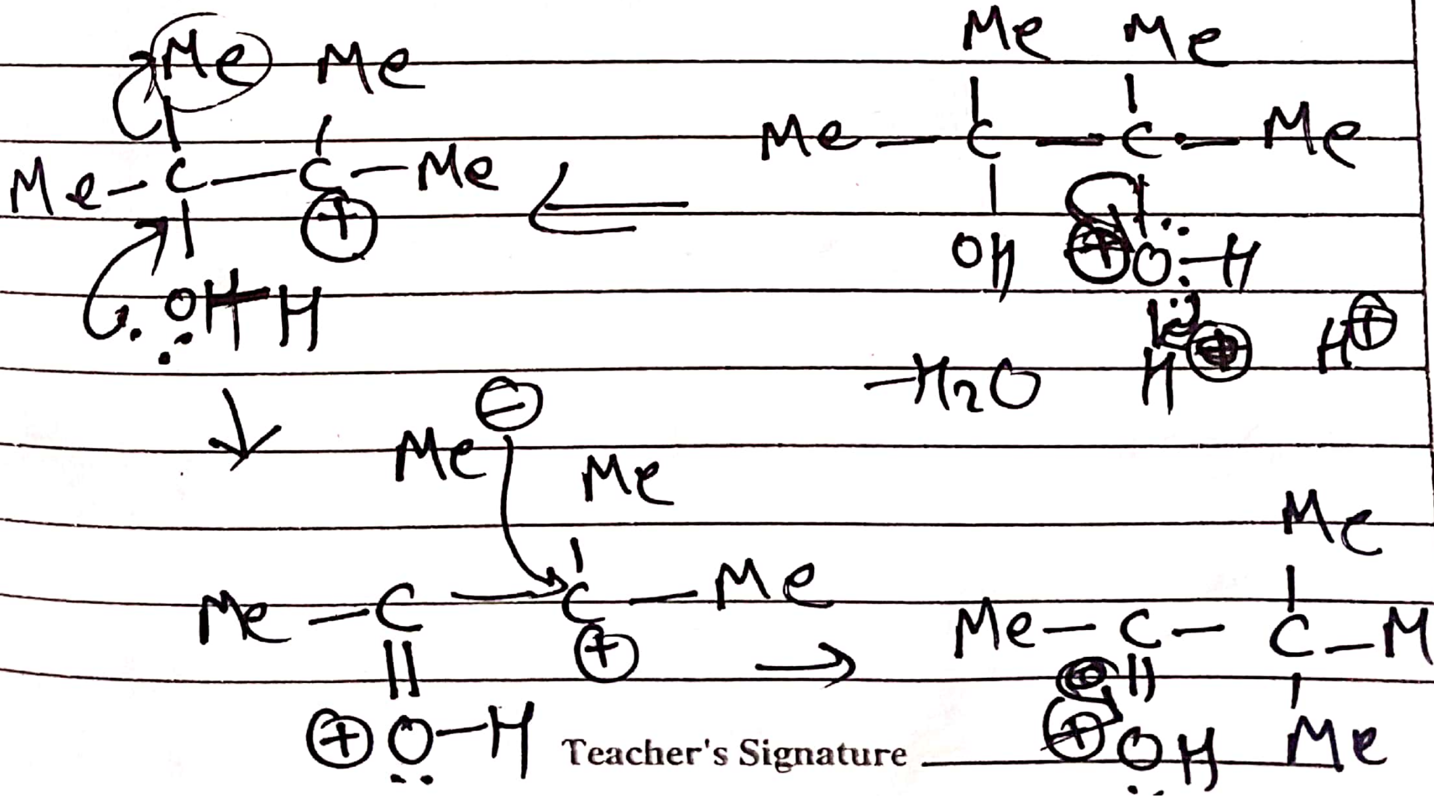
Pinacol - pinacolones rearrangement



(1) protonation





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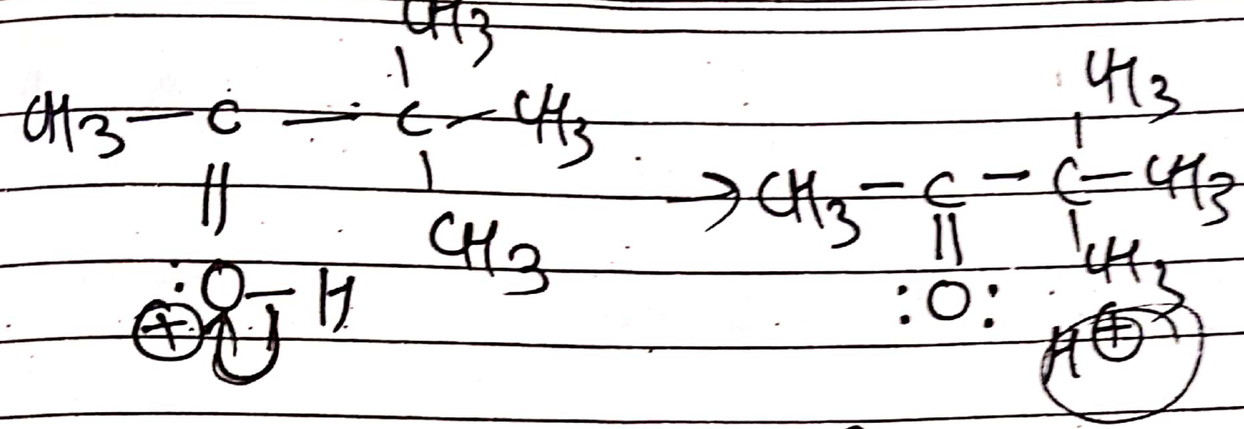

CH_3CH_2OH

(1) $CH_3OH \longrightarrow C_2H_5OH$

$$CH_3OH \xrightarrow[-H_2O]{KI} CH_3I \xrightarrow[-KI]{KCN} CH_3CN \xrightarrow{4H} $$

$$H_2O + CH_3CH_2OH \xleftarrow{HNO_2} CH_3CH_2NH_2$$

$+N_2$ $OH-NO$

(2) $CH_3CH_2OH \longrightarrow CH_3OH$

$$CH_3CH_2OH \xrightarrow[-H_2O]{(O)} CH_3CHO \xrightarrow{(O)} CH_3COOH$$

$\downarrow NaOH, -H_2O$

$$\xleftarrow{AgOH} CH_3Cl \xleftarrow[-HCl]{Cl_2} CH_4 \xleftarrow[+CaO]{NaOH} CH_3COONa$$

$-AgCl$

$\rightarrow CH_3OH$

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Victor meyer

P/I_2 $AgNO_2$ 3° HNO_2 $NaOH$

1° OH $R-CH_2OH \xrightarrow{P/I_2} RCH_2I \xrightarrow[-AgI]{AgNO_2}$

$RCH_2-NO_2 \xrightarrow[OH-NO]{HNO_2} R-\underset{\underset{N-OH}{\|}}{C}-NO_2 \xrightarrow[-H_2O]{NaOH}$

$R-\underset{\underset{N-ONa}{\|}}{C}-NO_2$

2° $\underset{R}{\overset{R}{>}}CH-OH \xrightarrow{P/I_2} \underset{R}{\overset{R}{>}}CH-I \xrightarrow[-AgI]{AgNO_2} \underset{R}{\overset{R}{>}}CH-NO_2$

$\underset{R}{\overset{R}{>}}CH-NO_2 \xrightarrow[OH-NO]{HNO_2} \underset{R}{\overset{R}{>}}\underset{\underset{N=O}{|}}{C}-NO_2 \xrightarrow{NaOH}$ Red colour

$3^\circ \rightarrow$

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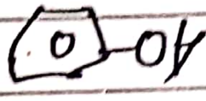
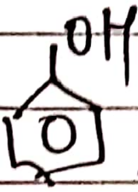
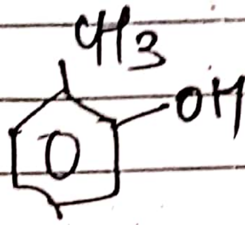
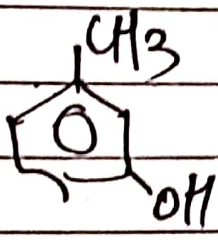
phenol

C_6H_5OH

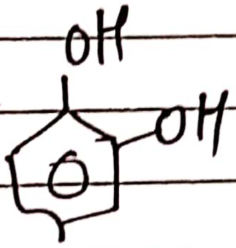
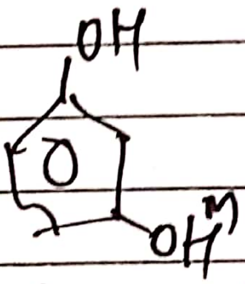
 C+C PhOH 

hydroxyl derivative

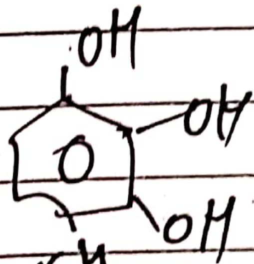
(1) mono phenol  

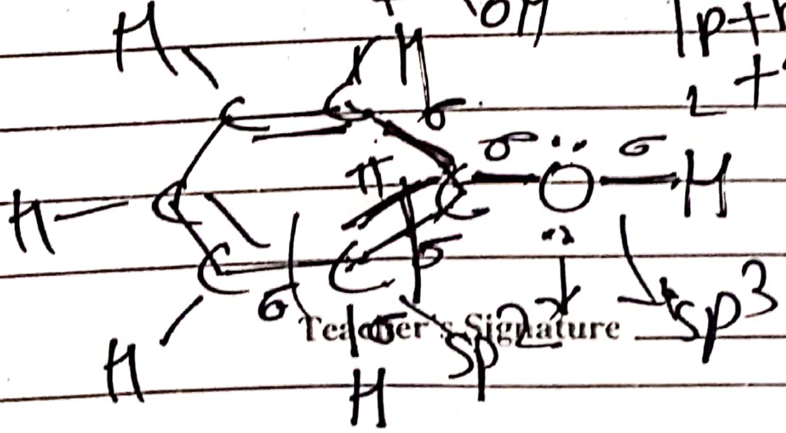
o-cresol

(II) Di phenol —   

Catechol Resorcinol Quinol

(III) tri phenol - 3-OH 

Stem



lp+bp = 4
+2 σ bond
2-sp
$3-sp^2$
$4-sp^3$

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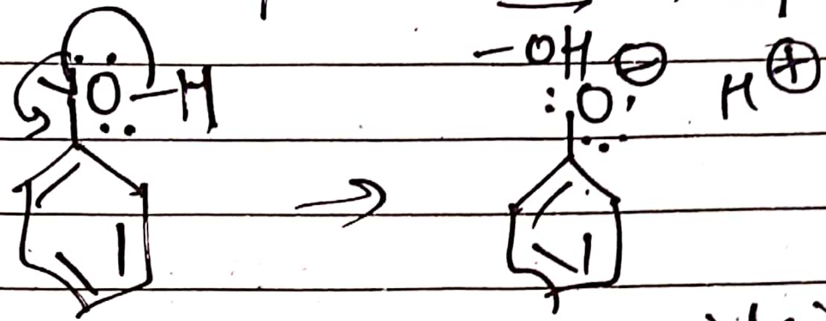
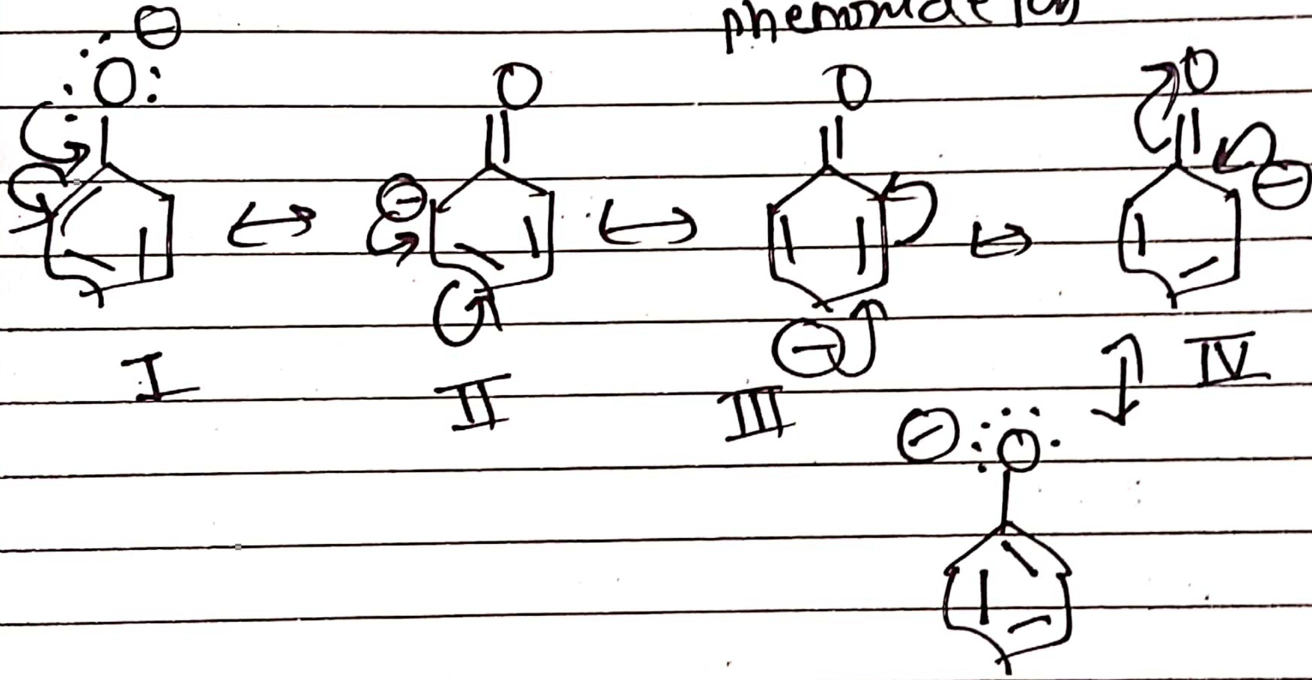
acidity → alcohol $\not>$ phenol > -COOH



phenoxide ion



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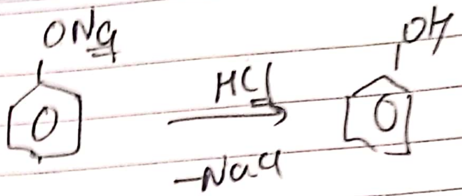
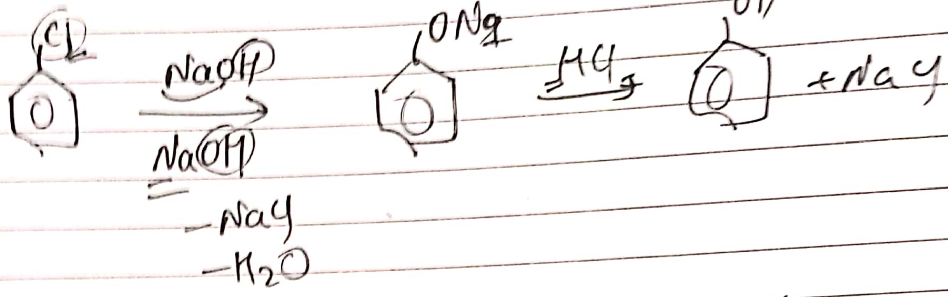
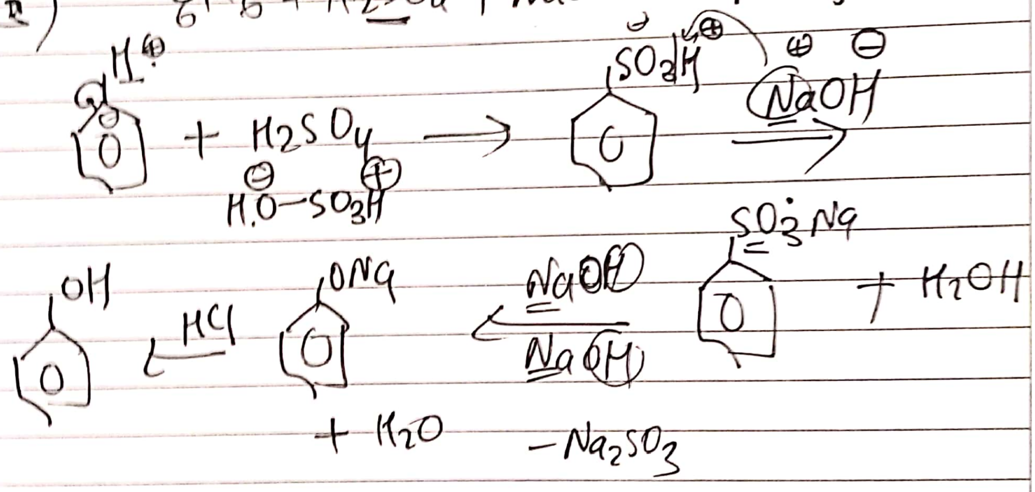
preparat^n of phenol – (1)



dows (·) $C_6H_5Cl \xrightarrow{NaOH/HCl}$ phenol



2) $C_6H_6 + H_2SO_4 + NaOH \rightarrow$ phenol



ph— → liq. less soluble, non polar, toxic

al < phenol < COOH

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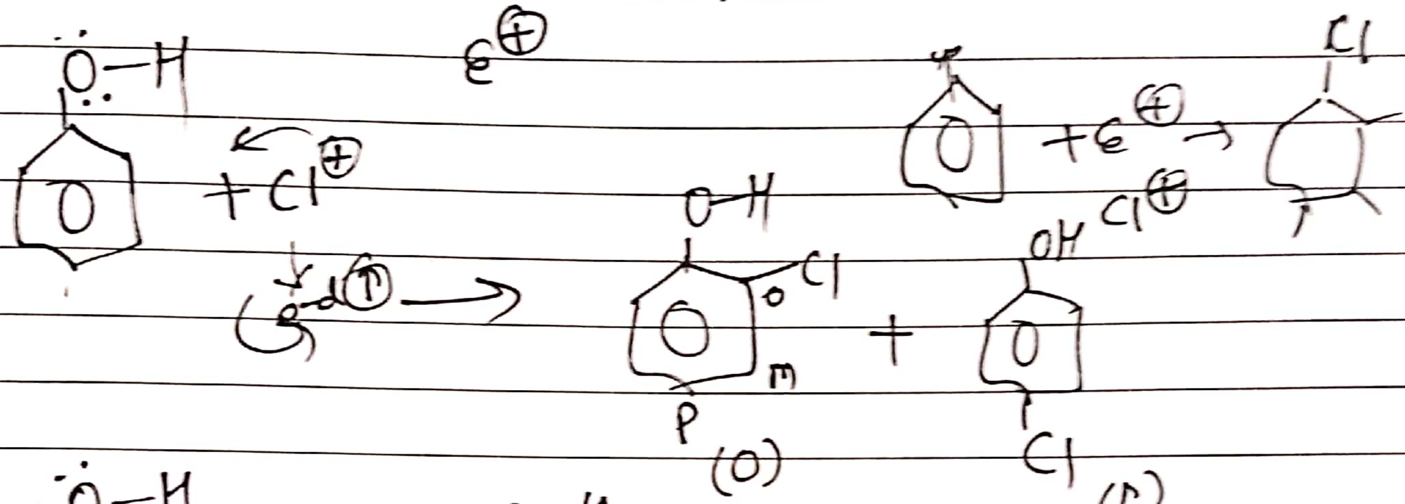
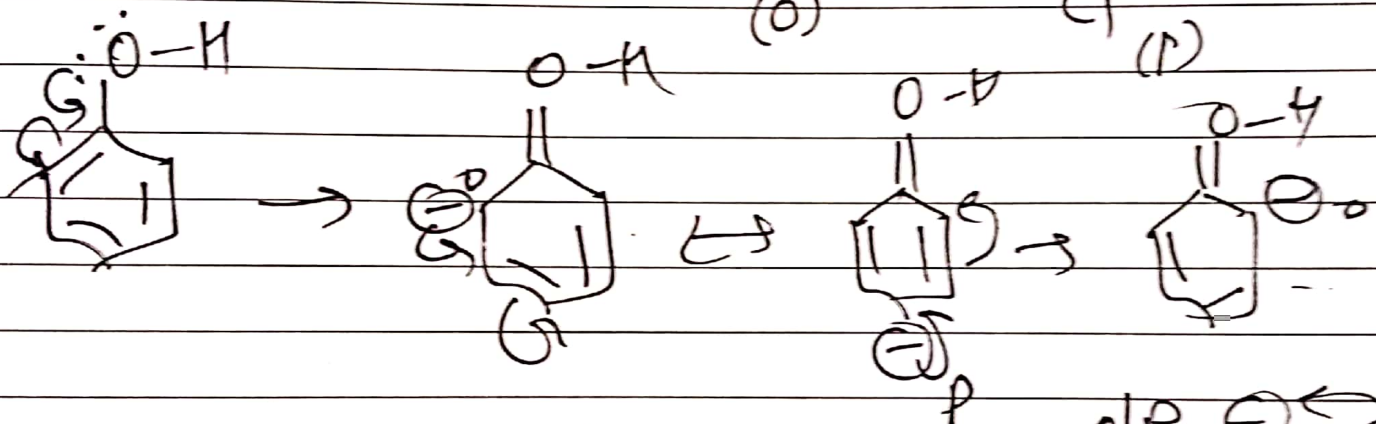
o/p dir g – $\ddot{O}H$, $\ddot{N}H_2$, $\ddot{N}HR$, $\ddot{S}H$

m dig. → NO_2, H–C=O

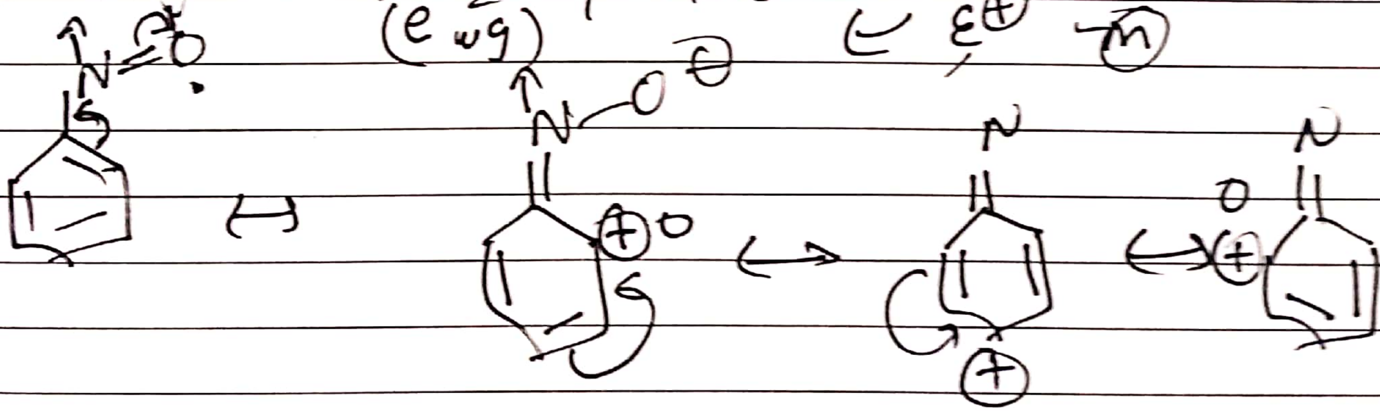
$E^{\oplus}$



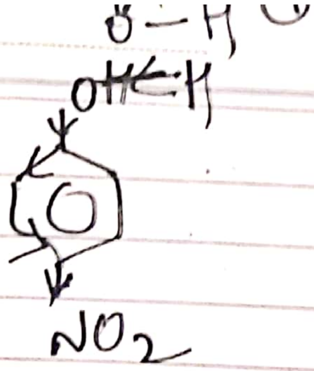


o/p ⊖ ← $E^{\oplus}$

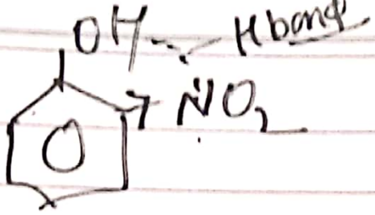
m-dir g – NO_2, –CHO (ewg) ← $E^{\oplus}$ m



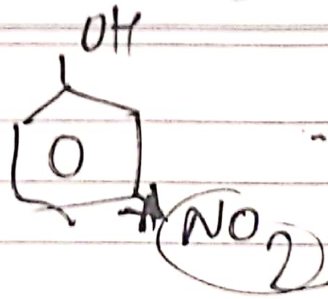
⊕ – o/p p m-e-den rich $E^{\oplus}$



P



O



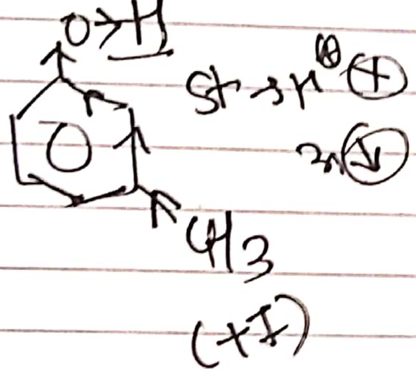
M

note → erg →

ewg → m push [illegible] effect

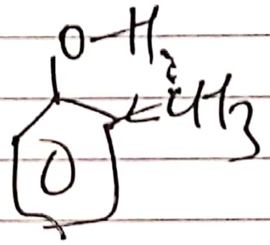
WAC →

P > O > M



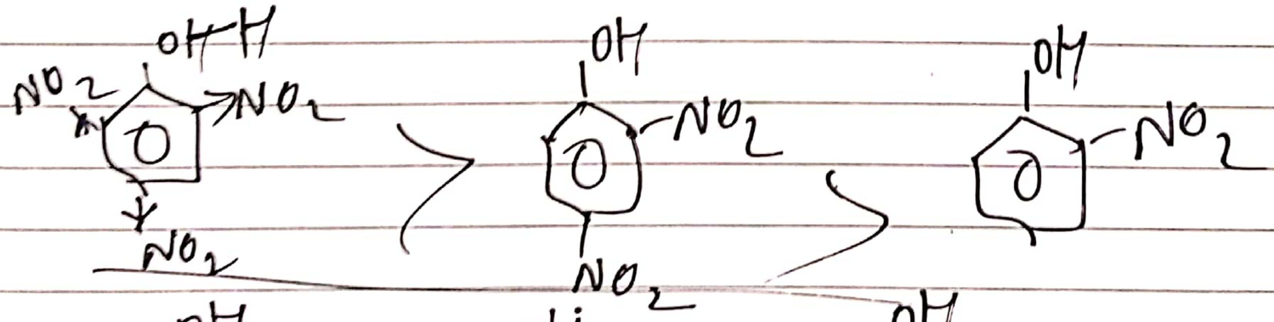
(m)

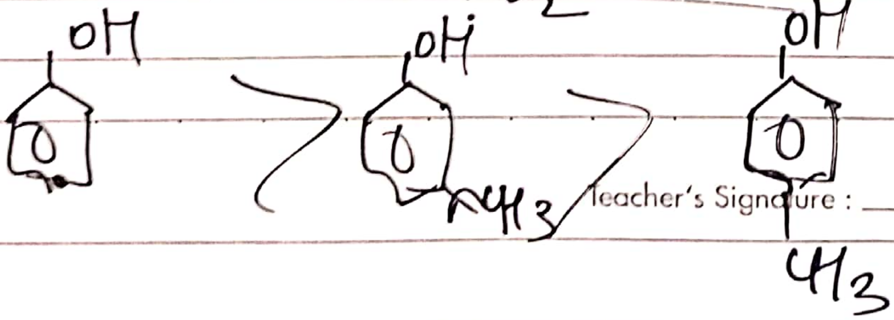
(p)



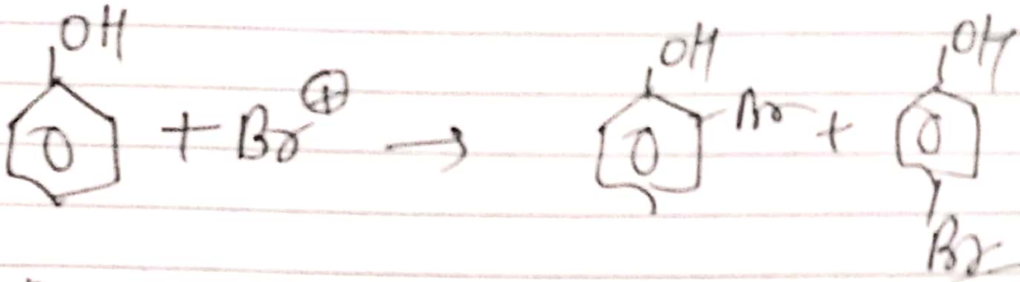
(o)

m > P > O

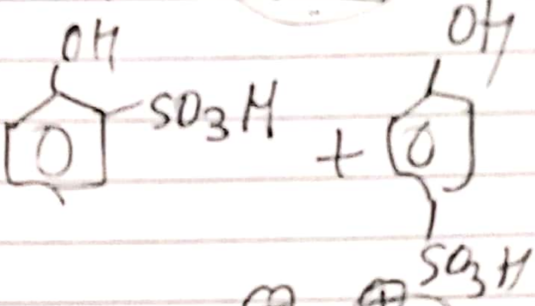




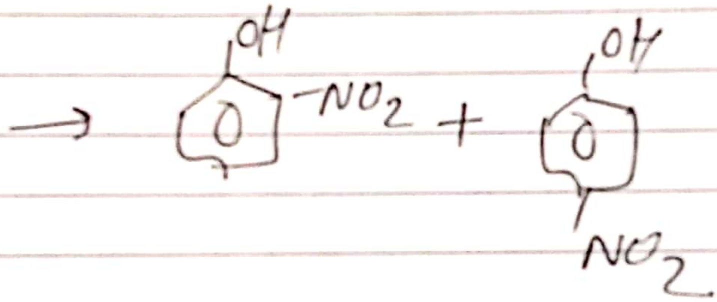
① halogenatn — $Br^{\oplus}$ $\quad Br^{\oplus}-Br^{\ominus}$



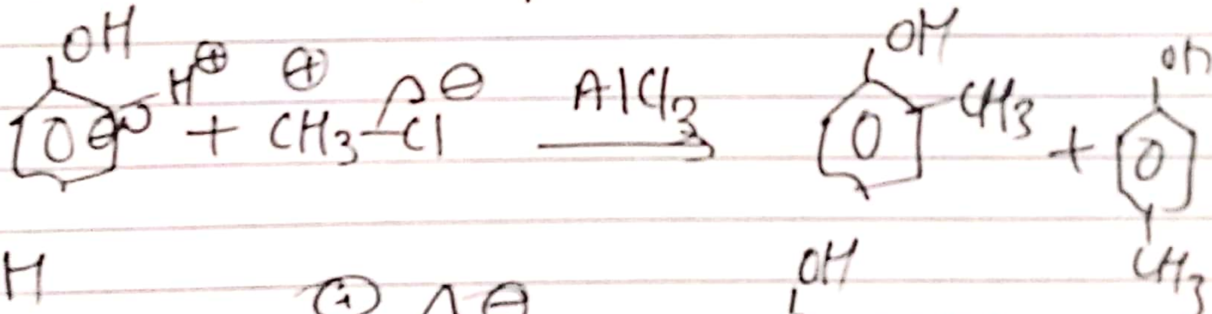
② sulphn ⇒ H_2SO_4 $\quad HO^{\ominus}-SO_3H^{\oplus}$

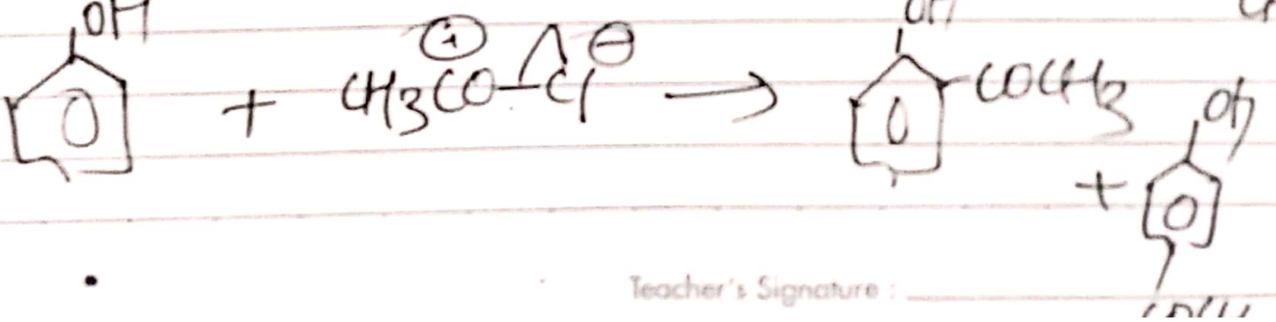


3) nitratn ⇒ $HNO_3 \rightarrow OH^{\ominus}-NO_2^{\oplus}$



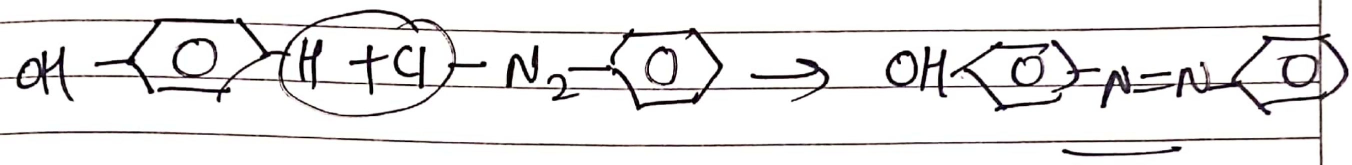
freidel craft reacn ⇒ phenol → cresol



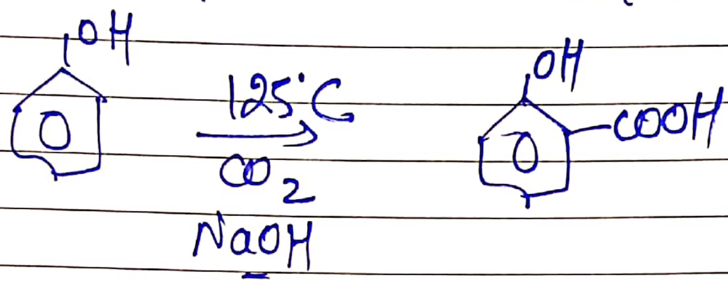


Coupling reacn

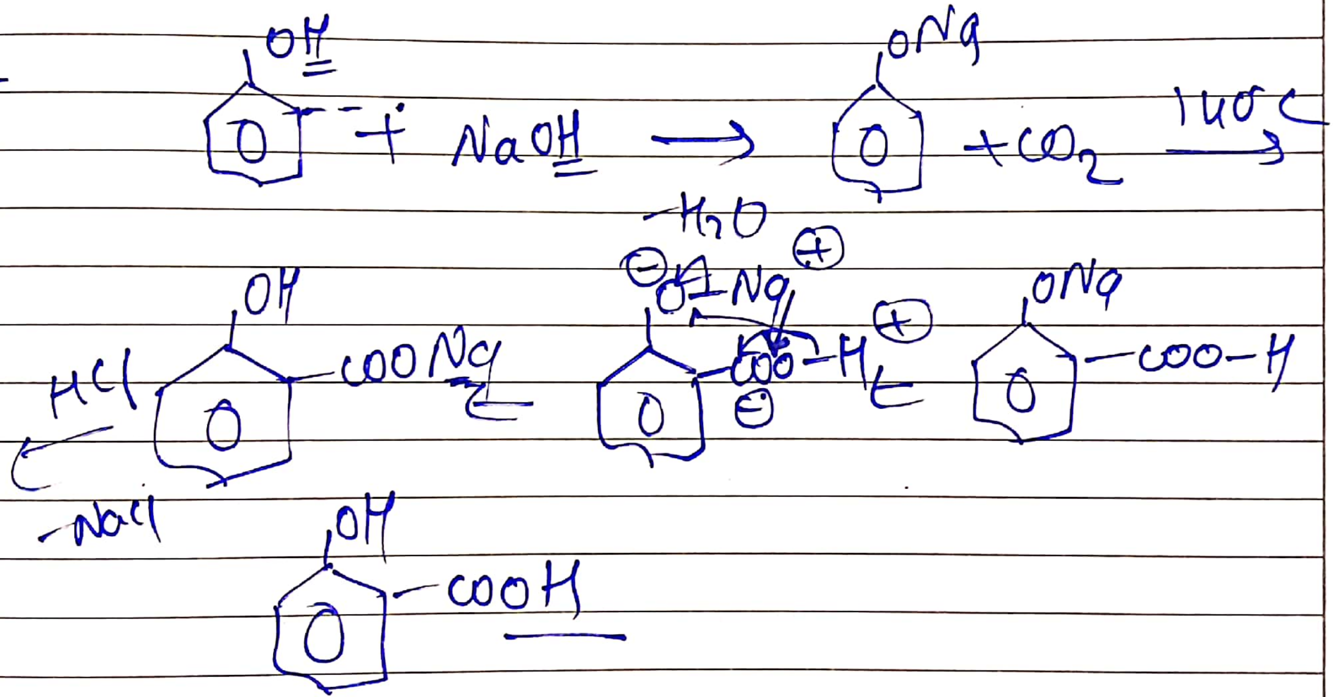
(2) $C_6H_5OH + C_6H_5N_2Cl \rightarrow$



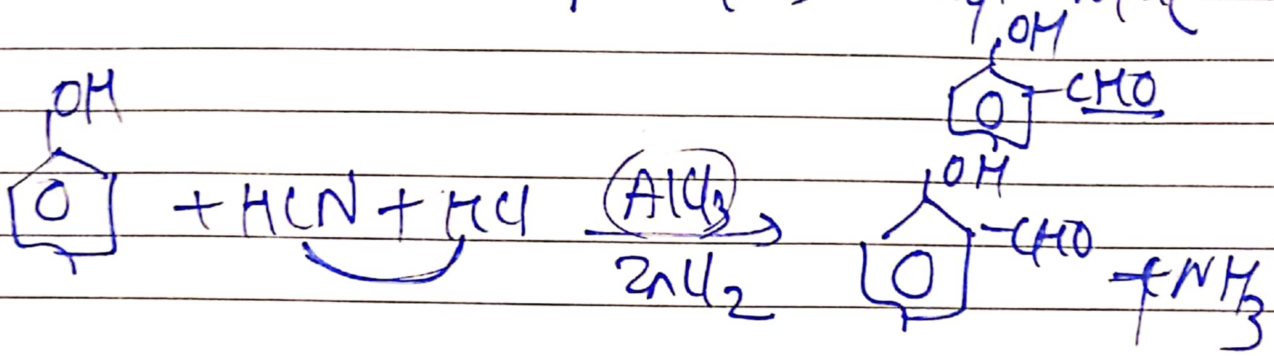
Kolbe's   phenol → Salicylic acid



mech



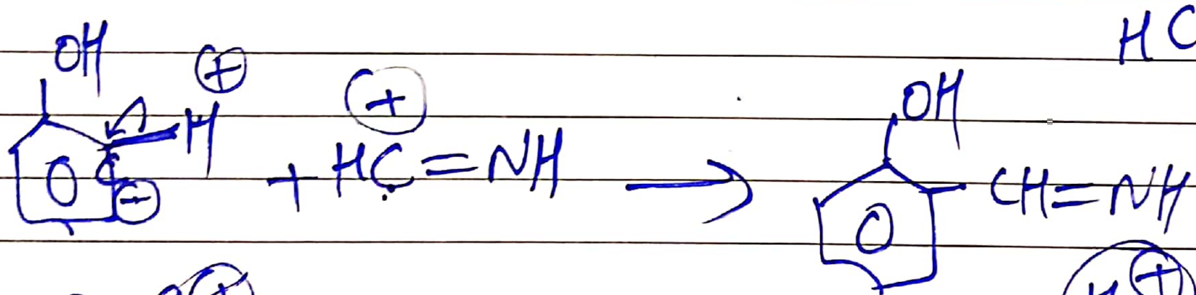
Gattermann Reaⁿ → phenol → salicylaldehyde



(i) $H-C\equiv N + HCl \rightarrow H-\underset{\underset{Cl}{|}}{C}=NH$

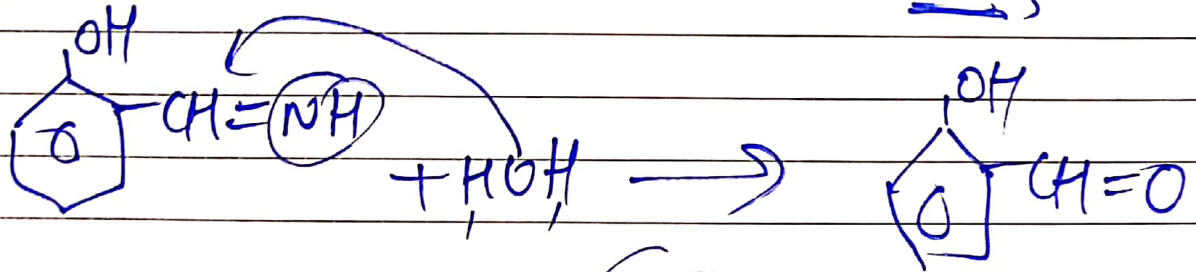
(ii) $H-\underset{\underset{Cl}{|}}{C}=NH + AlCl_3 \rightarrow AlCl_4^{\ominus} + H\overset{\oplus}{C}=NH$

(iii)



$AlCl_4^{\ominus} + H^{\oplus} \rightarrow HCl + AlCl_3$

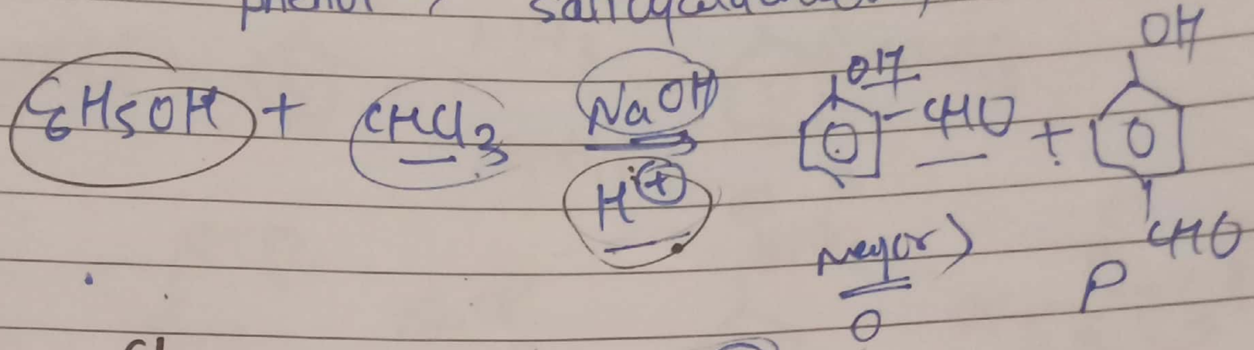
(iv)



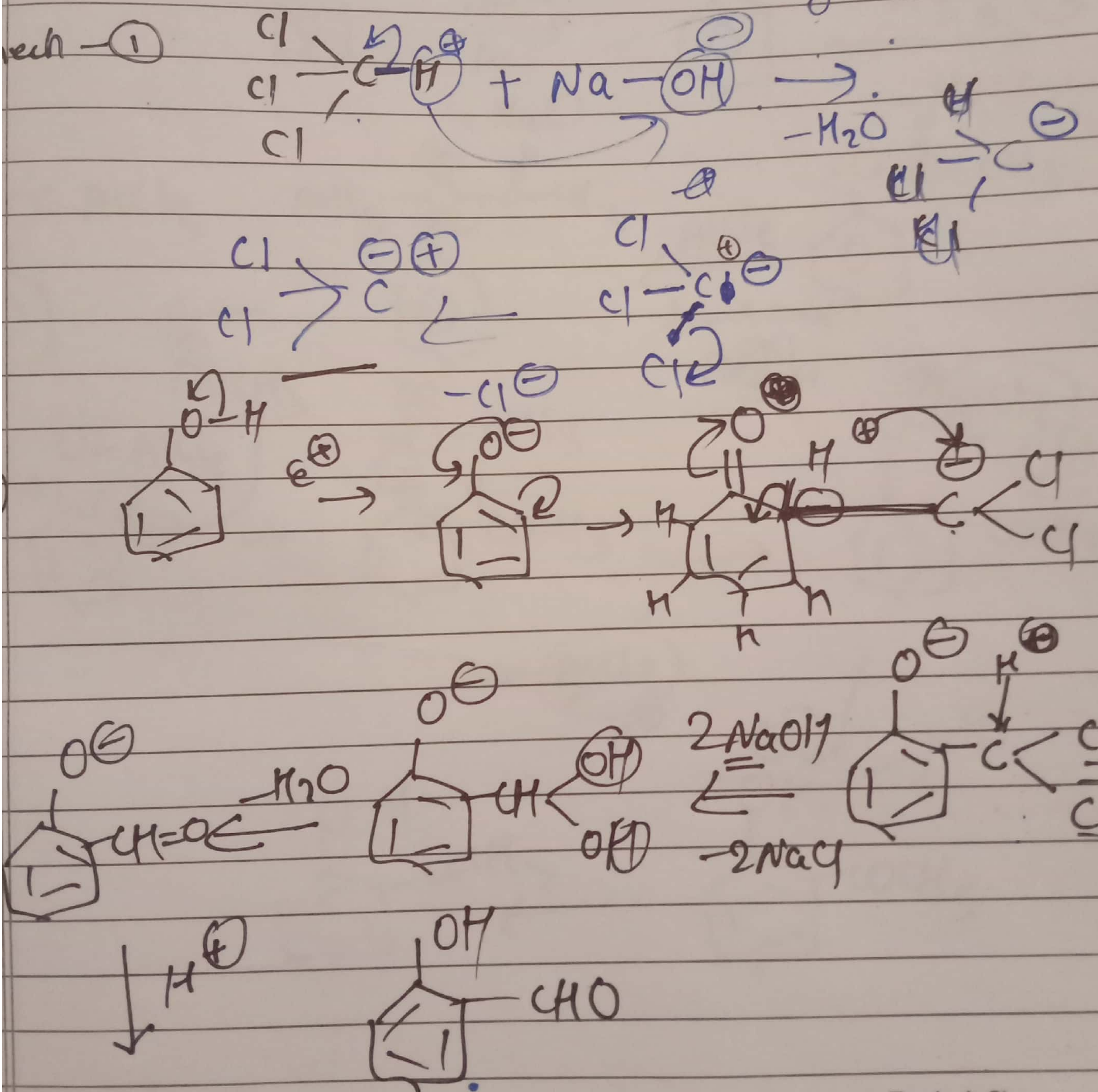
NH_3

Reimer-Teimann React^n ⇒

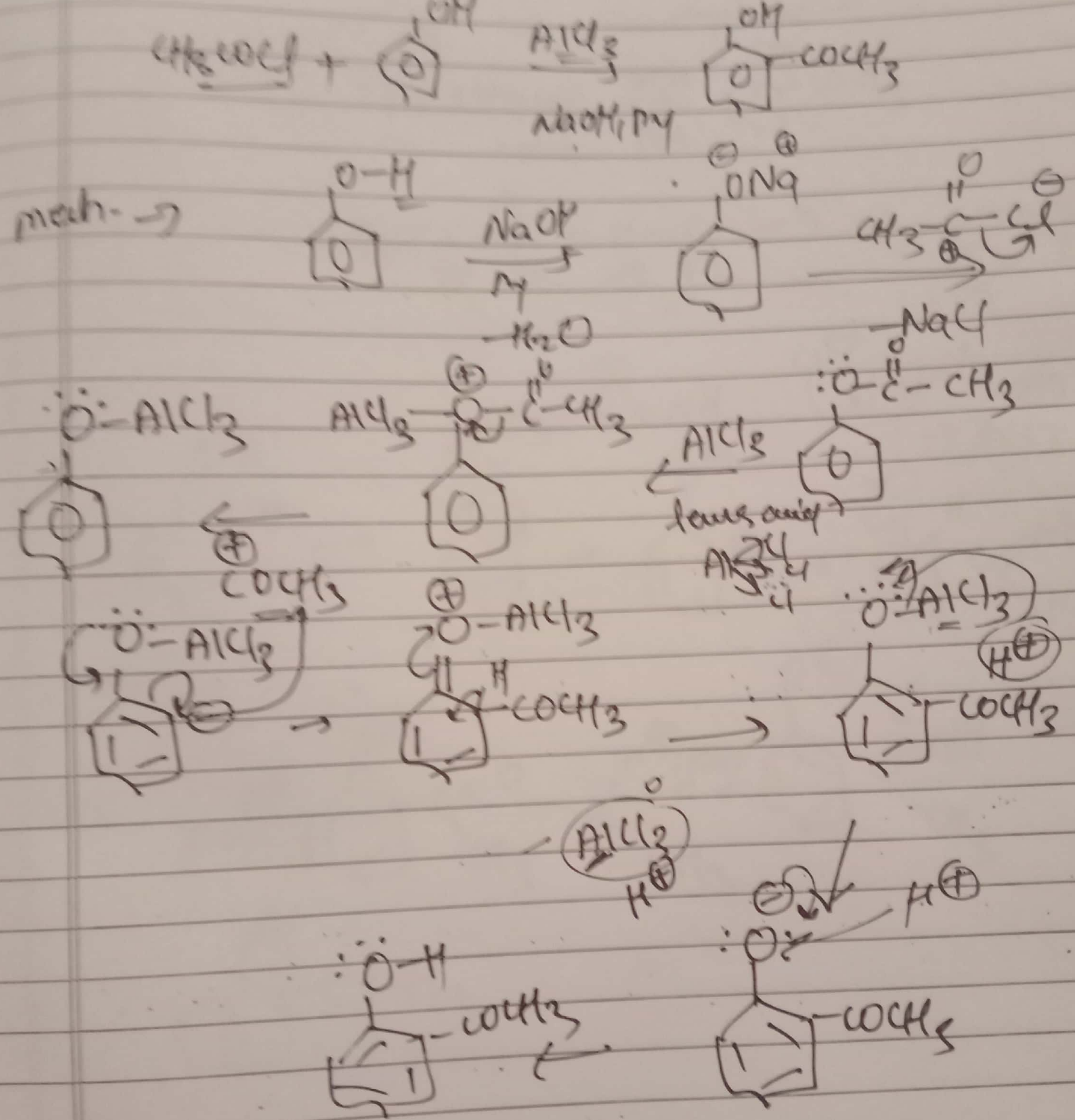
phenol → salicyaldehyde



Mech – 1



Fries – Rearrangement
phenol → acetophenone

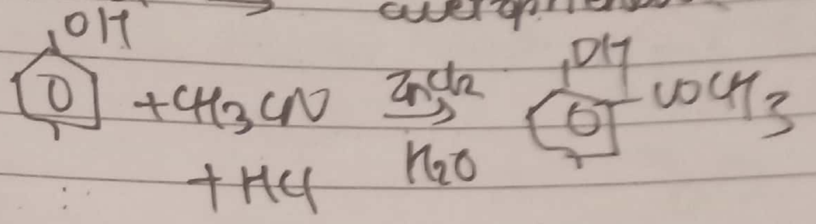


Teacher's Sign.

Remark

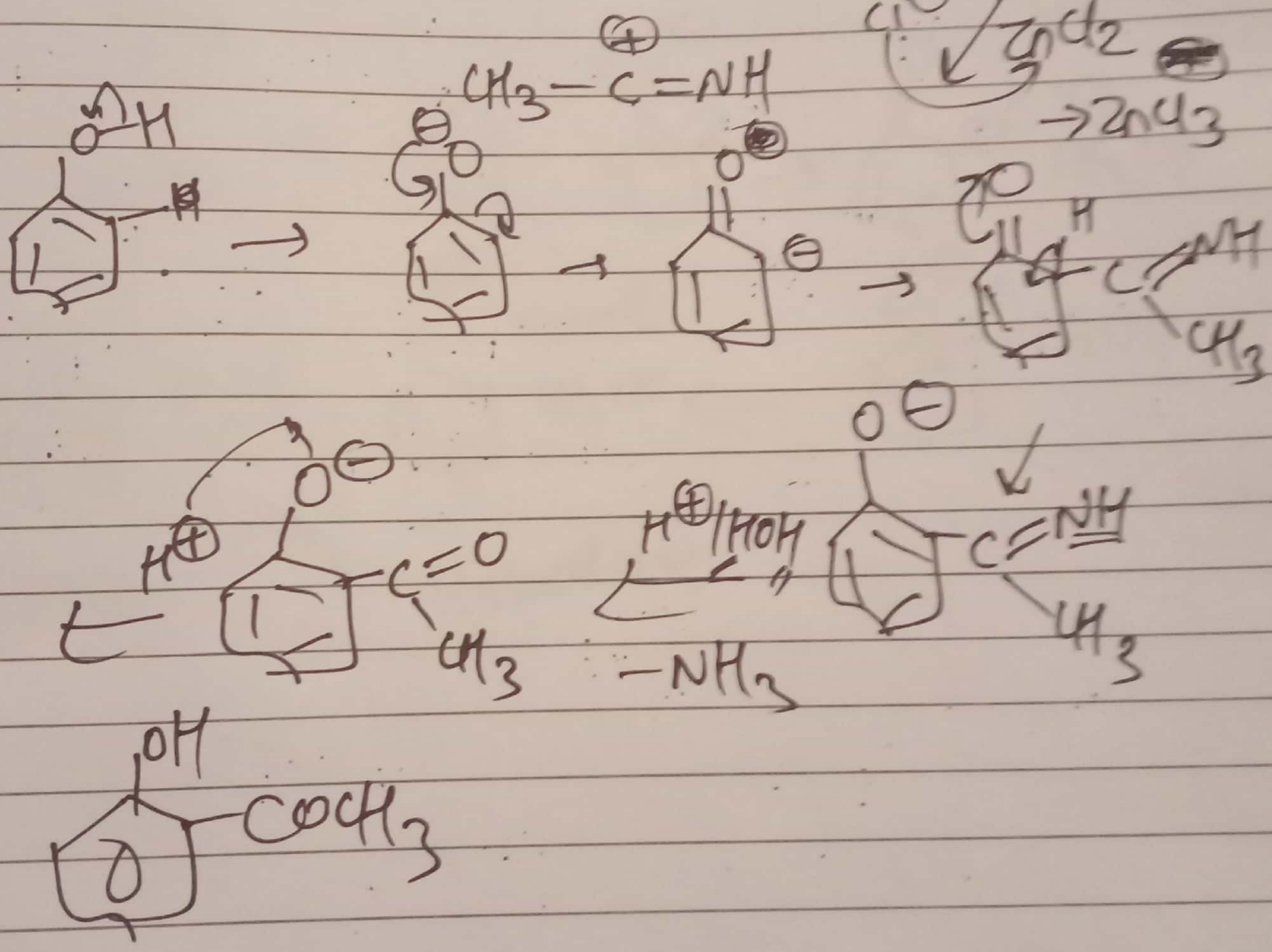
Hauben- hosch Rea^n ⇒

phenol → acetophenone

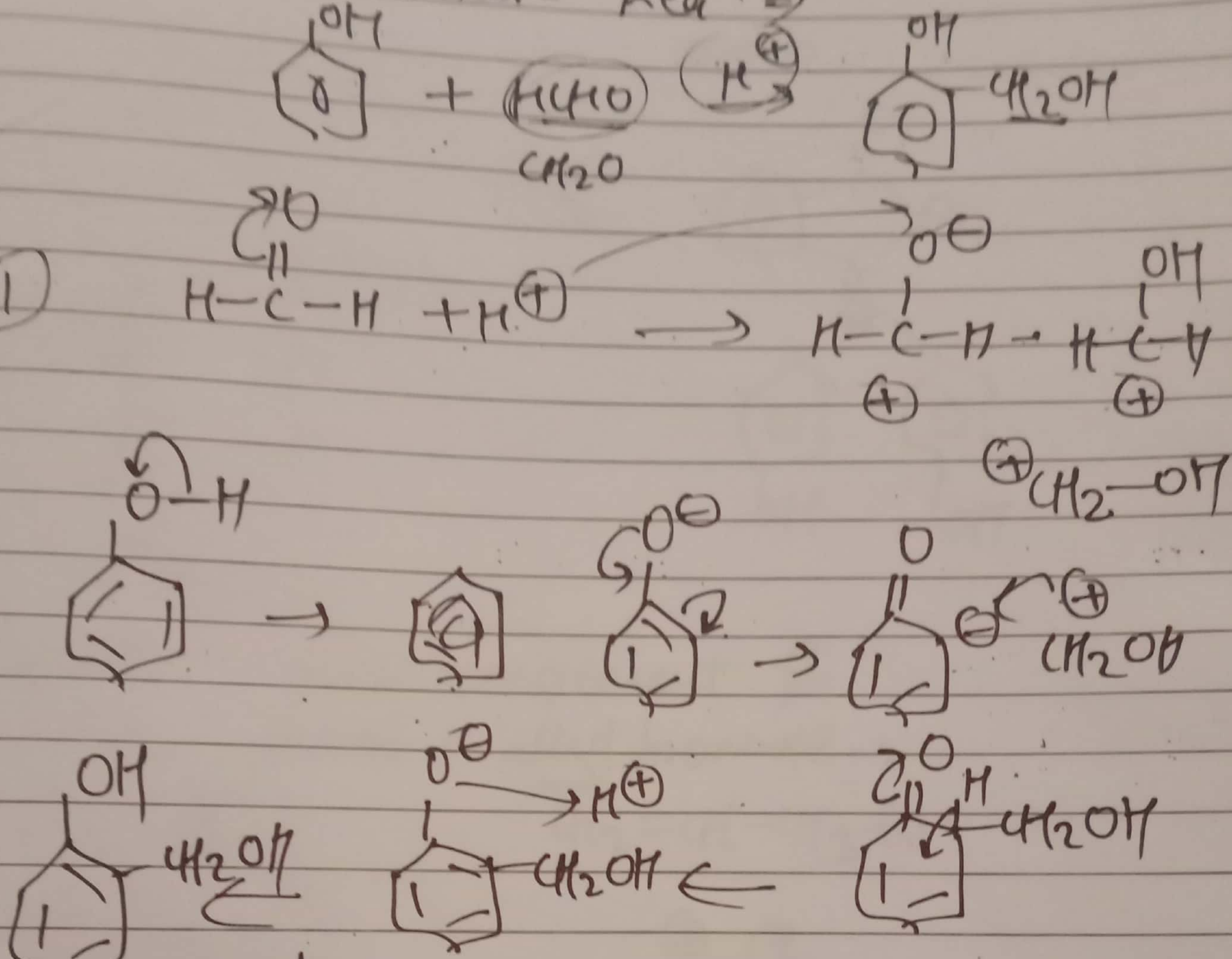


mech -

$$CH_3-C\equiv N + H-Cl \rightarrow CH_3-\underset{Cl}{\underset{|}{C}}=NH$$



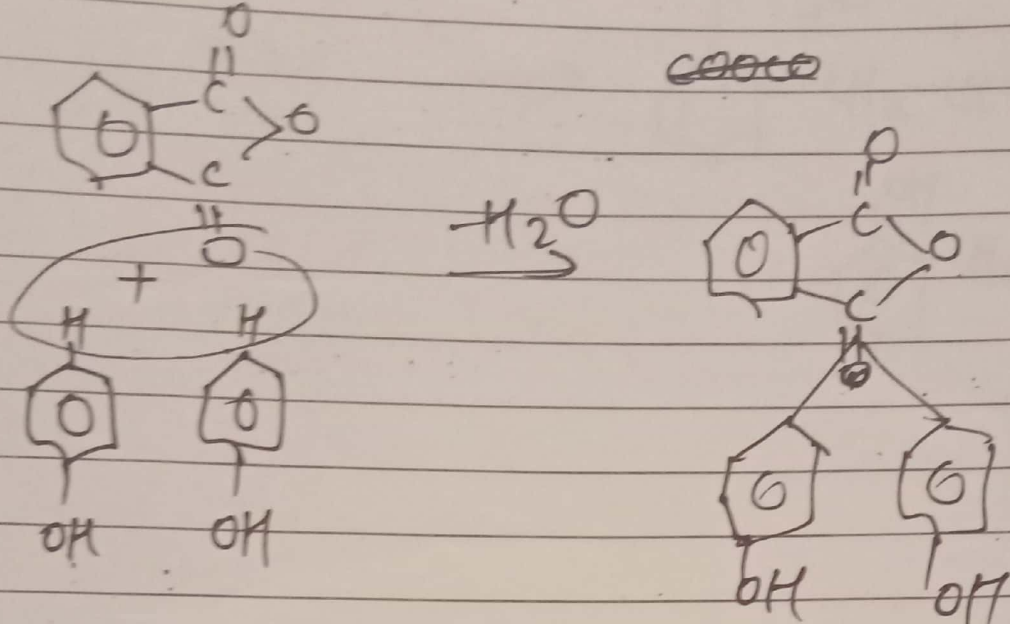
Lederer- Manasse Rea^n ⇒



Condn

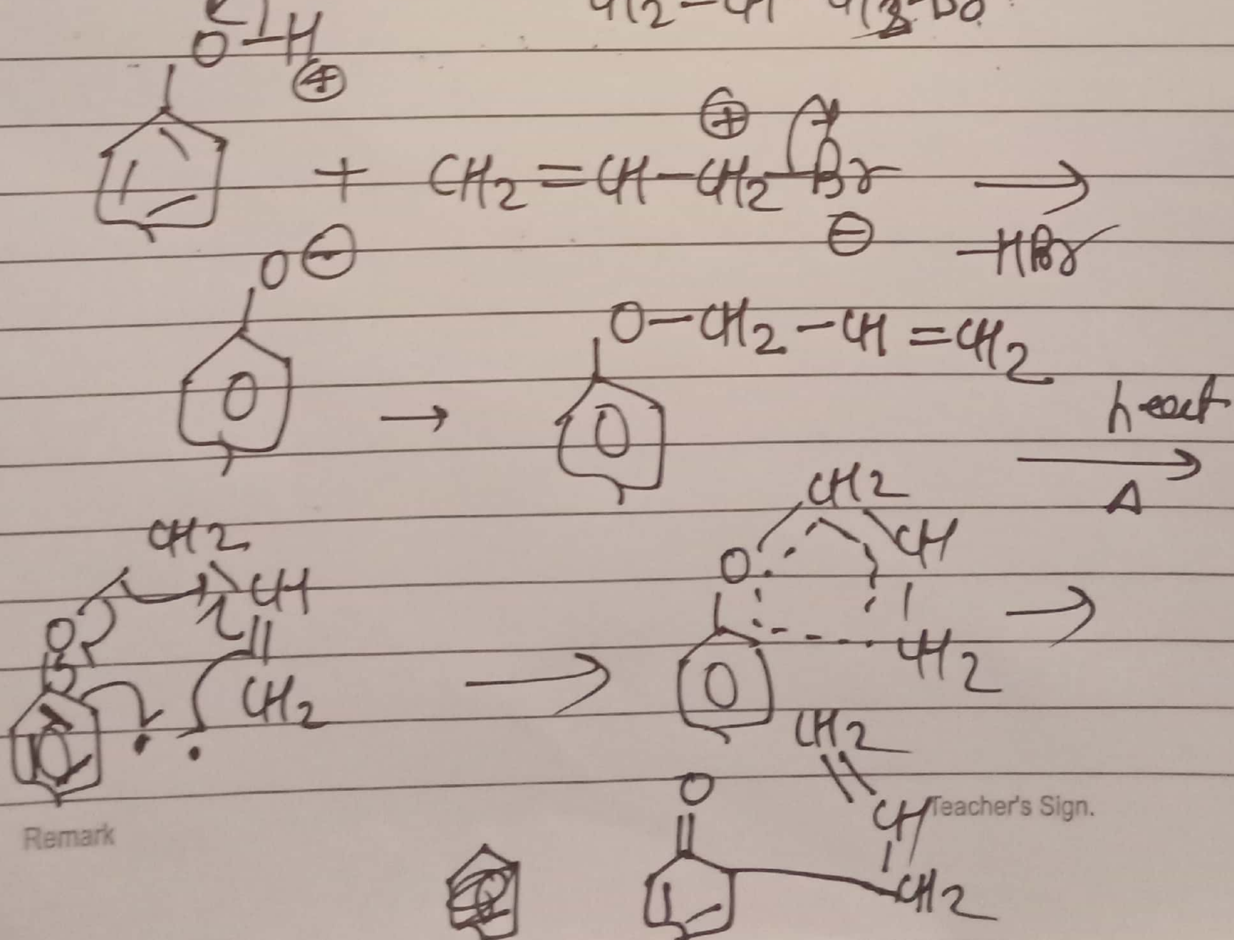
Bakellite

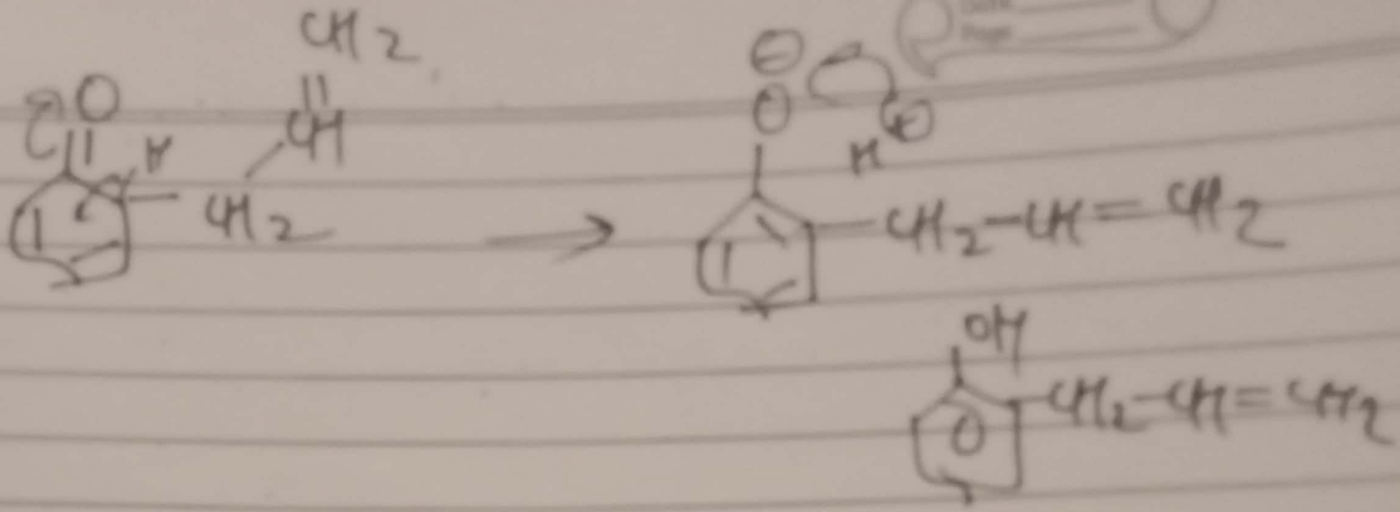
phenolpthalein synthesis



Clasein Rearrangement of
phenol + allyl bromide →

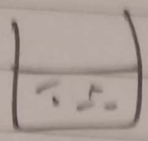
$CH_2=CH-CH_2-Br$





Thermodynamics

Thermo ↓ ऊष्मा — dynamics ↓ गति



भौतिक system

micro ↓ P, m, e

macro ↓ E, H, T, G

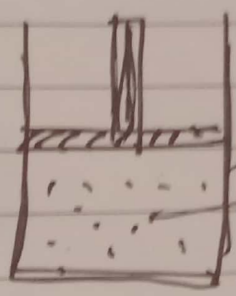
कमियां ⇒ (i) micro — ✗

(ii) process होने या न होने mech. ✗

(i) system ⇒

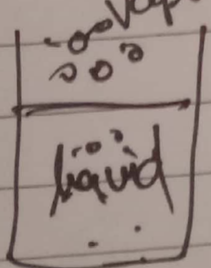
(ii) surr.

(iii) Boundry



Types of system –

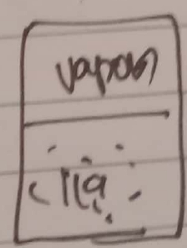
open



ऊष्मा ✓

द्रव्य ✓

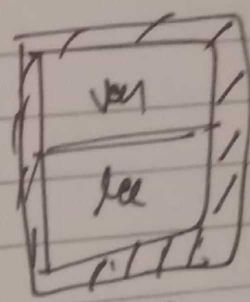
closed



ऊष्मा ✓

द्रव्य ✗

isolated



ऊष्मा ✗

द्रव्य ✗

composit^n के आधार पर

Homogeneous | Heterogeneous

$g \xrightarrow{g} g$

l l

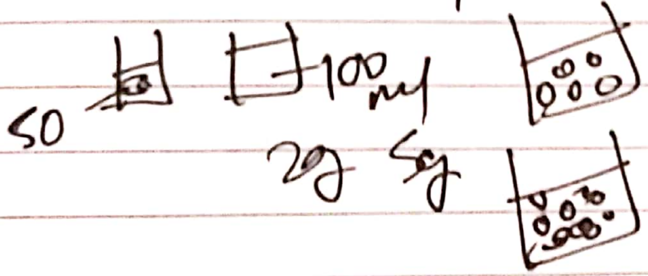
s s

$CaCO_3 (s) \xrightarrow{\Delta} CaO (s) + CO_2 (g) \uparrow$

Extensive property ⟹ पदार्थ मात्रा depend

↓

Volume, m, E



Intensive → मात्रा ⊗

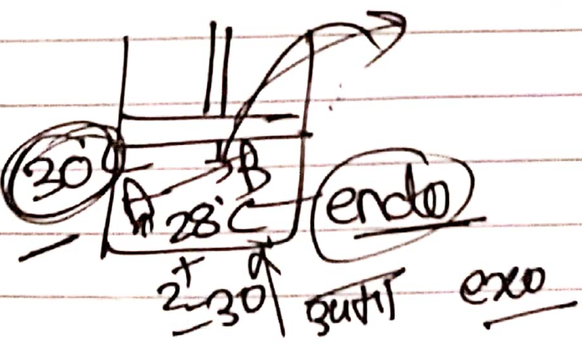
↓

Temp, P, density, surface

10ml 100ml

Thermodynamic process =

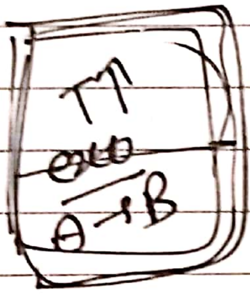
1. Isothermal $(dT=0)$ = q ⇄ sys surr.



closed

ii) Adiabatic $(dq=0)$ उष्मा ⇄ (X)
'heat'

isolated



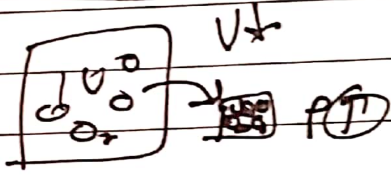
exo T (↑)

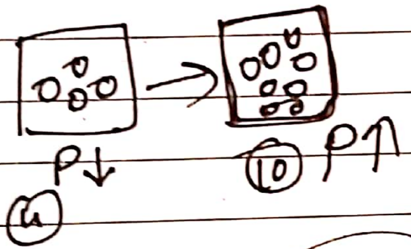
endo T (↓)

$dT \neq 0$

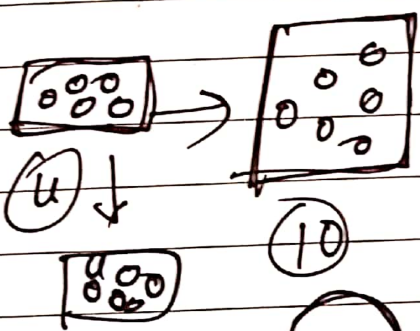
iii) Isochoric $dV=0$ $\boxed{V\downarrow = \frac{1}{P}}$

dp ✓

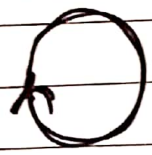




iv) Isobaric – $dP=0$ dV ✓



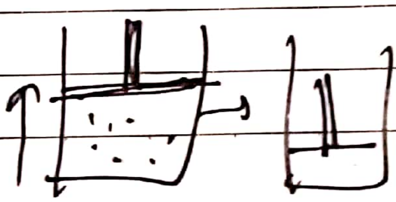
v) cyclic ⇒



$\Delta E = 0$

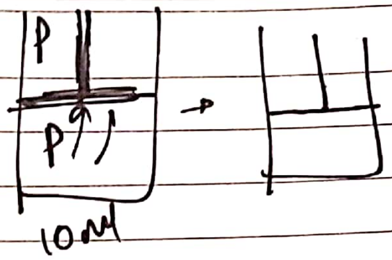
$dU = 0$

vi) Irreversible ⇒ →

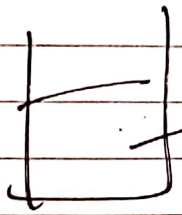


कार्य PV

reversible ⇒



10 atm



1000 l

State funct^n ⇒ — 2 final

— 1 initial

V, P, T

V_1 V_2 T_1 T_2

1 l 5 l 25 30

Path funct^n ⇒ 2 / 1   w   q

50 2 — 2

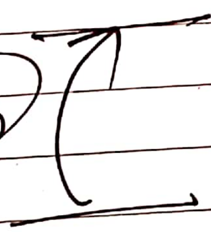
30 1 — 1

अलमारी

gas, stove

3rd floor

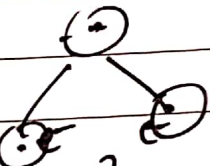
w path



सीढ़ी lift

Ist

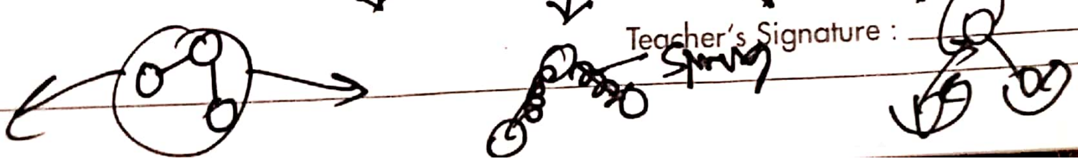
Internal energy < E, U



पदार्थ

CO_2

$$U = U_T + U_V + U_R + U_n + U_e$$



spring

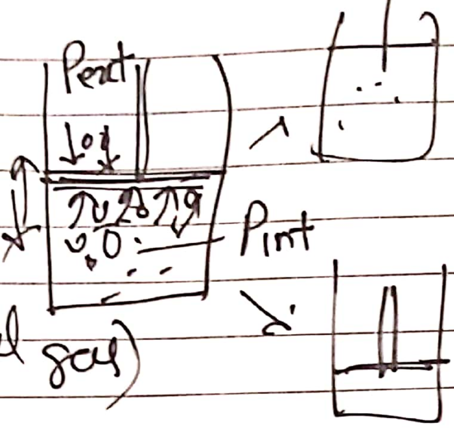
Expt. No. Date Page No.

Compression & Extension

(i) $P_{int} > P_{ext} \rightarrow$ प्रसार

(ii) $P_{int} < P_{ext} \rightarrow$ संपीडन

(iii) $P_{int} = P_{ext}$ equal (ideal gas)



कार्य = बल × विस्थापन

= दाब × क्षे × दूरी

$= P \underbrace{A \times dx}_{} \rightarrow$ Volume

$= P \times dV$

$$\boxed{W = PdV} \qquad dw = \int_{V_1}^{V_2} PdV$$

(A) निर्वात में Vacum हवा (X)

$$dw = \int_{V_1}^{V_2} P_{ext} \cdot dV, \quad P_{ext} = 0$$

$$\boxed{dw = 0}$$

(B) प्रसार कार्य at const P

$$w = \int_{V_1}^{V_2} PdV$$

$$= P \int_{V_1}^{V_2} dV = P[V]_{V_1}^{V_2}$$

Teacher's Signature :

$$= P(V_2 - V_1)$$

$V_2 - V_1$

$$\boxed{W = P\Delta V}$$

(c) reversible $\quad P_{int} = P_{ext}$

$$W = \int_{V_1}^{V_2} P\,dV \qquad PV = nRT$$

$$P = \frac{nRT}{V}$$

$$W = -\int_{V_1}^{V_2} \frac{nRT}{V}\,dV$$

$$W = nRT \int_{V_1}^{V_2} \frac{1}{V}\,dV$$

$$\left(\int_1^2 \frac{1}{x}\,dx = [\ln x]_1^2 \right)$$

$$W = nRT\,[\ln V]_{V_1}^{V_2}$$

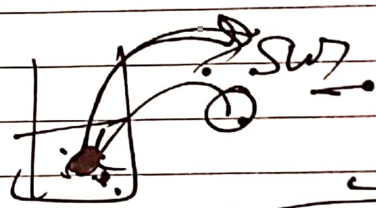
$$W = nRT\,(\ln V_2 - \ln V_1)$$

$$\boxed{W = nRT \ln \frac{V_2}{V_1}}$$

1 mol $\quad$ 1L → 10L

$V_1 \quad V_2$

I^{st} law thermody

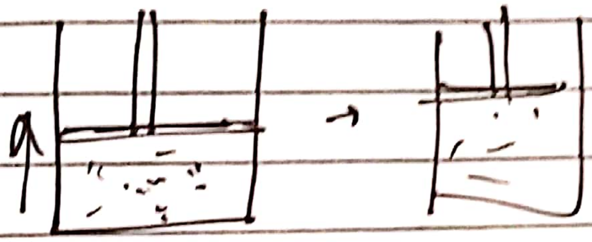


$$\boxed{dU = dq + dw}$$

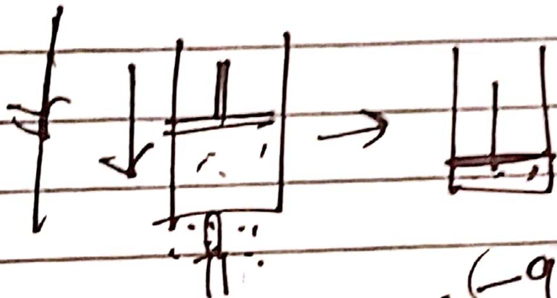
I law of thermodynamics

$$dU = dq + dw$$
$$dU = dq - dw$$

work done on the system $= +w$
by the sys. $= -w$



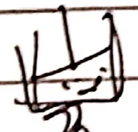
expansion $\rightarrow -w = \int p\,dV$
V (↑)
$w = -p\,dV$



comp^n $\rightarrow +w$ V (↓)
$w = p\,dV$

$q <$ $(-q)$ by the sy
$+q$ (↑) को दो

$dU = dq - dw$ $\qquad$ $dU = dq + dw$



2q T

Cond^n $\rightarrow$ adiabatic $\Rightarrow dq = 0$ [illegible] (X)

$$dU = dq + dw$$
$$dU = 0 + dw$$
$$dU = dw$$

a (+)

Teacher's Signature

(ii) cyclic $\Rightarrow$ $dU = 0$

$dU = dq + dw$

$0 = dq + dw$

$-dw = dq$

(iii) Isochoric ($dV = 0$), $dU = dq + dw$

$dU = dq + PdV$

$dU = dq$

limitⁿ $\Rightarrow$ (i) Rev $\rightarrow$ spontaneous

(ii) ऊष्मा $\rightarrow$ work (100%)

(iii)

Enthalpy $\rightarrow$ H

$H = U + PV$ E & H

$H_1 = U_1 + P_1V_1$

$H_2 = U_2 + P_2V_2$

$(H_2 - H_1) = (U_2 - U_1) + P_2V_2 - P_1V_1$ at P const

$\Delta H = \Delta U + P(V_2 - V_1)$

$\boxed{\Delta H = \Delta U + P\Delta V}$

$H = E + PV$

$dH = dE + PdV + VdP$

Teacher's Signature ....

$dH = dq + VdP$

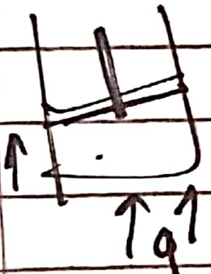
$dU = dq + dw$ at cons P_{ext}

$dU = dq - PdV$

$dU + PdV = dq_p$ — (II)

Let

$\boxed{dH = dq_p} + V dP$ $dP = 0$ — (I)

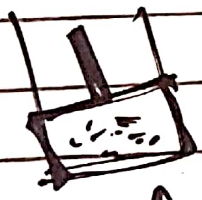


$\cancel{dH}\ dE + PdV = dq_p$

$dU = dq + dw$

at const $dV = 0$ $dU = dq + PdV$

$\boxed{dU = dq_v}$ — (II)



q

$dH = dU + PdV$

$dq_p = dq_v + PdV$ — (I)

$PV = nRT$ $PdV = \Delta nRT$

$P(V_2 - V_1) = (n_2 - n_1)RT$

$PdV = \Delta nRT$ — (II)

$\boxed{dq_p = dq_v + \Delta nRT}$

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$H_2 + Cl_2 \rightarrow 2HCl$ $\quad \Delta n = n_p - n_R$

$\quad 2 \qquad\quad 2 \qquad\qquad = 2 - 2$

(i) $dq_p = dq_v$ (ii) $dq_p > dq_v$ (iii) $dq_p < dq_v$

$dq_p = dq_v + \Delta n RT$

$dq_p = dq_v + 0$

$~~N_2 + 3H_2~~ \rightarrow 2NH_3 \rightarrow N_2 + 3H_2$

$\quad \cancel{4} \qquad\qquad \cancel{2} \qquad \Delta n = 4 - 2 = 2$

$dq_p = dq_v + 2RT$

$x = y + 2RT$

$dq_p > dq_v$

$x > y, \; x = y$

$dq_p = dq_v - 2RT$

$dq_p + 2RT = dq_v \rightarrow dq_v > dq_p$

$U > H$

Heat capacity $\rightarrow 1°C$

$dq \propto dT$

$\boxed{C_p - C_v = R}$

$dq = C\,dT$

$\boxed{C = \dfrac{dq}{dT}}$

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$C_p \rightarrow$ $dU = dq + dw$

cst P

$dU = dq - PdV$

$dU + PdV = dq$

$C = \frac{dq}{dT}$ $\quad dH = dq_P$

$$C_p = \left(\frac{dq_P}{dT}\right) = \left(\frac{dH}{dT}\right)_P$$

$C_v \Rightarrow$

$dU = dq + dw$

$dU = dq + PdV$

$dU = dq_V + 0$

$$C_v = \left(\frac{dq_v}{dT}\right) = \left(\frac{dU}{dT}\right)_V$$

$C_p - C_v = R$

$$C_p - C_v = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \quad \text{—(1)}$$

$H = U + PV$

T से diff. at cst P

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \quad \text{—(2)}$$

मान (2) का val (1) में

$$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \quad \text{—(3)}$$

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$$U = f(T, V) \text{ at cnt } P$$

आंशिक अवकलन

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

dT से भाग देने पर at cnt P

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \frac{dT}{dT} + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow \cancel{\left(\frac{\partial U}{\partial T}\right)_V} + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \cancel{\left(\frac{\partial U}{\partial T}\right)_V} \quad \text{— (4)}$$

$$C_p - C_v \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T^{0\times} \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$\Rightarrow$ ideal gas at T $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$C_p - C_v = P\left(\frac{\partial V}{\partial T}\right)_P \quad \text{— (5)}$$

$$PV = nRT \quad , \quad V = \frac{nRT}{P}$$

$$C_p - C_v = P\left(\frac{\partial\, nRT}{\partial T \times P}\right) \Rightarrow \frac{nR\cancel{P}}{\cancel{P}}\left(\frac{\cancel{\partial T}}{\cancel{\partial T}}\right) = (1)$$

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$C_p - C_v = nR$

for $n = 1$

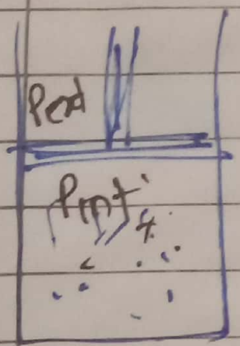
$$\boxed{C_p - C_v = R}$$

I Reversible isothermal expansion for ideal gas

$dT = 0$

$P_{ext} = P_{int}$

q w H U



① work $\Rightarrow dw = PdV$

$$dw = \int_{V_1}^{V_2} PdV \quad \text{—(I)}$$

$$PV = nRT, \quad P = \frac{nRT}{V}$$

$$dw = \int_{V_1}^{V_2} \frac{nRT}{V} dV \Rightarrow nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$dw = nRT \left[\ln V\right]_{V_1}^{V_2}$$

$$dw = nRT \ln V_2 - \ln V_1$$

$$dw = nRT \ln \frac{V_2}{V_1}$$

$$dw = nRT\, 2.303 \log \frac{V_2}{V_1}$$

$$dw = nRT\, 2.303 \log \frac{P_1}{P_2}$$

298K

$$P \propto \frac{1}{V}$$

$$\frac{V_2}{V_1} = \frac{\frac{1}{P_2}}{\frac{1}{P_1}} = \frac{P_1}{P_2}$$

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298K 2 mol $10 \to 20$, w

V_1 V_2

$R = 8.314$ $w = 2.303\, nRT \log \frac{V_2}{V_1}$

$= 2.303 \times 2 \times 8.314 \times 298 \log \frac{20}{10}$

$\times 0.3010$

$=$

$=$ J $1 \to 10$ cm

(2) $\underline{\underline{U}}$ $\Rightarrow$ $dU = 0$

$\underline{dT = 0}$ $dT = 0$, $\underline{dU = 0}$

$0 - 0$

(3) $q \Rightarrow$ $dq = dU + dw$

$dq = 0 + dw$

$dq = dw$

$dq = nRT \ln \frac{V_2}{V_1}$

$= 2.303\, nRT \log \frac{V_2}{V_1}$

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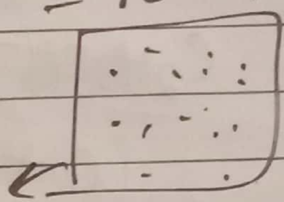
(4) $\underline{H}$ $\Rightarrow$ $H = U + PV$

$$dH = dU + d(PV)$$

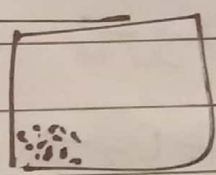
$$(PV = nRT)$$

$$dH = dU + d(nRT)$$

$$dH = dU + nR\,dT$$ – for ideal gas



$$dV = 0, \; \underline{dT = 0}$$



$$dH = 0 + 0$$

$$dH = 0$$

neglible →

dn

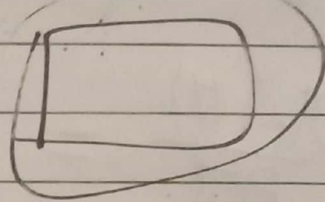
$P\,\underline{dV}$ $\underline{dn}$

real gas

II. Adiabatic expansion of ideal gas

$w \quad q \quad U \quad H$

$dq = 0$



(1) work (w) $\Rightarrow$ $dq = 0$

$$dq = dU + dw$$

$$0 = dU + dw$$

$$dw = -dU$$

$$= -\left[C_V(T_2 - T_1)\right] \Rightarrow C_V(T_1 - T_2)$$

(2) U or E $\Rightarrow$ $U = f(T, V)$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

ideal gas $dU = 0$

$dU \to T$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + 0$$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V, \quad C_P = \left(\frac{\partial H}{\partial T}\right)$$

$$dU = C_V dT$$

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$$dU = C_v \int_{T_1}^{T_2} dT$$

$$\boxed{dU = C_v [T_2 - T_1]}$$

ε at $\underline{V}$

(3) $\underline{H} \Rightarrow$ $H = U + PV$

$dH = dU + d(PV)$

$\left(\frac{dU}{dT}\right)_v = C_v$ $(PV = nRT)$

$= dU + d(nRT)$

$dU = C_v dT$

$dH = \underline{dU} + nR\,dT$

$dH = C_v \cdot \underline{dT} + nR\,d\underline{T}$

$dH = (C_v + nR)\,dT$

we know. $C_p - C_v = nR$

$C_p = nR + C_v$

$dH = C_p \cdot dT$

$$dH = C_p (T_2 - T_1)$$

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$V_1 \rightarrow V_2$

1 mol 127°C $10 \rightarrow 20$

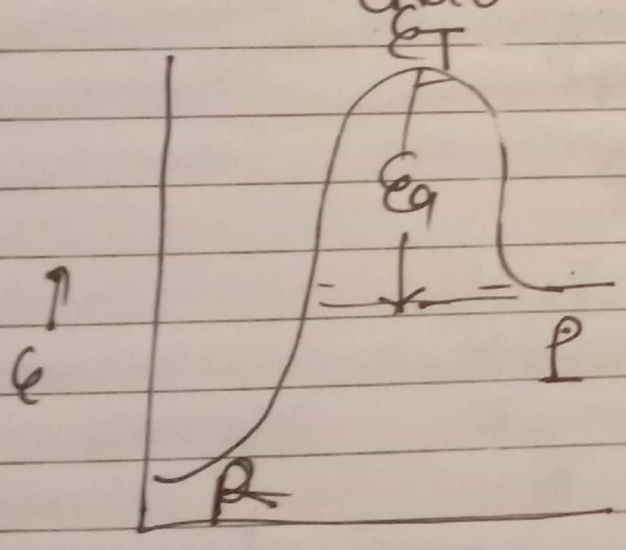
rev. iso. $q, w, \Delta U, \Delta H$

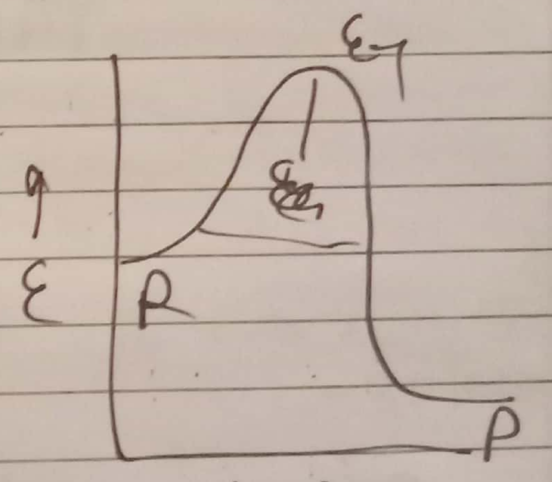
$$w = nRT \ln \frac{V_2}{V_1}$$

$dT = 0 \quad \Delta U = 0, \quad dH = 0$

Thermo chemistry

endo exo





R →

R ~

$E_R + E_a \Rightarrow E_T$

$\Delta H = H_P - H_R$

$= H_P > H_R$

$\Delta H = +ve$

$\Delta H = H_P - H_R$

$= H_R > H_P$

$\Delta H = -ve$

at con Volum $q_v = dU$

$q_p = dH$

$dH = dU + PdV$

$q_p = q_v + \Delta nRT$ real gas

$CaCO_3 \rightarrow CaO + CO_2$

$n_R = 1 \quad n_p = 2$

$\Delta n = n_p - n_r$

$= 2 - 1 = 1$

$q_p = q_v + RT$

$q_p > q_v$

Hess's law

-30 kcal

A → Z

-30 kcal

A → B → C → Z

-30 kcal

मुख्य ऊर्जा

multistep - A → B

B → C

C → Z

-50 kcal

मुख्य

A → Z

अवशोषित

ऊर्जा उत्पन्न Z — A 1 step

+30 kcal लगेगा

-20 kcal

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I $C + O_2 \rightarrow CO_2 + 93.4 kcal$

II - a $C + \frac{1}{2}O_2 \rightarrow CO + 26$

b $CO + \frac{1}{2}O_2 \rightarrow CO_2 + 68.3$

94

$C + O_2 \rightarrow CO_2$ $\Delta H = -93.4 kcal$

$C + O_2 + 10 \rightarrow$ $\Delta H = +10$ kcal

$P + 10$

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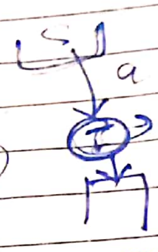
BSC-II

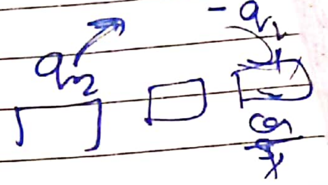
Entropy $\underline{\underline{S}}$

H, E, G, A

$$S = \frac{q_{rev}}{T}$$

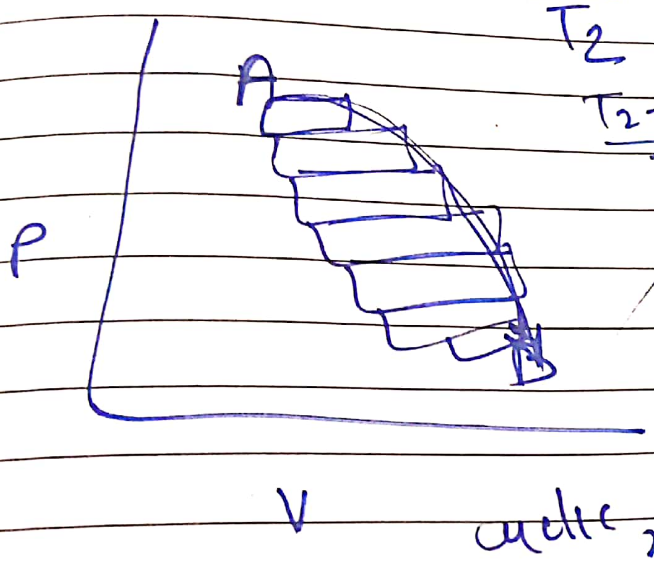


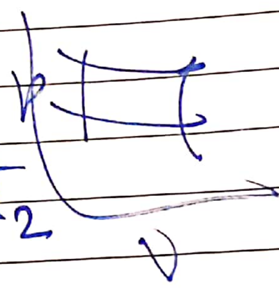
$$\eta = \frac{T_2 - T_1}{T_2} \quad \text{या} \quad \frac{q_2 - q_1}{q_2}$$



$$\frac{T_2 - T_1}{T_2} = \frac{q_2 - (-q_1)}{q_2}$$

$$\frac{T_2 - T_1}{T_2} = \frac{q_2 + q_1}{q_2}$$





$$1 - \frac{T_1}{T_2} = 1 + \frac{q_1}{q_2}$$

$$-\frac{T_1}{T_2} = \frac{q_1}{q_2}$$

cycle reve

$$-\frac{q_2}{T_2} = \frac{q_1}{T_1}$$

$$S = \frac{q}{T}$$

$$0 = \frac{q_1}{T_1} + \frac{q_2}{T_2}$$

$$dS = \frac{dq_{rev}}{T}$$

$$dS = \int_A^B \frac{dq_{rev}}{T}$$

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Calculation of S for ideal gas

① T & V variable

$$dS = \frac{dq}{T}$$

I law

$$dq = dE + PdV$$

$$\left(\frac{dE}{dT}\right)_V = C_V, \quad dE = C_V dT$$

$$dq = C_V dT + PdV$$

$$PV = RT, \quad P = \frac{RT}{V}$$

$$dq = C_V dT + \frac{RT}{V} dV$$

T से divide

$$\frac{dq}{T} = \frac{C_V dT}{T} + \frac{RT}{T}\frac{dV}{V}$$

$$\int_{S_1}^{S_2} dS = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$(S_2 - S_1) = C_V [\ln T]_{T_1}^{T_2} + R \ln [V]_{V_1}^{V_2}$$

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

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(II) T, P – variable

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \text{—(1)}$$

$$P_1 V_1 = R T_1 \qquad P_2 V_2 = R T_2$$

$$\frac{P_1 V_1}{P_2 V_2} = \frac{\cancel{R} T_1}{\cancel{R} T_2} \qquad \frac{V_1}{V_2} = \frac{T_1 P_2}{T_2 P_1}$$

$$\frac{V_2}{V_1} = \frac{T_2 P_1}{T_1 P_2} \quad \text{—(II)}$$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \left(\frac{P_1 T_2}{P_2 T_1} \right)$$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} + R \ln \frac{T_2}{T_1}$$

$$\left(C_p - C_v = R, \quad C_v = C_p - R \right)$$

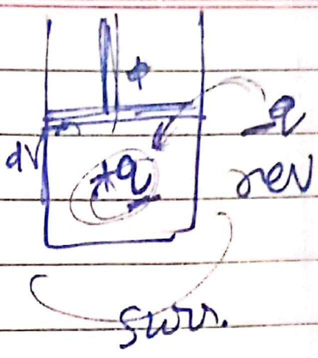
$$\Delta S = (C_p - R) \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} + R \ln \frac{T_2}{T_1}$$

$$\Delta S = C_p \ln \frac{T_2}{T_1} - \cancel{R \ln \frac{T_2}{T_1}} + R \ln \frac{P_1}{P_2} + \cancel{R \ln \frac{T_2}{T_1}}$$

$$\boxed{\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}}$$

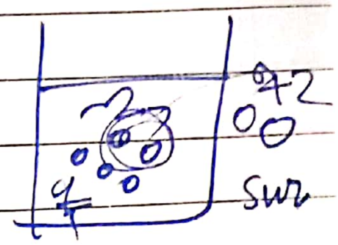
S chang in rev. process

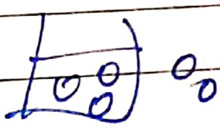
$\Delta S = \Delta S_{sys} + \Delta S_{surr.}$



$= +\frac{dq}{T} + \left(-\frac{dq}{T}\right)$

$= 0$





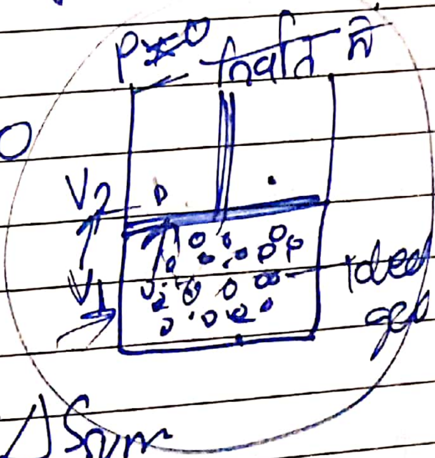
q irrev तो S change

$P = 0$

$dE = 0, \ dW = 0$

$dq = 0$

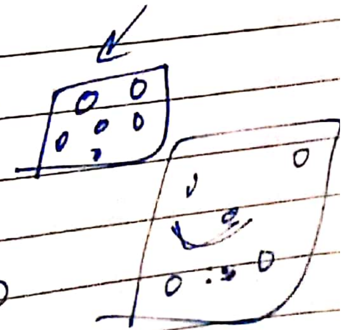
$dS_{surr} = 0$



$\Delta S = \Delta S_{sys} + \Delta S_{surr}$

$= \Delta S > + 0$

$\Delta S_{sys} = R \ln \frac{V_2}{V_1}$



$\Delta S = R \ln \frac{V_2}{V_1} + 0$

$\Delta S_{irr} > 0$

+ve

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$\Delta H \quad \Delta S \quad \Delta G \quad \Delta A$

$A \rightarrow B$

Imp

(I) isothermal $\quad dT = 0$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$dT = 0$

$$\Delta S = R \ln \frac{V_2}{V_1}$$

$$\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

$$\Delta S = R \ln \frac{P_1}{P_2}$$

(II) isobaric $\Rightarrow dP = 0$

$$\Delta S = C_p \ln \frac{T_2}{T_1}$$

(III) isochoric $\Rightarrow dV = 0$

$$\Delta S = C_v \ln \frac{T_2}{T_1}$$

(IV) adiabatic $\quad dq = 0, \; dS = 0$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$$-R \ln \frac{V_2}{V_1} = C_v \ln \frac{T_2}{T_1}$$

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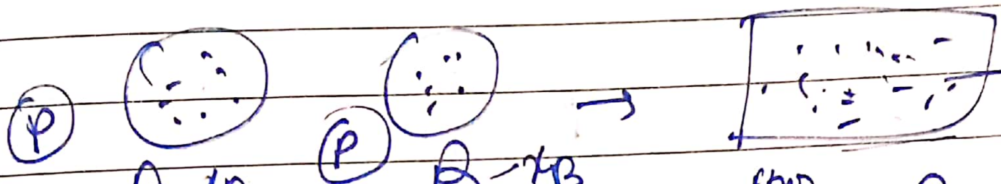
$$-R \ln \frac{P_1}{P_2} = C_p \ln \frac{T_2}{T_1}$$

entropy mixing of ideal gas

isothermal $dT = 0$

$$\Delta S = nR\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$$

$$\Delta S_{mix} = nR\ln\frac{P_1}{P_2} \quad \begin{matrix} P_1 - \text{int } P \\ P_2 - \text{final } P \end{matrix}$$



(P) A x_A (P) B – x_B → A+B

after M $P_i \rightarrow P_f$

$$\Delta S_{mix} = \Delta S_A + \Delta S_B$$

$$= n_A R\ln\frac{P_1}{P_2} + n_B R\ln\frac{P_1}{P_2}$$

$$= x_A R\ln\frac{P}{P\times x_A} + x_B R\ln\frac{P}{x_B\times P}$$

Partial $P = P\times x$

$$= x_A R\ln\frac{1}{x_A} + x_B R\ln\frac{1}{x_B}$$

$$= -x_A R\ln x_A - x_B R\ln x_B$$

$$\Delta S_{mix} = -R\left(x_A\ln x_A + x_B\ln x_B\right)$$

$$\boxed{\Delta S_{mix} = -R\sum x_i\ln x_i}$$

phase transition

(i) S & W ⇒ spontaneity

$$S = f(W)$$

( ) → liq → gas

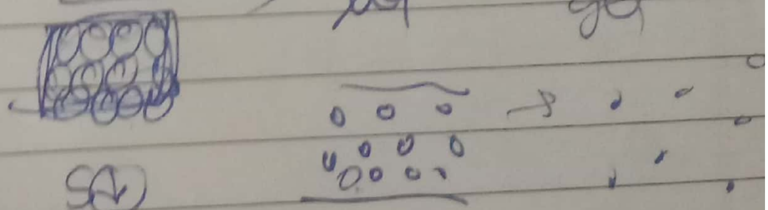
S ↗

$$\boxed{S = k \ln W}$$

↓ boltzmann const

(ii) disorderness measure

state → liq gas



H_2O S(↓) S(↑) S(↑)

(i) fusion S ⇒ s → l

$$\Delta S_f = \frac{\Delta H_f}{T}$$

(ii) Vap. S ⇒ l → gas

$$\Delta S_v = \frac{\Delta H_v}{T}$$

(III)

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C — graphite
Daimond

S — S_t, S_r, S_v

work function (A)

$$A_0 = E_0 - TS$$

$$\Delta A = \Delta E - T\Delta S \quad (1)$$

$$\Delta S = \frac{dq}{T}, \quad T\Delta S = dq$$

$$\Delta A = \Delta E - dq \quad (2)$$

1st law $dq = \Delta E + w$

$$-w = \Delta E - dq \quad (3)$$

fossil fuel → work (100) → useful (100% − 80%), waste (उपयोग) ($P\Delta V$)

$$\Delta A = -w$$

useful work

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

$$\Delta G = \Delta E + P\Delta V - T\Delta S$$

$$= \Delta E - T\Delta S + P\Delta V$$

$$\Delta G = \Delta A + P\Delta V$$

useful work, waste work

$$\Delta G = -w + P\Delta V$$

$$-\Delta G = w - P\Delta V$$

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Maxwells Relation

$_1dE, \; _2dH, \; _3dG, \; _4dA$

1st law $dE = dq - w$

$$\boxed{dE = dq - PdV} \quad (1)$$

$TdS - PdV$

$H = E + PV$

$dH = dE + PdV + VdP$

$dH = dq - \cancel{PdV} + \cancel{PdV} + VdP$

$dH = dq - VdP$

$\left(dS = \frac{dq}{T}, \; TdS = dq \right)$

$$\boxed{dH = TdS + VdP} \quad (2)$$

$G = H - TS$

$dG = dH - TdS - SdT$

$dG = \cancel{TdS} + VdP - \cancel{TdS} - SdT$

$$dG = VdP - SdT \quad (3)$$

$A = E - TS$

$dA = dE - TdS - SdT$

$dA = \cancel{TdS} - PdV - \cancel{TdS} - SdT$

$$dA = -PdV - SdT \quad (4)$$

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$$dE = TdS - PdV$$

$dS = 0$

$dE = -PdV$

$\left(\frac{dE}{dV}\right) = -P$

again diff w.r.t dS

$\frac{d}{dS}\left(\frac{dE}{dV}\right) = -\left(\frac{dP}{dS}\right)$

$dV = 0$

$dE = TdS$

$\frac{dE}{dS} = T$

agar diff w.r.t dV

$\frac{d}{dV}\left(\frac{dE}{dS}\right) = \left(\frac{dT}{dV}\right)$

$$\boxed{-\left(\frac{dP}{dS}\right) = \left(\frac{dT}{dV}\right)}$$

$$dH = TdS + VdP$$

(A, G)

$dS = 0$

$dH = VdP$

$\left(\frac{dH}{dP}\right) = V$

ag diff w.r.t dS

$\frac{d}{dS}\left(\frac{dH}{dP}\right) = \frac{dV}{dS}$

$dP = 0$

$dH = TdS$

$\frac{dH}{dS} = T$

diff w.r.t dP

$\frac{d}{dP}\left(\frac{dH}{dS}\right) = \frac{dT}{dP}$

$$\boxed{\left(\frac{dV}{dS}\right) = \left(\frac{dT}{dP}\right)}$$

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$$dA = -PdV - SdT$$

isotherm. A G

$$dG = VdP - SdT$$

$dT = 0$

$$dG = V\int_{P_1}^{P_2} dP$$

$PV = RT$

$V = \frac{RT}{P}$

$$= \quad dG = \int_{P_1}^{P_2} \frac{RT}{P} dP$$

$$= RT \int_{P_1}^{P_2} \frac{1}{P} dP \Rightarrow RT \left[\ln P \right]_{P_1}^{P_2}$$

$$= RT \ \ln P_2 - \ln P_1$$

$$\boxed{\Delta G = RT \ln \frac{P_2}{P_1}}$$

B.Sc-II

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Gibb's-Helmholtz eq^n

$A \Rightarrow$ work func^n

$A = E - TS$

$G = H - TS$ —

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

$dG = dH - TdS - SdT$

$G = E + PV - TS$

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

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

$dq = E + W$

$TdS = E + PdV$

$TdS - PdV = dE$

$(dE = TdS - PdV)$

$dG = VdP - SdT$

at con P

$dG = -SdT$

$G_1 \rightarrow G_2 \quad S_1 \rightarrow S_2$

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

$dG_2 - dG_1 = -S_2 dT - (-S_1 dT)$

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

$= -dT(S_2 - S_1)$

$d(\Delta G) = -dT \Delta S$

$$-\frac{d(\Delta G)}{dT} = \Delta S \quad (2)$$

शिक्षक के हस्ताक्षर :

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

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

↓ G–H eqⁿ

Spontaneous process

(1) ΔG spontan के लिए $\Delta G = -ve$

$\Delta G = -nFE$

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

$\Delta S = +ve$

ΔH

exo endo

(1) $\Delta H = -ve$ $\Delta H = +ve$

$\Delta S = +ve$

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

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

↓ lower temp.

(ii) $\Delta S = -ve$

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

$\Delta G = -ve$

(i) $\Delta H > T\Delta S$

↓ lower (↓)

endo - $\Delta H = +ve$

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

(I) $\Delta S = +ve$

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

$\Delta G = -ve$ होने के लिए

$\Delta H < T\Delta S$

high (T)

spontaneous

(II) $\Delta S = -ve$

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

$$= \Delta H + T\Delta S$$

(X) non-spontaneous

(II) entropy (S) ⇒

$$dS = \frac{dq_{rev}}{T}$$

$$TdS = dq_{rev}$$

$A \rightleftharpoons B$

rev → equil

equi → $TdS = dq_{rev}$

irrev → $TdS > q_{irrev}$

1st law → $dq = dE + w$

$dq = dE + PdV$ — (2)

$TdS \geq dq_{rev}$ — (1)

$TdS \geq dE + PdV$

$TdS - dE - PdV \geq 0$

at E & V const

$TdS \geq 0$

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$$(\Delta S)_{\varepsilon, V} \geq 0$$

irrev

reversi equy

(III) $A = \varepsilon - TS$

$$TdS - d\varepsilon - PdV \geq 0$$

w

$$TdS - d\varepsilon \geq w$$

$$d(TS - \varepsilon) \geq w \quad pdv$$

$$-d(\varepsilon - TS) \geq 0$$

$$-d(A) - PdV \geq 0$$

at con V & T

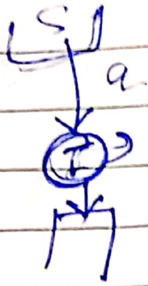
$$\boxed{-(\Delta A)_{T,V} \geq 0}$$

$$(\Delta A)_{T,V} < 0$$

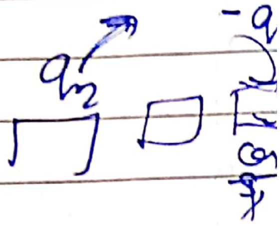
Entropy $\underline{\underline{S}}$

H, E, G, A

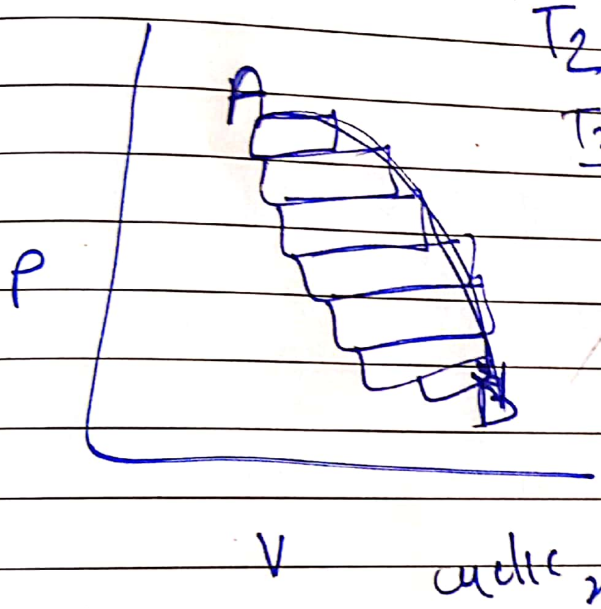
$$S = \frac{q_{rev}}{T}$$



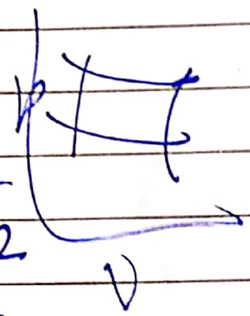
$$\eta = \frac{T_2 - T_1}{T_2} \quad \text{या} \quad \frac{q_2 - q_1}{q_2}$$



$$\frac{T_2 - T_1}{T_2} = \frac{q_2 - (-q_1)}{q_2}$$



$$\frac{T_2 - T_1}{T_2} = \frac{q_2 + q_1}{q_2}$$



$$1 - \frac{T_1}{T_2} = 1 + \frac{q_1}{q_2}$$

$$-\frac{T_1}{T_2} = \frac{q_1}{q_2}$$

cyclic reve

$$-\frac{q_2}{T_2} = \frac{q_1}{T_1}$$

$$S = \frac{q}{T}$$

$$0 = \frac{q_1}{T_1} + \frac{q_2}{T_2}$$

$$dS = \frac{dq_{rev}}{T}$$

$$dS = \int_A^B \frac{dq_{rev}}{T}$$

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Calculatn of S for ideal gas

(1) T & V variable

$$dS = \frac{dq}{T}$$

I law

$$dq = dE + PdV$$

$$\left(\frac{dE}{dT}\right)_V = C_V, \quad dE = C_V dT$$

$$dq = C_V dT + PdV$$

$$PV = nRT, \quad P = \frac{RT}{V}$$

$$dq = C_V dT + \frac{RT}{V} dV$$

T से divide

$$\frac{dq}{T} = \frac{C_V dT}{T} + \frac{R\cancel{T}}{\cancel{T}}\frac{dV}{V}$$

$$\int_{S_1}^{S_2} dS = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R\int_{V_1}^{V_2} \frac{dV}{V}$$

$$(S_2 - S_1) = C_V [\ln T]_{T_1}^{T_2} + R\ln(V)_{V_1}^{V_2}$$

$$\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

(II) T, P — variable

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \text{—(I)}$$

$$P_1V_1 = RT_1 \qquad P_2V_2 = RT_2$$

$$\frac{P_1V_1}{P_2V_2} = \frac{\cancel{R}T_1}{\cancel{R}T_2} \qquad \frac{V_1}{V_2} = \frac{T_1P_2}{T_2P_1}$$

$$\frac{V_2}{V_1} = \frac{T_2P_1}{T_1P_2} \quad \text{—(II)}$$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \left(\frac{P_1T_2}{P_2T_1}\right)$$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} + R \ln \frac{T_2}{T_1}$$

$$\left(C_p - C_v = R, \quad C_v = C_p - R \right)$$

$$\Delta S = (C_p - R) \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} + R \ln \frac{T_2}{T_1}$$

$$\Delta S = C_p \ln \frac{T_2}{T_1} - \cancel{R \ln \frac{T_2}{T_1}} + R \ln \frac{P_1}{P_2} + \cancel{R \ln \frac{T_2}{T_1}}$$

$$\boxed{\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}}$$

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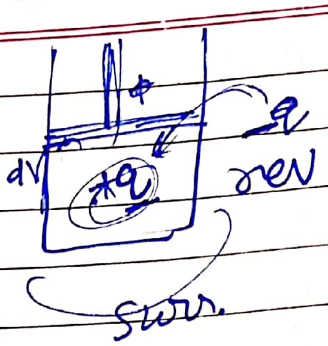
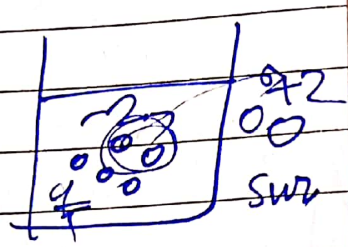
S change in rev process

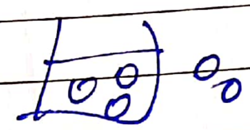


$$\Delta S = \Delta S_{sys} + \Delta S_{surr.}$$

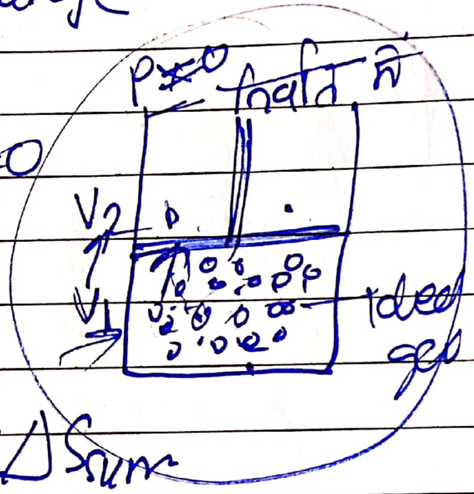
$$= +\frac{dq}{T} + \left(-\frac{dq}{T}\right)$$

$$= 0$$





q_{irrev} में S change



$$P = 0$$

$$dE = 0, \; dW = 0$$

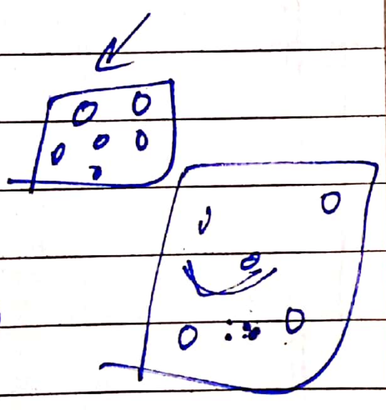
$$dq = 0$$

$$dS_{surr} = 0$$

$$\Delta S = \Delta S_{sys} + \Delta S_{surr}$$

$$= \Delta S + 0$$

$$\Delta S_{sys} = R \ln \frac{V_2}{V_1}$$



$$\Delta S = R \ln \frac{V_2}{V_1} + 0$$

$$\Delta S > 0$$

+ve

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ΔH ΔS ΔG ΔA

$A \rightarrow B$

Imp

(I) Isothermal

$dT = 0$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$dT = 0$

$$\Delta S = R \ln \frac{V_2}{V_1}$$

$$\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

$$\Delta S = R \ln \frac{P_1}{P_2}$$

(II) Isobaric $\Rightarrow$ $dP = 0$

$$\Delta S = C_p \ln \frac{T_2}{T}$$

(III) Isochoric $\Rightarrow$ $dV = 0$

$$\Delta S = C_v \ln \frac{T_2}{T_1}$$

(IV) adiabatic $dq = 0$, $dS = 0$

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

$$-R \ln \frac{V_2}{V_1} = C_v \ln \frac{T_2}{T_1}$$

शिक्षक के हस्ताक्षर :

$$-R \ln \frac{P_1}{P_2} = C_p \ln \frac{T_2}{T}$$

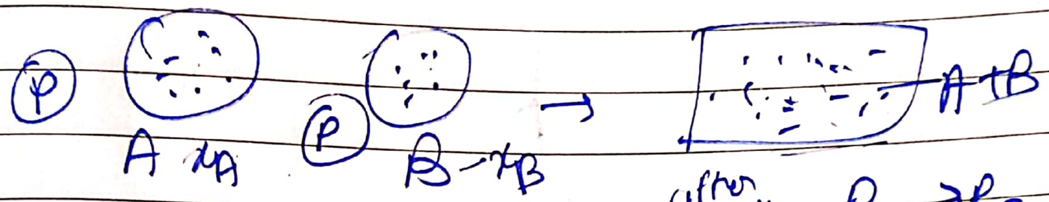
BSc IV

entropy mixing of ideal gas

isothal $dT=0$

$$\Delta S = nR\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$$

$$\Delta S = nR\ln\frac{P_1}{P_2}$$ P_1 – int P, P_2 – final P



after$_M$ $P_i \rightarrow P_f$

$$\Delta S_{mix} = \Delta S_A + \Delta S_B$$

$$= n_A R\ln\frac{P_1}{P_2} + n_B R\ln\frac{P_1}{P_2}$$

$$= x_A R\ln\frac{P}{P\times x_A} + x_B R\ln\frac{P}{x_B\times P}$$

Partial P = P × x

$$= x_A R\ln\frac{1}{x_A} + x_B R\ln\frac{1}{x_B}$$

$$= -x_A R\ln x_A - x_B R\ln x_B$$

$$\Delta S_{mix} = -R(x_A\ln x_A + x_B\ln x_B)$$

$$\boxed{\Delta S_{mix} = -R\sum x_i\ln x_i}$$

शिक्षक के हस्ताक्षर :

phys signicance

(I) S & W → spontaneity

$S = f(W)$

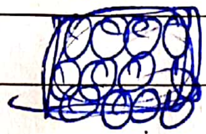
(s) → liq → gas

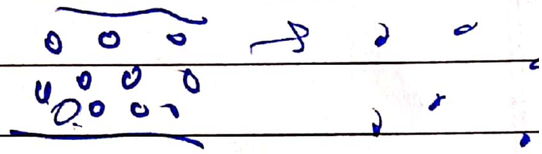
$\boxed{S = k \ln W}$

boltzm const

(II) disorderness measure

state → liq gas





H_2O S↓ S↑ S↑

(I) fusion S ⇒ [illegible]

s → l

$$\Delta S_f = \frac{\Delta H_f}{T}$$

(II) Vap. S ⇒ l → gas

$$\Delta S_v = \frac{\Delta H_v}{T}$$

(111)

E ← graphite
Diamond

$S \leftarrow S_e, S_r, S_v$

work function (A)

$$A_0 = E_0 - TS$$

$$\Delta A = \Delta E - T\Delta S \quad (1)$$

$$\Delta S = \frac{dq}{T}, \quad T\Delta S = dq$$

$$\Delta A = \Delta E - dq \quad (2)$$

1st law $dq = \Delta E + w$

$$-w = \Delta E - dq \quad (3)$$

$$\Delta A = -w$$

↓ useful work

100 → work → useful, work, 100%, 80%, $P\Delta V$

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

$$\Delta G = \Delta E + P\Delta V - T\Delta S$$

$$= \Delta E - T\Delta S + P\Delta V$$

$$\Delta G = \Delta A + P\Delta V$$

useful work, work

$$\Delta G = -w + P\Delta V$$

$$-\Delta G = w - P\Delta V$$

Maxwells Relation

1 dE, 2 dH, 3 dG, 4 dA

1st law $dE = dq - w$

$$\boxed{dE = dq - PdV} \quad \text{—} \ 1$$

$$TdS - PdV$$

$$H = E + PV$$

$$dH = dE + PdV + VdP$$

$$dH = dq - \cancel{PdV} + \cancel{PdV} + VdP$$

$$dH = dq - VdP$$

$$\left(dS = \frac{dq}{T}, \quad TdS = dq \right)$$

$$\boxed{dH = TdS + VdP} \quad \text{—} \ 2$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dG = \cancel{TdS} + VdP - \cancel{TdS} - SdT$$

$$dG = VdP - SdT \quad 3$$

$$A = E - TS$$

$$dA = dE - TdS - SdT$$

$$dA = \cancel{TdS} - PdV - \cancel{TdS} - SdT$$

$$dA = -PdV - SdT \quad \text{—} \ 4$$

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$$dE = TdS - PdV$$

$dS = 0$

$dE = -PdV$

$\left(\frac{dE}{dV}\right) = -P$

~~again~~ diff w.r.t dS

$\frac{d}{dS}\left(\frac{dE}{dV}\right) = -\left(\frac{dP}{dS}\right)$

$dV = 0$

$dE = TdS$

$\frac{dE}{dS} = T$

~~again~~ diff w.r.t dV

$\frac{d}{dV}\left(\frac{dE}{dS}\right) = \left(\frac{dT}{dV}\right)$

$$\boxed{-\left(\frac{dP}{dS}\right) = \left(\frac{dT}{dV}\right)}$$

$$dH = TdS + VdP$$

(A, G)

$dS = 0$

$dH = VdP$

$\left(\frac{dH}{dP}\right) = V$

ag diff w.r.t dS

$\frac{d}{dS}\left(\frac{dH}{dP}\right) = \frac{dV}{dS}$

$dP = 0$

$dH = TdS$

$\frac{dH}{dS} = T$

diff w.r.t dP

$\frac{d}{dP}\left(\frac{dH}{dS}\right) = \frac{dT}{dP}$

$$\boxed{\left(\frac{dV}{dS}\right) = \left(\frac{dT}{dP}\right)}$$

शिक्षक के हस्ताक्षर :

$dA = -PdV - SdT$ Navbodh

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Isotherm A G

$dG = VdP - SdT$

$dT = 0$

$$dG = \int_{P_1}^{P_2} V dP$$

$PV = RT$

$V = \frac{RT}{P}$

$$dG = \int_{P_1}^{P_2} \frac{RT}{P} dP$$

$$= RT \int_{P_1}^{P_2} \frac{1}{P} dP \Rightarrow RT \left[\ln P \right]_{P_1}^{P_2}$$

$$= RT \ \ln P_2 - \ln P_1$$

$$\Delta G = RT \ln \frac{P_2}{P_1}$$

शिक्षक के हस्ताक्षर :

BSc-II   Phy - Unit - II

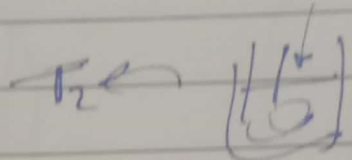
Thermodynamics - II

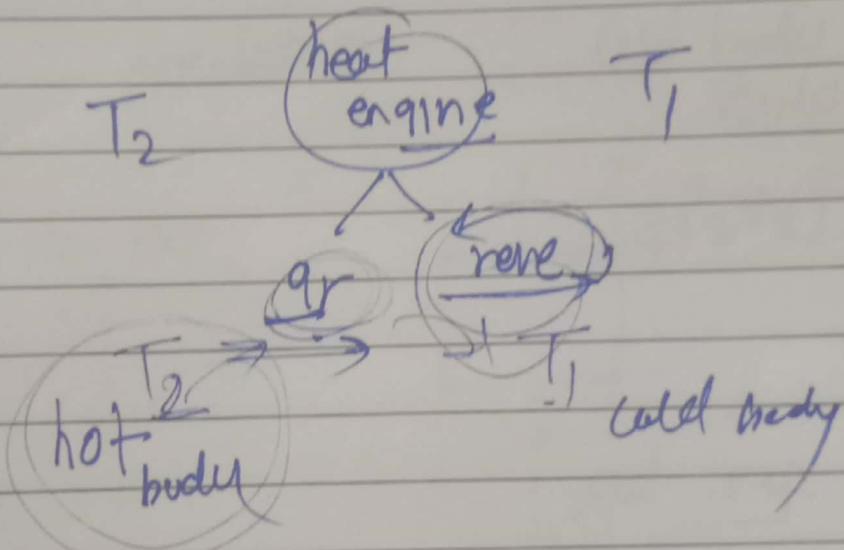
I law limitatⁿ

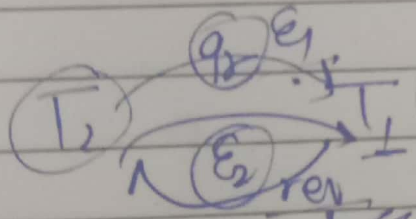
I) ऊष्मा → work मिलता %

II) directⁿ of any reacⁿ

III) Spontaneous ⊗







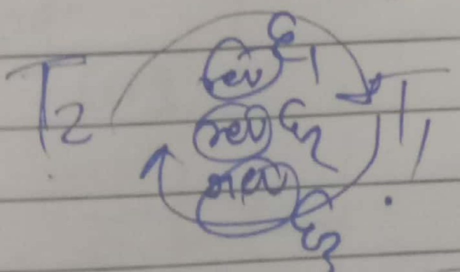
II plank / Clausius →

heat → work

100J → 100% conv ⊗

same   III carnot ⇒

Ir < rev



Teacher's Sign.

Remark

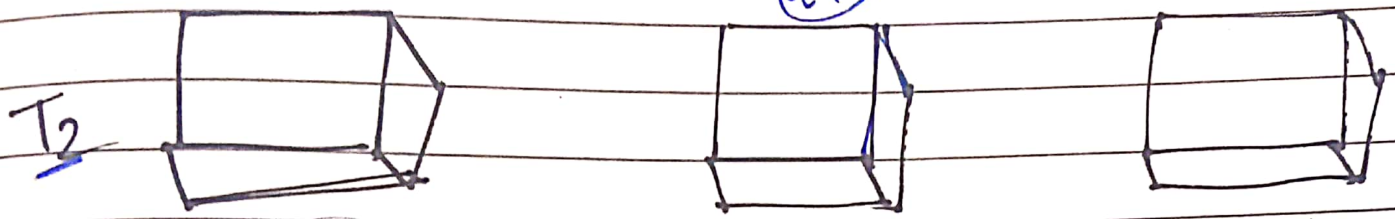
Carnot cycle

Sadi carnot 1824

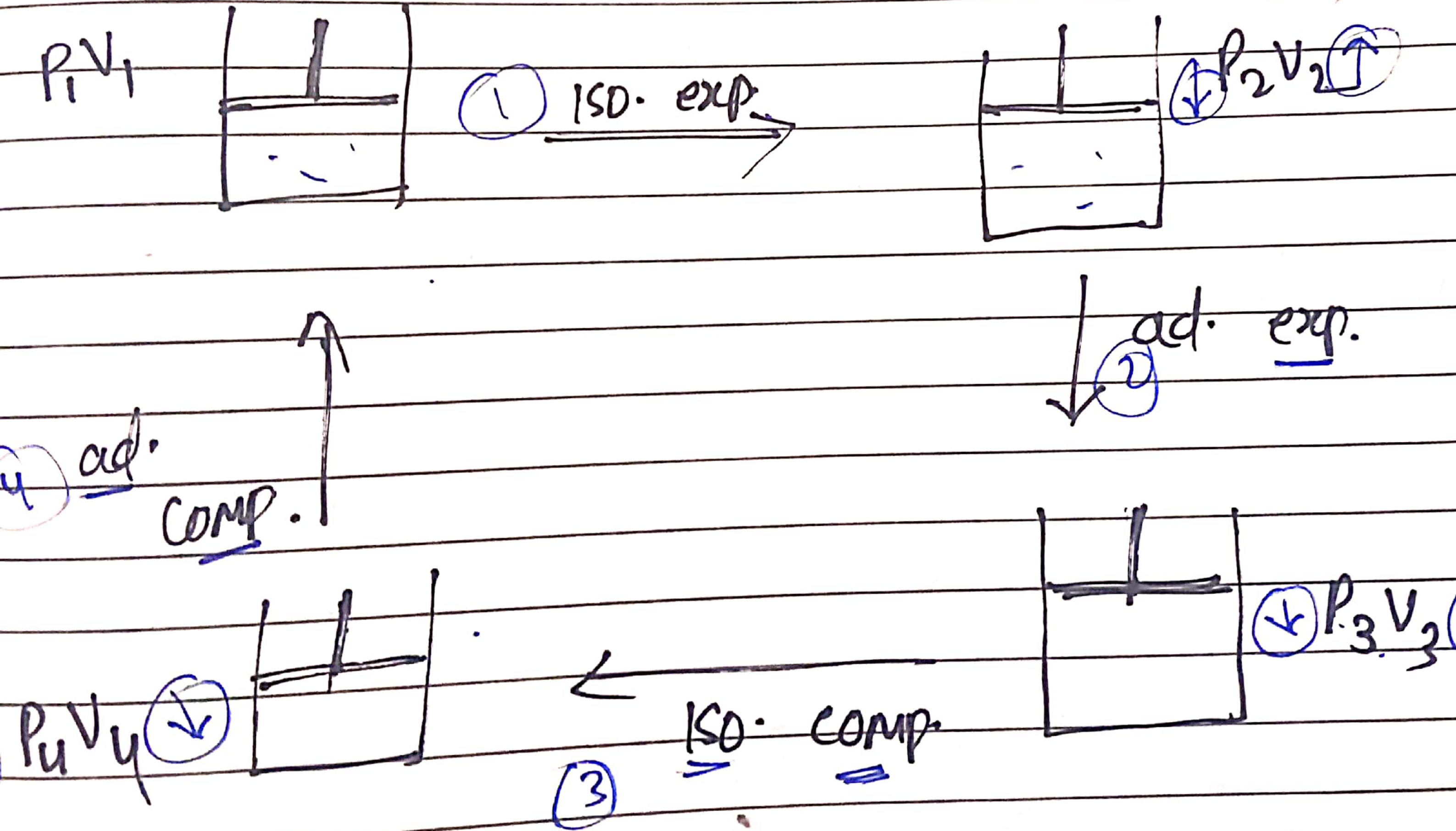
heat → work

100% → संभव (अ)संभव

q_2 लेगा $q_x = 0$ q_1 देगा

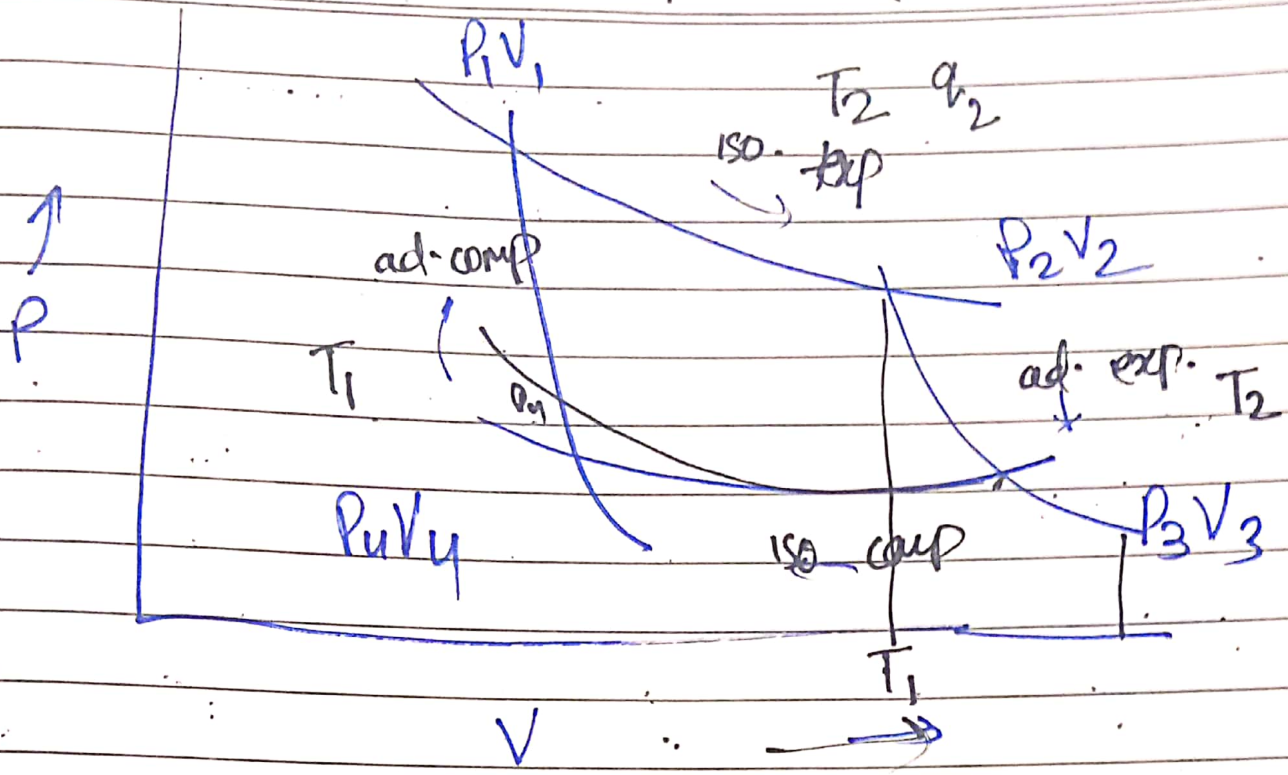


Hot source   insulator   Cold body (Sink)



Teacher's Sign.

Remark



① ISO. exp. $\Rightarrow$ $dT = 0$, $dE = 0$ $\quad q_2 \; P_1 V_1 \; T_2$

$$q_2 = dE + w_1$$

$$q_2 = w_1 = \int_{V_1}^{V_2} P\,dV \qquad \left(P = \frac{RT}{V}\right)$$

$$q_2 = w_1 = \int_{V_1}^{V_2} \frac{RT}{V}\,dV \Rightarrow RT\int_{V_1}^{V_2} \frac{1}{V}\,dV$$

$$\Rightarrow RT\,\left[\ln V\right]_{V_1}^{V_2} \Rightarrow RT \ln V_2 - \ln V_1$$

$$q_2 = w_1 \Rightarrow RT_2 \ln \frac{V_2}{V_1} \quad \text{—} ①$$

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(II) ad. expansⁿ $\Rightarrow$ $q = 0$ $\qquad P_2 V_2 q_2 T_2$

$$q_2 = dE + w_2$$

$$0 = dE + w_2$$

$$dE = -w_2$$

[we know $\left(\frac{dE}{dT}\right) = C_v$, $dE = C_v dT$]

$$C_v dT = -w_2$$

$(T_2 - T_1)$

$$C_v \int_{T_2}^{T_1} dT = -w_2$$

$$C_v (T_1 - T_2) = -w_2$$

$$C_v (T_2 - T_1) = w_2 \quad \text{--- (2)}$$

(3) iso. compressⁿ $\Rightarrow$ $dT_1 = 0 \rightarrow dE_1 = 0$

$$q_1 = dE + w_3$$

$$q_1 = w_3$$

$$q_1 = w_3 = \int_{V_3}^{V_4} PdV = RT \int_{V_3}^{V_4} \ln V$$

$$q_1 = w_3 \Rightarrow RT_1 \ln \frac{V_4}{V_3} \quad \text{--- (3)}$$

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Remark

Date ____
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(4) ad. compⁿ $\Rightarrow$ $dq_1 = 0$

$$dq_1 = dE + dw_4$$
$$0 = dE + w_4$$
$$dE = -w_4$$
$$\left(\frac{dE}{dT} = C_v, \quad dE = C_v dT \right)$$
$$C_v dT = -w_4 \qquad (T_1 \to T_2)$$
$$C_v \int_{T_1}^{T_2} dT = -w_4$$
$$\Rightarrow C_v (T_2 - T_1) = + w_4 \quad \text{— (4)}$$

total work $w = w_1 + w_2 + w_3 + w_4$

$$\Rightarrow RT_2 \ln \frac{V_2}{V_1} + \cancel{C_v(T_2 - T_1)} + RT_1 \ln \frac{V_4}{V_3} - \cancel{C_v(T_2 - T_1)}$$

$$w \Rightarrow RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3} \quad \text{— (5)}$$

$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1} \quad T/V$$

$$\frac{V_3}{V_4} = \frac{V_2}{V_1}$$

$$w = RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_3}{V_4}$$

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$$RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_2}{V_1}$$

$$\Rightarrow w = R(T_2 - T_1) \ln \frac{V_2}{V_1}$$

दक्षता η = $\dfrac{\text{किया गया कार्य}}{\text{दी गई ऊष्मा}}$ $\frac{100}{100}$ I (X) $\frac{400}{500}$ 20%

$$= \frac{w}{q_2}$$

$$\eta = \frac{R(T_2-T_1)\ln \frac{V_2}{V_1}}{RT_2 \ln \frac{V_2}{V_1}}$$

$$\boxed{\eta = \frac{T_2 - T_1}{T_2}}$$ (I)

0.495

0.35

$T_1 = 300$

$T_2 = 400$

$$\eta = \frac{400-300}{400} = \frac{100}{400} = 0.25$$

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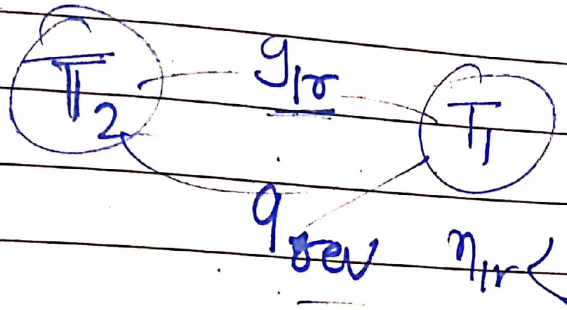
carnot theorum

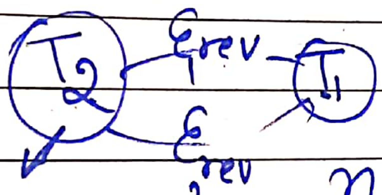
(I) —

(II)



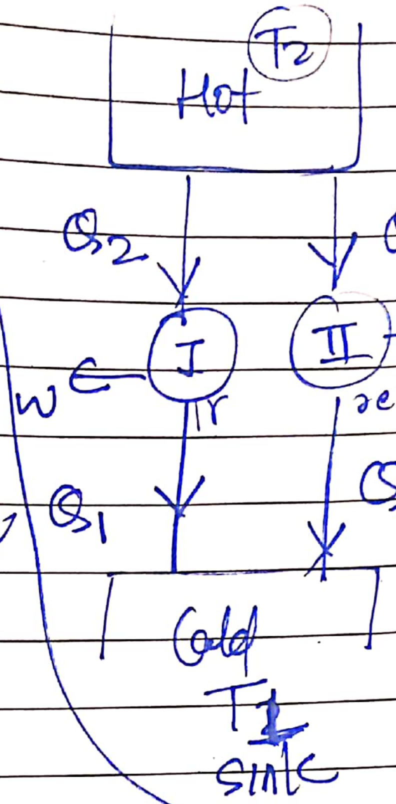
$\eta_{irr} < \eta_{rev}$

rev > irr



$\eta_{1\,rev} = \eta_{2\,rev}$

W



$T_2 > T_1$

(I) उपपत्ति

we know $\eta_{rev} > \eta_{irr}$

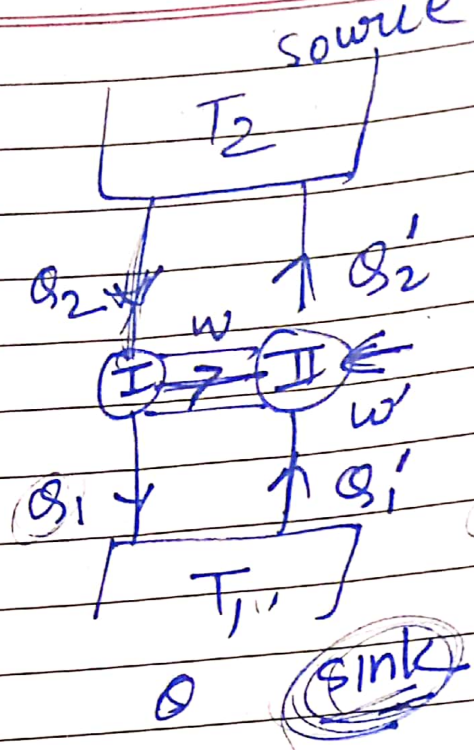
I	II
heat absorbed $= Q_2$	heat absorbed $= Q_2'$
work done $= W$	war $W' =$
heat rejected $= Q_1$	heat rejected $= Q_1'$
$W = Q_2 - Q_1$	$W' = Q_2' - Q_1'$

$\eta_{Ire} < \eta_{rev}$

जहाँ $\underline{w} > w'$

~~heat reject~~ ~~$Q_1' > Q_1$~~

(II) cond^n



I	II
heat absorbed $= Q_2$	heat absorbed $= Q_1'$
heat reject $= Q_1$	heat rejected $= Q_2'$
work done by the system $-w = Q_2 - Q_1 = -Q_2 + Q_1$	work done on the system $w' = Q_1' - Q_2'$

T_2 (source) पर ~~to~~ net heat change
$$Q_2 - Q_2' = 0$$

T_1 (sink) पर net heat change
$$\underline{Q_1' - Q_1}$$

net work $= w - w'$

$= -Q_2 + Q_1 - (Q_1' - Q_2')$

$= -Q_2 + Q_1 - Q_1' + Q_2'$

कार्य में change $= Q_1' - Q_1$

Thermodynamics scale of temp.

Hg — proper (temp) change

Kelvin scale

$$\eta = \left(\frac{T_2 - T_1}{T_2}\right) \text{ या } \frac{q_2 - q_1}{q_2}$$

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{q_1}{q_2} \qquad \frac{T_2}{T_1} = \frac{q_2}{q_1}$$

$$T_1 \downarrow \rightarrow \frac{T_2 - T_1}{T_2} \Rightarrow \frac{T_2 - 0}{T_2} = 1$$

0

temp — absolute temp.

$0°C \rightarrow 273\,K$

$-273°C \rightarrow 0K$ — परम शून्य ताप

const P पर gas का आयतन $0°C \rightarrow V_0$ है
(273K)

$1°C \rightarrow \frac{1}{2}$
$3°C - 2+\frac{1}{2}$

$t°C$ ताप पर $V_t = \left(V_0 + \frac{V_0 \times t}{273}\right)$

$= V_0\left(1 + \frac{t}{273}\right)$

शिक्षक के हस्ताक्षर :

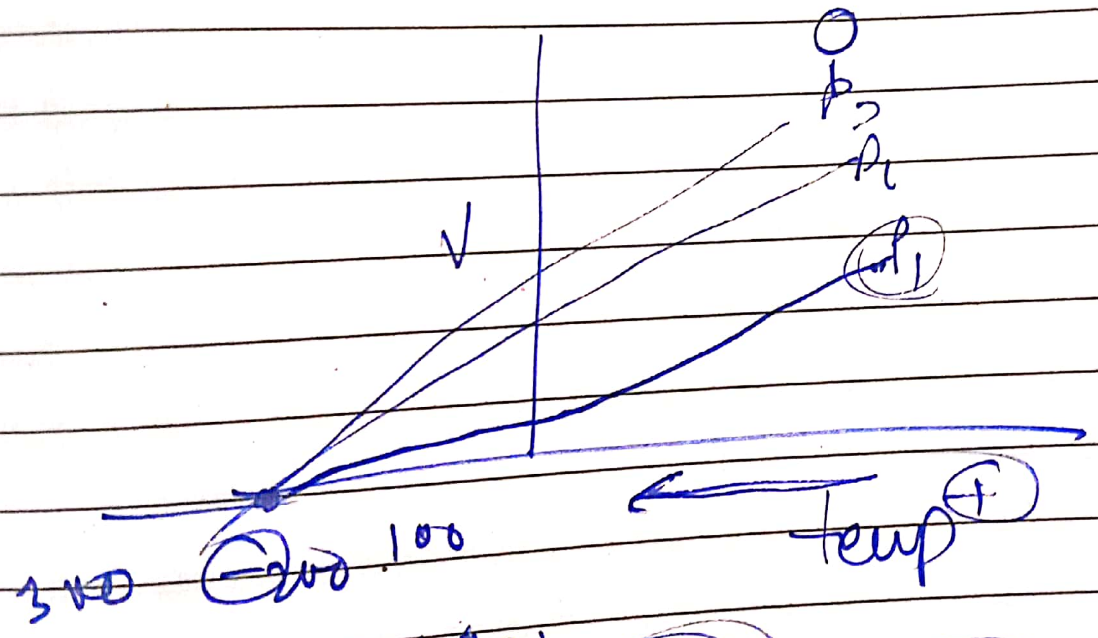
1°C घटाने पर $= V_0\left(1 + \frac{1}{273}\right)$

273°C घटाने पर

$$= V_0\left(1 - \frac{273}{273}\right)$$

$$= V_0(1-1)$$

$$= V_0 \times 0 = 0\ ml$$

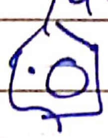
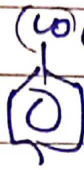


0 ml (°C) −273°C

Org. B Unit-3

aldehyde / ketone

$>C=O$ (carbonyl group)

aldehyde		ketone	
$-CHO$		$>C=O$	
aliphatic	aro	aliphatic	aro
$HCHO$	CHO	$CH_3>C=O$	$COCH_3$
CH_3CHO		CH_3	

$HCHO \rightarrow$

preparation methods ⇒

1) Alkenes ⇒

$CH_2=CH_2 + CO + H_2 \rightarrow$

CH_3-CH_2CHO

2) Ozonolysis →

$CH_3-CH=CH-CH_3 \xrightarrow{O_3/H_2O}$

$O=O$

ozonide

ozonolysis

$\rightarrow CH_3CHO + CH_3CHO$

Sc^{2+}

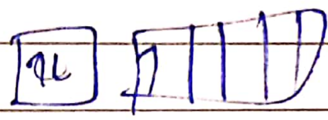
Metal-L

d-block

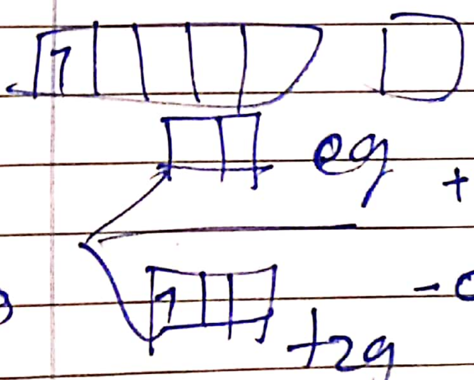
Sc^{2+}

21

$4s^2\,3d^1$



3d¹ 4s

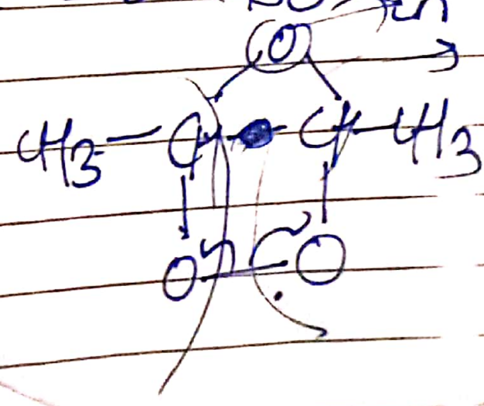


eg $+0.6\Delta_o$

t2g $-0.4\Delta_o$

$1\times -0.4+$

$CFSE = -0.4\Delta_o$



H

Li Py

Ag Mg

K Ca

Pb Sn

Cs Ba

Fr Ra

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(III) alkynes ⇒ hydration ⇒

$$CH_3-C\equiv CH \xrightarrow[\overset{\oplus}{H}-\overset{\ominus}{OH}]{60\%\ H_2SO_4/Hg^{2+}} CH_3-\underset{OH}{C}=\underset{H}{CH}$$

carbocation $2^\circ > 1^\circ$

M rule

⊖ आता

अधिक

स्थान

या

$$CH_3-\underset{OH}{C}=CH_2$$

(enolic)

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2 \leftarrow CH_3-\overset{O-H^{\oplus}}{C}=CH_2$$

$$\downarrow$$

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

(IV) Oppenauer's oxdn

$$\begin{matrix}R\\R\end{matrix}\!\!>CHOH + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O \xrightarrow{Al(-OC(CH_3)_3)_3}$$

oxdn ↓ Redn

$$\begin{matrix}R\\R\end{matrix}\!\!>C=O + \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CHOH$$

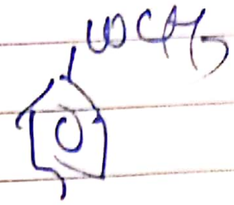
(V) Stephen's Redn ⇒

$$CH_3-C\equiv N \xrightarrow[(H_2)]{SnCl_2/HCl} [CH_3-CH=NH]HCl \xrightarrow{HOH}$$

Teacher's Signature $CH_3-CH=O + NH_4Cl$

(vi) Rosenmund Reaⁿ

$$CH_3-CO-Cl + H_2 \xrightarrow[\text{xylene}]{Pd/BaSO_4} CH_3CHO + HCl$$

$$C_6H_6 + CH_3CO^{\ominus}Cl^{\oplus} \xrightarrow{AlCl_3}$$ 

CH_3Cl

phy pro → (1) low mo gas → liquid → solid

C=O

(2) Solubility ⇒ non polar → CS_2, CCl_4, C_6H_6

(3) bp

OH alcohol > C=O > alkanes

H-bond

C=O

100°C ↑T ↑

chemical pro

structure

R

σ C π O σ sp²

R

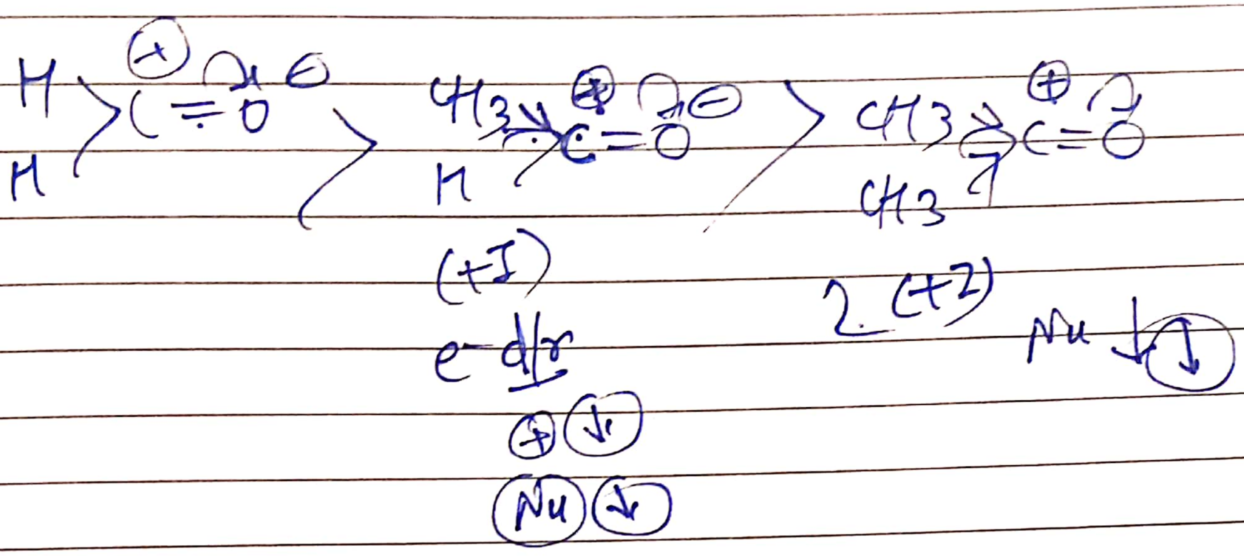
lp + bp

$\delta\oplus$ C = O $\delta\ominus$ 2+1 = 3 - sp²

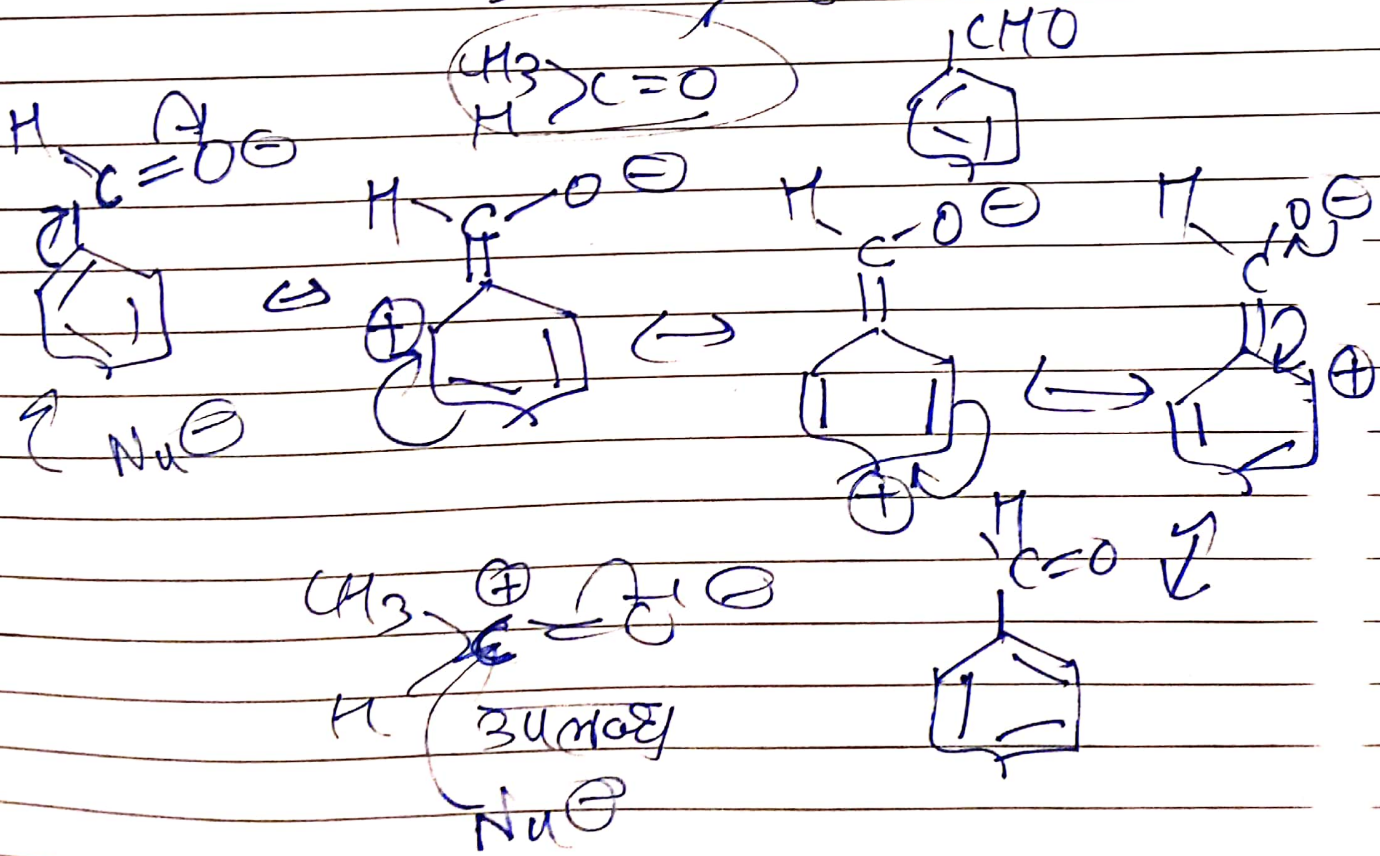
$Nu^{\ominus}$ reaⁿ

$HCHO$ CH_3CHO CH_3COCH_3

Nu add^n $\longrightarrow$

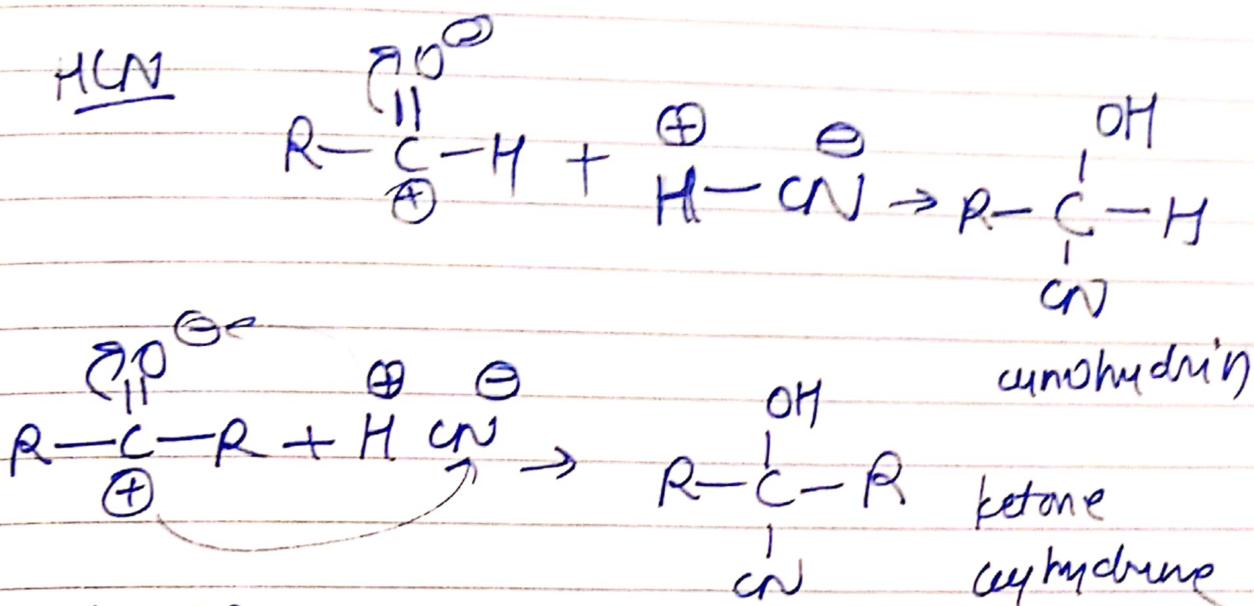


$CH_3CHO > C_6H_5CHO$

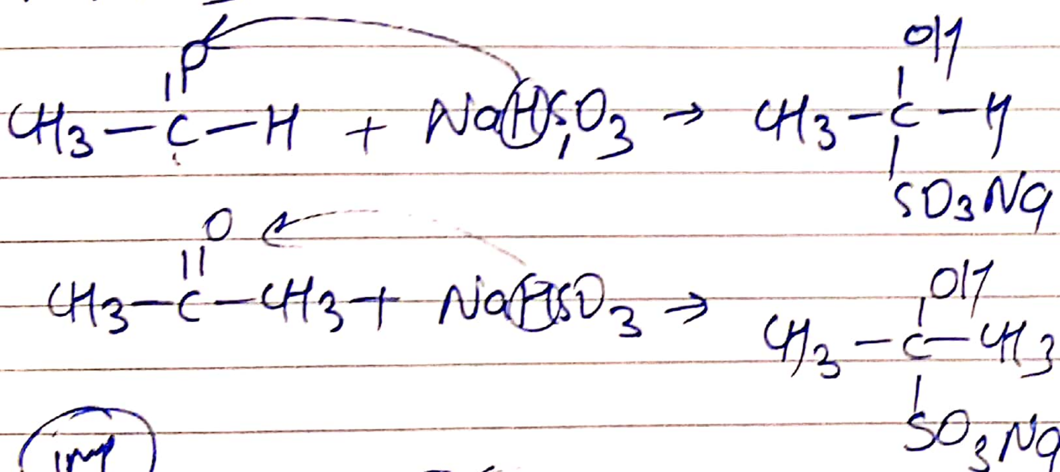


chemical properties

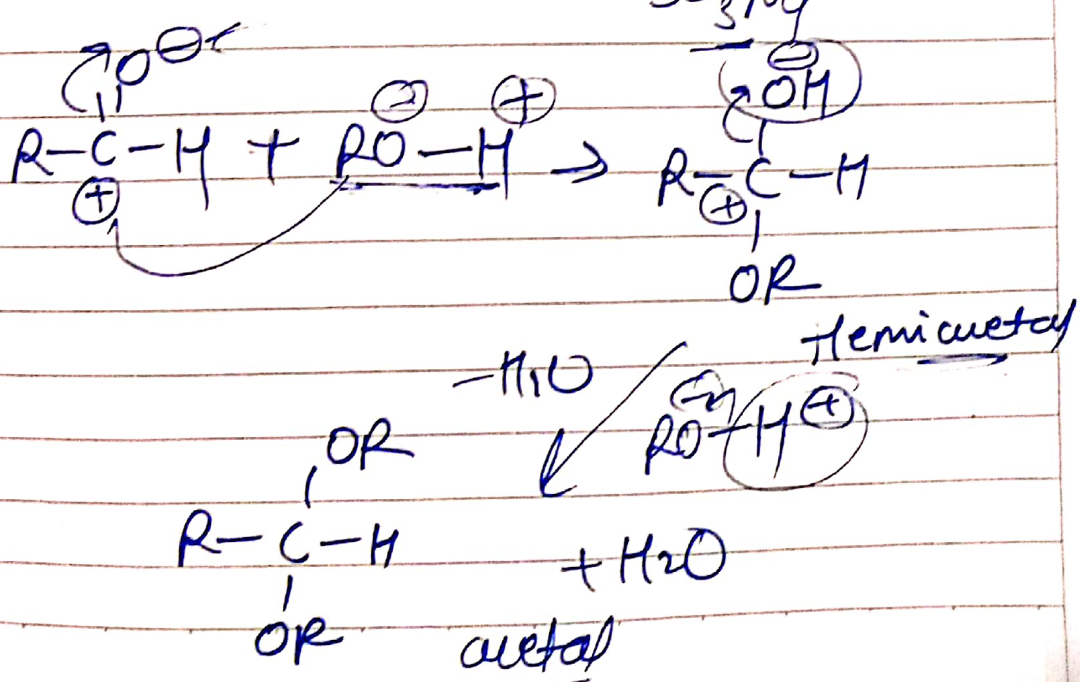
① HCN



② $NaHSO_3$



③ ROH ⇒ imp



$$R-\overset{O}{\overset{\|}{C}}-R + RO-H \rightarrow R-\overset{OH}{\underset{OR}{C}}-R \xrightarrow{RO-H} R-\overset{OR}{\underset{OR}{C}}-R + H_2O$$

Hemiketal (1 ROH)

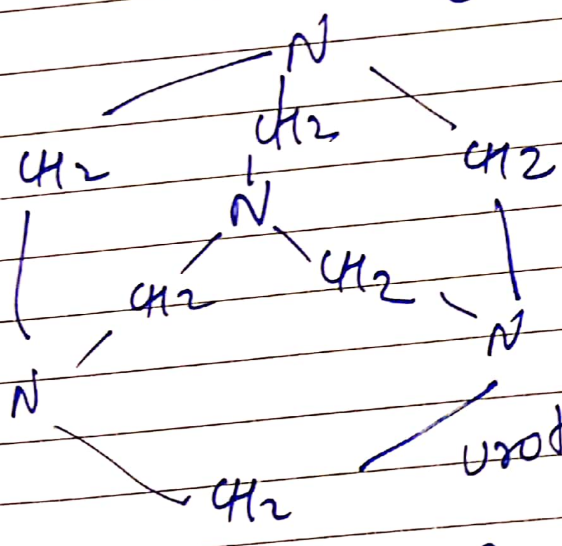
Ketal (2 ROH)

(5) Reaⁿ with NH_3

$6HCHO + 4NH_3 \rightarrow$ urotropin

hexamethylene tetra amine

$(CH_2)_6N_4 + 6H_2O$



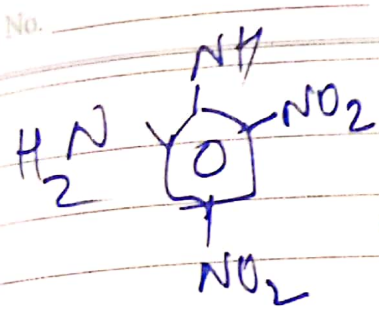
urotropin

NH_2-H / H_2N-OH

hydroxyl amine

H_2N-NH_2 hydrazine / $H_2N-NHCONH_2$ / $H_2N-NH-C_6H_3(NO_2)_2$

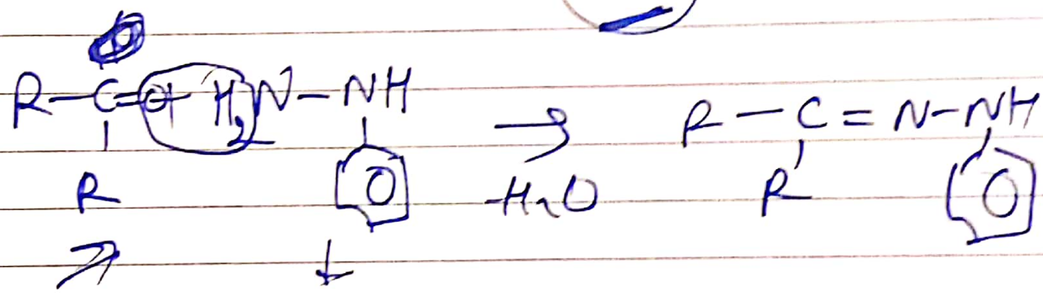
phenyl hydrazine



2,4 DNPH

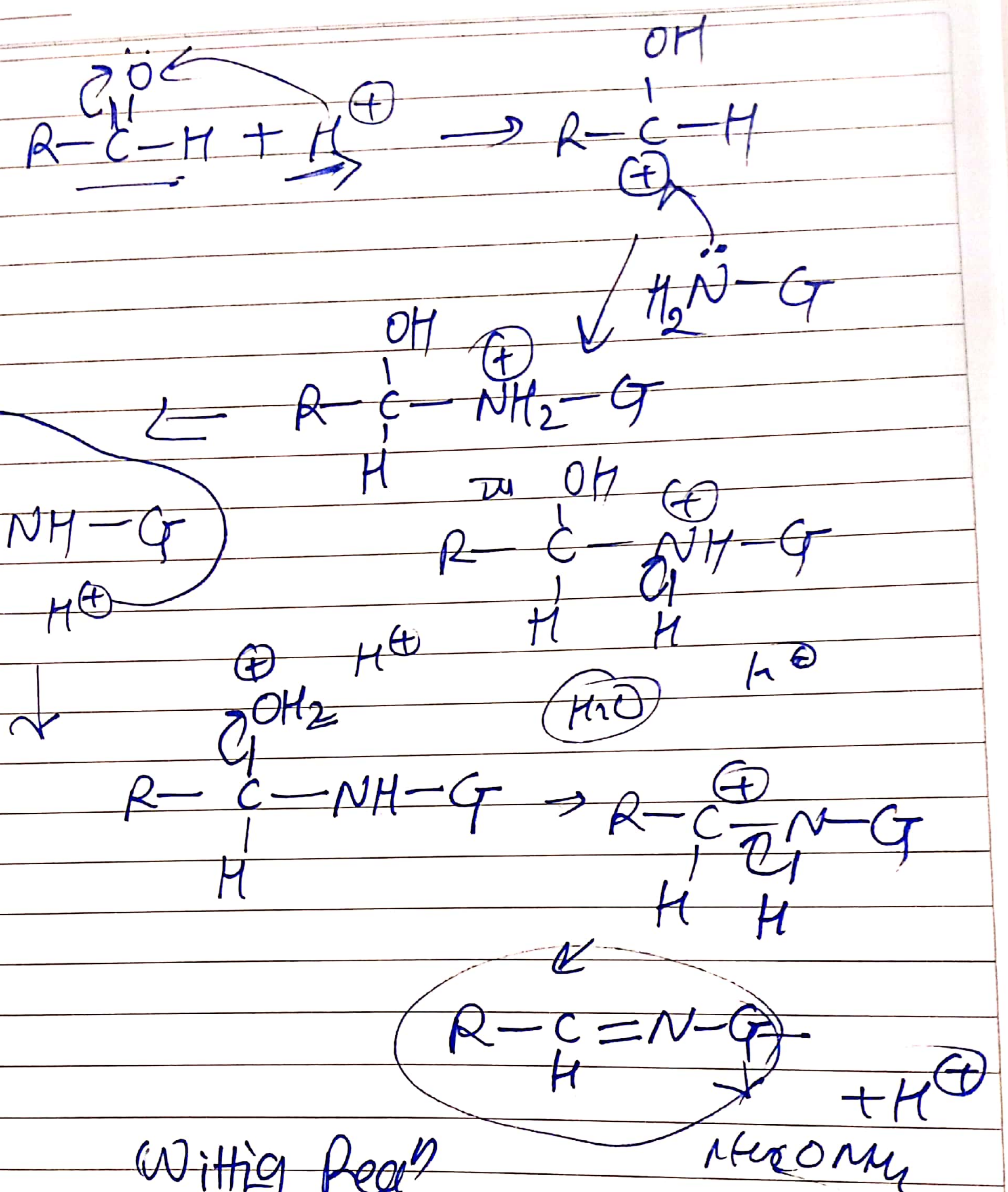
(1) $$R-\underset{\displaystyle H}{\underset{|}{C}}=O + H_2N-G \xrightarrow[-H_2O]{} R-\underset{\displaystyle H}{\underset{|}{C}}=N-G$$

$$R-\underset{\displaystyle H}{\underset{|}{C}}=O + H_2N-OH \xrightarrow[-H_2O]{} R-\underset{\displaystyle H}{\underset{|}{C}}=N-OH$$



$$R-\underset{\displaystyle H}{\underset{|}{C}}=O + H_2N-NH_2 \xrightarrow[H_2O]{} R-\underset{\displaystyle H}{\underset{|}{C}}=N-NH_2$$

mech. ⇒



Witting Reacⁿ

$$\begin{matrix}R\\R\end{matrix}\!\!>C=O + \underbrace{Ph_3P=CH-R}_{\text{ylide}} \rightarrow PPh_3=O + \underbrace{\begin{matrix}R\\R\end{matrix}\!\!>C=CH}_{\text{alkene}}$$

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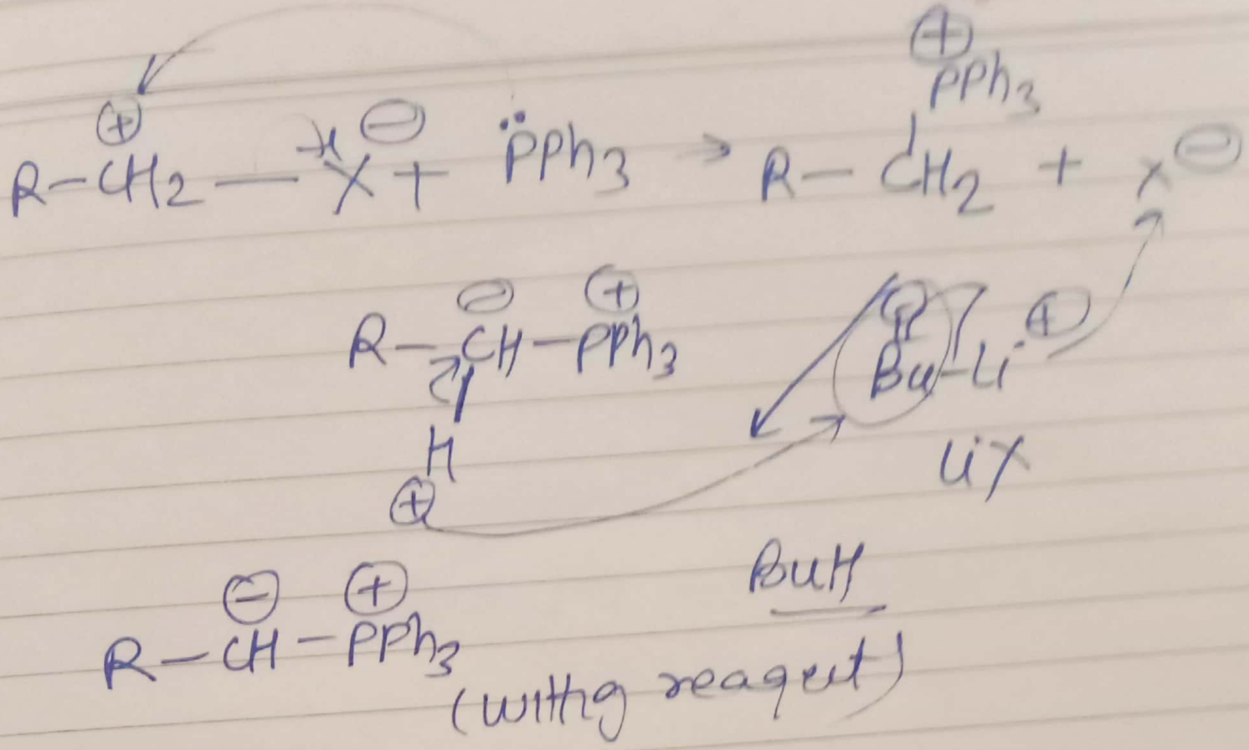
1



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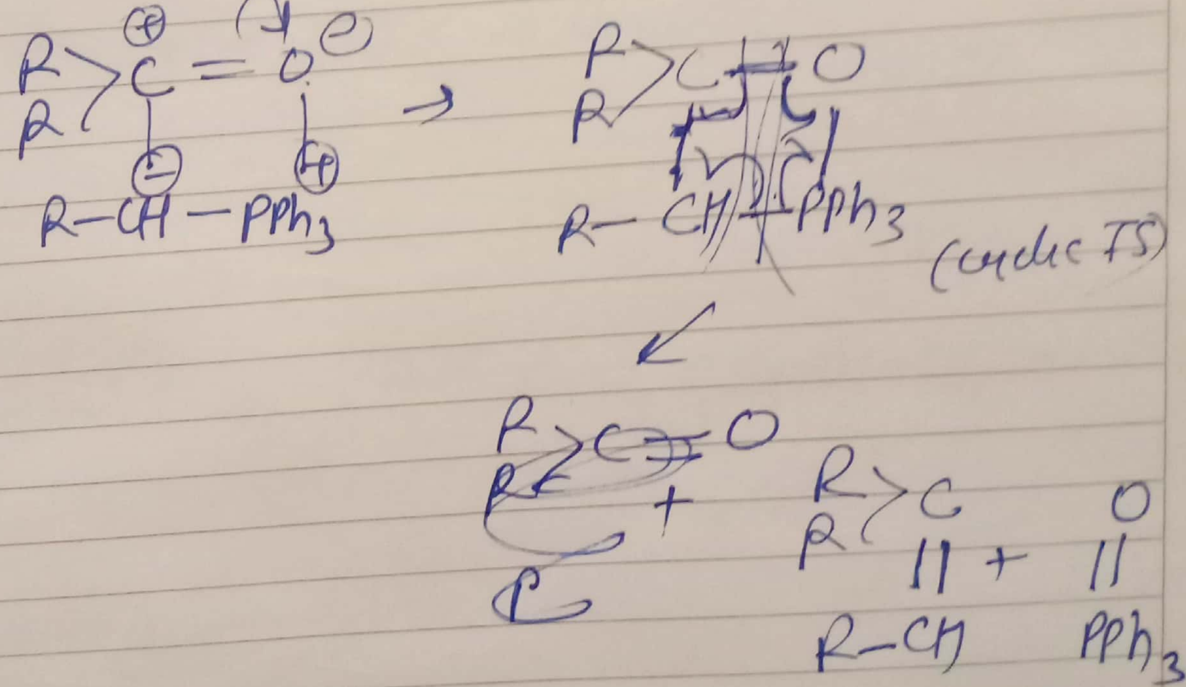

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(2) Perkin's Reaⁿ

$$C_6H_5CHO + \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>O \xrightarrow[180^\circ C]{CH_3COONa} C_6H_5CH=CH-COOH + CH_3COOH$$

cinnamic acid

Mech - (I) $CH_3COO|Na \rightarrow CH_3COO^{\ominus} + Na^{\oplus}$

(II)

$$\begin{matrix} CH_3CO \\ {}^{\ominus}CH_2-CO \\ | \\ H^{\oplus} \end{matrix}\!\!>O + CH_3COO^{\ominus} \rightarrow CH_3COOH + \begin{matrix} CH_3CO \\ {}^{\ominus}CH_2CO \end{matrix}\!\!>O$$

(III)

$$C_6H_5-\overset{O^{\ominus}}{\overset{|}{C^{\oplus}}}-H + \begin{matrix} CH_3CO \\ {}^{\ominus}CH_2-CO \end{matrix}\!\!>O \rightarrow C_6H_5-\overset{O^{\ominus}}{\overset{|}{CH}}-CH_2COOCOCH_3$$

$\swarrow H^{\oplus}$

(IV)

$$C_6H_5-\overset{OH^{\ominus}}{\overset{|}{C}}-\underset{H^{\oplus}}{CH}COOCOCH_3 \xrightarrow{-H_2O}$$

$$C_6H_5-\underset{H}{\overset{|}{C}}=CHCOO^{\ominus}|^{\oplus}COCH_3 \xrightarrow{HOH}$$

$H^{\oplus}$ $OH^{\ominus}$

$$C_6H_5CH=CH-COOH + CH_3COOH$$

Aldol condensation

* αH present * dil NaOH/KOH

(1) $2\,CH_3CHO \rightarrow$ aldol

$$CH_3-\overset{\overset{O}{\|}}{C}-H + CH_3-CHO \longrightarrow$$

αC

αH

$$CH_3-\underset{\underset{H}{|}}{C}=CH-CHO$$

HCHO

$$CH_3-\overset{\overset{O^{\ominus}}{\|}}{C}-H + H-CH_2-CHO \longrightarrow$$

$\oplus$ $\oplus$

αC

αH

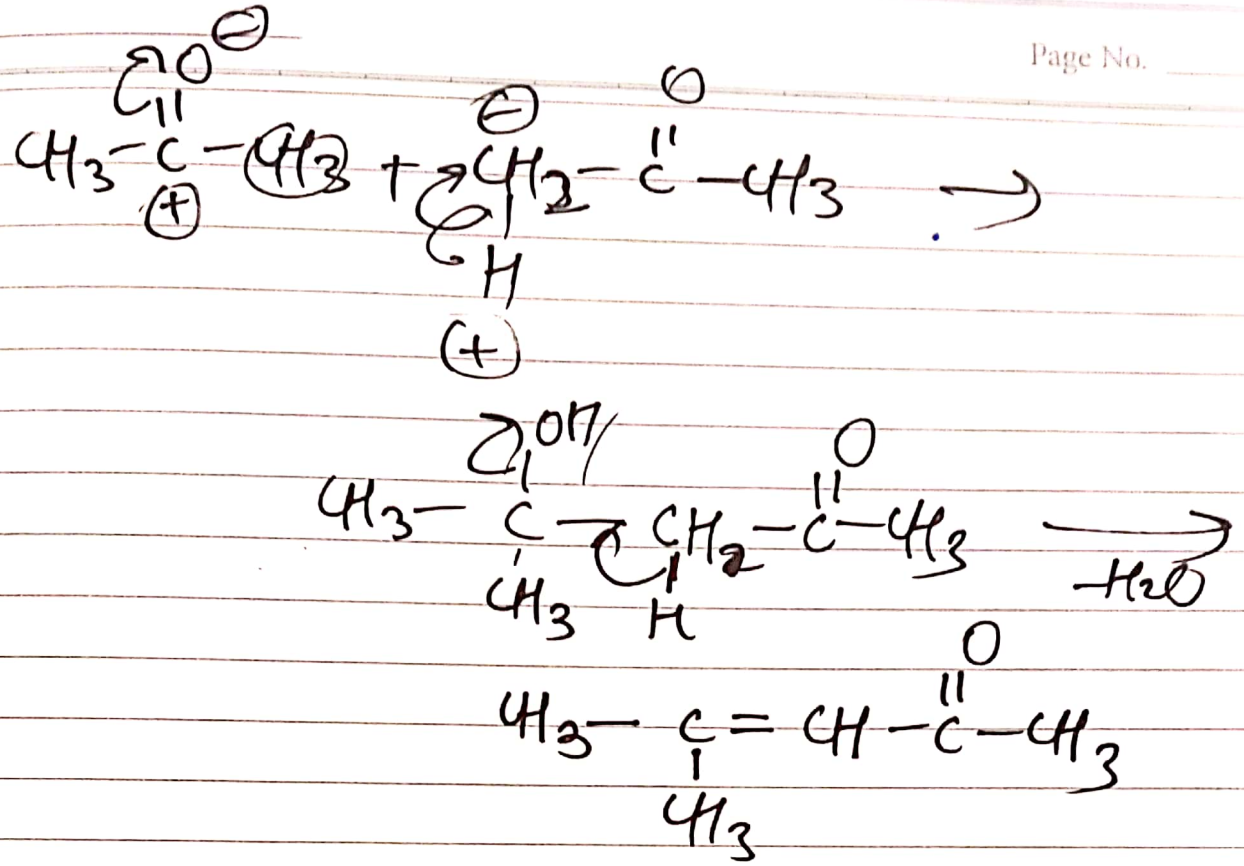
$$\begin{matrix} H \\ H \end{matrix}\!\!>C=O$$

$$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2-CHO \xrightarrow{\text{excess NaOH}}$$

(aldol)

$$CH_3-CH=CH-CHO$$

crotonaldehyde



$$CH_3-CH_2-CHO + CH_3-CH_2CHO \xrightarrow[\text{Pa}]{HCl}$$

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aldol → αH

$CH_3-\underset{\alpha C}{CH_2}-CHO + CH_3-\underset{\alpha C}{CH_2}-CHO \rightarrow$

$CH_3-CH_2-\underset{\oplus}{\overset{O^{\ominus}}{\overset{\|}{C}}}-H + H-\underset{CH_3}{\overset{\ominus}{C}}H-CHO \rightarrow$

$CH_3-CH_2-\underset{H}{\overset{OH}{C}}-\underset{CH_3}{C}H-CHO \xrightarrow{-H_2O}$

$CH_3-CH_2-\underset{H}{C}=\underset{CH_3}{C}-CHO$

C_6H_5CHO

αC αH ⊗

→ al ⊗

aldol	Cannizzaro
αH present	αH absent — HCHO
	C_6H_5CHO

base $OH^{\ominus}$ $NaOH \rightarrow Na^{\oplus} + OH^{\ominus}$

mech. (I) $\overset{\ominus}{C}H_2-CHO$

$H^{\oplus}-CH_2-CHO + OH^{\ominus} \rightarrow \overset{\ominus}{C}H_2-CHO + H_2O$

(II) $CH_3-CH=O \rightarrow CH_3-\overset{\oplus}{C}H-O^{\ominus}$

(III) $CH_3-\overset{\oplus}{C}H-O^{\ominus} + \overset{\ominus}{C}H_2-CHO \rightarrow CH_3-CH(O^{\ominus})-CH_2-CHO$

$HOH \rightarrow H^{\oplus}$

$CH_3-CH(OH)-CH(H)-CHO$

$CH_3-CH=CH-CHO \quad -H_2O$

Cross/mixed

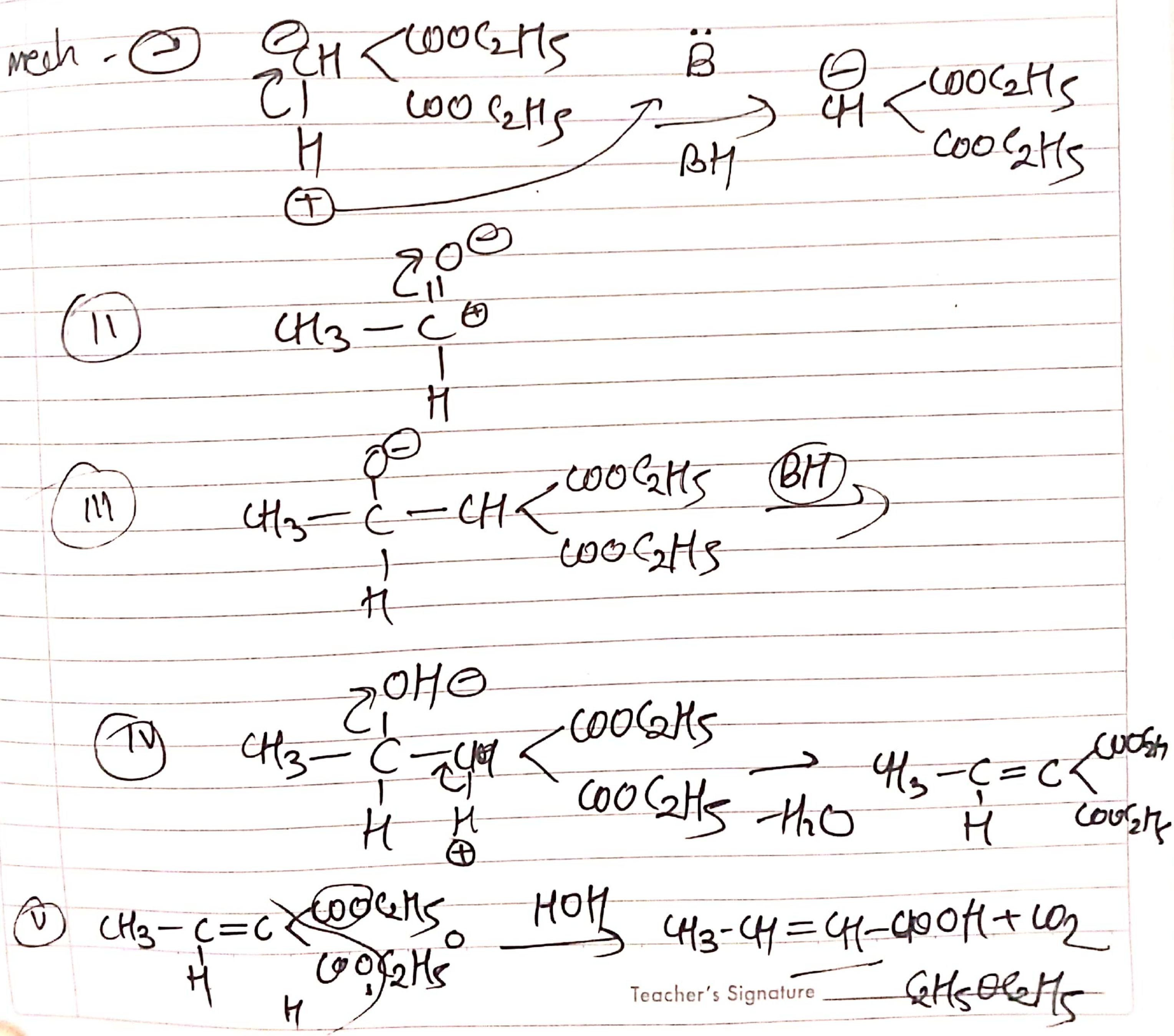
(I) $CH_3CHO + CH_3CH_2CHO$

(II) $CH_3COCH_3 + C_6H_5COCH_3$

Knoevenagel Reacn

$$CH_3CHO + CH_2 \begin{cases} COOC_2H_5 \\ COOC_2H_5 \end{cases} \xrightarrow{\text{base}} CH_3CH=CHCOOH + CO_2 + C_2H_5OC_2H_5$$

Mech -



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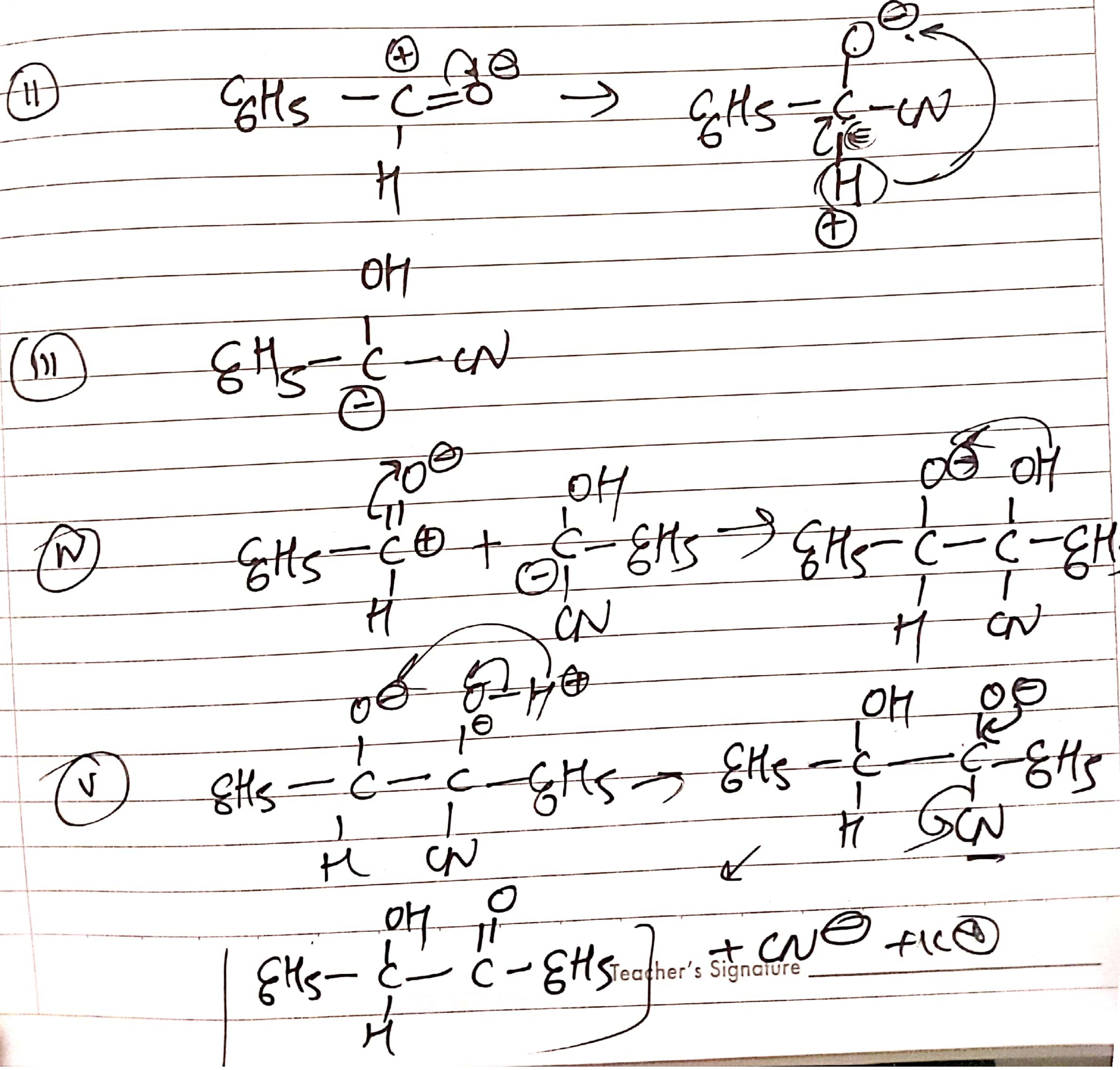
Benzoin condensⁿ

$$2\,C_6H_5CHO \xrightarrow{KCN} C_6H_5-\underset{OH}{\underset{|}{CH}}-\underset{O}{\overset{}{\underset{\|}{C}}}-C_6H_5$$

benzoin

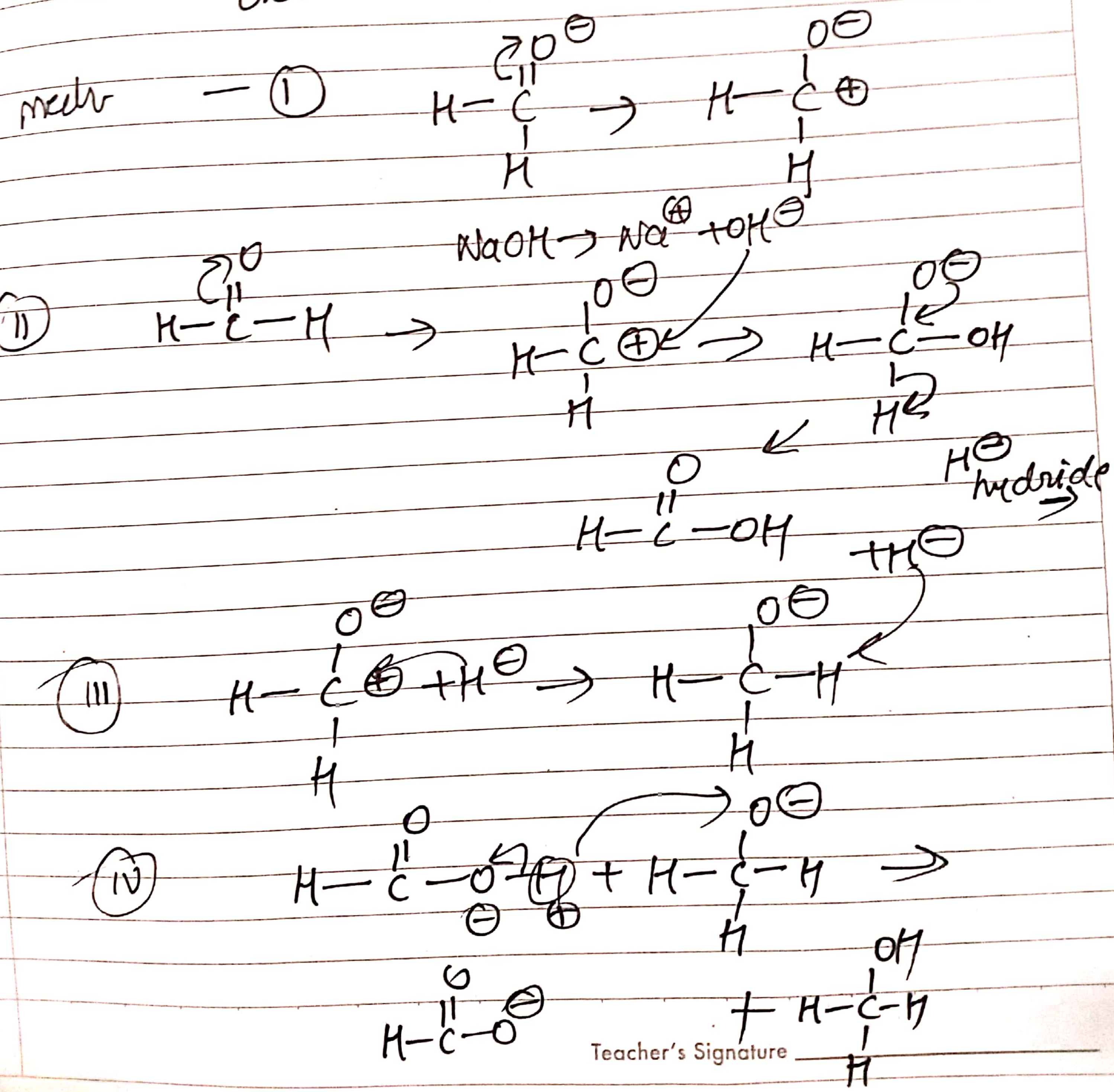
mech. :- (i) $KCN \longrightarrow K^{\oplus} + CN^{\ominus}$



Cannizzaro Reaⁿ

$$H-\overset{\overset{O}{||}}{C}-H + H-\overset{\overset{O}{||}}{C}-H \xrightarrow{\text{C}NaOH} CH_3OH + HCOO^{\ominus}$$

H donor (oxdⁿ) | H add (Redⁿ) | alcohol + acid



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Reformatsky Reacⁿ

ald / ketone + α-bromo ester $\xrightarrow[\text{(ii) } H_2O]{\text{(i) Zn/ ether}}$ β hydroxy ester

$Br-CH_2COOR$

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + Br-CH_2COOC_2H_5 \longrightarrow$$

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

mech → (i) $Br-CH_2COOC_2H_5 + Zn \longrightarrow$

orgmetal
M–C

$$Br-\overset{\oplus}{Zn}-CH_2COOC_2H_5$$

M–C

(ii) $CH_3-\overset{CH_3}{\overset{|}{\overset{\oplus}{C}}}=\overset{\ominus}{O} + Br-\overset{\oplus}{Zn}-\overset{\ominus}{C}H_2COOC_2H_5 \longrightarrow$

$$CH_3-\underset{CH_2COOC_2H_5}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-O\overset{\oplus}{Zn}Br \xrightarrow{\overset{\ominus}{H}OH}$$

$$CH_3-\underset{CH_2COOC_2H_5}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH$$

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Claisen - schmidt Condensn

$$C_6H_5CHO + CH_3CHO \xrightarrow{dil\ NaOH}$$

$$C_6H_5-\overset{O^{\ominus}}{\overset{\|}{\underset{\oplus}{C}}}-H + \underset{\oplus}{H}-\underset{\ominus}{C}H_2-CHO \longrightarrow$$

$$C_6H_5-\overset{OH}{\underset{\oplus}{\overset{|}{C}}}-H + \overset{\ominus}{C}H_2-CHO \rightarrow$$

$$C_6H_5-\overset{OH^{\ominus}}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\underset{\underset{\oplus}{H}}{\underset{|}{C}}H_2-CHO \xrightarrow[-H_2O]{}$$

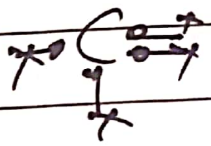
mixed aldol

$$C_6H_5-\underset{H}{\overset{\beta}{\underset{|}{C}}}=\underset{\alpha}{CH}-CHO$$

α, β unsaturated

या

unnemaldehyde



$$H-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-H$$

$$\left\{\begin{array}{l} C=C \\ C\equiv C \end{array}\right.$$

unsaturated

saturated alkane

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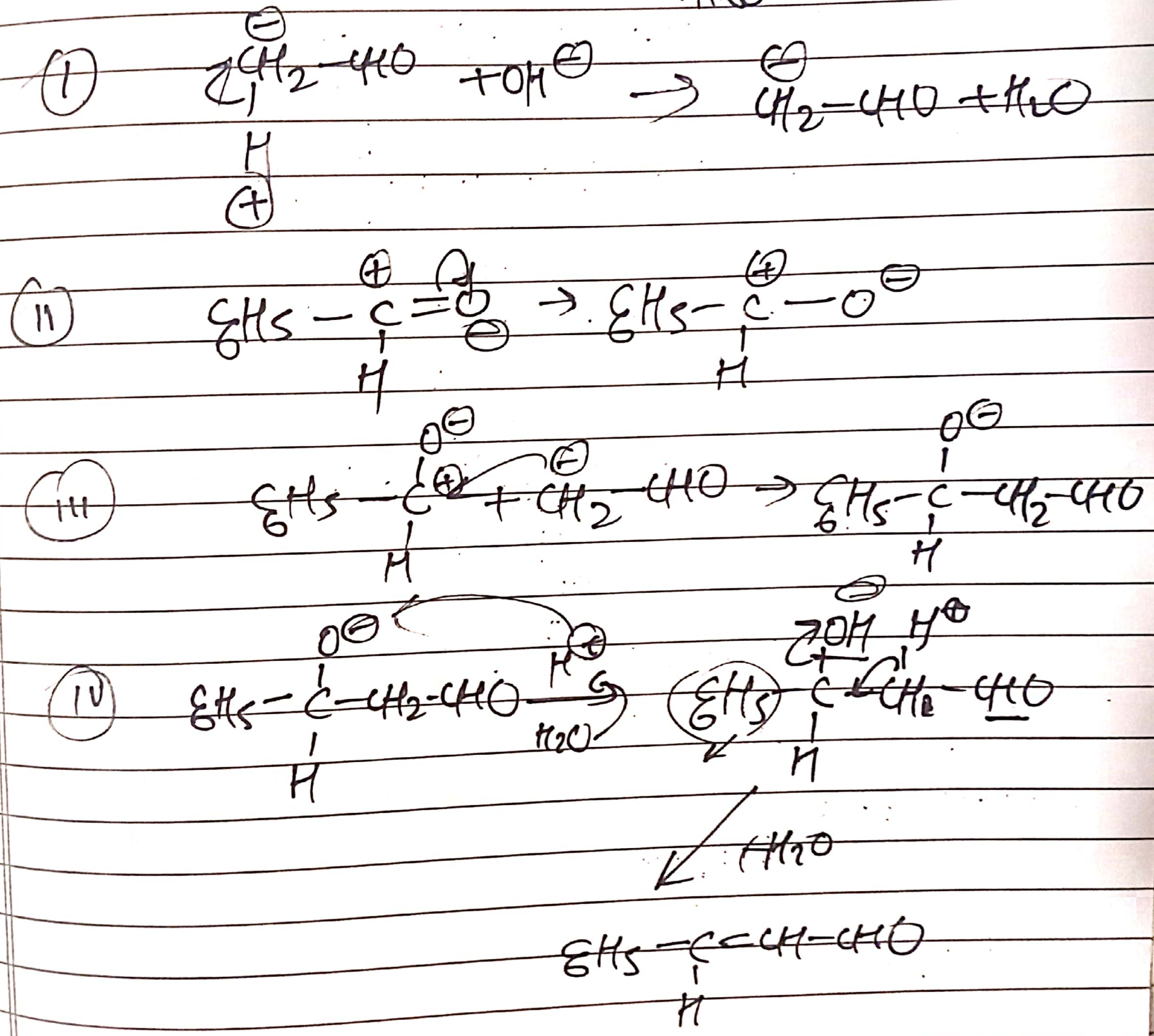
mech ⇒ $NaOH \rightarrow Na^{\oplus} + OH^{\ominus}$
$+ H_2O$



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oxidat^n of $>C=O$

(I) $R-CHO \xrightarrow[(O)]{KMnO_4 / K_2Cr_2O_7} R-COOH$

~~R-CO-R~~ ~~(O)~~

(II) Tollen's reagent

$R-CHO + \underset{(+1)}{Ag_2O} \longrightarrow R-COOH + 2\underset{0}{Ag}$

(III) Fehling reagent $\rightarrow$

$R-CHO + 2\underset{(+2)}{CuO} \rightarrow R-COOH + \underset{(+1)}{Cu_2O}$

(IV) Bayer-villiger Rea^n $\Rightarrow$

$\begin{matrix}R\\R\end{matrix}>C=O + C_6H_5\overset{O}{\overset{\|}{C}}-O-OH \rightarrow \underset{ester}{RCOOR} + C_6H_5COOH$

Reduction $>C=O \xrightarrow{Red^n}$ alcohol

(I) $CH_3CHO \xrightarrow[2H]{Ni / H_2} CH_3-CH_2OH$

1° OH

$\begin{matrix}CH_3-C=O,\\ \quad\ \ |\\ \quad\ \ H\end{matrix}$ Pd, Pa, Pt

LiAlH$_4$ / NaBH$_4$

$\begin{matrix}R\\R\end{matrix}>C=O \xrightarrow[2H]{} \begin{matrix}R\\R\end{matrix}>CH-OH$

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(4) Bouveault - blanc Reaⁿ → alcohol

$$CH_3CHO + 2H \xrightarrow{Na + C_2H_5OH} CH_3CH_2OH$$
1°

$$\frac{CH_3}{CH_3} > C=O + 2H \longrightarrow \frac{CH_3}{CH_3} > CH-OH$$
2°

(5) MPV →

$$CH_3 \cdot CHO \xrightarrow[2H]{Al\left(-CHO < \frac{CH_3}{CH_3}\right)_3} CH_3CH_2OH$$

$$\frac{CH_3}{CH_3} > C=O \longrightarrow \frac{CH_3}{CH_3} > CHOH$$

F F

IMP Haloform Reaⁿ Br Cl I

$$R-\overset{O}{\overset{\|}{C}}-CH_3 + 3Br_2 + 4NaOH \longrightarrow CHBr_3$$

$$R-COONa + 3NaBr + 3H_2O$$

α, β unsaturated aldᵉ

$$\underset{\beta}{CH_2}-CH=\underset{\alpha}{CH}-CHO$$ acrolde

$C_6H_5-CH=CH-CHO$ Remark cin

$CH_3-CH-CH=CH-CHO$ croton

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(I) $CH_2-CH=CH-CHO$

$CH_2-CH=CH-\overset{\oplus}{C}H=O^{\ominus} + \overset{\oplus}{H}\overset{\ominus}{CN} \longrightarrow$

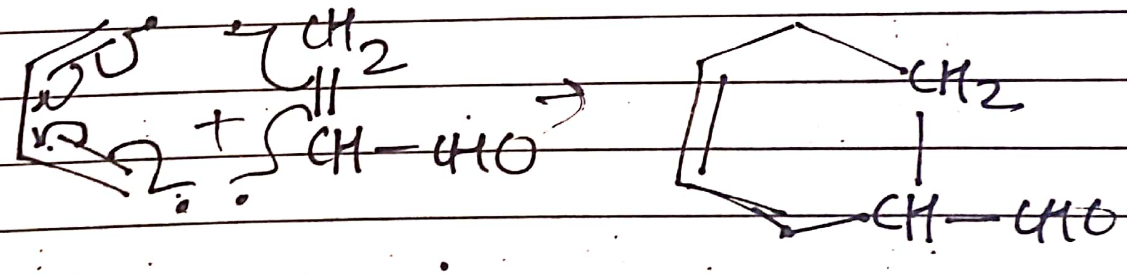
$CH_2-CH=CH-C(CN)(H)-OH$

$CH_2-CH=CH-CH(OH)CN$

(II) $CH_2-CH=CH-CHO + H_2N-NH-C_6H_5 \longrightarrow$

$CH_2-CH=CH-CH=N-NH-C_6H_5$

(III)



B-II

Unit - II (A) 1/10/19

Oxidatn / Reductn

Oxidatn → e देना, H removal, O addn (M-L)

Redn → e^- लेना, H addn, O - removal

$$FeCl_3 + SnCl_2 \rightarrow FeCl_2 + SnCl_4$$

+3 (+2) (+2) (+4)

Redn

Oxdn

e

oxidatn → (+) वृद्धि oxidate state (n)

$$+3 + e^- \rightarrow +2$$

$$+2 \rightarrow +4 + 2e^-$$

ऑक्सीकारक = Redn = e^- लेना

अपचायक = Oxdn = e^- बाहर/त्याग

$$2CuO \rightarrow Cu_2O$$

(+2) (+1) Redn

Ag_2O (+1) $\rightarrow$ $Ag_{(s)}$ (0)

Ag_2O

2x

CuO	Cu_2O
$x + (-2) = 0$	$2x + (-2) = 0$
$x - 2 = 0$	$2x - 2 = 0$
$x = +2$	$2x = 2$
	$x = \frac{2}{2} = +1$

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Be $\quad Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$

Mg $\quad Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-}$

$CaO \rightarrow Ca^{2+} + O^{2-}$

$H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$

$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$

$Al_2\,(SO_4)^{2-}$ $\quad PO_4 \quad CO_3$

$\quad\quad -2 \quad\quad -3 \quad -2$

Redox Rea^n $\rightarrow$ $FeCl_3 + SnCl_2 \rightarrow$

$FeCl_2 + SnCl_4$

oxid^n half rea^n $\rightarrow$ $\underset{+2}{SnCl_2} \rightarrow \underset{+4}{SnCl_4}$

Red^n rea^n $\rightarrow$ $\underset{(+3)}{FeCl_3} \rightarrow \underset{(+2)}{FeCl_2}$

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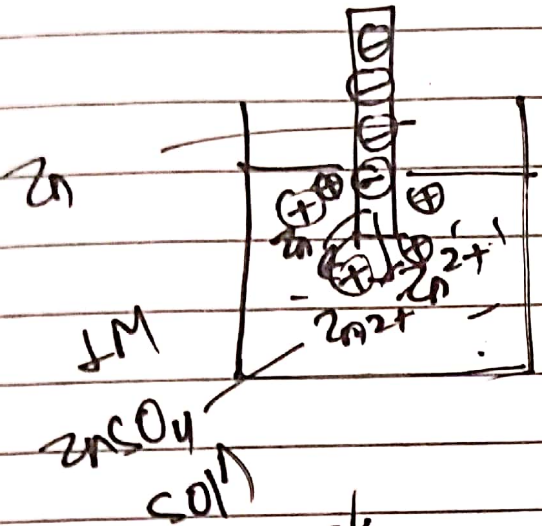
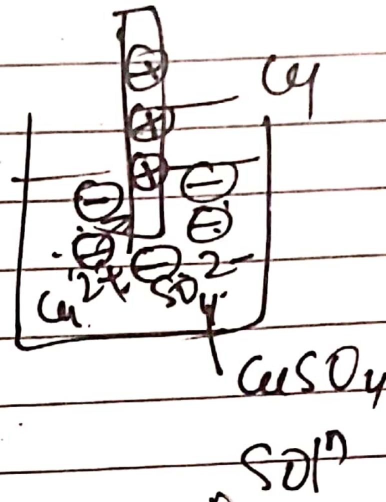
electrode potential





↓

oxidn

↓

Soln pressure

↓

Metal → soln में जाने के लिए आवश्यक

↓

SP > OP → oxidn

→ ~~Metal dissolve~~

→ wt कम

→ electrode ⊖ charge

Redn

↓

osmotic press

↓

Soln से Metal → सतह में जाना

low → high

OP > SP

↓

Redn

↓

metal wt ↑

↓

electrode ⊕

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SEP 1g/1litre

298 K   1M sol^n

$H/\frac{1}{2}H_2 \rightarrow 0.00$ V

Cell

electrochemical cell → electrolytic cell

gal / g/ voltaic
↓
chem → elect

electrolytic cell
↓
ele → chem

NaCl

$Na^{\oplus} + Cl^{\ominus}$

Cathode → $Na^{\oplus} + e^{\ominus}$
→ $Na_{(s)}$

anode $Cl^- \rightarrow Cl + e^-$

$Cl + Cl \rightarrow Cl_{2(g)}$

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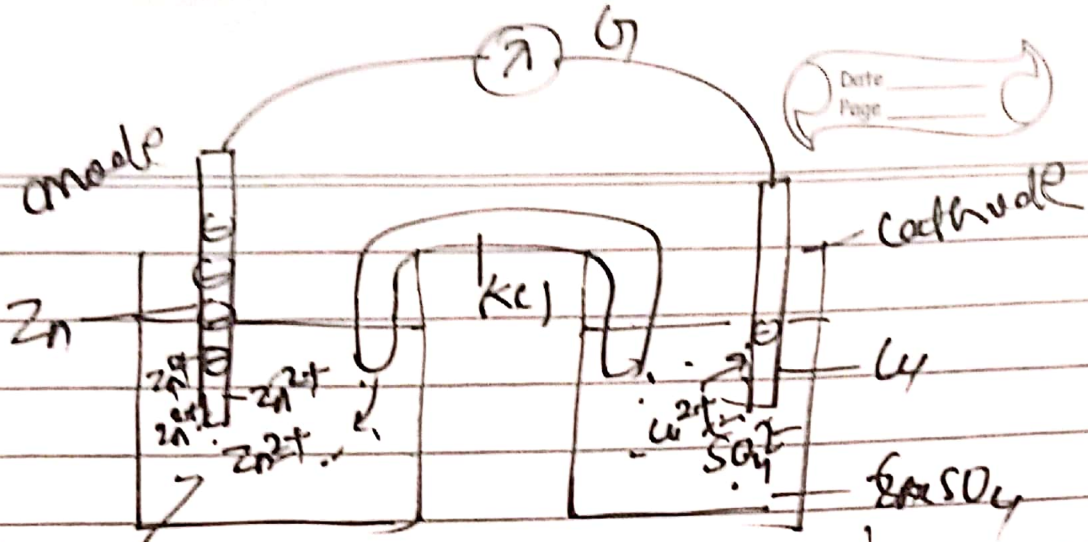
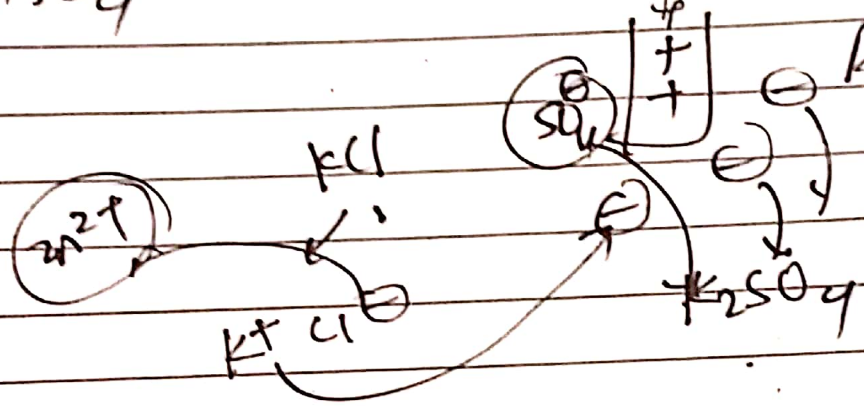


LHS $ZnSO_4$ RHS

oxdn Redn



$ZnCl_2$

$Zn_{(s)} | Zn^{2+}_{(aq)}$ (1M) ZnSO4 soln $|| Cu^{2+}_{(aq)} | Cu_{(s)}$

1M

Half cell → ~~Redn~~ oxdn

Half cell → Redn

$$E_{cell} = E_{cathode} - E_{anode}$$

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BSc II

$Zn \rightarrow Zn^{2+}$

$Cu^{2+} \rightarrow Cu(s)$

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$Zn | Zn^{2+}(1M) || Cu^{2+}(1M) | Cu(s)$

Nernst eq^n $\Rightarrow$ $M^{n+} + ne^- \rightarrow M_{(s)}$

$$E = E^0 - \frac{2.303}{nF} \log \frac{(Red)}{(Oxd)}$$

$$= E^0 - \frac{2.303}{n \times 96{,}500} \log \frac{[M]_{(s)}}{(M^{n+})}$$

$M_{(s)} = 1$

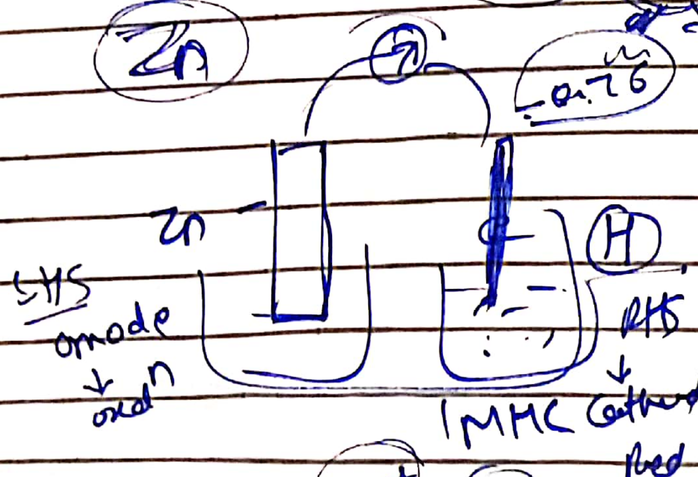
$$= E^0 - \frac{0.0591}{n} \log \frac{1}{(M^{n+})}$$

$$\boxed{E = E^0 + \frac{0.0591}{n} \log (M^{n+})}$$

R. E

1M

Volt H +0.0V



$E_{cell} = E_{cathode} - E_{anode}$

$E_{cell} = E_H - E_{Zn}$

$0.76 = 0.0 - E_{Zn}$

$-0.76 = E_{Zn}$

$H^+ + e^- \rightarrow H$

$H + H \rightarrow H_2$

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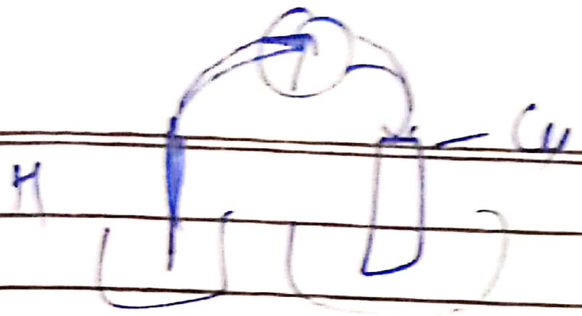


$\frac{1}{2}H_2 \rightarrow H^+ + e^-$

$E_{cell} = E_{cathode} - E_{anode}$

$+0.35 = E_{Cu} - E_{H}$

$\boxed{+0.35 = E_{Cu} - 0}$

electrochemical series

Li (−)	Li −	0.0 +
	$\xrightarrow{oxd^n}$	$\xrightarrow{Red^n}$
(+)	Zn →	−0.76
	Cu →	+0.35

सापेक्ष अपचयन विभव ⇒ (−)ve value

→ प्रबल अपचायक → e^-

−0.76

−0.43

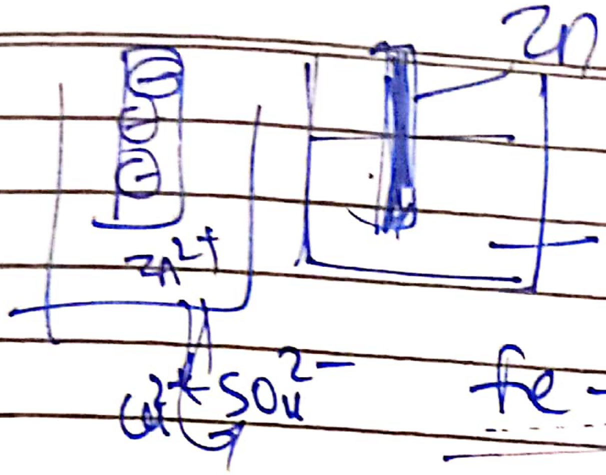
+0.35

देता → (−) ↑ e देता (+)

= आक्सीकारक

Applicat^n ⇒ (I) reactivity ⇒ e^- देना

(II) विस्थापन



$CuSO_4 \to Cu$

Fe = −0.44

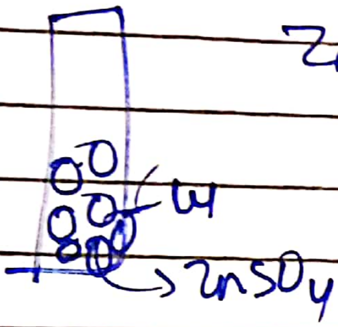
Zn = −0.76V

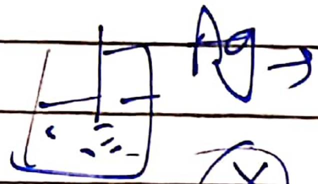
Cu = +0.35V

$Zn \to Zn^{2+} + 2e^-$

$Zn^{2+} + SO_4^{2-} \to ZnSO_4$

$Cu^{2+} + 2e^- \to Cu(s)$





(X)

III) अपचायक शक्ति →

IV) H का H − 0.0

(v) metal

$$Na[Ag(CN)_2] + Zn \to Na_2[Zn(CN)_4] + 2Ag\downarrow$$

$(+1) + x + (-2)$

$x - 1 = 0$

$x = +1$

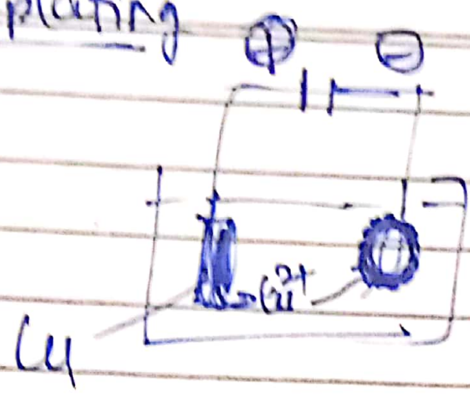
$+2 + x - 4$

$x - 2 = 0$

$x = +2$

0

electroplating



Redox Rea^n संभावना बताओ

$$Cu^{2+} + 2e^- \rightarrow Cu_{(s)} \qquad 0.34V$$

$$Zn^{2+} + 2e^- \rightarrow Zn(s) \qquad -0.76V$$

$$E_{cell} = E_{cath} - E_{anode}$$

कमी e ⊕

⊖

⊗

⊖ अपचायक = oxd^n

anode

$$E_{cell} = E_{Cu} - E_{Zn}$$

$$= 0.34 - (-0.76)$$

$$= +1.10V$$

$\Delta G = -ve$

$\Delta E = +ve$

rea^n

$$\Delta G = -nFE_{cell}$$

E_{cell} = +ve

$$\Delta G = -nFE$$

(-V)

$\Delta G = +nFE$

$\Delta = -ve$

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Q. $Zn + CdSO_4 \rightarrow ZnSO_4 + Cd$

$E_{Zn} = -0.76V$

$Cd = +0.40V$

reaction होगी या नहीं।

Bk IV

Inorg — unit – I, unit – II – co ords

Unit III – co - chem

org – phenol & alcohol

phys — unit - I - 20

—o—

Metallurgy

↓

Metal

reactive — less reactive

↓ संयुक्त ~~मुक्त~~ — ↓ free state

↓ Fe, Cu, Zn, — ↓ Au, Ag, Pt

ores — Mineral

↓ → सस्ता → easily — ↓ impurity ज्यादा ↓ खर्चीला ज्यादा

1) crush of ores
II) concentn ores
III) ores (M) → Metal oxide
IV) reductn → O_2 का removal $MO \rightarrow M + O_2$
V) M → purificatn → Metal शुद्ध

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1) mechanical → Au, Ag, Pt

2) Thermal dec → $NaN_3 \rightarrow 2Na + 3N_2$

$Ni(CO)_4 \xrightarrow{230°C} Ni + 4CO$

$2HgO \rightarrow Hg + O_2$

3) displacement ⇒ CuS

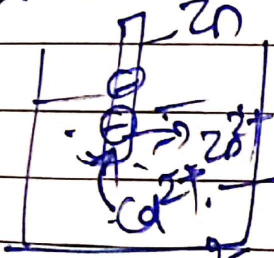
↓ भर्जन

O_2 + water → $(CuSO_4)$

$\downarrow Fe$

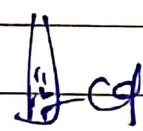
$Cu_{(s)} + FeSO_4$

$CdSO_4 \rightarrow Cd$



$\rightarrow ZnSO_4 + CdSO_4 \rightarrow Cd^{2+} \rightarrow Cd_{(s)}$

SO_4^{2-}



Reduction method

$MO \xrightarrow[C/CO/M]{} M + O_2\uparrow$

blast furnace

CO_3
$O \rightarrow$
$C \rightarrow$
$S \rightarrow$
SO_4

$Fe_2O_3 + C \rightarrow Fe + CO\uparrow$

$ZnO + C \rightarrow Zn + CO\uparrow$

$PbO + C \rightarrow Pb + CO\uparrow$

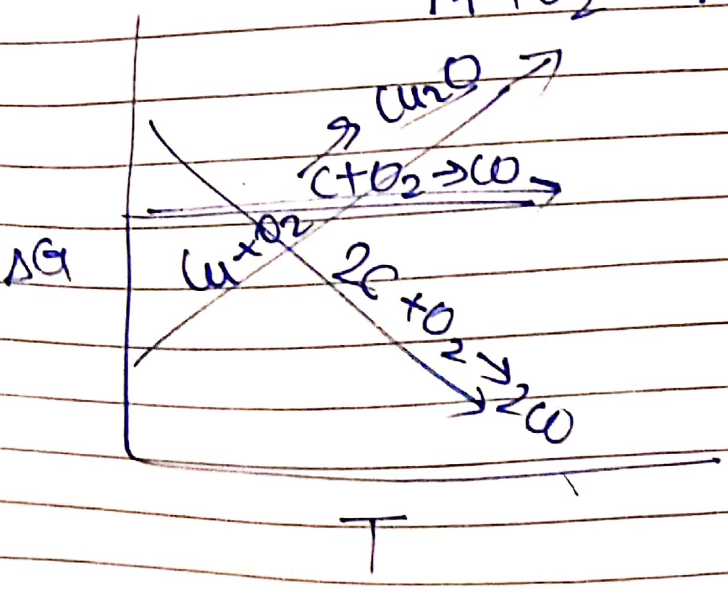
Thermody of redn process

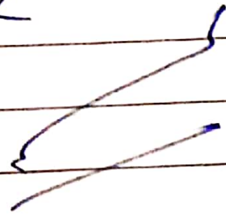
$MO \rightleftharpoons M + O_2\uparrow$

help → Ellingham diagram

* metal easily reduce / easily
* plot ΔG of O_2 vs Temp

$M + O_2 \rightarrow MO_2$





line → $M + O_2$

रेखा → MO_2

$\Delta H = -ve$

exo

$M + O_2 \rightarrow MO_2$

$-\Delta H$

★ $\Delta G = \Delta H - T\Delta S$

(-ve) Spontaneous

0

+ve

$S \rightarrow l$

$\Delta S = +ve$

① $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

1 1

$\Delta S = 0$

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

$= -\Delta H - 0$

$\Delta G = -\Delta H$

$T\uparrow$ $T\downarrow$ G X

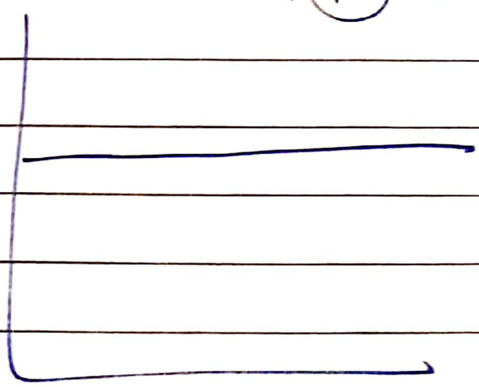
$\Delta G = \Delta H - T\Delta S$

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

$-20 - 10$

$\Delta G = -ve$

T (T)



② $4Cu_{(s)} + O_{2(g)} \rightarrow 2Cu_2O_{(s)}$ ΔG

$1 \rightarrow 0$

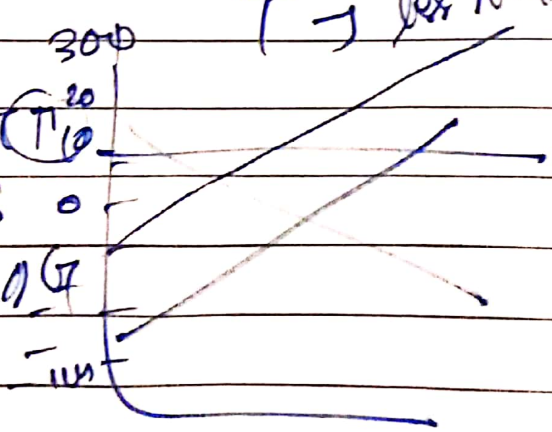
$\Delta S \Rightarrow -ve$

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

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

$\Delta G = +ve$

T → less negative



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