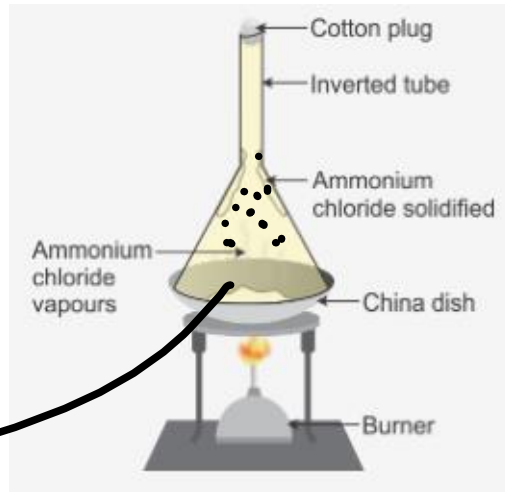


Methods of Purification of Organic Compounds:

1. Sublimation: The phenomenon of a solid directly passing to vapor state without passing to liquid state.

Applicable for volatile substances

Eg. Iodine is purified by this method



Purification of Organic compounds
e.g. Benzene, Naphthalene, Salicylic acid, Ammonium chloride etc.

Crystallization - : Process of atoms or molecules arranging into a well-defined, rigid crystal lattice in order to minimize their energetic state.

Steps:

1. Selection of a suitable solvent.
2. Dissolve the material to be purified in the minimum amount of warm solvent.
3. Once the material is fully dissolved,

filter the heated soln. & bring to the point of saturation by evaporating a part of the solvent.

4. Cool the warm, saturated soln. to reduce the solubility of the solute which will generally cause the material to precipitate out.
5. Isolate the pure solid by filtration & remove the traces of solvent.
6. The cycle may be repeated for recrystallization to further purify the compound.

3. Distillation . . .

Distillation is a process used to separate

Substances that have different boiling points

Volatile substances from non-volatile impurities .

Caution: During the distillation process some cautions should be observed -

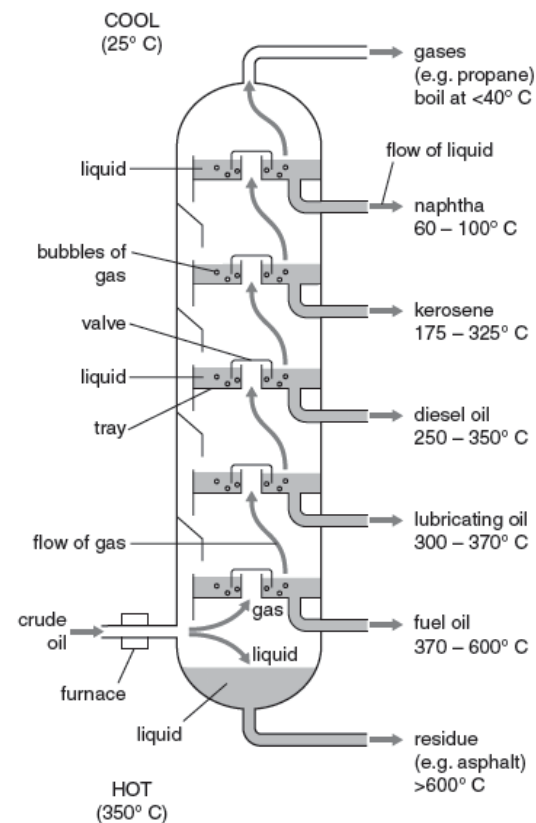
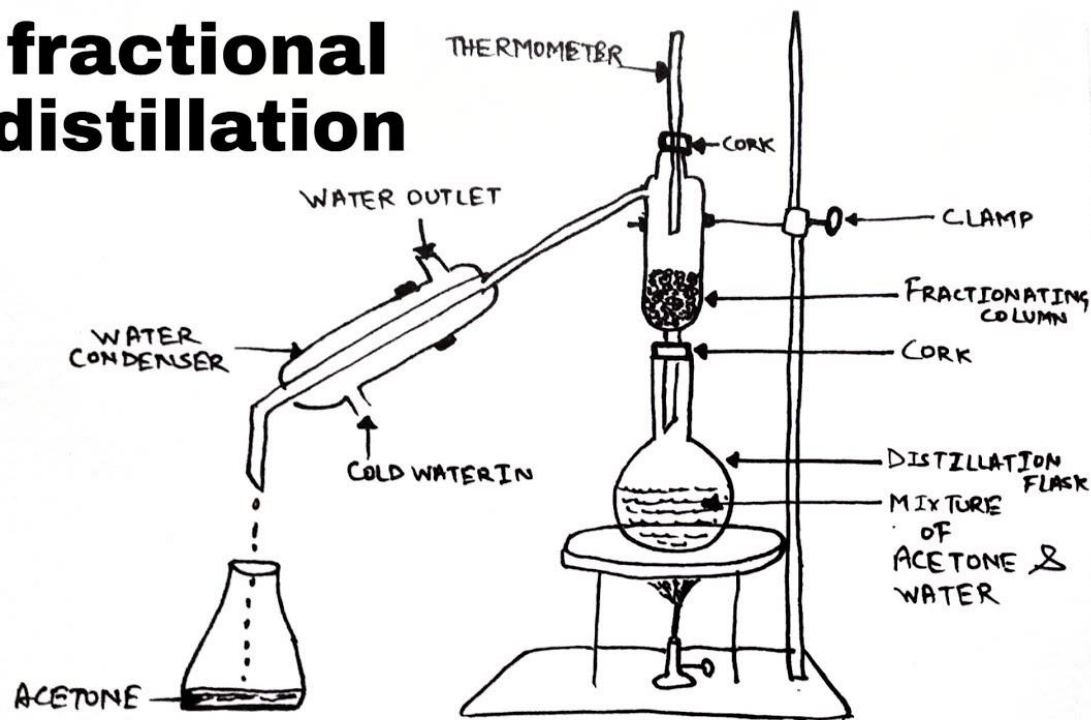
1. The flask should not be more than one-half full.
2. The bulb of the thermometer should be near the side tube of the distillation flask & not dipping in the solution.
3. Add pieces of porous plates in the flask to eliminate the risk of bumping.
4. Regulate the heating during distillation by removing the burner.

5. Distillation of volatile organic compounds should be carried out in heated water bath rather than on direct flame.

Fractional distillation :- This process is used when the boiling point of the components to be separated differ by less than $30 - 40^{\circ}\text{C}$ & a fairly complete separation is desired. Mixtures such as hexane-toluene, chloroform-

aniline can be separated by simple distillation.
 Fractional distillation is used in petroleum industry for fractional distillation of crude oil.

fractional distillation



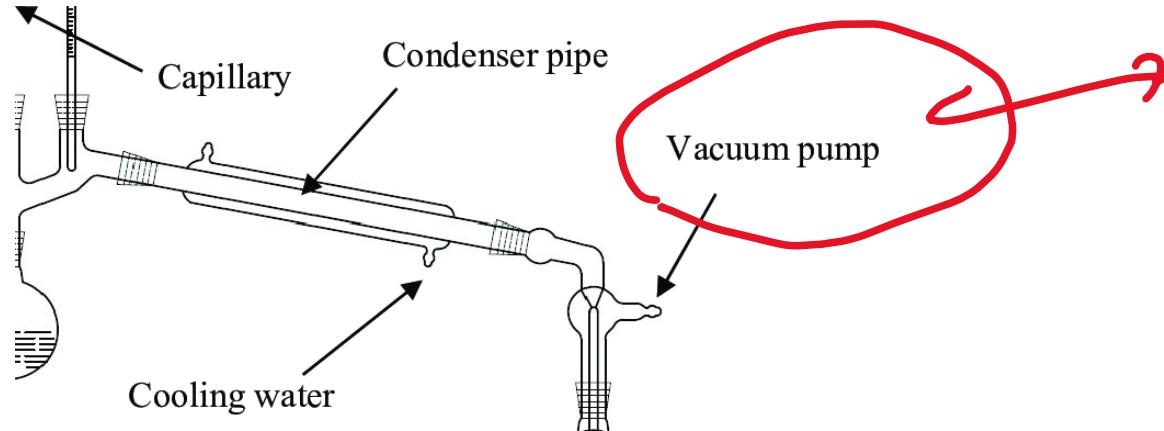
Reduced Pressure Distillation

Liquids which boil at very high temperatures or decompose below their boiling points or undergo chemical changes upon heating are separated by carrying out distillation under reduced pressure. The pressure of the mixture in the round-bottomed flask is reduced using a water or vacuum pump to make

it fall below the normal atmospheric pressure.

The reduction in pressure makes the liquids boil below their normal b.p.

Application: Purification of D.M.S.O.
Separation of glycerol from spent lye in the soap industry.

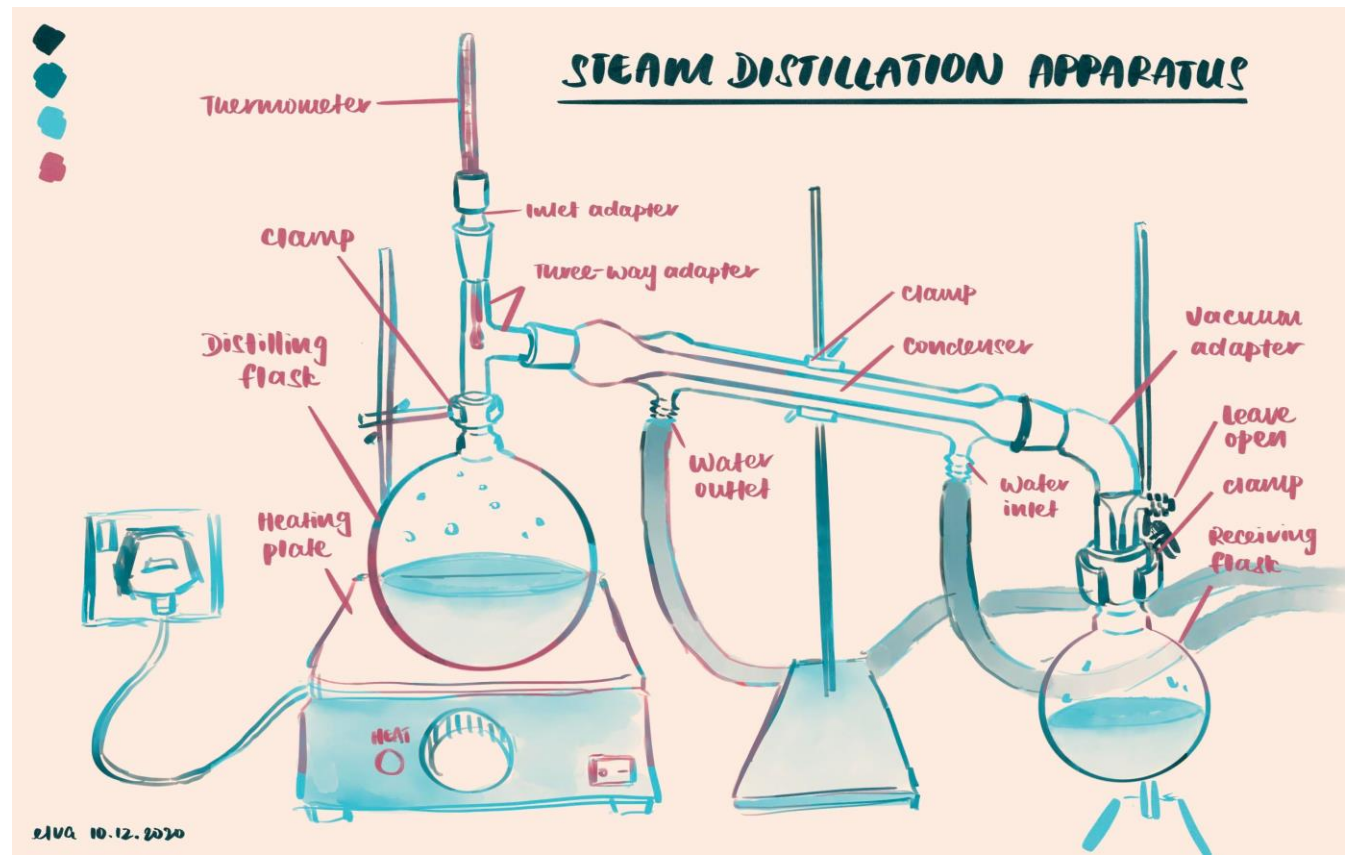


used for reducing pressure

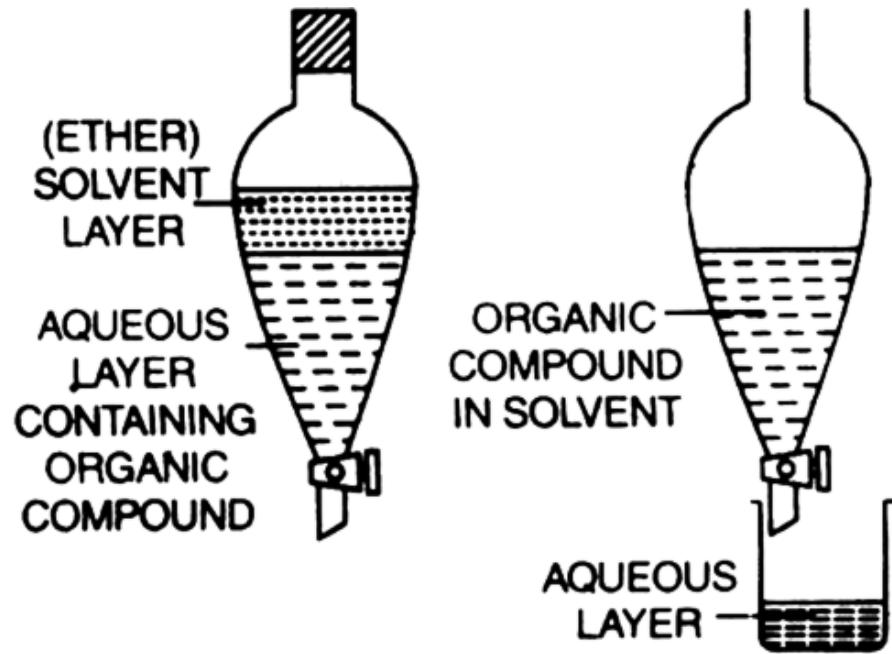
Steam Distillation

This technique is used for purifying substances that are steam volatile & immiscible with water

Air line -
Water
Mixture
Separation



Differential Extraction



Solvent separation is used in the laboratory to separate out the desired compound out of the mixture or from impurities depending upon their solubility in various solvents.

The solubility of a given compound governs its distribution between two phases of immiscible solvents in which the material

has been dissolved
mixture thoroughly.
compound can be
mixture by shaking
solvent in a

The mixture forms two distinct layers
which are separated & the organic compound
is obtained by evaporation of solvent.

Multiple or continuous extractions are
carried out to separate out compounds

when these phases are
Thus an organic
separated from aqueous
with an organic
separating funnel!

that are not very soluble in the organic solvent. The same solvent is repeatedly used for extraction & it becomes enriched with for each extraction.

In case of liquid-liquid extraction, the desired properties of solvent extraction are -

1) It must be immiscible with the solvent.

2) It should readily separate from the desired component after extraction by evaporation i.e. it should be low boiling.

3) It should not react chemically with any of the component in the aqueous mixture.

Chromatography

Chromatography may be defined as a method of separating a mixture of components into individual components by equilibrium distribution between the two phases: one stationary & the other mobile.

Various methods of chromatography

1. Solid - Liquid Chromatography -
2. Liquid - liquid "
3. Vapor phase "

Stationary Phase

Mobile Phase

Type

1. Alumina

Liquid

Column chromatography

2. Silica gel

"

T.L.C

Thin Layer

3. MgO

Liquid

c.c)

chromatography
○ Spin chromatography

	Stationary phase	Mobile phase	Type
4.	Paper	Liquid	Paper chromatography.
5.	Amino acid	Gas	Gas chromatography.

Two principles involved in chromatographic separation:

- i) Adsorption chromatography
- ii) Column chromatography

Adsorption chromatography

Steps:

1. Adsorption or retention of a substance on the stationary phase.
2. Separation of adsorbed substance by the moving phase.
3. Recovery of the separated substance by a continuous flow of the mobile phase.
4. Qualitative & Quantitative analysis of the eluted substances.

A description

Chromatography

Column

Thin Layer

For separation
obtained from
or purification
synthesis

of mixture
natural extracts
of compounds
in the laboratory

Rapid
analysis of
purity of
samples &
as a preparative
technique for
obtaining small
amounts of
materials with high purity

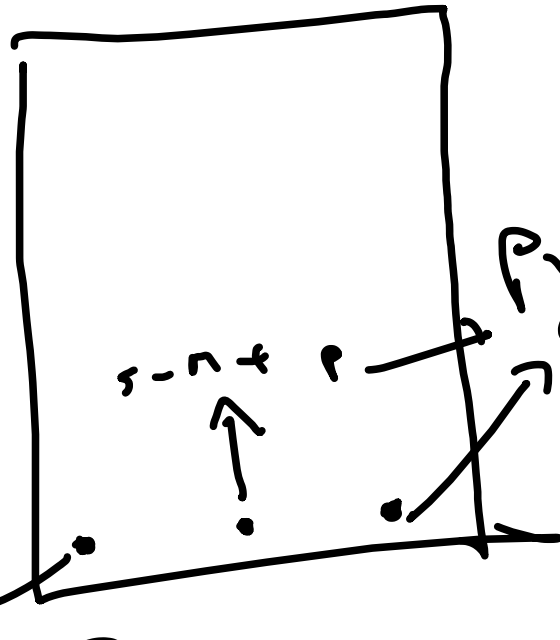
stationary
phase



components separated
chromatography
column

S.M: $R_f = 100:0 \rightarrow 90:10 \rightarrow 80:20 \rightarrow 70:30$

metal
TLC plate
silica coated

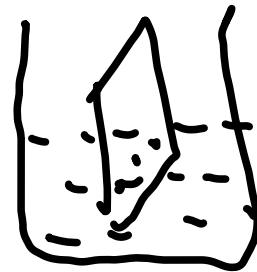
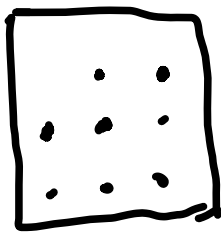


Product
 ω -sift
 $A + B \rightarrow$ rxn. mixture
 $C + D$

Glass plate
coated
with silica
gel.

S.M
T.L.C. Plate

Starting material



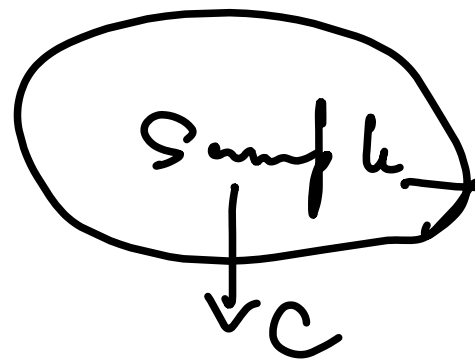
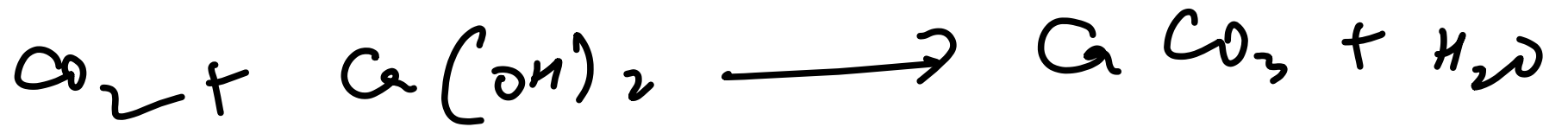
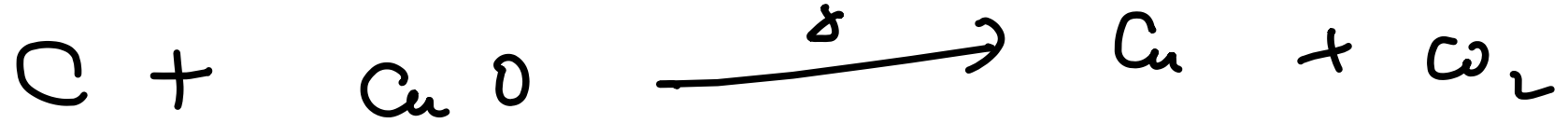
Polar solvent
 CH_2OH

Nonpolar
hexane
Pet ether

Ethyl acetate

Qualitative analysis of organic compound.

1. Detection of C & H:

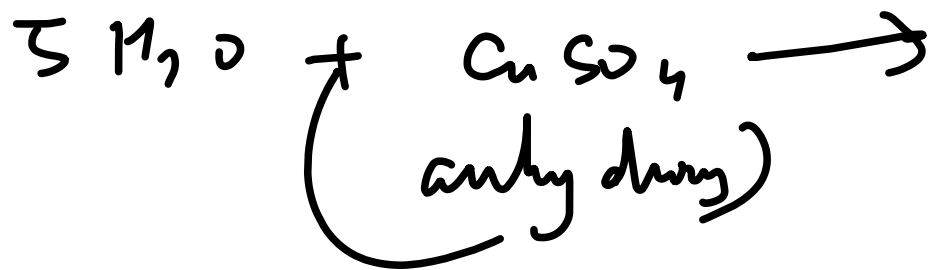
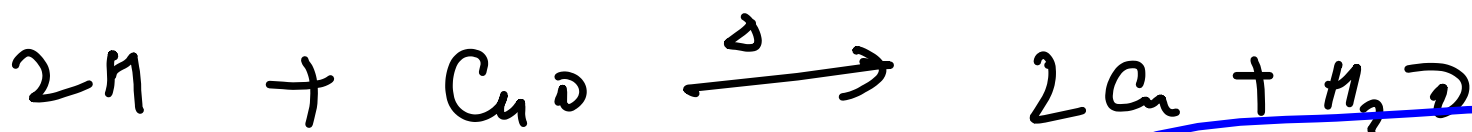


$[O]$ oxidized
 $Cu + CO_2$
 CO_2 turns lime water milky due to $CaCO_3$ pptn.

Carbon in the compound is oxidized to carbon dioxide.

2.

detection
of H

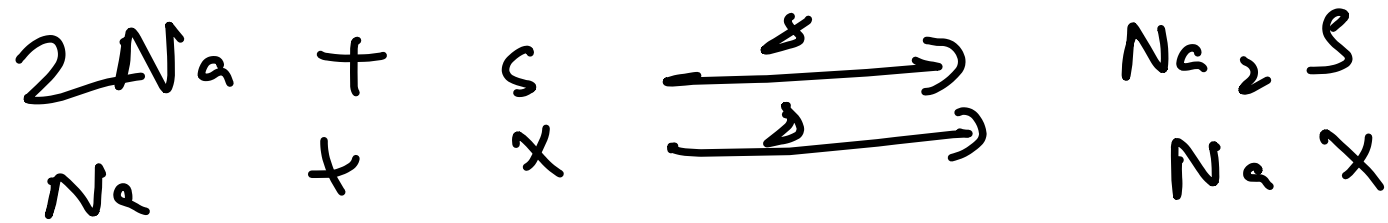


Blue

3. Detection of other elements.

To detect the presence of N, S, P, & halogens, organic compound is fused with metallic sodium. This reaction converts these heteroatoms to water soluble

inorganic compounds & their presence can be determined by inorganic qualitative analysis tests.

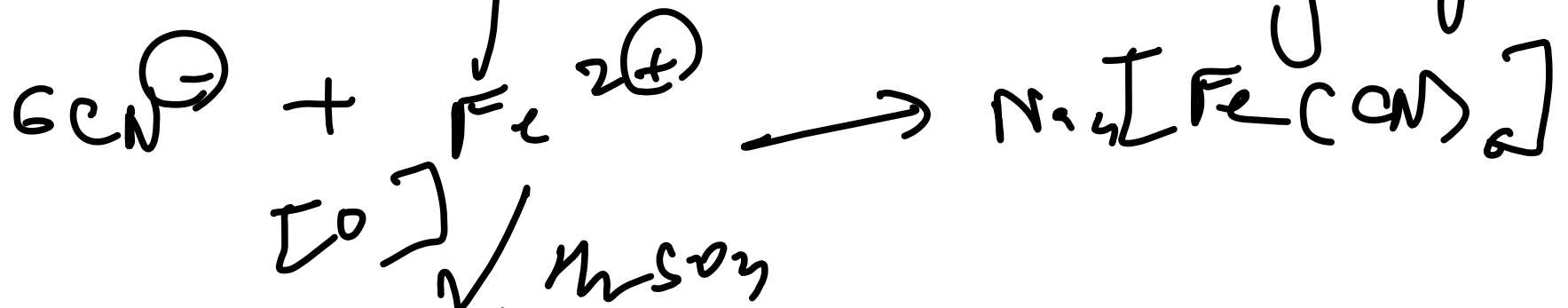


(X = Cl, Br, I)

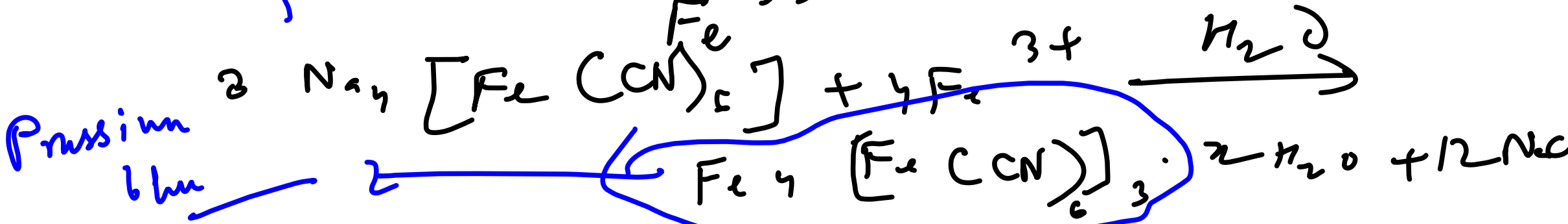
Test for N:

1. Na fusion extract is boiled with Na_2SO_4 & acidified with sulfuric

acid. Appearance of blue coloration confirms the presence of nitrogen. NaCN formed in Lassaigne's test first reacts with FeSO_4 to form sodium hexacyanoferrate(II).

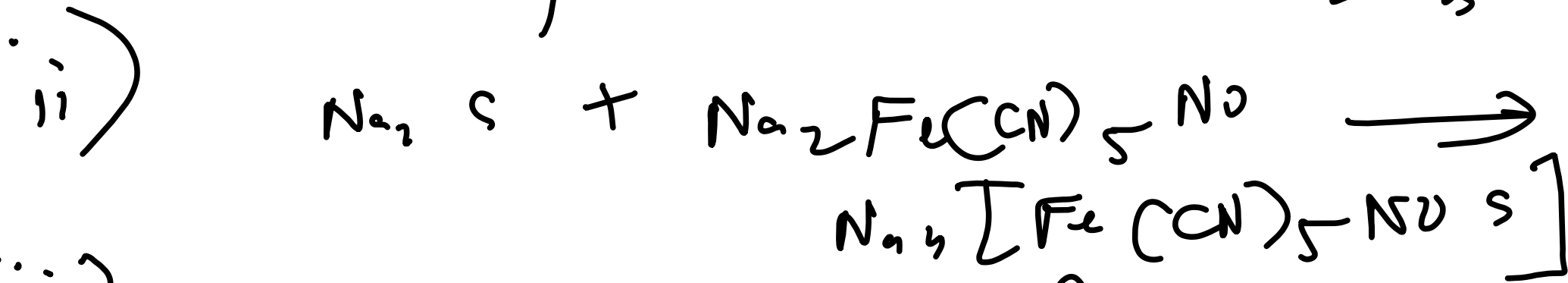
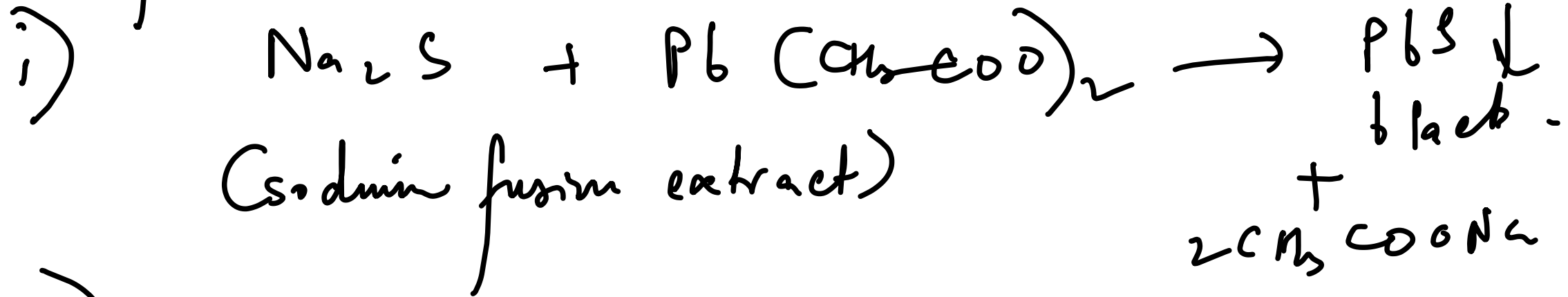


nitrogen



Prussian blue

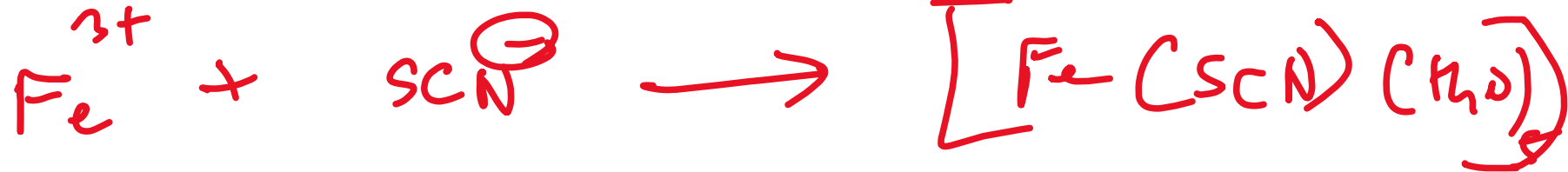
Test for S:



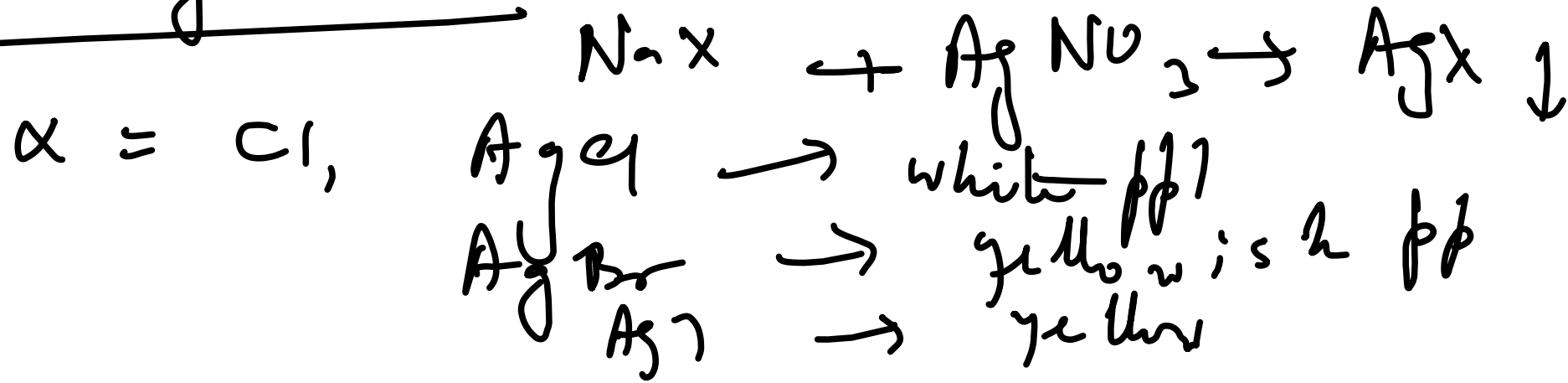
iii) If both N & S are present, sodium thiocyanate is formed in fusion mixture. Blue-violet complex.

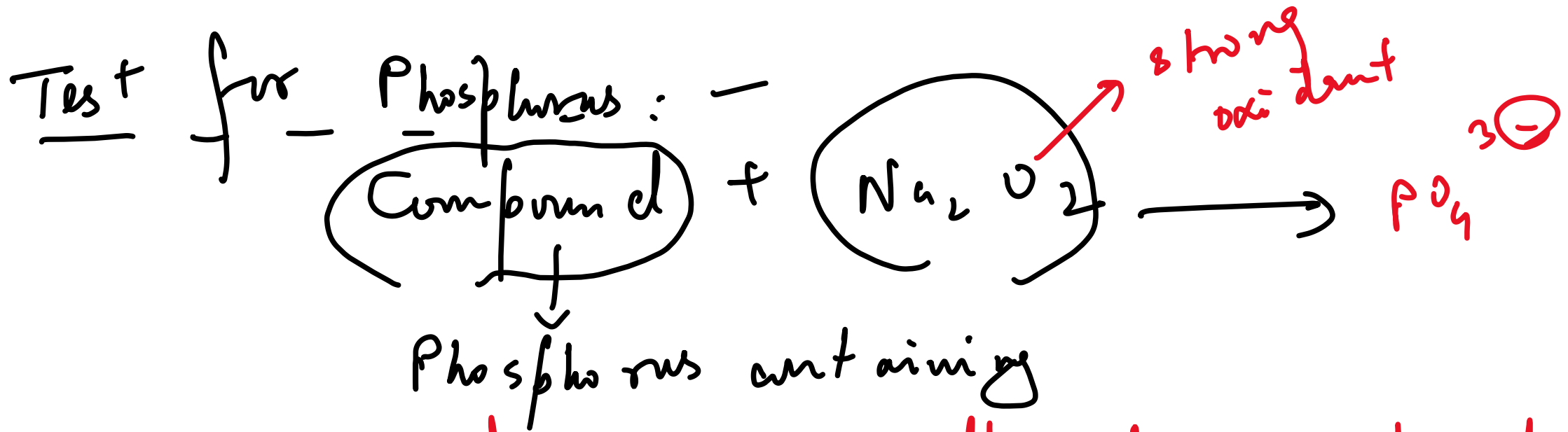


Blood red coloration



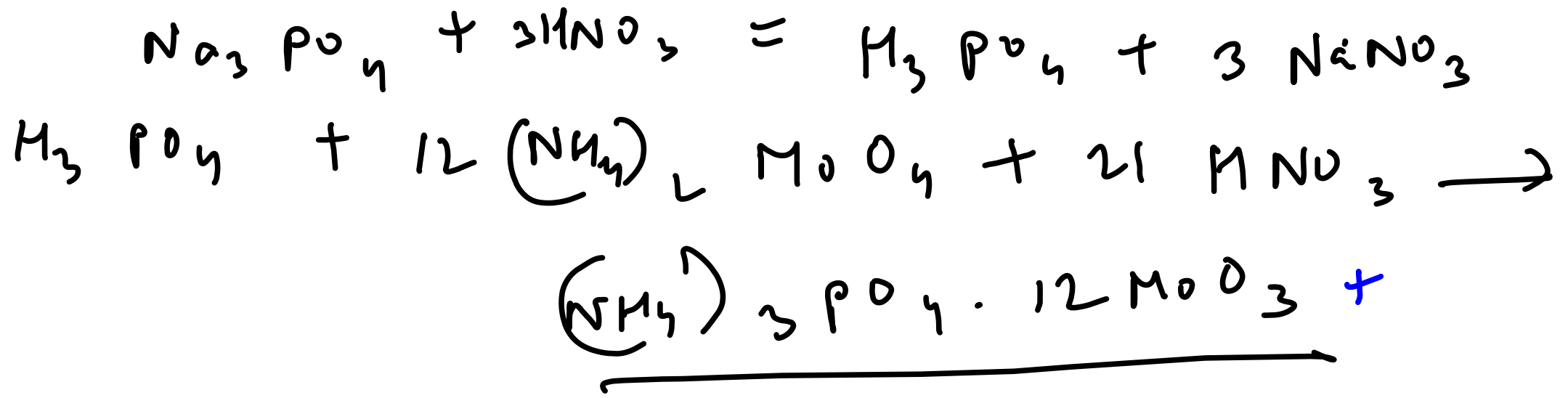
Test for halogens





Na_2O_2 oxidizes P in the test compound to phosphate.

Ammonium molybdate is added in the presence of strongly acidic solution of HNO_3 which reacts with the PO_4^{3-} to form a canary yellow ppt. of ammonium molybdate.



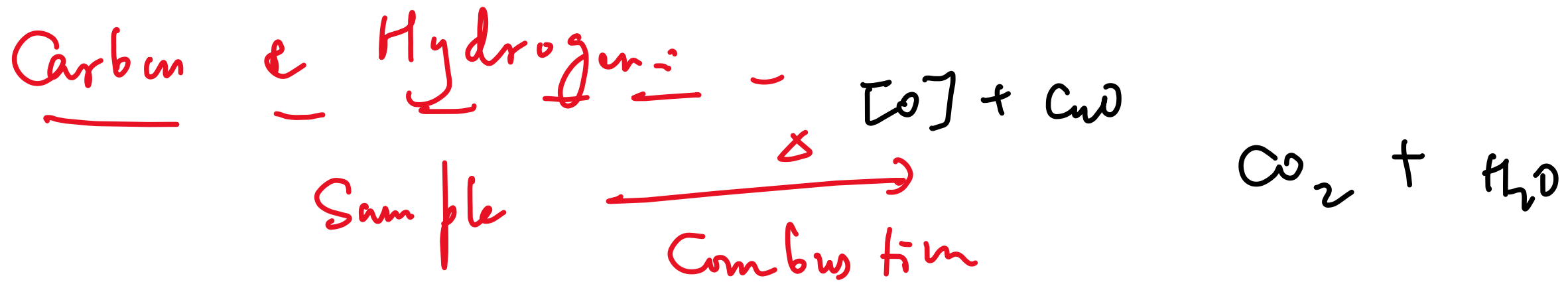
Ammonium phosphomolybdate



Arsenic also gives similar reaction under boiling conditions. To distinguish between P & As with Arsenic, the filtrate is heated with silver nitrate (AgNO_3) \rightarrow Brown ppt.

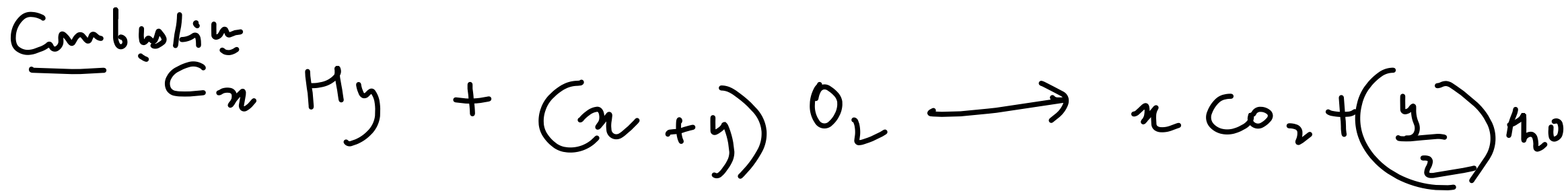
Quantitative Analysis —
↓

Qualitative analysis → identity confirmation
Quantitative " → amount of each elements



(Leibig's combustion tube)

Combustion



The amounts formed are determined by passing these through previously weighed U-tubes containing concentrated solution of KOH & anhydrous $CaCl_2$, respectively, and determining the increase in their mass.

If nitrogen, sulphur & halogens are also present in the organic compound, the

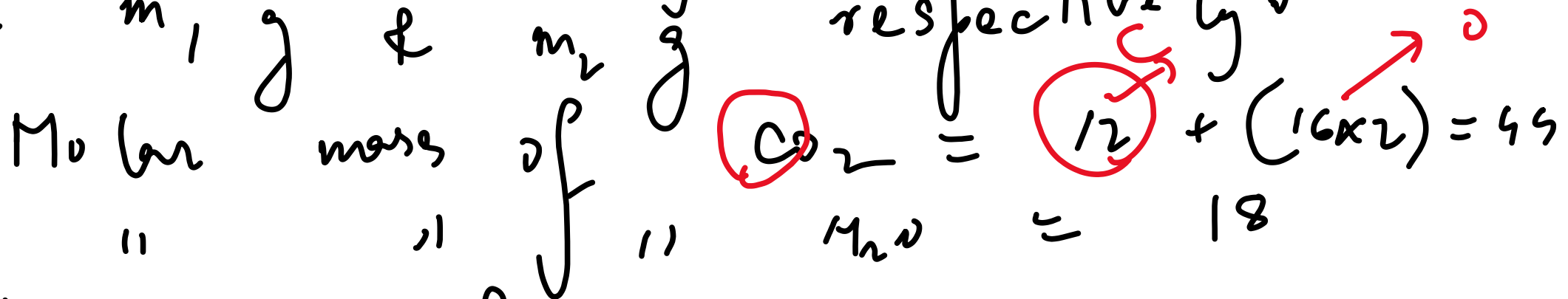
apparatus is modified to include a copper spiral for decomposing oxides of N.

Cu spiral → Decompose N-oxides
Silver gangue → Sulfur & halogen oxidation
Prevention of absorption of N, S, & Ag in KOH tube.

Calculation: From the mass of H_2O & CO_2 obtained, we can calculate the

% of C & H in the organic compound.

Let the mass of organic compound be m g
 & the amount of CO_2 & H_2O formed
 be m_1 g & m_2 g respectively



The amount of C in 44 gm CO_2 is -
 $44 \text{ g } \text{CO}_2 \rightarrow 12 \text{ g C}$
 $m_1 \text{ g } \text{CO}_2 \rightarrow \frac{12}{44} \times m_1$

$\frac{\%}{\text{H}_2\text{O}: 18\text{g}}$ of C: $\frac{12}{44} \times \frac{m_1}{m} \times 100$

$\frac{\%}{\text{H}_2\text{O}: 18\text{g}}$ of H: $\frac{2}{18} \times \frac{m_2}{m} \times 100$

Nitrogen Quantification

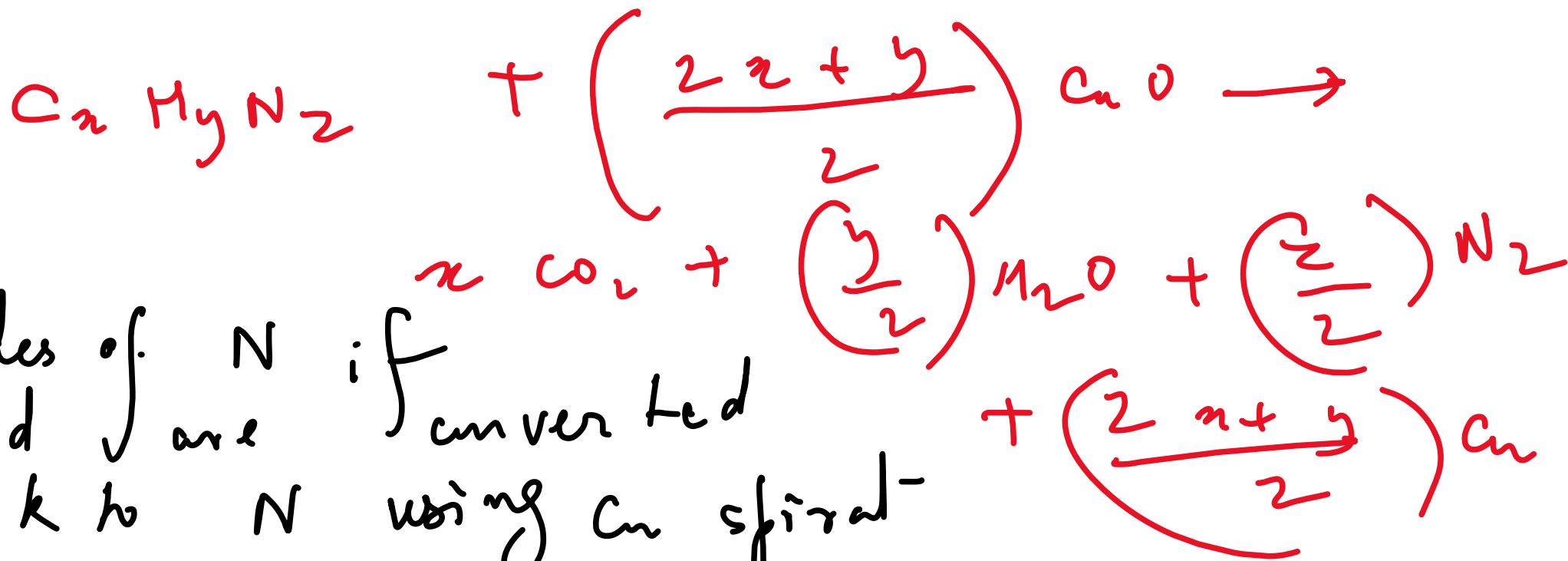
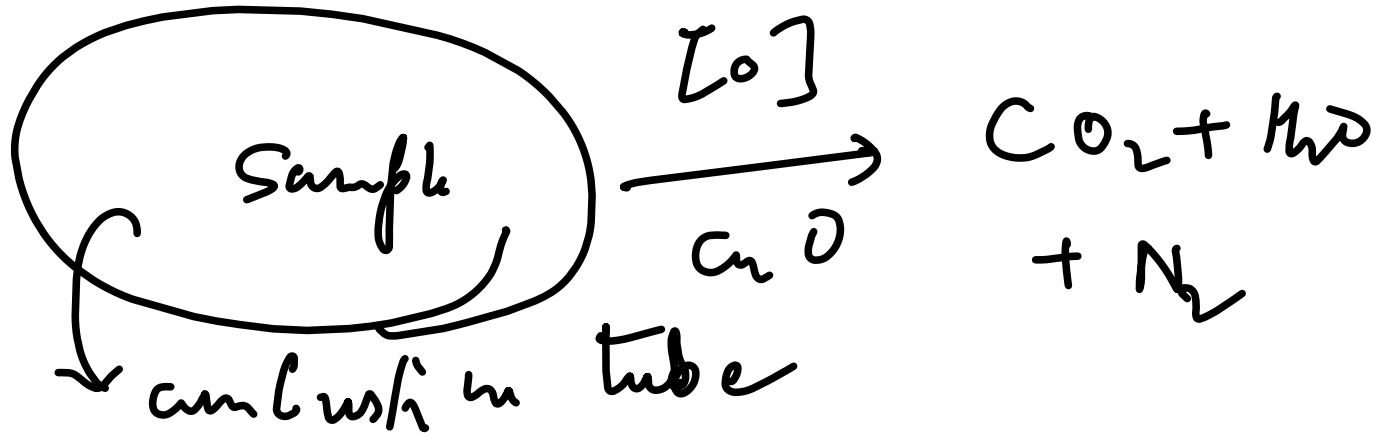
↓
Duma's method

↓
Conversion to N

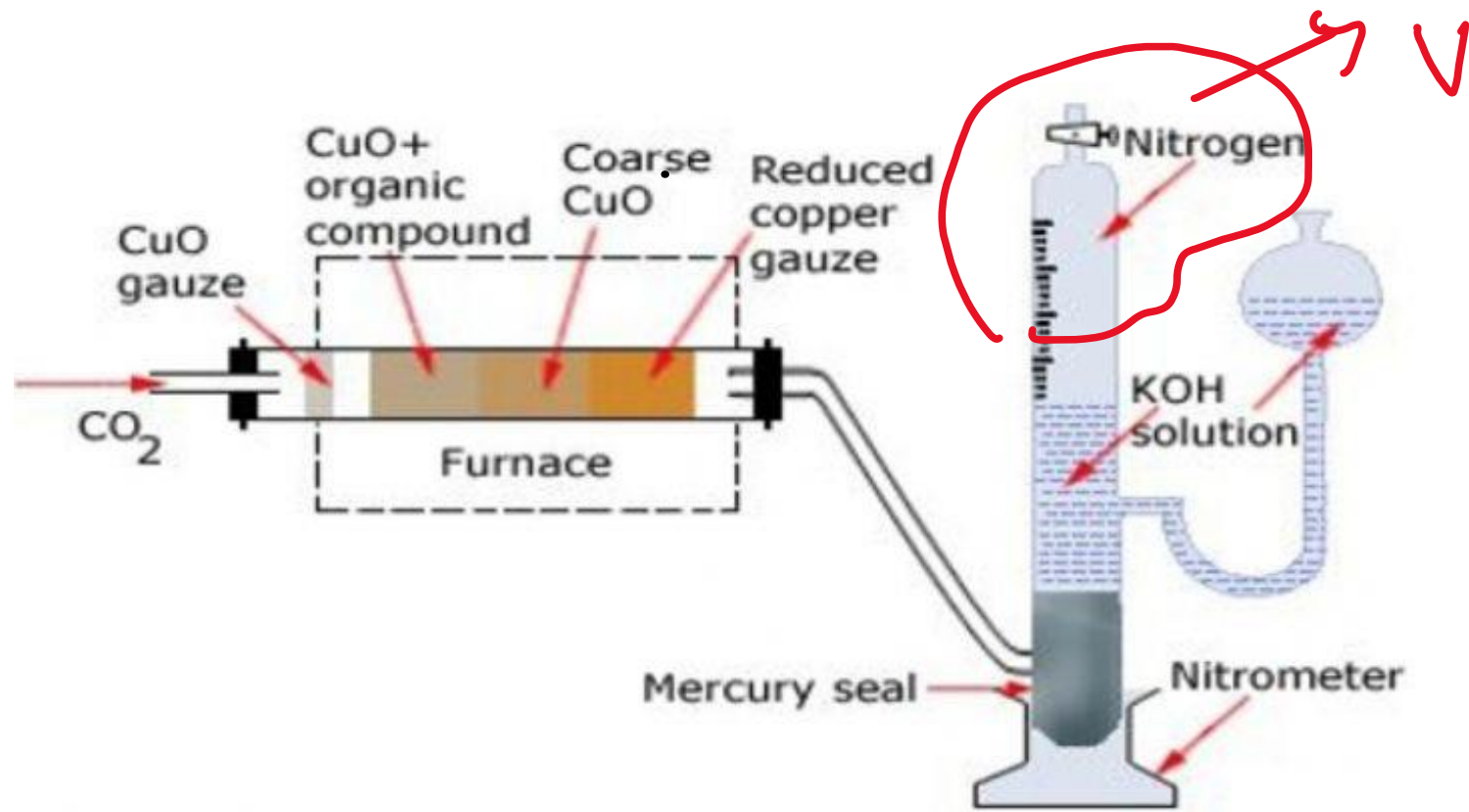
↓
Kjeldahl's method

↓
Conversion to NH_3
followed by titration
with std. acid

Dumas's method



Oxides of N if converted back to N using Cu spiral-



CO₂ formed is absorbed in the KOH soln. & N₂ is collected in the upper part of the graduated tube.

Calculation :

Let the mass of organic compound = m g
 " " volume of N₂ collected = V_1 ml
 room temp. = T_1 K.

Then the volume of gas collected at STP is

$$V = \frac{p_1 v_1 \times 273}{760 \times T}$$

where p_1 is pressure of N_2 which is diff. from atm pressure at which the gas is collected.

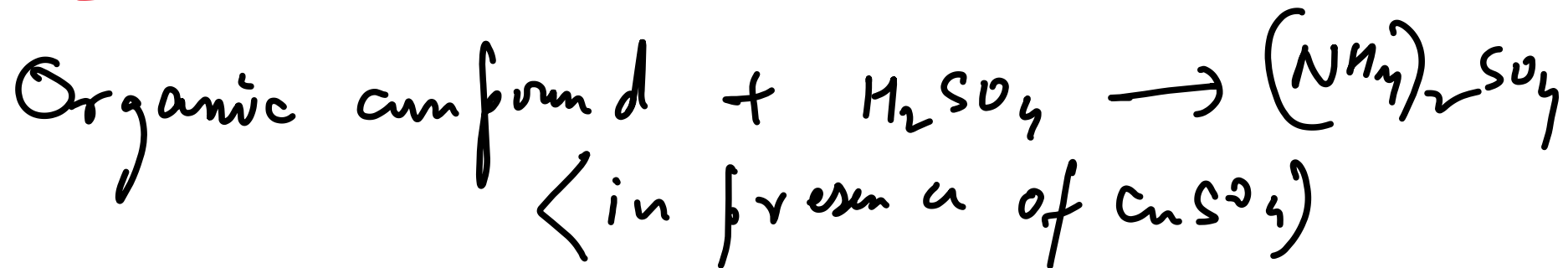
Corrected pressure (p_1) = atm pressure of vapour pressure $\frac{z}{4}$ aqueous tension

Using the relation that 22400 ml of N_2 at S.T.P weighs - 28 g

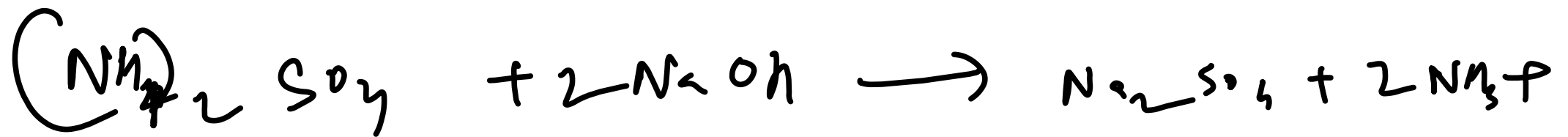
V ml of N_2 gas weighs $\frac{V \times 28}{22400}$

$$\% N_2 = \frac{V \times 28 \times 100}{22400 \times m} \%$$

Kjeldahl's method:



The soln. containing $(\text{NH}_4)_2\text{SO}_4$ is heated with excess NaOH to liberate NH_3 which is absorbed by H_2SO_4



Calculation: Let the mass of organic compound taken = m .
 molecular weight M & V ml of H_2SO_4 of
 of molecular weight M used for titration of NaOH

excess acid is $\sim V_1$ ml.

We know that for soln. of same molarity,
 V_1 ml. of $\text{NaOH} \equiv V_1/2$ ml. H_2SO_4

Vol. of H_2SO_4 left un consumed after
absorption of $\text{NH}_3 = (V - V_1/2)$ ml.

If molarity of NH_3 soln. is M ,
then $(V - V_1/2)$ ml of H_2SO_4
 $= 2(V - V_1/2)$ ml of NH_3 .
1000 ml. of 1M. soln. of NH_3 contains

179 NH_3 or 14 g N.

2 $(V - V_{1/2})$ ml NH_3 soln. of
 molarity M contains —

$$14 \times M \times 2 (V - V_{1/2})$$

$$\% N = \frac{14 M \times 2 (V - V_{1/2})}{1000} \times \frac{100}{m}$$

Exception

NO_2 , As_2O_3 ,
 hetero dydic compounds does not respond
 as N present in them does not get %

converted to $(\text{NH}_4)_2\text{SO}_4$ under test conditions.

Problems:

1.4 g of an organic compound was digested according to Kjeldahl's method & the ammonia evolved was absorbed in 60 ml. of $\text{M}/10 \text{ H}_2\text{SO}_4$ solution. The excess H_2SO_4 requires 20 ml. of $\text{M}/10 \text{ NaOH}$ solution for neutralization. The % of N in the compound is

i) 3 ii) 5 iii) 90 iv) 24

% of N = $1.4 \times \text{m. eq. of } \text{H}_2\text{SO}_4 \text{ used to neutralize } \text{NH}_3$

Mass of the compound

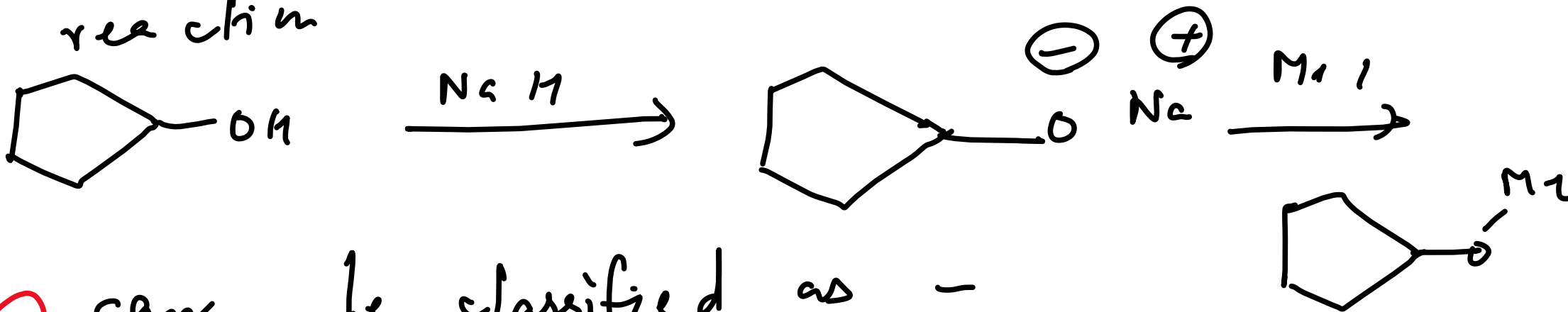
$$= 1.4 \times \left(60 \times \frac{1}{10} \times 2 - 20 \times \frac{1}{10} \right)$$

14

$$= 10\%$$

Problems:

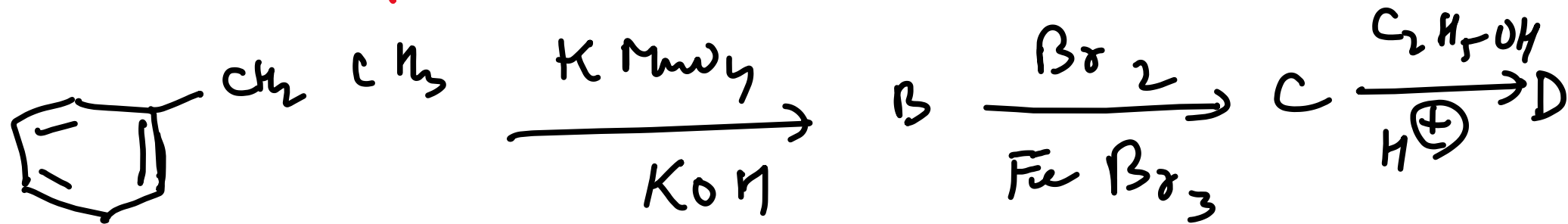
1. The reaction



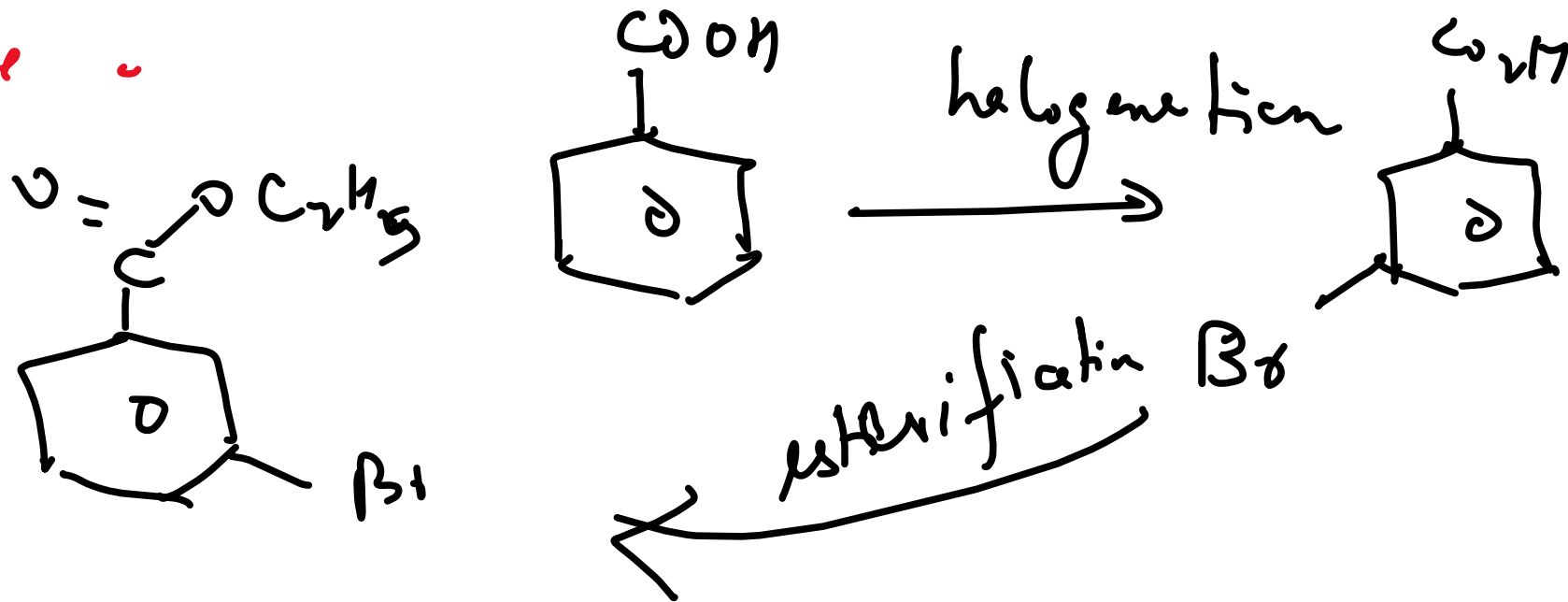
can be classified as -

- i) ✓ William son ether synthesis reaction -
- ii) Alcohol formation reaction
- iii) Dehydration reaction
- iv) William son alcohol synthesis reaction.

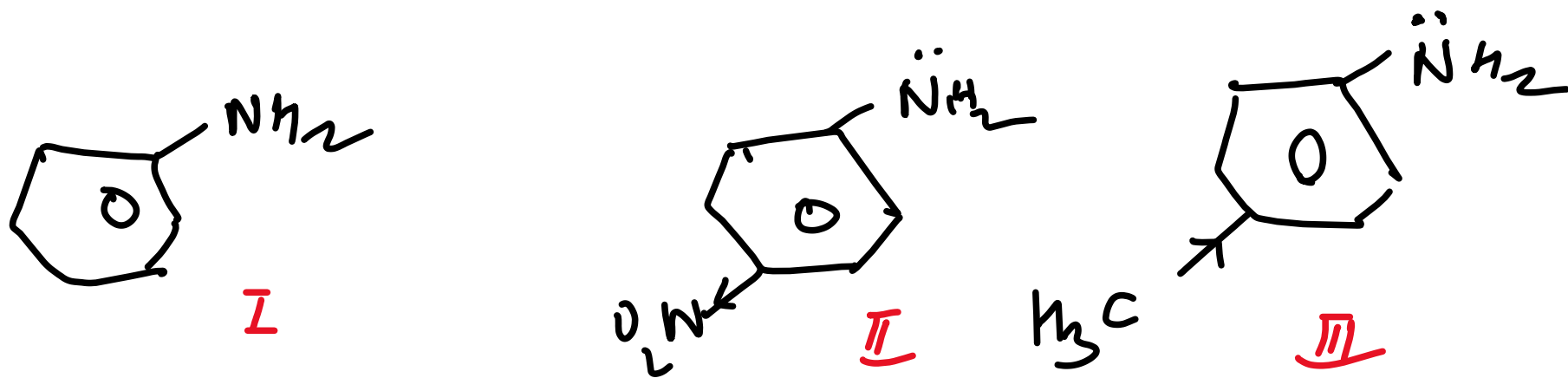
2. In a set of reaction, ethyl benzene yields a product D.



D would be -



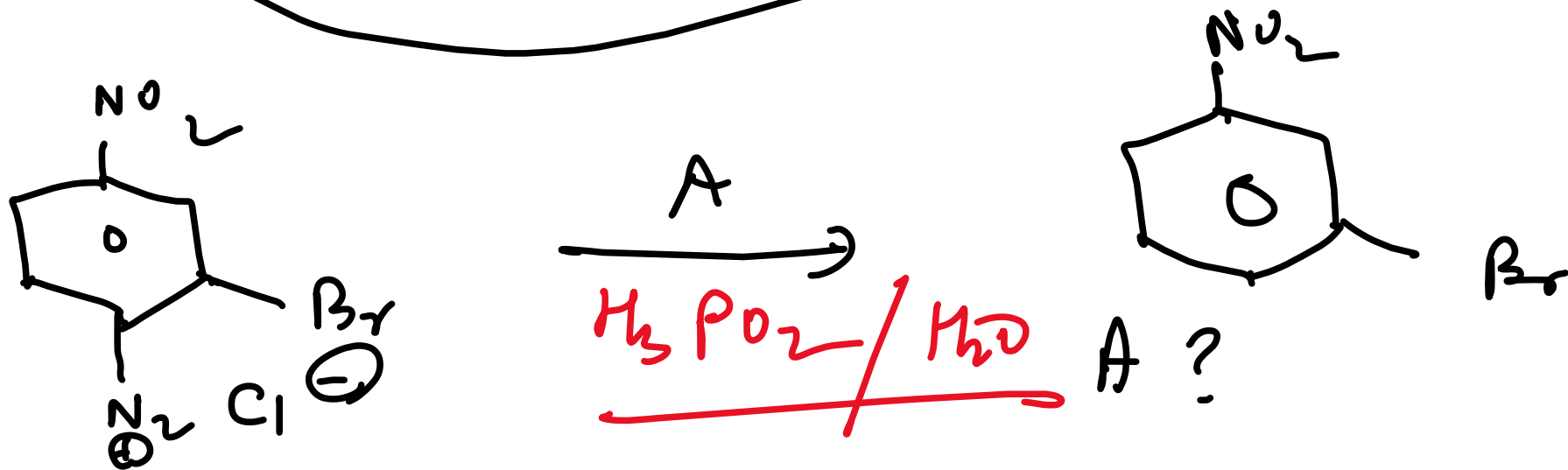
3.

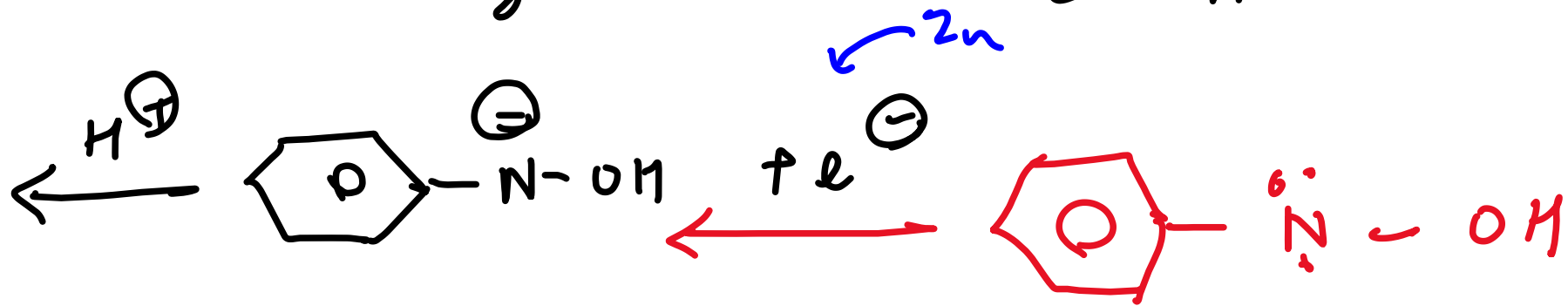
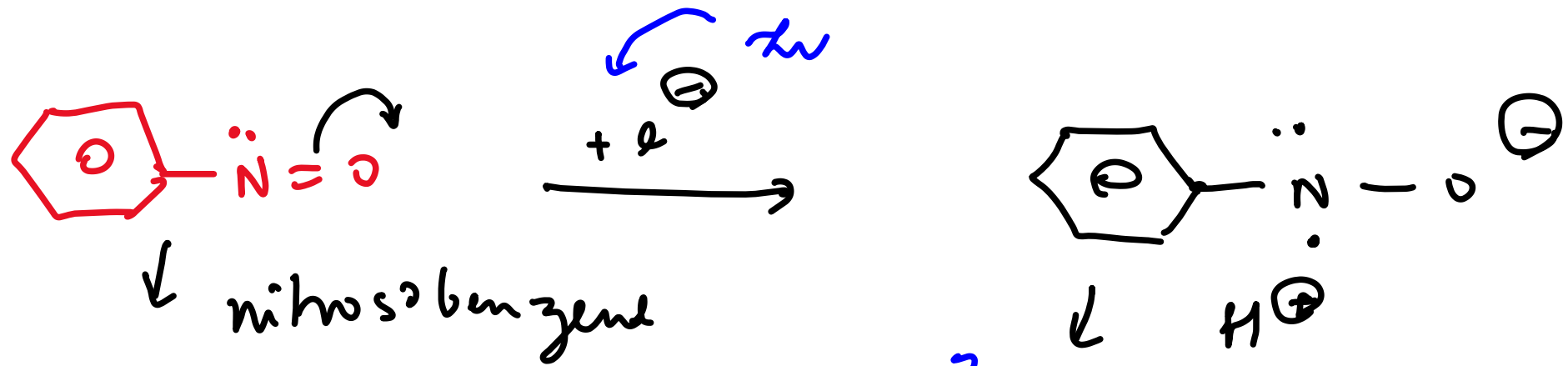


Correct in increasing order of base strength



4.



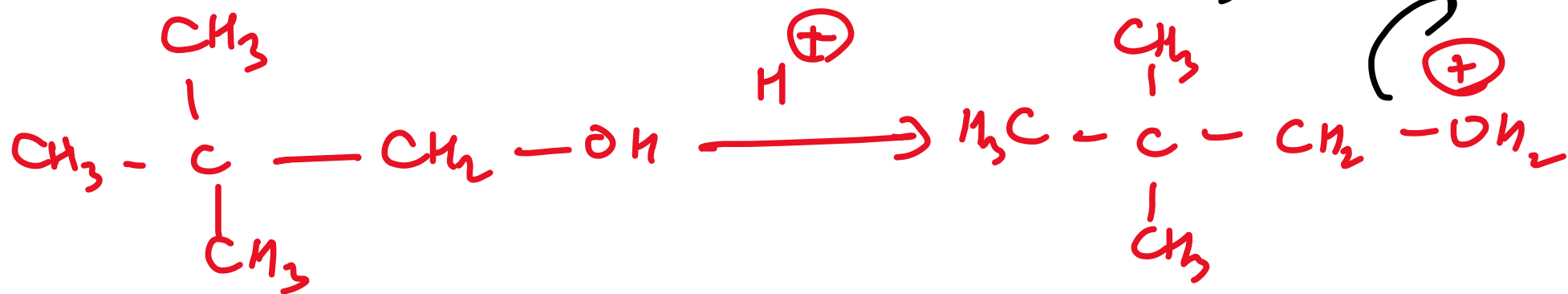
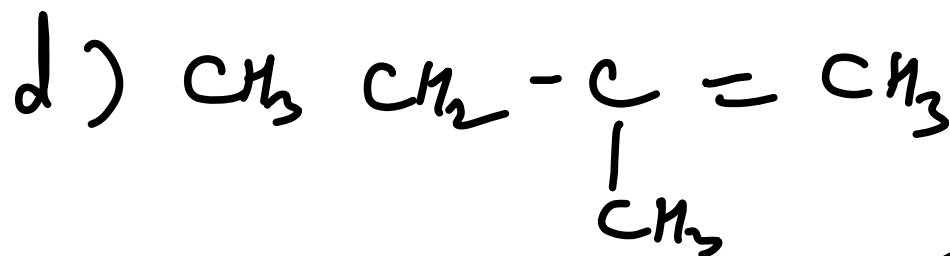
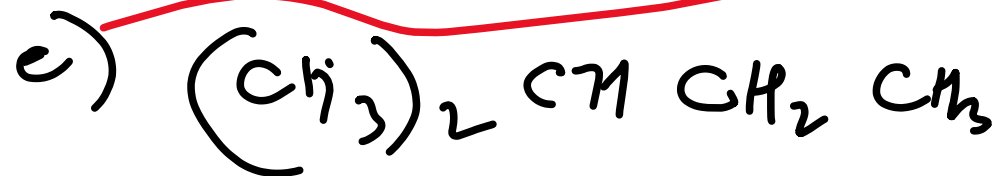
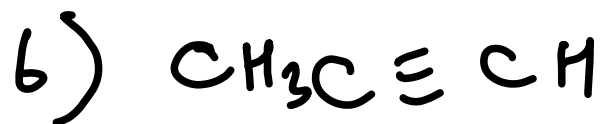
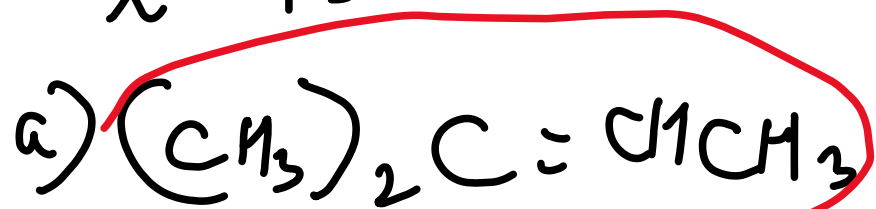


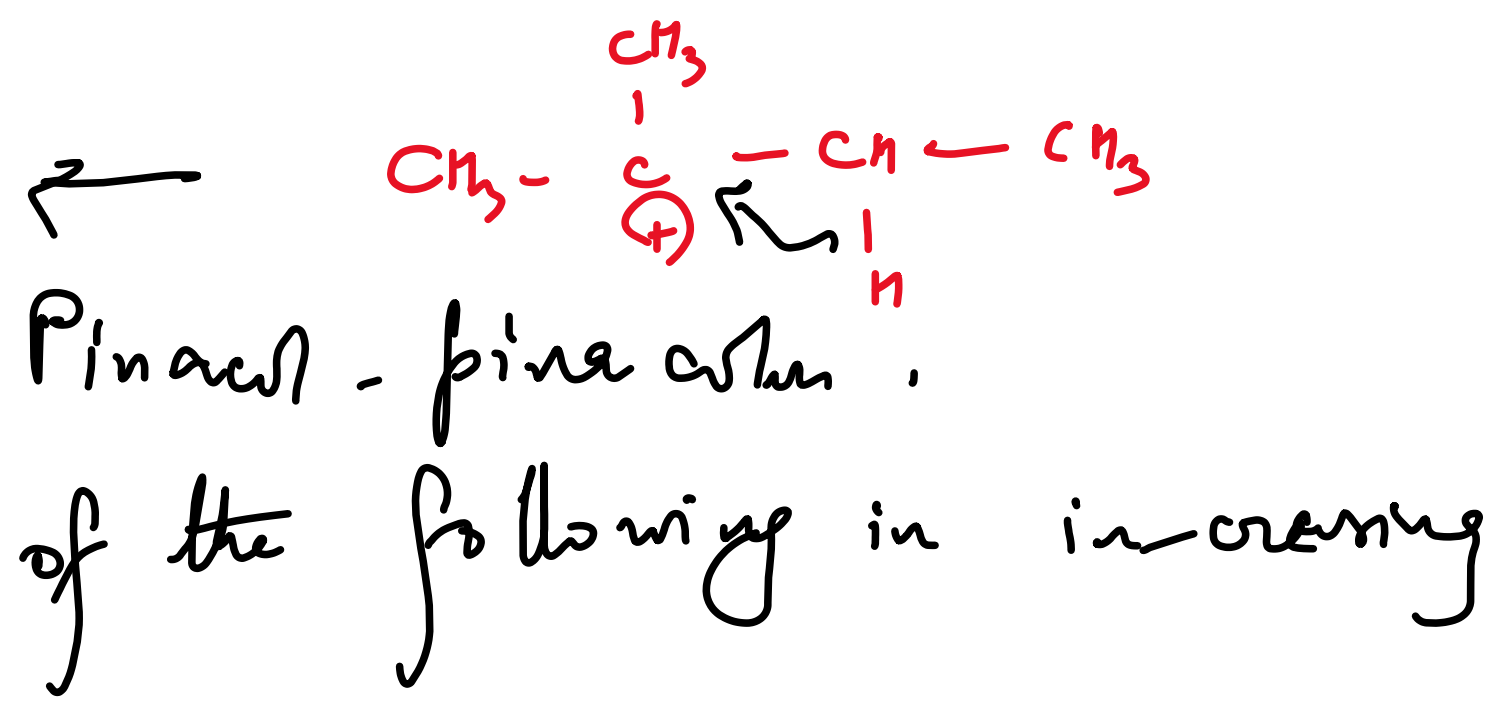
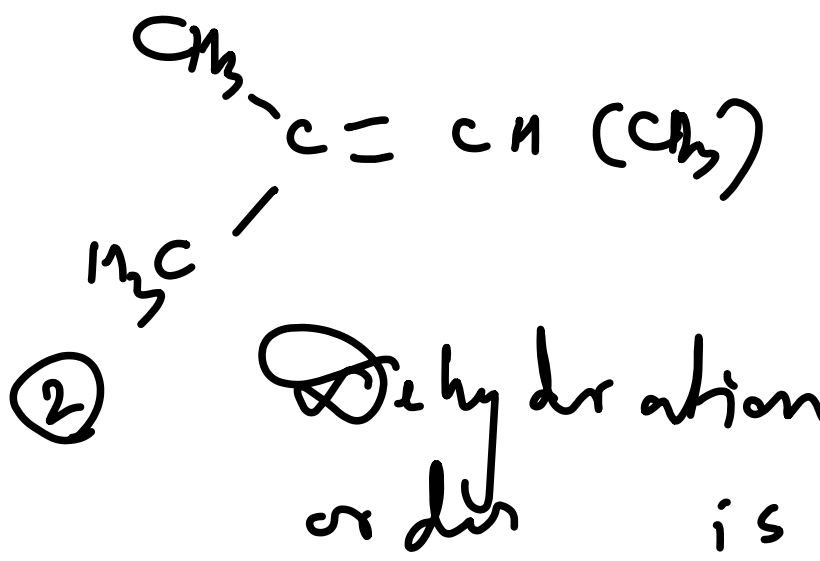
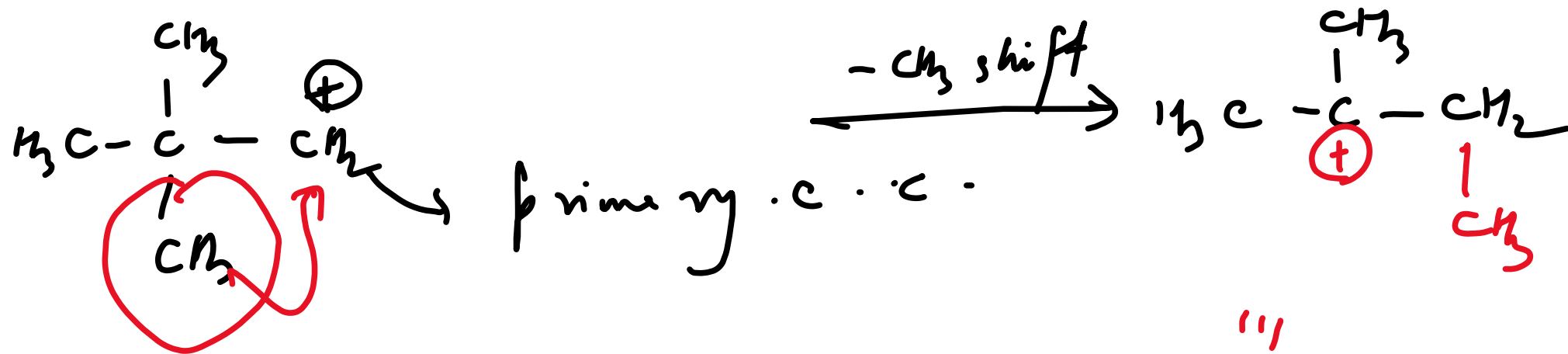
Phenyl hydroxylamine

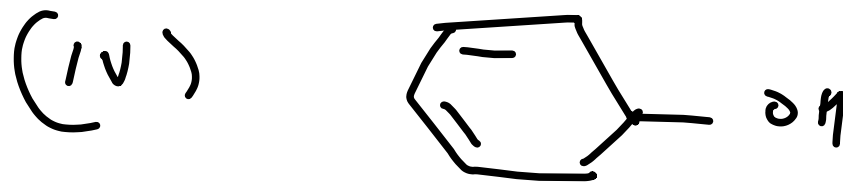
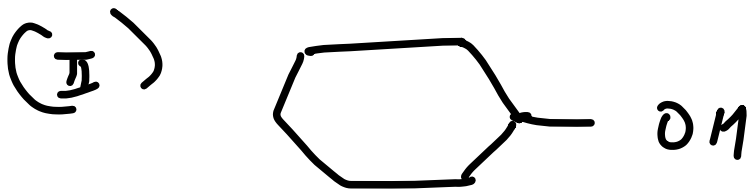
Problems

In the reaction, $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{OH} \xrightarrow[170^\circ\text{C}]{\text{conc. H}_2\text{SO}_4} \text{X}$

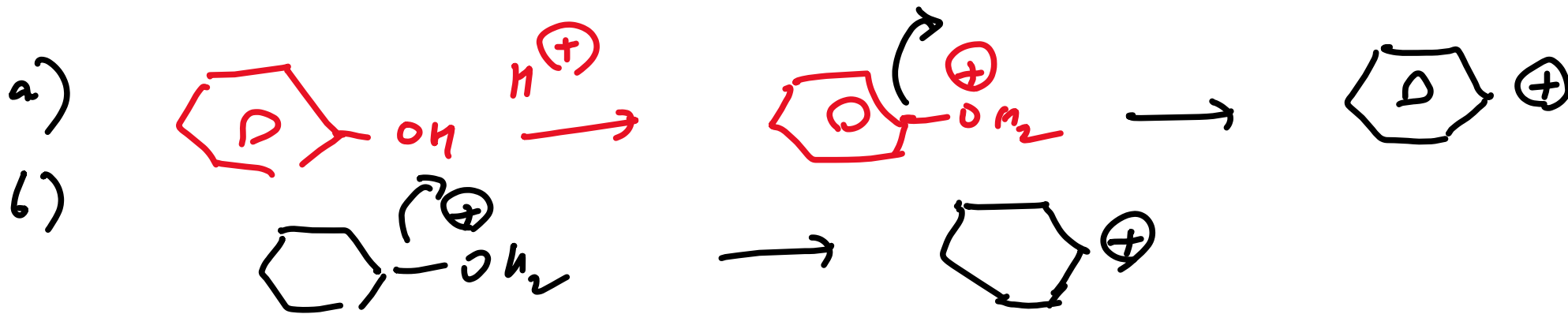
X is

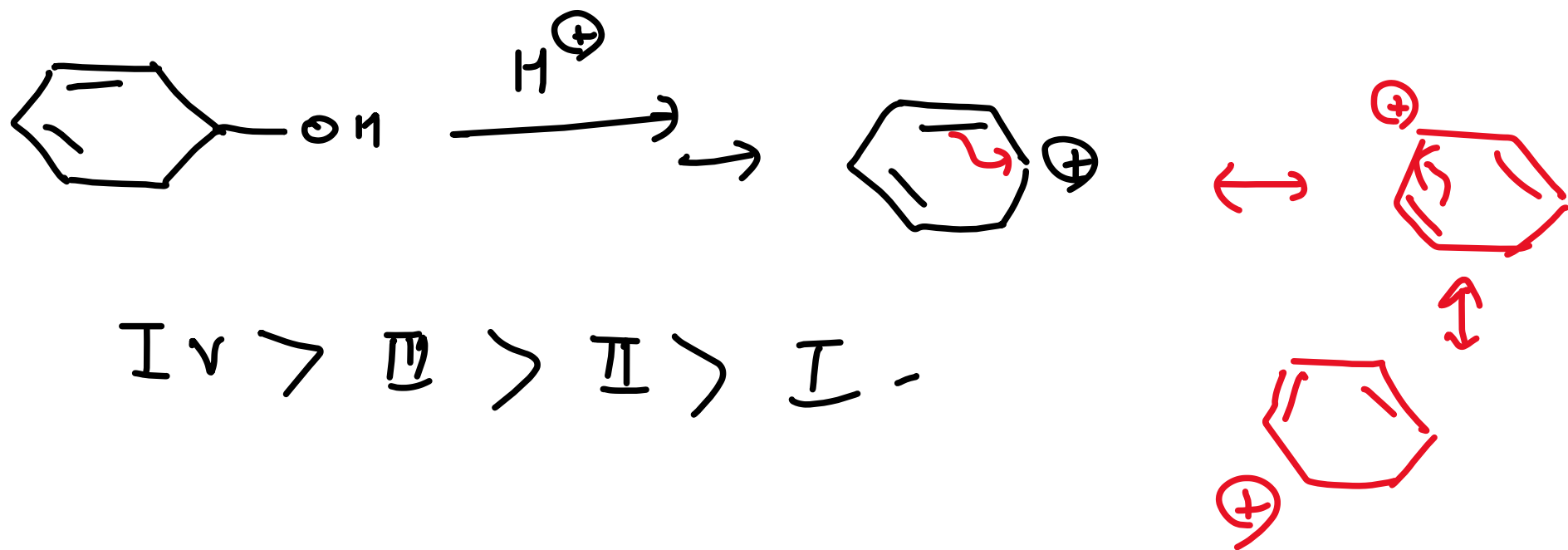
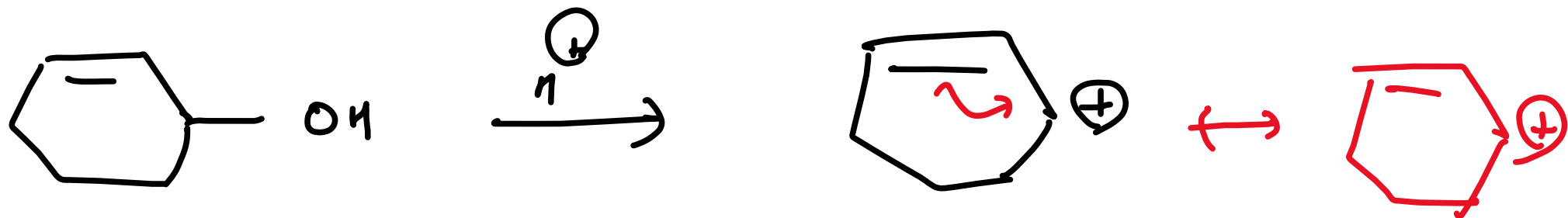






- a) I < II < III < IV b) II < III < IV < I
- c) I < IV < IV < II d) None of these





$IV > III > II > I -$

