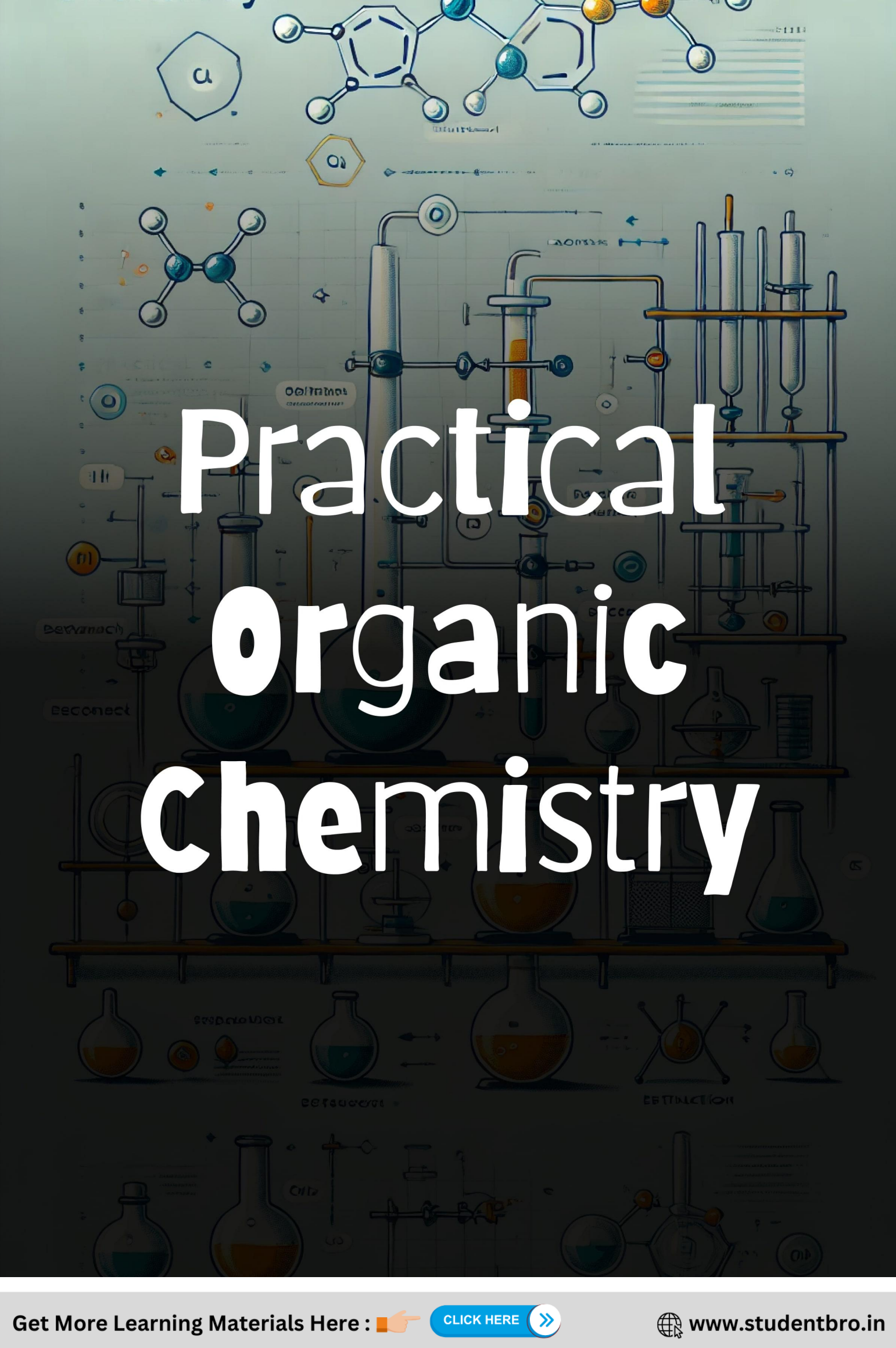


In this section, we study about organic compounds having different elements like C, S, halogen, H, P etc.

Test for Hydrogen and Carbon

Organic substance is passed through CuO at high temperature. CO_2, H_2O will produce if organic substance contains carbon & hydrogen respectively. If CO_2 is passed through lime water ($Ca(OH)_2$), it becomes milky due to formation of $CaCO_3$.

If H_2O is present, it is passed through anhydrous $CuSO_4$, & it gives blue to formation of blue vitriol" ($CuSO_4 \cdot 5H_2O$)

($CuSO_4 \cdot 5H_2O$)

$$C + 2CuO \longrightarrow CO_2 + 2Cu$$

$$2H + CuO \longrightarrow H_2O + Cu$$

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

$$5H_2O + CuSO_4 \longrightarrow CuSO_4 \cdot 5H_2O$$

(white) (blue vitriol)

Test for Nitrogen, Sulphur and Halogen

The test is called "Lassaigne's Test"

In this process, organic substance is heated in an ignition tube in presence of sodium metal and we will get "sodium extract" (ionic in-nature).

$$Na + C + N \longrightarrow NaCN$$

$$Na + X \longrightarrow NaX$$

$$2Na + S \longrightarrow Na_2S$$

i Test for Nitrogen

- Sodium extract is passed through ferrous sulphate solution in presence of concentrated sulphuric acid. "Prussion Blue" colour will obtain due to presence of ferri ferro cyanide.

$$NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6]$$

$$[Fe(CN)_6]^{-4} + Fe^{+3} \longrightarrow Fe_4[Fe(CN)_6]_3$$

(Fe^{+3}: same Fe is oxidised; $Fe_4[Fe(CN)_6]_3$: (Prussion blue))

ii TEST FOR SULPHUR

a. Sodium extract is passed through lead acetate in presence of acetic acid. Black precipiate will be obtained due to formation of PbS.

$$Na_2S \xrightarrow[Pb(CH_3COO)_2]{CH_3COOH} PbS \downarrow \text{Black}$$

b. Sodium extract is passed through sodium nitro prussid, violet colour will be obtained.

$$S^{2-} + N_2[Fe(CN)_5NO] \longrightarrow Na_2[Fe(CN)_5NO_5]$$

($Na_2[Fe(CN)_5NO_5]$: (Violet))

iii TEST FOR HALOGEN

- Sodium extract is passed through silver nitrate ($AgNO_3$) in presence of nitric acid (HNO_3). If precipitate is obtained there will be a halogen.

$$AgNO_3 + SE \xrightarrow{HNO_3} AgX \downarrow$$

(AgX ↓: precipitate)

If white precipitate which is soluble in aqueous ammonia solution it confirms that "halogen is chlorine".

$$AgCl \xrightarrow{NH_4OH} \text{soluble}$$

(AgCl: white)

If yellow precipitate which is partially soluble in aqueous ammonia solution it confirms that halogen is bromines.

$AgBr \xrightarrow{NH_4OH}$ Partially soluble

(AgBr: yellow)

If yellow precipitate which is insoluble in aqueous ammonia sol, then iodine is confirmed.

$AgI \xrightarrow{NH_4OH}$ insoluble

iv TEST FOR PHOSPHORUS

- organic compound is passed through sodium proxide, all phosphorus will be converted into phosphate which is passed through HNO_3 to give phosphoric acid which on passing through ammonium molybdate. It will give yellow colour of ammonium phosphate molybdate.

organic compound $\xrightarrow{Na_2O_2}$ Na_3PO_4 $\xrightarrow{HNO_3}$ H_3PO_4 $\xrightarrow{(NH_4)_2MoO_4}$ $(NH_4)_3PO_4.12MoO_3$ (yellow)

QUANTATIVE ANALYSIS

In this section we will calculate percent composition of elements present in organic compounds.

Leibig's Method / combustion Method

- W is mass of organic substance.
- W_1 is mass of CO_2 obtained after combustion.

→ W_2 is mass of H_2O obtained after combustion.

$$\underset{w}{C_xH_y} + \left(x - \frac{y}{4}\right)O_2 \longrightarrow \underset{W_1}{xCO_2} + \underset{W_2}{\frac{y}{2} \cdot H_2O}$$

$$\%C = \frac{W_1}{44} \times \frac{12}{W} \times 100\%$$

$$\%H = \frac{W_2}{18} \times \frac{2}{W} \times 100\%$$

Aqueous KOH absorbs CO_2 Anhydrous $CaCl_2$, absorbs H_2O,

Mass of CO_2 is obtained due to weight increase in aqueous KOH tube.
Mass of H_2O is obtained from weight increase in anhydrous $CaCl_2$ tube.

POC

Analysis of Nitrogen

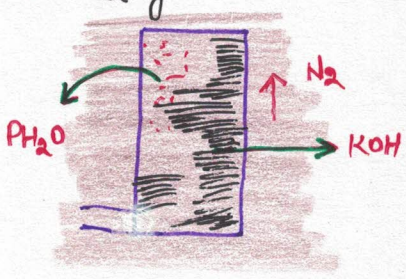
There are two methods for determining % nitrogen in organic compounds

1. DUMA's method
2. KJELDAHL's method

1 DUMA'S METHOD (DM)

In this method, organic substance is burnt in presence of CuO, it'll give CO_2, N_2, H_2O and copper metal. These products are collected in a glass tube containing aqueous KOH solution. N_2 gas will be collected over the solution. so, at that temperature there will be some vapour pressure. so pressure due to N_2 gas –

$$P_{N_2} = P_{moist} - \text{aqueous tension}$$



where aq. tension is vapour pressure of water at that temperature.

$$C_2H_yN_2 + (2x + y/2)\,CuO \longrightarrow xCO_2 + \frac{y}{2}H_2O + \frac{2}{2}N_2 + (2x + y/2)\,Cu$$

For volume of N_2, there will be marking on glass tube. Now with the help of $PV = nRT$ we can calculate moles of N_2 gas.

Hence $\% N = \left(\frac{n_{N_2} \times 28 \times 100}{w}\right)\%$

w = Total weight of organic substance

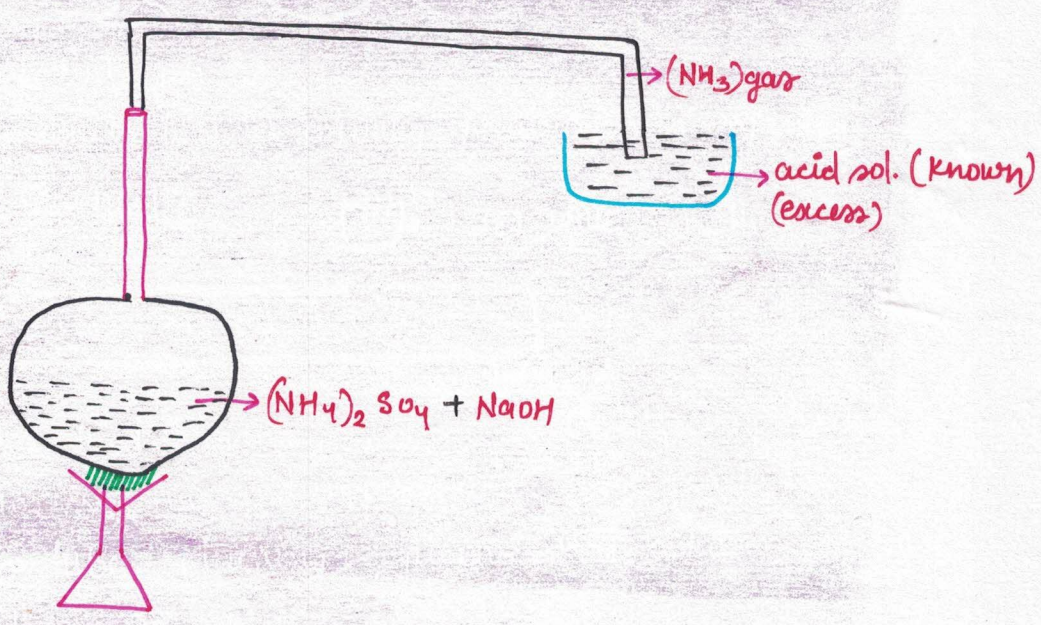
n = moles of N_2 gas

2. KJELDAHL's METHOD

An organic compound is digested in a closed flask in presence of sulphuric acid & copper sulphate ($H_2SO_4 + CuSO_4$)

Then this flask is added to a distillation column before addition of column NaOH is added. In product we will get ammonia gas.

$$\text{Organic compound} \xrightarrow[CuSO_4]{H_2SO_4} (NH_4)_2SO_4 \xrightarrow{2NaOH} 2NH_3 + Na_2SO_4 + H_2O$$



IMPORTANT

Ammonia gas is collected (absorbed) in excess acid solution (known). Excess amt. of acid is neutralised with known basic solution.

This is called "Black Titration".

So, equivalent of ammonia = Moles of ammonia because valence factor is 3.

If moles of ammonia = n

$$\%N = \left(\frac{n_{NH_3} \times 14 \times 100}{10}\right)\%$$

W = mass of organic compound.

ANALYSIS OF SULPHUR AND HALOGEN

FOR RALOGENS

(i) Carius Method – In this method, organic substance is passed through fuming HNO_3 in presence of $AgNO_3$ and AgX precipitate will be formed.

Organic compound (W) $\xrightarrow[AgNO_3]{\text{fuming } HNO_3}$ AgX (W_1)

For $AgCl$:- $\left(\frac{W_1}{143.5} \times \frac{35.5}{W} \times 100\right)\% \longrightarrow Cl\%$

$AgBr$:- $\left(\frac{W_1}{188} \times \frac{80}{W} \times 100\right)\% \longrightarrow Br\%$

AgI :- $\left(\frac{W_1}{235} \times \frac{127}{W} \times 100\right)\% \longrightarrow I\%$

FOR SULPHUR

(i) Carius Method – organic substance is passed through fuming HNO_3 to get H_2SO_4. H_2SO_4 is then passed through $BaCl_2$ to form $BaSO_4$ which precipitates.

Organic compound (W) $\xrightarrow{\text{fuming } HNO_3}$ H_2SO_4 $\xrightarrow{BaCl_2}$ $BaSO_4\downarrow$ (W_1)

$$\%S = \left(\frac{W_1}{233} \times \frac{32}{W} \times 100\right)\%$$

V TEST FOR OXYGEN

organic substance is reated which gives O_2. But O_2 is absorbed by carbon to form carbon monoxide. CO can be passed through I_2O_5 to form CO_2.

$$(\text{organic compound}) \xrightarrow{\Delta} O_2 + \text{other compound}$$

$$[O_2 + 2C \longrightarrow 2CO] \times 5$$

$$[5CO + I_2O_5 \longrightarrow 5CO_2 + I_2] \times 2$$

W_1

It can be seen that 5 mole O_2 is giving 10 mole CO_2.

So, 1 mole $O_2 \longrightarrow$ 2 mole CO_2

$$\%.O = \left(\frac{W_1}{44} \times \frac{16}{W} \times 100\right)\%$$

"16" is written because 1 mole $O_2 \longrightarrow$ 2 mole CO_2

MOLECULAR WT. DETERMINATION FOR ORGANIC COMPOUNDS

(i) Cryoscopic Method

– when non volatile solute is added to volatile solvent, then vapour pressure of solution will decrease, boiling point will increase and freezing point will decrease.

$\Delta P \downarrow \propto$ B.P $\uparrow$

ΔT_B = boiling point
ΔT_f = freezing point

$\Delta T_f \propto$ molality

$\Delta T_f = K_f \times$ molality

W gram solvent & w gram solute.

M → molecular wt. of organic compound (solute).

ΔT_f → depression in freezing point

$$M = \frac{W \times 1000}{\text{Molality} \times W} = \frac{10 \times 1000}{\frac{\Delta T_f}{K_f} \times W}$$

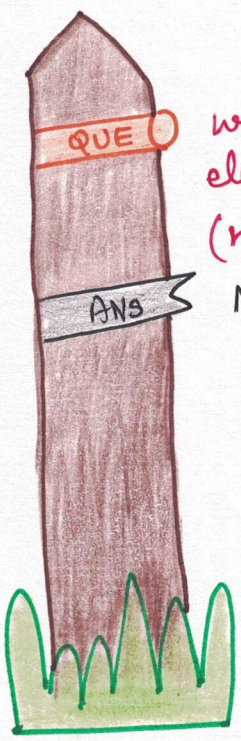
$$M = \frac{K_f \times W \times 1000}{\Delta T_f \times W}$$

(ii) Ebullioscopic Method

$$M = \frac{K_b \times 10 \times 1000}{\Delta T_B \times W}$$

same method
($T_B \propto$ molality)

K_B = ebullioscopic constant or metal elavation constant
W = weight of solute
W = weight of solvent
ΔT_B = elevation in B.P
M = Molecular wt. of organic compound



when one gram organic substance is added to 10 gram water, elevation in boiling point is 2°C.
(molal elevation constant for water is 0.52)

Molality $\frac{1}{M}$ $\frac{100}{10}$ $\frac{100}{M}$

2 $\frac{100}{M}$ 0.52

M $\frac{100 \quad 0.52}{2}$

26 gram Ans.....

(iii) Silver Salt Method

– It is used for determining molecular weight of organic acids. (R–COOH)

$RCOOH \longrightarrow RCOOAg$ (W_1)

$RCOOAg$ (W) $\longrightarrow Ag$ (W_1)

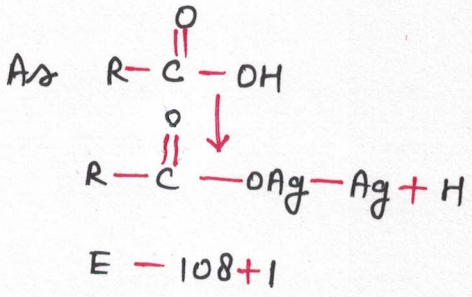
Equivalents will be equal.

$$\frac{W}{E} = \frac{W_1}{108}$$

E will be known.

$E - 180 + 1$ = Equivalent wt. of acid

$$E - 107 = \frac{M}{V \cdot E}$$

As 

$E - 108 + 1$

> Molar mass of acid = $(E - 107) \times V \cdot F$

(vi) Platinum Salt method (RNH_2) (base)

It is used for determining molecular wt. of organic base.

B is any base.

$$2B + 2HCl \longrightarrow B_2H_2Cl \longrightarrow B_2H_2{}^{+}Cl \longrightarrow \underset{W_1}{Pt.}$$

$$195 = E_3$$

Eq. will be same.

$$\frac{W}{2B \;\; 410} = \frac{W_1}{195}$$

B is eq. wt. of base

> Molar mass $B \times V \cdot F$

> No. of equivalents = $\frac{\text{weight}}{\text{equivalent wt.}}$

Victor Meyer's Test

This is for volatile organic substances.

$$PV = nRT$$

$$PV = \frac{WRT}{M}$$

> $M = \frac{WRT}{PV}$

when volatile substance is heated, it becomes "vapour" and follows ideal gas equation.

Organic substance ignite at high temperature & convert to gas. so, we can use ideal gas equation.

DEGREE OF UNSATURATIONS

$C_x\ H_y\ N_z\ O_p\ X_q$

$$D.O.U = (x+1) - \left(\frac{y+q-z}{2}\right)$$

Q. C_2H_2

$D.O.U = (2+1) - \frac{(2)}{2} = 3-1 \Rightarrow 2$

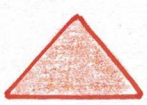
Q. C_2H_4

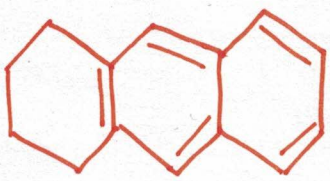
$D.O.U = (2+1) - \left(\frac{4}{2}\right) = 3-2 \Rightarrow 1$

DEGREE OF UNSATURATION – No. of π bonds present.

if D.U=1, either 1 double bond or cyclic compound is present.

E.g. $C_3H_6 \Rightarrow (3+1) - \frac{6}{2} = 1$

$(CH_3 - CH = CH_2)$ or 

Q. 

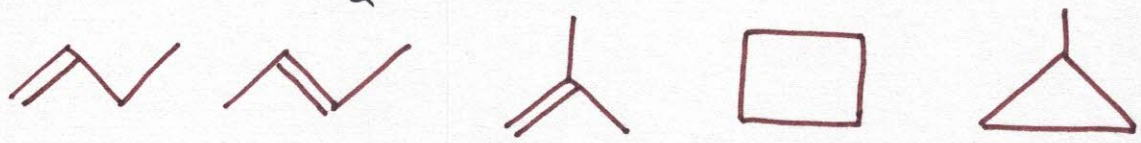
D.U ⇒ No. of π bond + No. of cycles

⇒ 5 + 3

⇒ 8

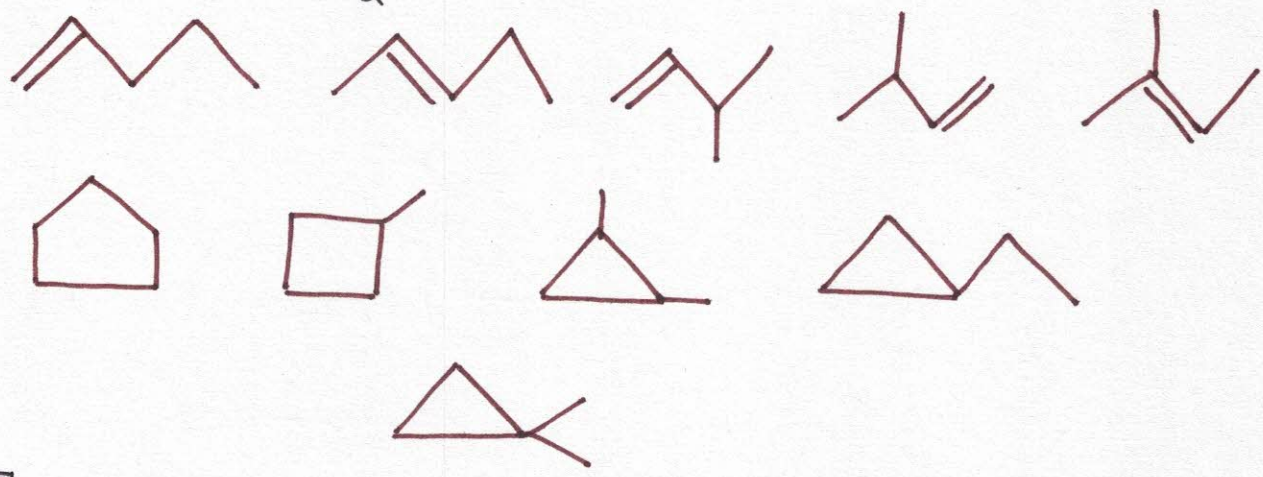
Q. No. of isomers of C_4H_8

ANS → D.U $= (4+1) - \frac{8}{2} = 1$



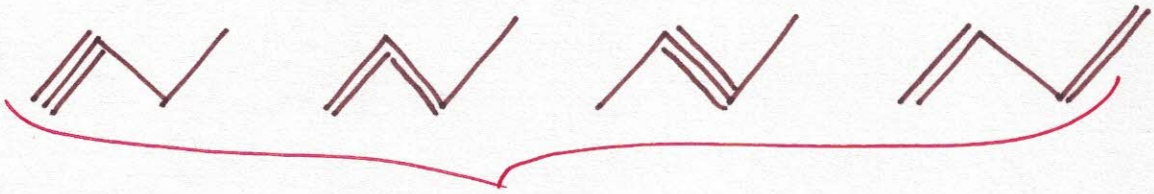
Q. C_5H_{10}

ANS → D.U $= (5+1) - \frac{10}{2} = 1$



Q. C_4H_6

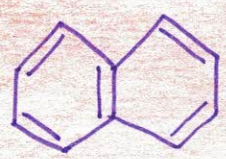
ANS → $(4+1) - \frac{6}{2} \Rightarrow 5 - 3 \Rightarrow 2$



(acyclic)

(cyclic)

Q.



ANS → D.U = 5 double bonds + 2 cyclic ⇒ 7