



# **PURIFICATION AND CHARACTERISATION OF ORGANIC COMPOUNDS - II**



# Objectives

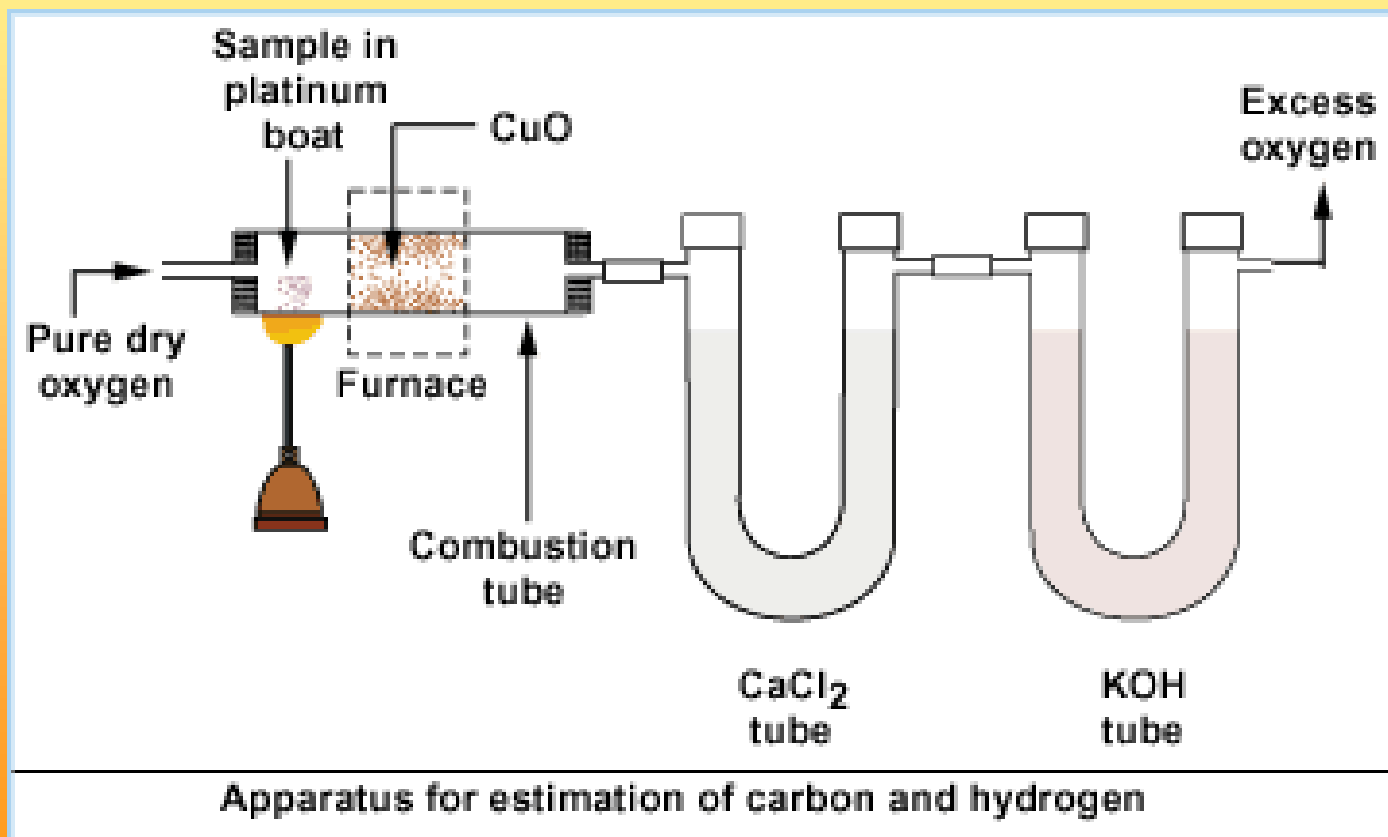
- **Methods of purification of organic compounds**
- **Detection of elements in compounds**
- **Quantitative analysis of organic compounds**
- **Determination of empirical and molecular formula**

# Estimation of carbon (C) & hydrogen (H)

$$\% \text{ of Carbon (C)} = \frac{12}{44} \times \frac{\text{mass of CO}_2 \text{ evolved}}{\text{mass of organic compound taken}} \times 100$$

$$\% \text{ of Hydrogen (H)} = \frac{2}{18} \times \frac{\text{mass of H}_2\text{O formed}}{\text{mass of organic compound taken}} \times 100$$

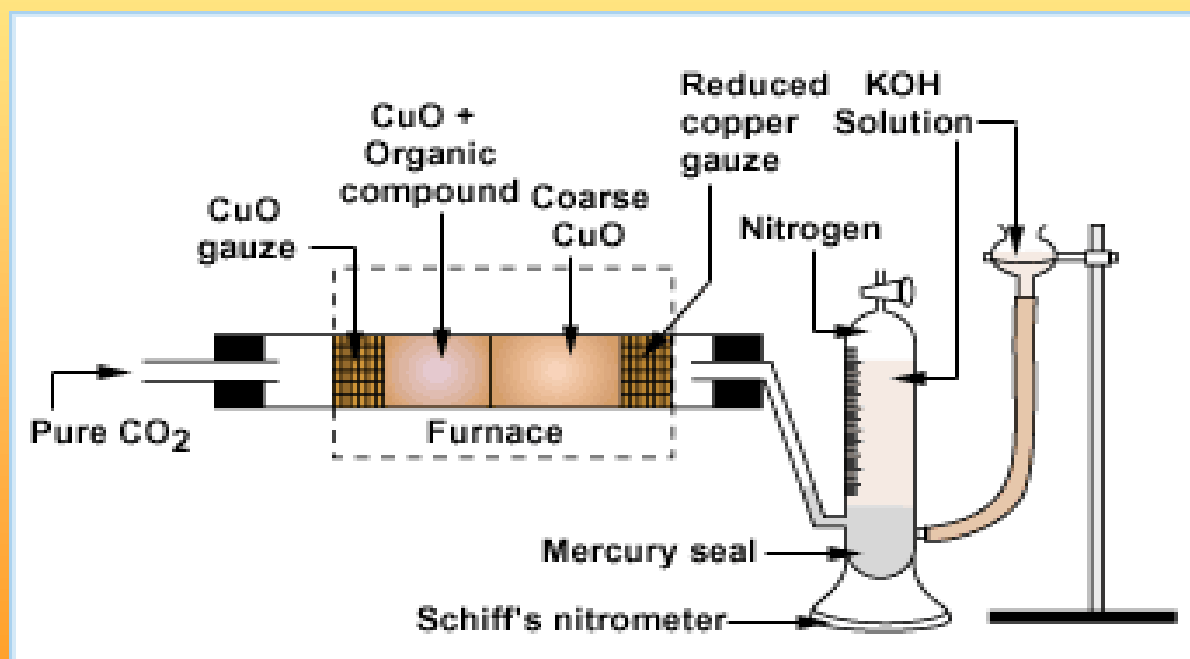
# Estimation of carbon (C) & hydrogen (H)



# Estimation of nitrogen

Duma's method:

$$\% \text{ of N} = \frac{28}{22400} \times \frac{\text{Volume of N at STP}}{\text{Mass of organic compound}} \times 100$$



Apparatus for the estimation of nitrogen by Duma's method



# Estimation of nitrogen

Kjeldahl's method:

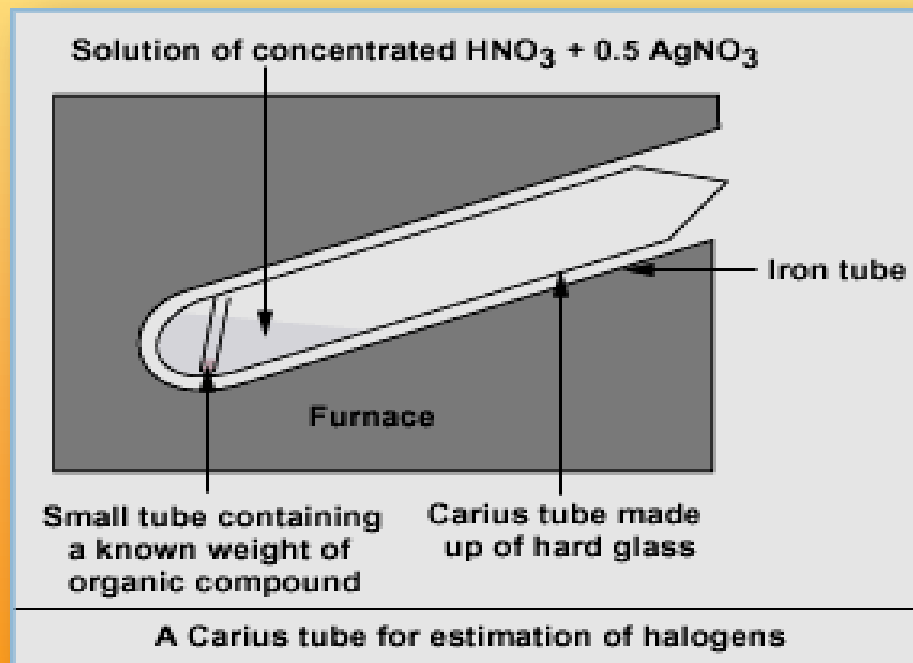
$$\% \text{ of N} = \frac{1.4 \times \text{Volume of acid} \times \text{normality of acid used}}{\text{Mass of organic compound taken}}$$

# Estimation of halogens (Carius method)

% Halogen

$$= \frac{\text{At.wt. of halogen}}{\text{M.wt. of AgX}} \times \frac{\text{Mass of AgX}}{\text{Mass of organic compound}} \times 100$$

Atomic mass of Ag	= 108
Atomic mass of F	= 19
Atomic mass of Cl	= 35.5
Atomic mass of Br	= 80
Atomic mass of I	= 127



# Dumas method

From organic compound,



From organic compound,



From organic compound,





# Calculation

**Weight of organic compound taken for combustion = Wg**

**Volume of nitrogen collected =  $V_1 \text{ cm}^3$**

**Atmospheric pressure = P mm of mercury**

**Room temperature =  $t^\circ\text{C} = (273 + t)\text{K} = T_1\text{K}$**

**Aqueous tension at  $t^\circ\text{C}$  = p mm of mercury**

**$\therefore$  Pressure of dry nitrogen at  $t^\circ\text{C}$  temp.**

**= Atmospheric pressure –  
Aqueous tension**

**=  $(P - p)$  mm of the mercury**

**=  $P_1$  mm Hg**

# Calculation

To find the volume of nitrogen at STP:

In experimental conditions:

Pressure of nitrogen =  $P_1$  mm Hg

Temperature =  $T_1$  K

Volume of nitrogen =  $V_1$  cm<sup>3</sup>

In STP conditions:

Pressure of nitrogen ( $P_2$ ) = 760 mm Hg

Temperature ( $T_2$ ) = 273 K

Volume of nitrogen ( $V_2$ ) = ?

Applying gas equation,

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

$$\therefore V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{P_1 V_1 \times 273}{760 \times T_1} = X \text{ cm}^3$$



# Calculation

**$\therefore$  Volume of nitrogen gas at STP =  $X \text{ cm}^3$**

**1 mole of any gas will occupy a volume of  $22,400 \text{ cm}^3$  at STP.**

**$\therefore$  1 mole of  $\text{N}_2$  gas  $22400 \text{ cm}^3$  at STP.**

**$\therefore$  28 g of  $\text{N}_2$  gas  $22400 \text{ cm}^3$  at STP.**

**Thus, a volume of  $22,400 \text{ cm}^3$  at STP will contain 28 g of  $\text{N}_2$  gas.**

# Calculation

∴ **A volume of  $X \text{ cm}^3$  at STP will contain**

$$= \frac{28 \times X}{22400} \text{ g of N}_2$$

∴ **Mass of  $X \text{ cm}^3 \text{ N}_2$  gas at STP**  $= \frac{28 \times X}{22400} \text{ g}$

∴ **Amount of nitrogen present in  $W \text{ g}$  of the**

**organic compound**  $= \frac{28X}{22400} \text{ g}$

∴ **Amount of nitrogen present in  $100 \text{ g}$  of the organic**

**compound**  $= \frac{28X}{22400 \times W} \times 100 \text{ g}$

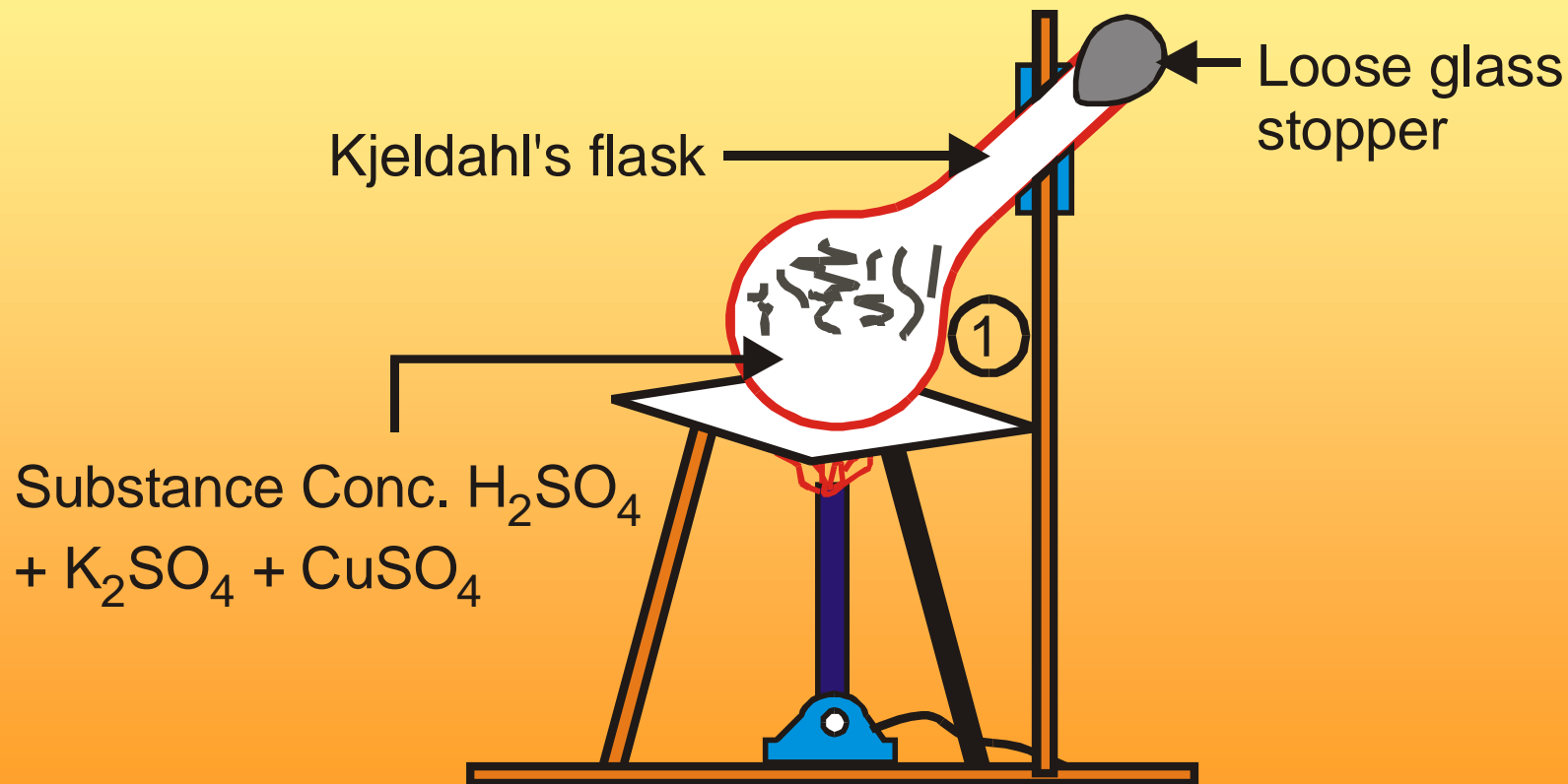


# Calculation

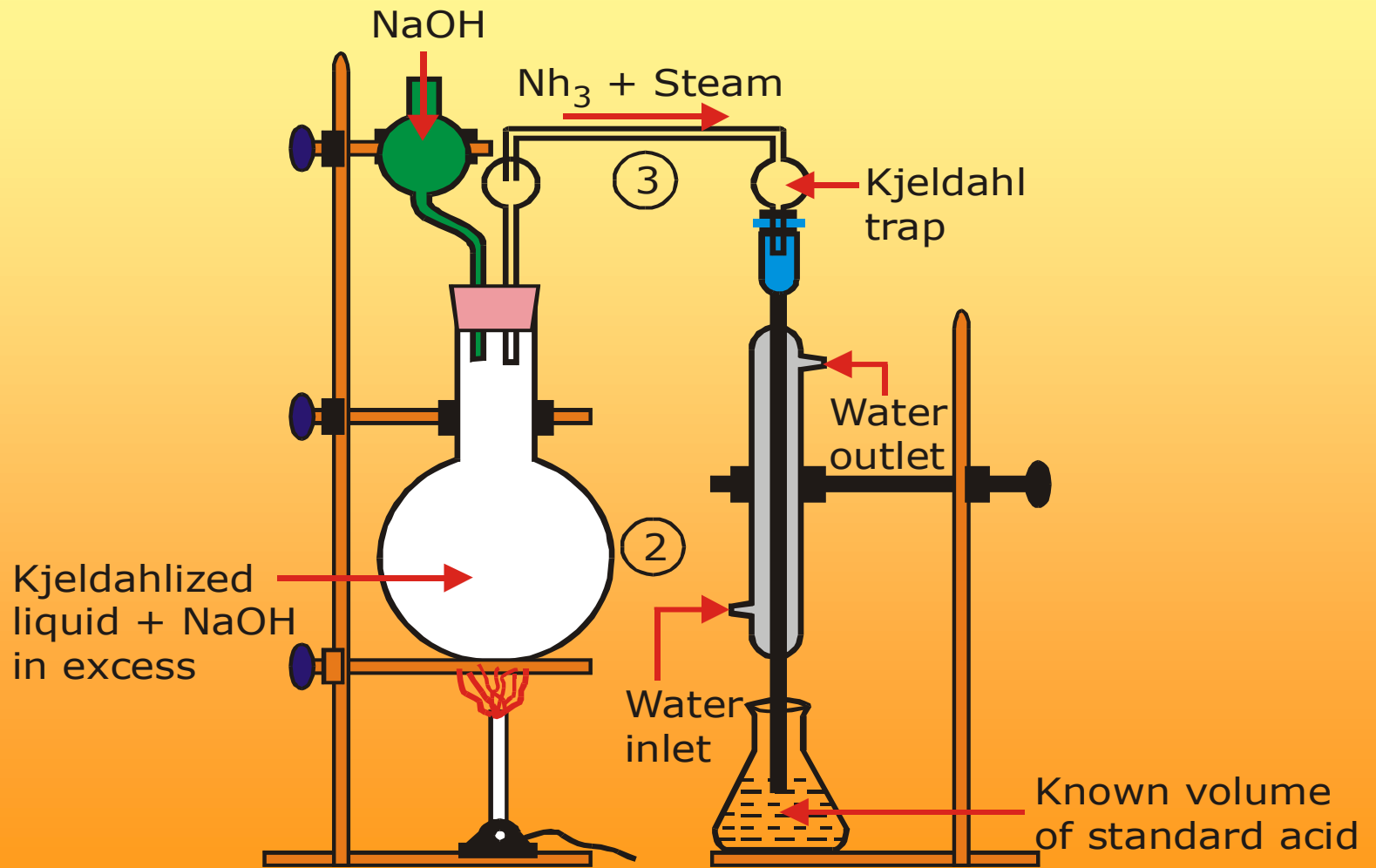
∴ **Percentage of nitrogen present in the organic**

**compound** =  $\frac{28X}{22400 W} \times 100$

# Kjeldahi method



# Kjeldahi method



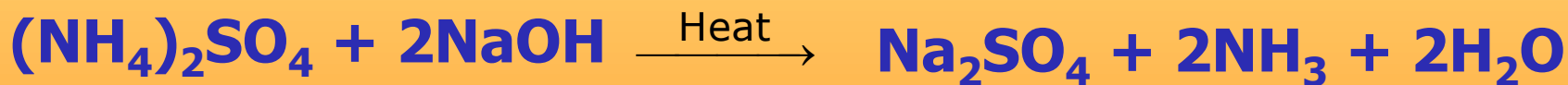
# Reactions involved

Reactions involved are as the following

Nitrogen from organic compound is converted to ammonium sulphate.



Ammonium sulphate reacts with sodium hydroxide to give ammonia gas.



Ammonia is absorbed in sulphuric acid or hydrochloric acid.



# Reactions involved

Excess of  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  remaining unreacted is back titrated using standard alkali.



# Carius method

Reaction involved



Reaction



Sulphur from organic compound



# Reactions involved



Phosphorus from organic compound

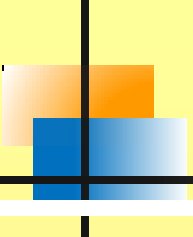




# Estimation of phosphorus (Modified Carius method)

% of Phosphorus (P)

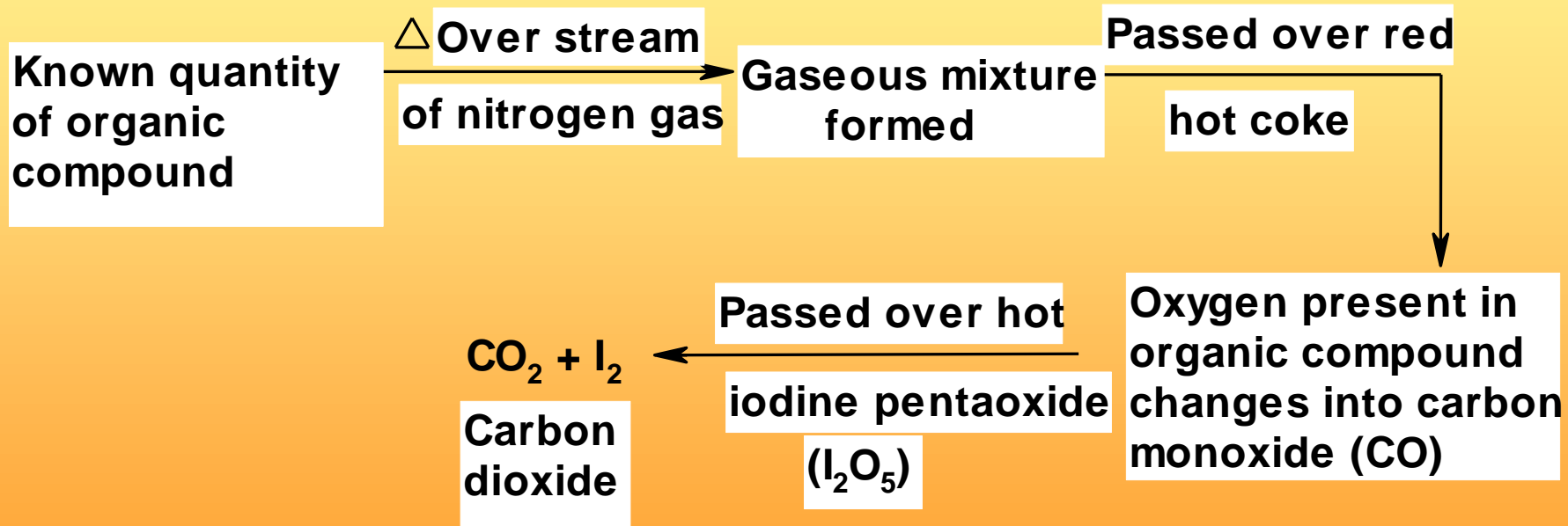
$$= \frac{62}{222} \times \frac{\text{Mass of magnesium pyrophosphate}(\text{Mg}_2\text{P}_2\text{O}_7)}{\text{Mass of organic compound taken}} \times 100$$



# Estimation of Sulphur (Modified Carius method)

$$\% \text{ of Sulphur(S)} = \frac{32}{233} \times \frac{\text{Mass barium sulphate(BaSO}_4\text{) formed}}{\text{Mass of organic compound taken}} \times 100$$

# Estimation of oxygen





# Oxygen

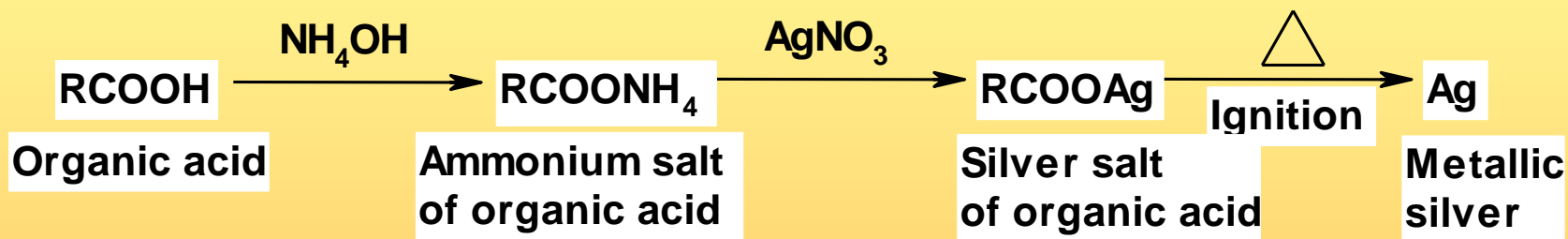
$$\% \text{ of Oxygen(O)} = \frac{32}{44} \times \frac{\text{Mass of Carbon dioxide(CO}_2\text{) formed}}{\text{Mass of organic compound taken}} \times 100$$



# **Determination of molecular mass**

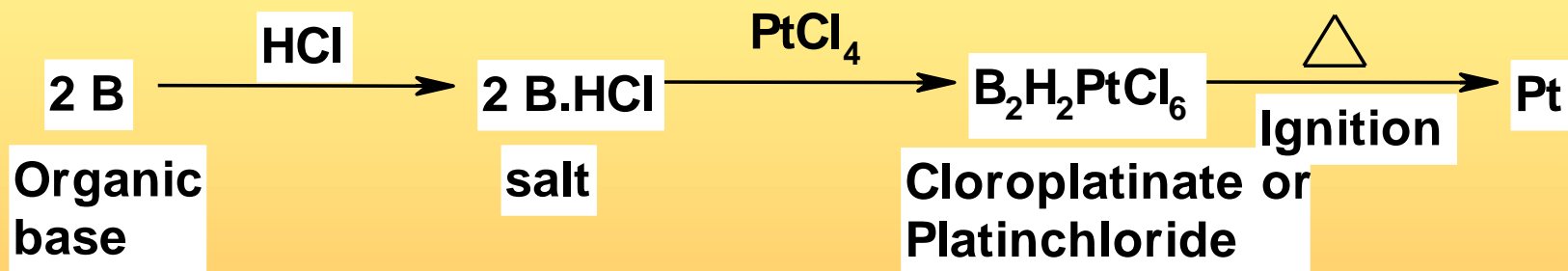
- **Silver salt method**
- **Chloroplatinate method**
- **Victor Meyer method**
- **Volumetric method**
- **Cryoscopic method**
- **Ebullioscopic method**
- **Modern techniques – spectroscopy and X-ray analysis**

# Silver salt method



$$\text{M.wt. of organic acid} = \left[ \left( \frac{\text{Mass of silver salt of organic acid}}{\text{Mass of silver left after ignition}} \times 108 \right) - 107 \right] \times \text{basicity}$$

# Chloroplatinate method



$$\text{M. wt. of organic base} = \left[ \frac{1}{2} \left( \frac{\text{Mass of platinchloride taken}}{\text{Mass of platinum (Pt) as residue}} \times 195 \right) - 410 \right] \times \text{acidity}$$

# Victor Meyer's method

Used for volatile organic compounds.

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

$$\text{M.wt. of organic compound} = \frac{\text{Mass of organic compound}}{\text{Volume of air displaced at NTP}} \times 22400$$



# Volumetric method

**Used for determination of molecular weight of organic acids and bases.**

$$\text{M.wt .of organic acid} = \frac{\text{Mass of acid taken} \times \text{basicity of acid}}{\text{Volume of base taken to neutralise the organic acid} \times \text{Normality of base}} \times 1000$$

$$\text{M.wt .of organic base} = \frac{\text{Mass of base} \times \text{acidity of base}}{\text{Volume of acid used to neutralise the organic base} \times \text{Normality of acid}} \times 1000$$

# Cryoscopic method or depression in freezing point method

$$M = \frac{1000 \times K_f \times W_1}{\Delta T_f \times W_2}$$

**Where**

- m** = molecular weight of solute
- K<sub>f</sub>** = molal depression constant
- W<sub>1</sub>** = mass of solute
- W<sub>2</sub>** = mass of solvent
- Δ T<sub>f</sub>** = depression in freezing point

# Ebullioscopic or elevation in boiling point method

$$M = \frac{1000 \times K_b \times W_1}{\Delta T_b \times W_2}$$

**Where**

- m** = molecular weight of solute
- K<sub>b</sub>** = molal depression constant
- W<sub>1</sub>** = mass of solute
- W<sub>2</sub>** = mass of solvent
- Δ T<sub>b</sub>** = depression in freezing point



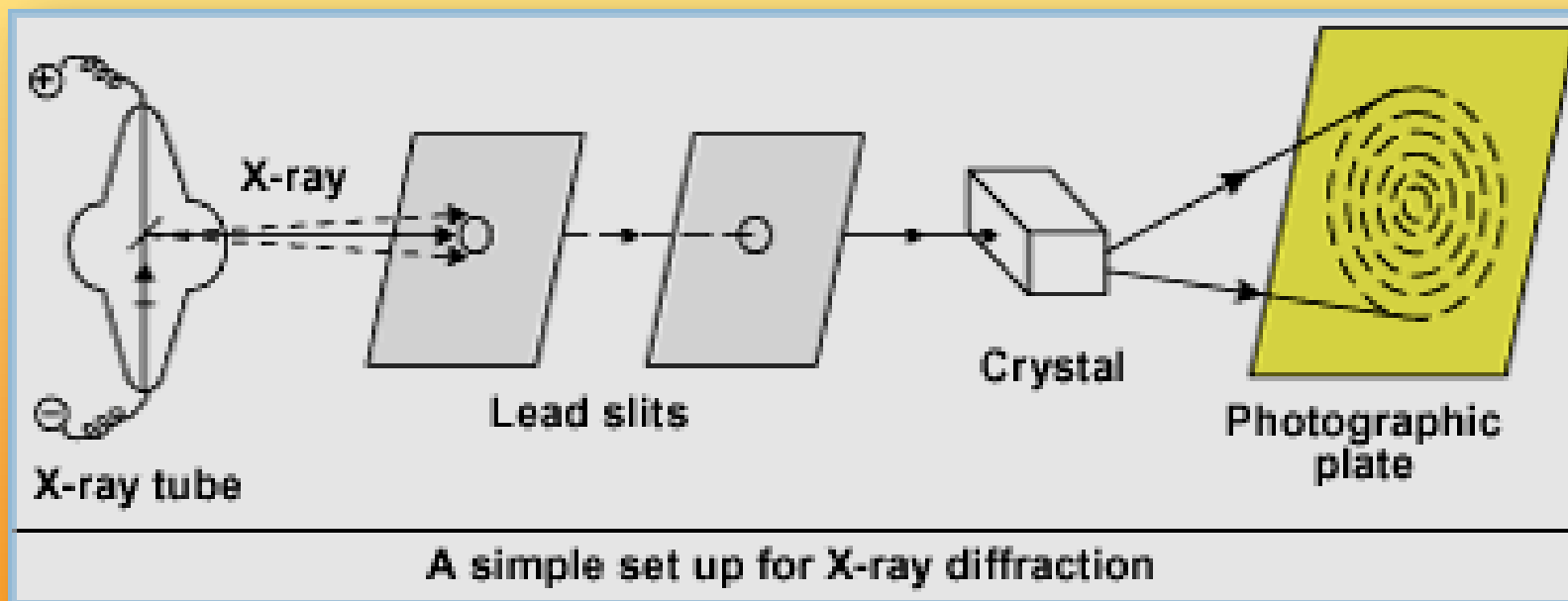
# Modern techniques

## 1. Spectroscopy

- (a) Mass spectroscopy – determines molecular mass and molecular formula of organic compound.**
- (b) Ultraviolet (UV) spectroscopy.**
- (c) Infrared (IR) spectroscopy.**
- (d) Nuclear magnetic resonance (NMR) spectroscopy**  
**U.V., I.R. and NMR are to determine type of bond and functional group in organic compound.**

# X-ray diffraction

Used to determine bond lengths and bond angles in organic compounds.





# Determination of empirical and molecular formula

- 1. Empirical formula – simplest whole number ratio of atoms of different elements present in it.**
- 2. Molecular formula – Gives actual number of atoms of each element present in molecule.**
- 3. Molecular formula =  $n \times$  empirical formula.**
- 4.  $n = \frac{\text{Molecular mass of organic compound}}{\text{Empirical formula mass of organic compound}}$**
- 5. Molecular mass =  $2 \times$  vapour density.**
- 6. Approximate molecular mass =  $6.4 \times$  specific heat of organic compounds.**



## **Illustrative problem**

**An organic compound containing C, H and N gave the following analysis.**

**C = 40%, H = 13.33% and**

**N = 46.67%. Its empirical formula is**



# Solution

Element	Percentage	Atomic mass	Atomic ratio	Simplest ratio
C	40.0	12	$40/12 = 3.33$	$3.33/3.33 = 1$
H	13.33	1	$13.33/1=13.33$	$13.33/3.33=4$
N	46.67	14	$46.67/14=3.33$	$3.33/3.33= 1$

Therefore, empirical formula =  $\text{CH}_4\text{N}$ .

Hence, answer is (c).



## Illustrative problem

A compound with empirical formula  $\text{CH}_2\text{O}$  has a vapour density of 30. Its molecular formula is



# Solution

$$\begin{aligned}\text{Empirical formula weight of CH}_2\text{O} \\ &= 12 + 2 \times 1 + 16 \\ &= 30\end{aligned}$$

$$\begin{aligned}\text{Molecular weight} &= 2 \times \text{vapour density} \\ &= 2 \times 30 \\ &= 60\end{aligned}$$

$$n = \frac{\text{Molecular weight}}{\text{Empirical formula weight}} = \frac{60}{30} = 2$$

$$\begin{aligned}\text{Molecular formula} &= n \times \text{empirical formula} \\ &= 2 (\text{CH}_2\text{O}) \\ &= \text{C}_2\text{H}_4\text{O}_2\end{aligned}$$

Hence, answer is (b).



## **Illustrative problem**

**Haemoglobin contains 0.334% of iron by weight. If the molecular weight of haemoglobin is approximately 67200, then number of iron atoms present in one molecule of haemoglobin are (at.wt. of Fe = 56)**

- (a)1**
- (b)6**
- (c)4**
- (d)2**



# Solution

$$\begin{aligned}\text{Number of iron atoms} &= \frac{\text{M. wt. of haemoglobin} \times \text{percentage of iron}}{\text{M.wt. of iron} \times 100} \\ &= \frac{67200 \times 0.334}{56 \times 100} = 4\end{aligned}$$

**Hence, the answer is (c).**



**Thanks...**