# Distillation Techniques :

Туре		Conditions	Examples
(A)	Simple distillation	(i) When liquid sample has non volatile impurities	(i) Mixture of chloroform (BP = 334K) and Aniline (BP = 457K)
		(ii) When boiling point difference is 80° K or more.	<ul> <li>(ii) Mixture of Ether (BP = 308K) &amp; Toluene (BP = 384K)</li> <li>(iii) Hexane (342K) and Toulene(384K)</li> </ul>
(B)	Fractional distillation	When BP difference is 10°	(i) Crude oil in petroleum industry (ii) Acetone (329) and Methyl alcohol(338K)
(C)	Distallation under reduced pressure (Vacuum distillation)	When liquid boils at higher temperature and it may decompose before BP is attained.	<ul><li>(i) Concentration of sugar juice</li><li>(ii) Recovery of glycerol from spent lye.</li><li>(iii) Glycerol</li></ul>
(D)	Steam distillation	When the substance is immiscible with water and steam volatile. $P = P_1 + P_2$ $Vapour Vapour Vapour pressure pressure of of waterOrganicliquid$	<ul> <li>(i) Aniline is separated from water</li> <li>(ii) Turpentine oil</li> <li>(iii) Nitro Benzene</li> <li>(iv) Bromo Benzene</li> <li>(v) Naphthalene</li> <li>(vi) o-Nitrophenol</li> </ul>





LASSAIGNE METHOD : 1. Nitrogen (N) : Na + C + N  $\longrightarrow$ NaCN (Sodium extract)  $NaCN + FeSO_4 + NaOH$ Test :  $\downarrow$  boil & cool  $\text{FeCl}_3 + \text{conc.}$  HCl Blue or green colour  $[Fe_4[Fe(CN)_6]_3]$ Prussian blue 2. Sulphur (S) :  $2Na + S \longrightarrow Na_2S$ (Sodium extract) Na<sub>2</sub>S Test (1)  $\downarrow$  Sodium nitro prusside A deep voilet colour  $Na_2S + CH_3COOH + (CH_3COO)_2Pb$ Test (2) Black colour (PbS) 3. Halogen (X) : Na + Cl  $\longrightarrow$  NaCl (Sodium extract) **Test** :  $NaCl + HNO_3 + AgNO_3$ White ppt soluble in aq. NH<sub>3</sub> confirms Cl (a) (b) Yellow ppt partially soluble in aq. NH<sub>3</sub> confirms Br (c) yellow ppt insoluble in aq. NH<sub>3</sub> confirms I 4. Nitrogen and Sulphur together :  $Na + C + N + S \longrightarrow NaCNS$ (Sodium thiocynate) As in test of nitrogen, instead of green or blue colour, blood red coloration confirms presence of N and S both. 5. Phosphorous (P) :  $P \xrightarrow[boils, \Delta]{Na_2O_2} Na_3PO_4$ Solution in boiled with nitric acid and then treated with ammonium molybdate  $(NH_4)_2 MoO_4$ Formation of yellow ppt indicate presence of phosphate hence phosphorous present in organic compounds. THE QUANTITATIVE ANALYSIS : Quantitative analysis involves the estimation of percentage composition of various element by suitable method. The molecular mass of the compound is also determined by suitable methods. The knowledge of molecular mass and percentage composition help us to determine the molecular formula of the compound. ESTIMATION OF CARBON AND HYDROGEN OR LIEBIG COMBUSTION METHOD : Organic compound + dry, black CuO  $\downarrow$  Heat strongly in combustion tube (w g) mixture of oxide

 $\downarrow$  Pass through

(i) anhydrous CuSO<sub>4</sub>(ii) anhydrous CaCl<sub>2</sub>

say increase in weight = a g  $\downarrow$  Pass through (i) KOH (aq) (ii) Saphnolite resin say increase in weight = b g For % of H - The increase in weight is 'a' g due to the formation of H<sub>2</sub>O  $\therefore$  18 g H<sub>2</sub>O has H = 2 g

$$\therefore$$
 ag H<sub>2</sub>O has  $H = \frac{2a}{18}g$ 

Since w g organic compound has =  $\frac{2a}{18}$  g hydrogen.

$$\therefore$$
 100 g organic compound has=  $\frac{2a \times 100}{18 \times w}$  g hydrogen

$$\therefore \quad \%H = \frac{2}{18} \times \frac{\text{weight of } H_2O \text{ formed}}{\text{weight of subs tance}} \times 100$$

For % of C -

The increase in wt is b g due to formation of  $CO_2$ 

$$\therefore$$
 44 g CO<sub>2</sub> has C = 12 g

$$\therefore \text{ b g CO}_2 \text{ has } \text{C} = \frac{12}{44} \times \text{b g}$$

Since w g organic compound has  $\left(\frac{12}{44} \times b\right)$  g carbon

$$\therefore$$
 100 g organic comound has  $\frac{12}{44} \times b \times \frac{100}{w}$  g carbon

	$\frac{12}{\%}$	weight of CO <sub>2</sub> formed	×100
	$100 - \frac{1}{44}$	weight of subs tan ce	×100

**Note** : This method is suitable for estimation if organic compound contains C and H only. In case if other elements e.g., N,S, halogens are also present the organic compound will also give their oxides which on being absorbed in KOH will increase the percentage of carbon and therefore following modification should be made.

(a) If N is also present : The gaseous oxide mixture is first passed over heated Cu gauze which reduces all oxides of N to  $N_2$  which are neither absorbed by  $H_2O$  nor by KOH

 $2NO + 2Cu \longrightarrow N_2 + 2CuO$ 

(b) If halogens are present : A roll of silver gauze is placed at the exit end of combustion tube which retains all the halogens on itself.

 $2Ag + X_2 \longrightarrow 2AgX$ 

 $2Ag + CuX_2 \longrightarrow 2AgX + Cu$ 

(c) If S is present : A layer of fused lead chromate is placed near the exit end, all the oxides of sulphur are oxidised to  $PbSO_4$  & left in tube it self.

$$\begin{array}{rrrr} Cr^{+6} &+ 3e^- &\rightarrow & Cr^{+3} \\ S^{+4} &\rightarrow & S^{+6} &+ 2e^- \\ (\text{in SO}_2) & (\text{in SO}_4^{-2}) \end{array}$$

## GENERAL CONCEPT FOR DRYING AND DEHYDRATING AGENTS

- Acidic oxides ( non metals oxides such as CO<sub>2</sub>, NO<sub>2</sub>, SO<sub>2</sub> P<sub>2</sub>O<sub>5</sub> etc.) are absorbed by alkali (KOH, NaOH, Ca(OH)<sub>2</sub> etc.)
- (ii) Basic oxides (Na<sub>2</sub>O,  $K_2O$  etc.) are dissolved in acids ( $H_2SO_4$ , HCl etc.)
- (iii) Acidic oxides can not be dried by basic dehydrating agent (e.g CaO) but they are dried by acid dehydrating agent (e.g  $H_2SO_4$ ,  $P_2O_5$  etc). However  $H_2S$  can be dried by  $H_2SO_4$  because it reacts with  $H_2SO_4$ .  $H_2S + H_2SO_4 \rightarrow 2H_2O + S + SO_2$
- (iv) Basic substances can not be dried by acidic dehydrating agent but are dried by basic dehydrating agent (e.g CaO). It is because  $NH_3$  is dried by CaO but not by  $H_2SO_4$ .

# ESTIMATION OF NITROGEN

## (a) Duma's method :

 $\begin{array}{ccc} \text{Organic compound} & & \underbrace{\text{CuO}}_{\text{heated strongly}} \rightarrow & \text{Mixture of oxides} & \underbrace{\text{Pass over Cu gauze}}_{\text{Ngauze}} \rightarrow & \text{N}_2 + & \text{Other oxides} \\ & (w \text{ g}) & & \downarrow \end{array}$ 

Dry N<sub>2</sub> 
$$\leftarrow$$
 drying agent N<sub>2</sub> + Moisture  $\leftarrow$  Pass through KOH(aq.)

(Let Vml at N.T.P.)

 $\therefore$  22400 ml N<sub>2</sub> weigh at N.T.P. = 28 g

$$\therefore \text{ V ml } N_2 \text{ weigh at NTP} = \frac{28}{22400} \times \text{V g}$$

since w g organic compound gives  $\frac{28}{22400} \times \frac{V}{w} \times 100$  g

$$N = \frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at NTP}}{\text{weight of the compound}} \times 100$$

Note : This method can be used to estimate nitrogen in all types of organic compounds.

### KJELDAHL'S METHOD :

This method is based on the principle that a nitrogenous organic compound on heating with conc.  $H_2SO_4$  converts all its nitrogen quantitatively to ammonium sulphate ;

organic compound + conc. 
$$H_2SO_4 + K_2SO_4 + CuSO_4$$
  
(w g) (raises the B.P. of  $H_2SO_4$ ) (catalyst)  
 $\downarrow$  Heating in Kjeldahl flask  
 $(NH_4)_2SO_4 \xrightarrow{addKOH}{dropbydrop} NH_3$  is formed  
Pass this gas through  $V_1$  ml of  $N_1 H_2SO_4$ 

Now titrate the  $H_2SO_4$  by another alkali say of  $N_1 H_2SO_4$  ( $NH_3$  is absorbed here)

V<sub>2</sub> ml of N<sub>2</sub> ,KOH are used

Meq of  $H_2SO_4$  taken =  $N_1V_1$ 

Meq. of KOH used for  $H_2SO_4 = N_2V_2$ 

 $\therefore$  Meq. of H<sub>2</sub>SO<sub>4</sub> for NH<sub>3</sub> = N<sub>1</sub>V<sub>1</sub> - N<sub>2</sub>V<sub>2</sub>

 $\therefore$  Meq. of NH<sub>3</sub> formed = (N<sub>1</sub>V<sub>1</sub> - N<sub>2</sub>V<sub>2</sub>) or say NV)

(the difference obtained or V ml of N  $H_2SO_4$  are used to absorb NH<sub>3</sub>)

$$\therefore \quad \frac{W_{NH_3}}{17} \times 1000 = NV$$
$$\therefore \quad W_{NH_3} = \frac{17}{100} \times NV$$

$$\therefore W_{\rm NH_3} = \frac{17}{1000} \times \rm NV$$

Now  $:: 17 \text{ g NH}_3$  has 14 g Nitrogen

$$\therefore \frac{17}{1000} \times \text{NV g NH}_3 \text{ has } \frac{14 \times 17 \times \text{NV}}{17 \times 1000} \text{ g Nitrogen}$$

$$= \frac{14 \text{NV}}{1000} \text{ g Nitrogen}$$

$$\therefore \text{ w g organic compound has } \frac{14 \text{NV}}{1000} \text{ g nitrogen}$$

$$\therefore .100 \text{ g organic compound has } \frac{14 \text{NV} \times 100}{\text{w} \times 1000} \text{ g nitrogen.}$$

$$= \frac{1.4 \text{NV}}{\text{w}} \text{ g nitrogen}$$

$$\therefore \frac{\text{\%Nitrogen} = 1.4 \times \frac{\text{Normality of the acid} \times \text{volume of the acid}}{\text{wright of the compound}}$$

- %INitrogen = 1.4 × weight of the compound
- Note : This method is simpler and more convenient and is mainly used for finding out the percentage of nitrogen in food stuffs, soil, fertilizers and various agricultural products. This method cannot be used for compound having nitro groups, azo gp. (-N = N-) and nitrogen in the ring (pyridine, quinole etc.). Since nitrogen in these compounds is not quantitatively converted in to ammonium sulphate.

### ESTIMATION OF SULPHUR (CARIUS METHOD) :

Organic compound + con.  $HNO_3 + BaCl_2 \rightarrow ppt (BaSO_4)$  is dried and weighed say "a" g (w g)

$$S \xrightarrow{Furming,HNO_3} H_2SO_4 \xrightarrow{BaCl_2} BaSO_4 + HCl$$
233 g BaSO<sub>4</sub> has 32 g sulphur (a g)

$$\therefore$$
 a g BaSO<sub>4</sub> has  $\frac{32 \times a}{233}$  g sulphur

$$\therefore \% \text{ of Sulphur} = \frac{32 \times a \times 100}{233 \times w}$$

...

 $\frac{32}{233} \times \frac{\text{weight of BaSO}_4 \text{ formed}}{\text{weight of compound}} \times 100$ %S =233 (

### ESTIMATION OF HALOGENS (CARIUS METHOD) :

Organic compound + con  $\rm HNO_3$  +  $\rm AgNO_3 \rightarrow ~ppt$  (AgX) is dried and weighed say a g

% of Cl = 
$$\frac{35.5}{143.3} \times \frac{\text{weight of AgCl}}{\text{weight of compound}} \times 100$$
  
% of Br =  $\frac{80}{188} \times \frac{\text{weight of AgBr}}{\text{weight of compound}} \times 100$   
% of I =  $\frac{127}{1225} \times \frac{\text{weight of AgI}}{1225} \times 100$ 

o of I = 
$$\frac{1}{235} \times \frac{1}{\text{weight of compound}} \times 1$$

# □ ESTIMATION OF PHOSPHORUS - (CARIUS METHOD) :

Organic compound + con.  $HNO_3$  + Magnesia mixture (MgSO<sub>4</sub> + NH<sub>4</sub>OH + NH<sub>4</sub>Cl) (w g)

$$2 \text{ MgNH}_4\text{PO}_4 \longrightarrow \text{ Mg}_2\text{P}_2\text{O}_7 + 2\text{NH}_3 + \text{H}_2\text{O}$$

Precipitate is dried and ignited to give magnesium pyrophosphate ( $Mg_2P_2O_7$ ) weighed say a g

% of P = 
$$\frac{62}{222} \times \frac{\text{weight of } Mg_2P_2O_7 \text{ formed}}{\text{weight of compound}} \times 100$$

Atomic weight of P = 31 42 = 62 gmolecular weight of  $Mg_2P_2O_7 = 222 \text{ } g$ 

# □ ESTIMATION OF OXYGEN :

There is no direct formula and method for estimation of oxygen however, percentage of oxygen is calculated by

% of oxgyen = 100 - [Sum of the % of all other elements]

**Note** - A direct method for estimation of oxygen has been given by Alusive in 1947 known as Alusive method.