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Purification and Characterisation of Organic Compounds

In the chapter, organic compounds purification and characterisation various important techniques and methods such as chromatography sublimation, distillation and more to purify the organic compounds.

It is essential to remove these impurities from the organic compound. The process of removal of impurities is called **purification**.

The pure compound is tested quantitatively and qualitatively. The elements present in organic compound may have elements such C, H, O, N, S, X and P. The percentage composition of elements present in an organic compound is determined by **quantitative analysis**.

Methods of Purification

Various methods used for the purification of organic compounds are based on the nature of the compound and the impurity present in it.

Common techniques used for purification are as follows

1. Filtration

- (i) **Principle** It is based on the difference in filterability of different component of a solution.
- (ii) Process Filtration is used to separate the insoluble solid component of the mixture from the soluble components in a given solvent. Sometime we use the filtrate of hot solution for separation. If the process of filtration is slow then it is carried out under reduced pressure using a Buchner funnel and a filter pump.
- (iii) **Applications** Separation of sand from salt by dissolving in water, separation of tea leaves from tea is done by this method.

IN THIS CHAPTER

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 - Estimation of Nitrogen
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2. Crystallisation

- (i) **Principle** It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent.
- (i) Process The impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to get a nearly saturated solution.

On cooling the solution, pure compound crystallises out and removed by filtration. The filterate contains impurities and small quantity of the compound. The solvents commonly used for dissolving organic solids are water, alcohol, ether, chloroform, benzene, petroleum ether, etc.

Solvents used for crystallisation are given below

Solvents to be Used for Crystallisation of Different Substances

Substances	Solvents	Polarity of solvents
Hydrocarbons	Pentane, hexane, benzene, petroleum ether	Hydrophobic (non-polar)
Ethers	Diethyl ether; methylene chloride (CH_2Cl_2)	
Halohydrocarbons	Chloroform	
Tertiary amines	Acetone	
Ketones, aldehydes, esters	Ethyl acetate/ methyl acetate	
Phenols, alcohols	Ethanol	
Carboxylic acids	Methanol	
Sulphonic acid	Water	
Organic salts	Water	Hydrophilic (polar)

(iii) Applications Sugar having common salt as impurity, can be crystallised through hot ethanol as it is soluble in hot ethanol but, common salt does not. Similarly, hot water is used to separate a mixture of benzoic acid and naphthalene.

3. Fractional Crystallisation

- (i) **Principle** It is based on the slight difference in solubilities of different components of a mixture in the same solvent.
- (ii) Process In this method, a hot concentrated solution of mixture is prepared and is allowed to cool. The less soluble component crystallises out earlier as compared to more soluble one. The various fractions are separated from time to time. Now, these fractions are subjected to crystallisation.
- (iii) Applications The mixture of glucose and fructose; sodium sulphate and sodium dichromate, KClO₃ + KCl are separated by this method.

4. Sublimation

(i) **Principle** This process is employed for those solids which convert directly into vapours on heating without converting into liquid phase and the vapours upon cooling give back solid.

(ii) Process In this process, the impure solid is taken into China dish and is covered with a perforated filter paper. An inverted funnel is placed over the dish and its stem is plugged with cotton.

The diagram is shown below.



The dish is heated gently and the substance volatilises as result. The substance now called **sublimate** is collected over the inner cold surface of the funnel. The non-volatile impurities are left behind in the China dish.

The perforated filter paper allows only the vapours to go upwards and check the sublimate from falling back down into the dish.

(iii) **Applications** Impure samples of naphthalene, anthracene, camphor, benzoic acid, $NH_4Cl, HgCl_2$, dry ice, salicylic acid, iodine etc., can be purified by this method provided the impurities are non-volatile.

Note A mixture of two or more sublimates cannot be separated by sublimation. Such mixtures are separated by **chemical methods**.

5. Distillation

- (i) Principle It is based upon the difference in the boiling points of two liquids or two components and is generally used to separate volatile liquids from non-volatile in purities. The liquids having sufficient difference in their boiling points.
- (ii) Process When a given liquid is heated to its boiling point, it is converted into vapours and the vapours on cooling condense to give back the original liquid in its pure form. The liquid obtained is **distillate** and the process is called distillation.

Several distillation methods employed to separate mixtures are as follows

(a) Simple distillation It is used only for the purification of liquids which boil without decomposition at atmospheric pressure and contain non-volatile impurity. Generally, the impurity and liquid which differ in their boiling points by 30-50K are separated by this process.

In this method, the liquid mixture is taken in a round bottom in flask and heated carefully. On boiling, the vapours of lower boiling component are formed first. The vapours are condensed by using a condenser and the liquid is collected in a receiver. The vapours of higher boiling component form later and the liquid can be collected separately.

A mixture of ether and toluene, hexane and toluene; benzene and aniline etc., is separated by this method.

(b) Fractional distillation For the separation of two liquids which have nearly equal boiling points, i.e. their boiling points are within the limit of 10 to 15 K (e.g. acetone 329 K and methyl alcohol 338 K), the process of simple distillation cannot be used as vapours of both the liquids will be formed simultaneously and thus, the distillate will also contain both of them.

In such case, the distillation is done with the help of **specially designed fractionating columns** and this type of distillation is called **fractional distillation**.

A mixture of acetone and methyl alcohol is separated by this process.

(c) **Distillation under reduced pressure** It is used to purify liquids having very high boiling points and those which decompose at or below their boiling points.

As we know, at boiling point and vapour pressure of liquid is equal its atmospheric pressure.

Hence, under reduced pressure the liquid will boil at low temperature. Thus, temperature for decomposition is not reached.

e.g. Boiling point of glycerol is 563 K but it decomposes much before its boiling temperature. However at 12 mm of Hg pressure, glycerol boils at 453 K without decomposition. Other examples include H_2O_2 , concentration of **sugar cane** juice in sugar industry etc.

- (d) **Steam distillation** It is used to purify the substances which
 - are volatile in steam but are immiscible with water.
 - possess sufficiently high vapour pressure at the boiling point of water.
 - contain non-volatile impurities.

The compound to be purified is distilled with steam under reduced pressure at a temperature below its boiling point.

The pure compound comes out with steam (as it is volatile with steam) and separates on cooling down (as it is immiscible with water). The impurities being non-volatile remains in mother liquor.

In steam distillation, the liquid boils when the sum of vapour pressure due to the organic liquid (p_1) and that due to water vapour (p_2) becomes equal to the atmospheric pressure.

$$p = p_1 + p_2$$

Since, $p_1 < p_2$, the compound vaporises at lower temperature than its boiling point.

The process of steam distillation can also be used to separate a mixture of two organic compounds one of which is steam volatile while the other is not. e.g. *ortho* and *para* nitrophenols (the latter is non-volatile) compounds like aniline, nitrobenzene, sandal wood oil, terpentine oil, bromobenzene, *o*-hydroxy acetophenone etc., are purified or obtained by this process.

6. Azeotropic Distillation

The liquid mixtures which have constant boiling point and distill with unchanged composition are called **azeotropes.** These mixtures behave as pure liquids and cannot be separated with simple distillation. The method designed to separate **azeotropes** is called **azeotropic distillation.**

- (i) **Principle** It is based on the more solubility of a component of azeotrope in another solvent as compared to the other component of the azeotrope.
- (ii) **Process** In this process a suitable solvent is added to form a new azeotrope resulting to removal of one of the components of older azeotrope with the solvent.
- (iii) Applications Dehydration of 96% ethanol (azeotrope with 96% $C_2H_5OH + 4\%$ water) to absolute alcohol with the help of benzene, as ethanol is more soluble in benzene as compared to water.

Example 1. The distillation technique most suitable for separating glycerol from spent lye in the soap industry is (a) fractional distillation (JEE Main 2018)

(b) steam distillation

(c) distillation under reduced pressure

(d) simple distillation

Sol. (c) Glycerol with high boiling point (290°C) can be separated from spent lye by distillation under reduced pressure. This process is used to purify liquids having very high boiling points.

By this process, liquid is made to boil at lower temperature than its boiling point by lowering the pressure on its surface.

7. Differential Extraction

- (i) Principle It is based on the more solubility of solute in a suitable organic compound as compared to water.
- (ii) Process The process of differential extraction is used to separate a given organic compound an aqueous solution. The process involves shaking of solution with a suitable organic solvent in which compound is more soluble such as ether, chloroform or benzene, in a separating funnel.

At one point, the solvent and aqueous solution must not be miscible with each other. In order to get the more amount of organic solvent, the process is repeated again and again with same sample. The process is shown in the figure below.



(iii) **Application** Benzoic acid is separated from water by using benzene.

8. Chromatography

It is the modern technique used for separation, isolation, identification and purification of organic compounds (available in small amounts). This method was discovered by **Tswett** (a Russian botanist) in 1906. He used the technique for the separation of coloured pigments from a plant.

- (i) Principle The process is based upon the principle of distribution of components of a given organic mixture between two phases, i.e. the stationary phase and the mobile phase, it is based upon the difference in the rates at which the components of a mixture move through a porous medium (stationary phase) under the influence of some solvent or gas (mobile phase).
- (ii) Process and Application In this technique, the mixture of substances is applied to a stationary phase which may be solid or a liquid. A pure solvents, a mixture of solvents, or a gas is allowed to move slowly over the stationary phase. The components of the mixture get gradually separated from one another. The moving phase is called the **mobile phase**.

Over the year's the number of techniques has been developed under chromatography which are used in the separation of different compounds according to the need.

For example, column or adsorption chromatography, paper chromatography, thin layer chromatography, gas-liquid chromatography etc.

A brief outline review of these has been given in the following table below.

Types	of	Chromatograph	iy
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	Types of chromatography	Mobile/ Stationary phase	Uses
(i)	Adsorption or column chromatography	Liquid/Solid	Large scale separations
(ii)	Thin layer chromato- graphy (TLC)	Liquid/Solid	Qualitative analysis
(iii)	High performance liquid chromatography (HPLC)	Liquid/Solid	Qualitative and quantitative analysis
(iv)	Gas liquid chromatography (GLC)	Gas/Liquid	Qualitative and quantitative analysis
	Paper or partition chromatography	Liquid/Liquid	Qualitative and quantitative analysis

Important Facts Related to Chromatography

- In chromatography, stationary phase is solid Al_2O_3 , SiO_2 , starch and charcoal mainly, while mobile phase is pure solvent.
- The relative adsorption of each constituent of the mixture is expressed in terms of its **retardation** factor, i.e. R_f .
- $R_{f} = \frac{\text{Distance moved by the substance from base line}(x)}{\sum_{i=1}^{n}}$
- f_f Distance moved by the solvent from base line(y)

 $R_f = \frac{x}{y}$

- The R_f value of a substance depends on the (i) nature of the substance,
 - (ii) nature of the solvent,
 - (iii) nature of the filter paper used, and (iv) temperature.
- The spots of the coloured compounds are visible on the TLC plate.
- The spots of colourless compounds are seen under UV- (ultra violet) light. Another detection method is to place the TLC plate in a covered jar containing crystals of I₂ (iodine). The compound which absorbs I₂ will be seen as brown spots.
- Sugars are separated by using the solvent BAW (*n*-butanol acetic acid-H₂O) in the volume ratio of 4:1:3 and detected by spraying the plate with aniline hydrogen phthalate solution.
- If the solvent is placed at the top and the upper end of the filter paper dips in it, the solvent moves downwards. This is called **descending paper chromatography**.
- If the condition is **reversed**, it is called **ascending paper chromatography**.

Note In the purification of petroleum and coal tar products for their acidic, basic and neutral components, Sulphuric acid is used to separate the basic component and caustic soda solution to separate the acid component.

Example 2. In chromatography, which of the following statements is incorrect for R_f? (JEE Main 2019)

(a) R_f value depends on the type of chromatography

- (b) Higher R_f value means higher adsorption
- (c) R_f value is dependent on the mobile phase
- (d) The value of R_f can not be more than one

Sol. (b) In chromatography, the expression of retention factor (R_f) is

$$R_f = \frac{\text{Distance travelled by the compound from origin}}{\text{Distance travelled by the solvent from origin}} < 1$$

The value of R_f signifies the relative ratio of migration of each component of the mixture with respect to the developing solvent used.

Example 3. During hearing of court case, the judge suspected that some changes in the documents had been carried out. He asked the forensic department to check the ink used at two different places. According to you which technique can give the best results? **(NCERT Exemplar)**

- (a) Column chromatography (b) Solvent extraction
- (c) Distillation (d) Thin layer chromatography

Sol. (*d*) Thin layer chromatography is based on different rates of adsorption of different substances, thus found useful for identification and separation of two different dyes.

Qualitative Analysis

The qualitative analysis of an organic compound implies that the detection of all the major elements at which can be present in it with the help of suitable chemical tests. Some qualitative analysis are as follows

1. Detection of Carbon and Hydrogen

The detection of carbon and hydrogen is done by heating the compound with copper oxide. Carbon present in the compound is oxidised to carbon dioxide and hydrogen to water.

In this test, the compound is mixed with the double amount of pure and dry copper oxide.

The mixture is heated in a hard glass test tube which is fitted with a bulb containing delivery tube as shown in the figure below



Detection of carbon and hydrogen inorganic compounds

The other end of the delivery tube is dipped in a tube containing lime water. The bulb of delivery tube contains anhydrous CuSO_4 in it. The organic compound on combustion gives following reaction

C of organic compound + 2CuO $\xrightarrow{\Delta}$ CO₂ + 2Cu

H of organic compound + CuO $\xrightarrow{\Delta}$ H₂O + Cu

 $\rm H_2O$ vapours turns an hydrous $\rm CuSO_4$ blue and $\rm CO_2$ evolved turns lime water milky.

$$\begin{array}{c} \operatorname{CuSO}_4 + 5\operatorname{H}_2 O \longrightarrow \operatorname{CuSO}_4 \cdot 5\operatorname{H}_2 O \\ \text{White} & \operatorname{Hydrated \ copper \ sulphate} \\ \operatorname{Ca}(OH)_2 + \operatorname{CO}_2 \longrightarrow \operatorname{CaCO}_3 \downarrow + \operatorname{H}_2 O \\ \text{Milky} \end{array}$$

Since, oxygen is present almost everywhere, no direct method is available for its detection.

Note While testing for hydrogen, it is necessary that the apparatus, copper oxide and the substance are absolutely dry. Cupric oxide being hygroscopic in nature and strongly heated just before use.

2. Sodalime Test for Nitrogen

Sodalime test involves strong heating of compound with sodalime (NaOH/CaO). The evolution of NH_3 gives the indication of nitrogen.

 $\begin{array}{c} \mathrm{CH}_{3}\mathrm{CONH}_{2} + \mathrm{NaOH}/\mathrm{CaO} \longrightarrow \mathrm{CH}_{3}\mathrm{COO}^{-}\mathrm{Na}^{+} + \mathrm{NH}_{3} \uparrow \\ \mathrm{Acetamide} & \mathrm{Sodium\ acetate} \end{array}$

3. Detection of Other Elements

(Using Lassaigne's Test)

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by Lassaigne's test.

It involves two steps are as follows

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- (i) Preparation of Lassaigne's extract.
- (ii) Detection of elements using Lassaigne's extract.

To prepare Lassaigne's extract, the organic substance is fused with small quantity of Na pieces in a fusion tube. The red hot tube is plunged into distilled water contained in a China dish. The contents of dish are boiled for couple of minutes, then cooled and filtered.

The filtered liquid is called **sodium extract** or **Lassaigne's extract**. The Lassaigne's extract is usually alkaline. If not, it is made alkaline by adding a few drops of NaOH.

During fusion, the elements like N, S, C, F, Cl, Br, I, etc., are present in the organic compound, get fused with Na and convert into their ionic form.

.g.
$$\operatorname{Na} + \operatorname{C} + \operatorname{N} \xrightarrow{\operatorname{Fusion}} \operatorname{Na}^+\operatorname{C}^- \equiv \operatorname{N}_{\operatorname{Sodium cyanide}}$$

 $2\operatorname{Na} + \operatorname{S} \xrightarrow{\operatorname{Fusion}} \operatorname{Na}_2\operatorname{S}_{\operatorname{Sodium sulphide}}$
 $\operatorname{Na} + \operatorname{C} + \operatorname{N} + \operatorname{S} \longrightarrow \operatorname{NaSCN}_{\operatorname{Sodium sulphocyanide}}$
(when N and S both are present)
 $\operatorname{Na} + \underset{\operatorname{Halogen}}{X} \xrightarrow{\operatorname{Sodium halide}}$

Note Li and K both cannot be used in Lassaigne's test in place of Na as the former reacts very slowly and forms covalent compounds while later reacts vigorously and thus, cannot be handled properly.

Detection of Nitrogen

The soda extract is first boiled with $FeSO_4$ solution. After that a few drops of $FeCl_3$ is added and the resulting solution is acidified with conc. HCl. The formation of bluish green or prussian blue confirms presence of nitrogen.

The reactions that occur during this test are as

• On heating the extract with FeSO₄, sodium ferrocyanide is formed.

$$\begin{array}{ccc} 2NaCN + FeSO_4 & \longrightarrow & Na_2SO_4 + Fe(CN)_2 \\ Fe(CN)_2 + 4NaCN & \longrightarrow & Na_4[Fe(CN)_6] \\ & & \text{Sodium ferrocyanide} \end{array}$$

• The treatment with FeCl_3 , it form ferric ferrocyanide which has bluish green or Prussian blue in colour. $3\operatorname{Na}_4[\operatorname{Fe}(\operatorname{CN})_6] + 4\operatorname{FeCl}_3 \longrightarrow \operatorname{Fe}_4[\operatorname{Fe}(\operatorname{CN})_6]_3 \cdot x\operatorname{H}_2\operatorname{O}_{\operatorname{Ferric ferro}_{\operatorname{Cyanide}_{\operatorname{Cyanide}_{\operatorname{CPUssian blue}}}}$

$$+ 12 NaCl$$

- The function of conc. HCl is destruction of $\rm Fe(OH)_2$ which might have been formed by the action of $\rm FeSO_4$ with NaOH.

$$\label{eq:FeSO4} \begin{split} \text{FeSO}_4 + 2\text{NaOH} & \longrightarrow & \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4 \\ & \text{Green} \end{split}$$

 $Fe(OH)_2 + 2HCl \longrightarrow FeCl_2 + 2H_2O$

• If this is not done, the green colour of $Fe(OH)_2$ will interfere with the detection of nitrogen.

Note In the above test, if Fe^{3+} ions are in excess, green colour appears instead of blue.

Example 4. Lassaigne's test for the detection of nitrogen fails in

(a) $NH_2CONHNH_2 \cdot HCl$	(b) NH ₂ NH ₂ ·HCl
(c) NH ₂ CONH ₂	(d) $C_6H_5NHNH_2 \cdot HCl$

Sol. (b) Lassaigne's test is positive for nitrogen only when the compound contains carbon along with nitrogen. $NH_2NH_2 \cdot HCl$ contains nitrogen but does not contain carbon. Thus, NaCN is not formed and test of N is negative.

Detection of Sulphur

Mainly two tests are used to detect the presence of sulphur in organic compounds.

 (i) A part of Lassaigne extract is acidified with CH₃COOH and then (CH₃COO)₂Pb solution is added. Formation of black precipitate confirms the presence of sulphur in the compound.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow PbS \downarrow + 2CH_3COO^-Na^-$$

Black ppt.

(ii) A few drops of sodium nitroprusside solution are added to a part of soda extract. The appearance of purple colouration confirms the presence of sulphur.

$$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$$

Purple colour

If the compound contains both sulphur and nitrogen then Lassaigne's extract forms sodium thiocyanide, which gives blood red colouration of $Fe(SCN)_3$ with $FeCl_3$.

$$Na + C + N + S \longrightarrow NaSCN \xrightarrow{\text{Sodium}} Sodium and a sulphocyanide.}$$

Tests for Halogens

The soda extract of organic compound is boiled with conc. HNO_3 to expel the gases. Here, the HNO_3 decomposes NaCN and Na₂S (if present) in the soda extract.

e.g.
$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN^{\uparrow}$$

 $Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S^{\uparrow}$
 $Na + X \longrightarrow NaX (X = Cl, Br, I)$
Soda extract

It is then cooled and treated with AgNO_3 solution. It will form

• A white ppt. soluble in NH₄OH solution indicates the presence of chlorine in organic compound.

$$NaCl + AgNO_3 \longrightarrow AgCl \downarrow + NaNO_3$$

White ppt.

- A dull yellow ppt partially soluble in $\rm NH_4OH$ solution indicates the presence of bromine in the organic compound.

$$NaBr + AgNO_3 \longrightarrow AgBr \downarrow + NaNO_3$$

Dull yellow ppt.

• A yellow ppt insoluble in NH₄OH indicates the presence of iodine in the organic compound.

Note

- In the detection of halogens if cyanide and sulphide are not removed before adding silver nitrate solution, these radicals will combine with silver nitrate and produce white and black precipitate of AgCN and Ag₂S respectively.
- H_2SO_4 cannot be used instead of HNO_3 as it gives white ppt. of Ag_2SO_4 with $AgNO_3$ which interfere with the test of chlorine.

Beilstein Test for Halogens

If organic compound gives blue or green colour at the tip of red hot copper wire, it indicates the presence of halogens in the organic compound. Several halogen free compounds such as pyridine, purines, urea, thiourea, etc., also give green colour to the flame, thus this test is not very reliable.

Note Since, CuF₂ is non-volatile, fluorine does not give this test.

Layer Test for Bromine and Iodine

The presence of nitrogen and sulphur does not interfere in this test. In this test, add a little sodium extract and acidify with dil. HNO_3 or dil. H_2SO_4 . Then add $CHCl_3$ or CCl_4 and excess of chlorine water. If organic layer becomes yellow or brown, bromine is present and if violet, iodine is present.

Test for Phosphorus

For the detection of phosphorus, organic compound is fused with sodium peroxide, hence phosphorus is converted into sodium phosphate.

$$5Na_2O_2 + 2P_{Compound} \xrightarrow{Fuse} 2Na_3PO_4 + 2Na_2O$$

Sodium
phosphate

The fused mass is extracted with water and obtained extract is boiled with conc. HNO_3 . Upon cooling, a few drops of ammonium molybdate solution are added, a yellow ppt. confirms the presence of phosphorus in the organic compound.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

 $H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow$

$$(\mathrm{NH}_4)_3\mathrm{PO}_4\cdot 12\mathrm{MoO}_3 \downarrow + 21\mathrm{NH}_4\mathrm{NO}_3 + 12\mathrm{H}_2\mathrm{O}$$
Yellow ppt.

Example 5. An organic compound A is oxidised with Na_2O_2 followed by boiling with HNO_3 . The resultant solution is then treated with ammonium molybdate to yield a yellow precipitate.

Based on above observation, the element present in the given compound is (JEE Main 2019)

(a)	nitrogen	(b)	phosphorus
(C)	fluorine	(d)	sulphur

Sol. (b) Organic compound 'A' contain phosphorus as it gives positive test with ammonium molybdate. Phosphorus present in organic compound 'A' get oxidised with Na_2O_2 and form Na_3PO_4 .

 Na_3PO_4 in presence of HNO_3 form H_3PO_4 and $NaNO_3$.

 $Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$

Upon cooling, a few drops of ammonium molybdate solution are added. A yellow ppt. confirms the presence of phosphorus in the organic compound.

$$\begin{array}{c} \mathsf{H_3PO_4+12} \ (\mathsf{NH_4})_2\mathsf{MoO_4}+2\mathsf{1}\mathsf{HNO_3} \longrightarrow \\ (\mathsf{NH_4})_3\mathsf{PO_4}.\mathsf{1}\mathsf{2}\mathsf{MoO_3} \downarrow + 2\mathsf{1}\mathsf{NH_4}\mathsf{NO_3}+\mathsf{1}\mathsf{2}\mathsf{H_2}\mathsf{O} \\ \text{Yellow ppt.} \end{array}$$

Quantitative Analysis

The next step after the identification of elements is their estimation, i.e. to know the percentage of various elements present in an organic compound. It is determined by the methods based on the following principles.

Estimation of Carbon and Hydrogen

The C and H in an organic compound are estimated by **Liebig method.** In this method, the organic compound is heated with dry cupric oxide in an atmosphere of dry oxygen (or air) free from CO_2 . Thus, the C and H present in the organic compound are oxidised to CO_2 and water vapours respectively.

$$\begin{array}{ccc} \mathrm{C} + 2\mathrm{CuO} & \longrightarrow & \mathrm{CO}_2 + 2\mathrm{Cu} \\ \mathrm{2H} + 2\mathrm{CuO} & \longrightarrow & \mathrm{H_2O} + 2\mathrm{Cu} \end{array}$$

• CO_2 vapours are passed through weighed potash bulb which absorbs CO_2 completely. Increase in the weight of potash bulb corresponds to the weight of CO_2 produced.

$$2\text{KOH} + \text{CO}_2 \longrightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$$

• Water vapours are passed through weighed calcium chloride tube (U-shaped). Increase in the weight of CaCl₂ corresponds to the weight of H₂O produced.



Apparatus for the estimation of carbon and hydrogen

From the respective weights, the percentage of C and H can be determined as

(i) % of carbon =
$$\frac{12 \times \text{mass of } \text{CO}_2 \times 100}{44 \times \text{mass of organic compound}}$$

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

Note In this method, near the exit, a silver foil and a bright copper spiral is placed in order to remove halogen and oxides of nitrogen respectively. As, Ag foil converts halogens into AgX while copper reduces oxides of nitrogen into N_{2} .

Example 6. An organic compound contains 69% carbon and 4.8% hydrogen, the remaining being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

(a) 0.69 g and 0.048 g	(b) 0.506 g and 0.086 g
(c) 0.345 g and 0.024 g	(d) None of the above

Sol. (b) %C =
$$\frac{12}{44} \times \frac{\text{mass of CO}_2 \text{ formed}}{\text{mass of substance taken}} \times 100$$

$$69 = \frac{12}{44} \times \frac{\text{Mass of CO}_2 \text{ formed}}{0.2} \times 100$$

$$\therefore \text{ Mass of CO}_2 \text{ formed} = \frac{69 \times 44 \times 0.2}{12 \times 100} = 0.506 \text{ g}$$

$$\% \text{H} = \frac{2}{18} \times \frac{\text{mass of H}_2\text{O formed}}{\text{mass of substance taken}} \times 100$$

$$4.8 = \frac{2}{18} \times \frac{x}{0.2} \times 100$$

$$x = \frac{4.8 \times 18 \times 0.1}{100} = 0.086 \text{ g}$$

Estimation of Nitrogen

Estimation of nitrogen can be done by following two methods

1. Duma's Method

In this method, organic compound is heated with dry copper oxide in a combustion tube in the presence of atmosphere of CO_2 , which is created by heating NaHCO₃ and removing its moisture by passing it in conc H₂SO₄. Upon heating, C and H present, in organic compound are oxidised to CO_2 and water vapours respectively, while N₂ is set free.

A roll of oxidised copper gauze is placed in combustion tube which prevents the backward diffusion of gases evolved. A small amount of N_2 might be oxidised to its oxides but they are reduced back to N_2 with the help of Cu placed at the end of the combustion tube.

$$2C + 2CuO \xrightarrow{\Delta} 2Cu + 2CO_2 \uparrow$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O \uparrow$$

$$N + CuO \longrightarrow N_2 + oxides of N$$

Oxides of nitrogen + Cu \longrightarrow CuO + N₂

The volume of N_2 evolved is recorded with the help of **Schiff's nitrometer tube** which contains 40% KOH solution and provided with Hg seal at the bottom to check the backward flow of the liquid.

Apparatus for estimation of nitrogen are given below.





The volume is reduced to STP by applying the gas p_1V_1 p_2V_2

From the volume of
$$N_2$$
 at STP, the percentage of nitrogen is calculated as

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

Here, V = volume of N₂ evolved at STP m = mass of organic compound taken

Example 7. An organic compound is estimated through Duma's method and was found to evolved 6 moles of CO_2 , 4 moles of H_2O and 1 mole of nitrogen gas. The formula of the compound is (JEE Main 2019)

(a)
$$C_6H_8N$$
 (b) $C_{12}H_8N$
(c) $C_{12}H_8N_2$ (d) $C_6H_8N_2$

Sol. (d) In Duma's method, organic compound is heated with dry cupric oxide in a combustion tube in the atmosphere of CO_2 . Upon heating, C and H present are oxidised to CO_2 and water vapours while N_2 is set free.

Let, the molecular formula of the organic compound (1 mol) be $C_x H_v N_z$. In Duma's method,

$$C_{x}H_{y}N_{z} + \left(2x + \frac{y}{2}\right)CuO \longrightarrow xCO_{2} + \frac{y}{2}H_{2}O + \frac{z}{2}N_{2}$$

$$x \operatorname{mol} + \frac{y}{2}\operatorname{mol} + \frac{z}{2}\operatorname{mol} + \left(2x + \frac{y}{2}\right)Cu$$

Now, $x = 6, \frac{y}{2} = 4 \implies y = 8 \text{ and } \frac{z}{2} = 1 \implies z = 2$

:. Molecular formula of the compound is $C_6H_8N_2$.

2. Kjeldahl's Method

This method is based on the principle that when the nitrogenous compound is heated with conc H_2SO_4 in the presence of potassium sulphate, (which raises the boiling point of H_2SO_4) and $CuSO_4$ (catalyst), the nitrogen present in the compound is converted to ammonium sulphate.

The ammonium sulphate formed, is decomposed with excess of alkali and NH_3 evolved is estimated volumetrically, i.e. by the titration of an acid and NH_3 .

The percentage of N_2 is then calculated from the amount of NH_3 .

Thus, % of nitrogen in a compound =
$$\frac{1.4 \times N \times V}{1.4 \times N \times V}$$

where, N =normality of acid used for the estimation of NH_3 volumetrically

m

- V = volume of acid used
- m = mass of organic compound taken

or %N =
$$\frac{1.4 \times M \times 2\left(V - \frac{V_1}{2}\right)}{\text{mass of organic compound}}$$

equation, $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$



Estimation of Nitrogen by Kjeldahl's Method

Note Kjeldahl's method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring, as nitrogen of these compounds is not quantitatively converted into ammonium sulphate.

Example 8. Which of the following compounds will be suitable for Kjeldahl's method for nitrogen estimation? (JEE Main 2018)



Sol. (b) Estimation of nitrogen through Kjeldahl's method is not suitable for organic compounds containing nitrogen in ring or nitrogen in nitro or azo groups. This is to the nitrogen of these compounds does not show conversion to ammonium sulphate $((NH_4)_2SO_4)$ during the process.

Hence, among the given compounds only aniline can be used suitably for estimation of nitrogen by Kjeldahl's method.

Example 9. A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of $0.50 \text{ MH}_2\text{SO}_4$. The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound. (NCERT)

(a)	46%	(b)	53%
(C)	56%	(d)	87%

Sol. (c) Volume of the acid taken

= 50 mL of 0.5 M
$$H_2SO_4$$

= 25 mL of 1.0 M H_2SO_4

Volume of alkali used for neutralisation of excess acid = 60 mL of 0.5 M NaOH = 30 mL of 1.0 M NaOH

$$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$$

1 mole of $H_2SO_4 = 2$ moles of NaOH

Hence, 30 mL of 1.0 M NaOH = 15 mL of 1.0 M H_2SO_4

:. Volume of acid used by ammonia = 25 - 15 = 10 mL

% of nitrogen =
$$\frac{1.4 \times N_1 \times \text{vol. of acid used}}{m}$$

(where, N_1 = normality of acid and m = mass of the organic compound taken)

% of nitrogen =
$$\frac{1.4 \times 2 \times 10}{0.5}$$
 = 56.0%

Estimation of Halogens

In case of halogens, estimation is done with **Carius method.** In this method, the known mass of organic compound is heated in a sealed tube with fuming HNO_3 in the presence of $AgNO_3$.

As a result, halogen present in the organic compound is converted into AgX which is weighed.

The percentage of halogens can be calculated with the help of direct formulae as

% of chloring $-\frac{35.5}{}$	$\sim \frac{\text{mass of AgCl} \times 100}{\text{mass of AgCl} \times 100}$
143.5	mass of compound
% of bromine $-\frac{80}{3}$ ×	mass of AgBr \times 100
188 ⁻¹⁸⁸	mass of compound
% of joding $-\frac{127}{127}$	mass of AgI \times 100
1000000000000000000000000000000000000	mass of compound

Example 10. 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound. **(NCERT)**

(a) 40%	(b) 37%
(c) 25%	(d) 85%

Sol. (b) The mass of the organic compound taken = 0.3780 g

Mass of AgCl formed
$$= 0.5740$$
 g

Percentage of chlorine =
$$\frac{35.5}{143.5} \times \frac{\text{mass of AgCl formed}}{\text{mass of substance taken}} \times 100$$

$$=\frac{35.5}{143.5}\times\frac{0.5740}{0.3780}\times100=37.566\%$$

Estimation of Sulphur

It is also estimated by **Carius method.** In this case, a known mass of compound is heated with conc. HNO₃, resulting to oxidation of its sulphur to $\rm H_2SO_4$, which is collected as $\rm BaSO_4$ by using barium chloride solution.

The percentage of sulphur is calculated by the formula

% of sulphur = $\frac{32}{233} \times \frac{\text{mass of BaSO}_4 \times 100}{\text{mass of organic compound}}$

Estimation of Phosphorus

For the estimation of phosphorus weighed amount of organic compound is heated with conc. HNO_3 in a **Carius tube.** Phosphorus present in the compound is converted into phosphoric acid.

Contents of the tube are heated with $MgCl_2$ solution in the presence of NH_4Cl and NH_4OH (magnesia mixture), the $MgNH_4PO_4$ so formed is collected, washed, dried and ignited to get magnesium pyrophosphate ($Mg_2P_2O_7$) which is weighed and the percentage of P is calculated with the help of formulae as,

% of P =
$$\frac{62}{222} \times \frac{\text{mass of Mg}_2 P_2 O_7 \text{ formed } \times 100}{\text{mass of organic compound}}$$

Estimation of Oxygen

It is usually found by difference between the total percentage composition and the sum of the percentages of all other elements.

It can also be estimated directly. In this method, a known mass of organic compound is decomposed by heating in a stream of N_2 gas.

The gaseous product is passed over a red hot coke that forms CO. It is further passed through warm I_2O_5 where, CO gets converted to CO_2 .

Percentage of oxygen can be find out from amount of CO_2 produced by the formulae as

% of oxygen =
$$\frac{32}{44} \times \frac{\text{mass of CO}_2 \times 100}{\text{mass of organic compound}}$$

Calculation of Molecular Weight

Mainly following two methods can be employed to calculate the molecular weight of a compound.

1. Molecular Weight (*m*) of Volatile Substances

Victor Meyer's method (applicable only to volatile substances).

$$m = 2 \times V.D.$$

Here, V.D = vapour density

or
$$m = \frac{\text{mass of compound} \times 22400}{\text{volume of vapour given by substance at NTH}}$$

2. Molecular Weight of Non-Volatile Substances

These are of following two types

(i) **Silver salt method** (for organic acids only) A known mass of an organic acid is converted into its silver salt by using ammonical silver nitrate solution.

On ignition, the silver salt of the acid leaves a residue of metallic silver.

 $\begin{array}{c} R\text{COOH} \xrightarrow[\text{AgNO}_3]{} R\text{COOAg} \xrightarrow[\text{Ignition}]{} \text{Ag}\\ m = \text{equivalent wt.} \times \text{basicity}\\ \text{Eq. wt.} = \left(\frac{\text{wt. of silver salt} \times 108}{\text{wt. of silver}}\right) - 107 \end{array}$

(ii) Chloroplatinate method (for organic bases only) Amines and most organic bases react with chloroplatinic acid (H_2PtCl_6) to form salts. Chloroplatinates of general formula, $B_2H_2PtCl_6$ where, *B* is a monoacidic base.

On heating, the salt decomposes to yield platinum metal.

$$2R\mathrm{NH}_{3} + \mathrm{H}_{2}\mathrm{PtCl}_{6} \longrightarrow (R\mathrm{NH}_{3})_{2}\mathrm{PtCl}_{6} \xrightarrow{\mathrm{Ignition}} \mathrm{Pt}$$

$$m = \mathrm{equivalent} \ \mathrm{wt.} \times \mathrm{acidity}$$

$$\frac{\mathrm{Wt. of chloroplatinate} (W)}{\mathrm{Wt. of platinum} (w)} = \frac{2B + 410}{195}$$
or
$$2B = \left(\frac{W}{w} \times 195\right) - 410$$

or
$$B = \left(\frac{W}{w} \times \frac{195}{2}\right) - 205$$

where, B is the equivalent weight of base.

Note For problems based on organic qualitative analysis see chapter experimental chemistry.

Example 11. 0.759 g of a silver salt of a dibasic organic acid on ignition left 0.463 g metallic silver. The equivalent weight of acid is

(a)	50	(b)	65
(C)	70	(d)	85

Sol. (c) Equivalent weight of silver salt = Equivalent weight of Ag

$$\frac{0.759}{E} = \frac{0.463}{108}$$

:. Equivalent weight of silver salt = 177

 \therefore Equivalent weight of acid = 177 - 108 + 1 = 70

Practice Exercise

ROUND I Topically Divided Problems

Purification of Organic Compounds

1. Mixture of sugar and common salt is separated by crystallisation by dissolving in

(a)	H_2O	(b)	C_2H_5OH
(c)	C_6H_6	(d)	None of these

- **2.** Fractional crystallisation is carried out to separate a mixture of
 - (a) organic solids mixed with inorganic solids
 - (b) organic solids slightly soluble in water
 - (c) organic solids having small difference in their solubilities in suitable solvent
 - (d) organic solids having great difference in their solubilities in suitable solvent
- **3.** A mixture of iodine and sodium chloride can be easily separated by
 - (a) fractional distillation(b) steam distillation(c) chromatography(d) sublimation
- 4. Anthracene is purified by
 - (a) filtration(b) distillation(c) crystallisation(d) sublimation
- **5.** Sublimation is a process in which a solid
 - (a) changes into vapour form
 - (b) changes into another allotropic form
 - (c) changes into liquid form
 - (d) None of the above
- **6.** Which of the substance is purified by sublimation?

(a)	Naphthalene	(b)	Benzoic acid
(c)	Camphor	(d)	All of these

c)) Campl	hor	((d)	All	0İ	these

- **7.** In a solution, solvent can be separated from solute by one of the following process
 - (a) decantation (b) filtration
 - (c) distillation (d) sedimentation
- **8.** Which of the following is useful for making pure water from a solution of salt in water?
 - (a) Filtration (b) Distillation
 - (c) Chromatography (d) Steam distillation
- **9.** Impure glycerine can be purified by
 - (a) steam distillation (b) simple distillation
 - (c) vacuum distillation (d) extraction with a solvent

- **10.** Absolute alcohol cannot be obtained by simple fractional distillation because
 (a) pure C₂H₅OH is unstable
 - (b) C_2H_5OH forms hydrogen bonds with water
 - (c) boiling point of C_2H_5 OH is very close to that of water
 - (d) constant boiling azeotropic mixture is formed with
 - water
- 11. A mixture of acetone and methanol can be separated by(a) steam distillation(b) vacuum distillation
 - (a) steam distillation(b) vacuum distill(c) fractional distillation(d) None of these
- **12.** Fractional distillation is useful to obtain
 (a) petroleum
 (b) coal tar
 (c) crude alcohol
 (d) All of these
- **13.** Steam distillation is based on the fact that vaporisation of organic liquid takes place at (a) lower temperature than its boiling point
 - (b) higher temperature than its boiling point
 - (c) its boiling point
 - (d) water and organic liquid both undergo distillation
- **14.** Glycerol can be separated from spent-lye in soap industry by
 - (a) steam distillation
 - (b) fractional distillation
 - (c) distillation under reduced pressure
 - (d) ordinary distillation
- **15.** If dichloromethane (DCM) and water (H_2O) are used for differential extraction, which one of the following statements is correct? (JEE Main 2019)
 - (a) DCM and $\rm H_2O$ would stay as lower and upper layer respectively in the separting funnel (SF)
 - (b) DCM and $\rm H_2O$ would stay as upper and lower layer respectively in the separating funnel (SF)
 - (c) DCM and $\rm H_2O$ will be miscible clearly
 - (d) DCM and H_2O will make turbid/colloidal mixture
- **16.** Which of the following compounds cannot be purified by steam distillation?
 - (a) Nitrobenzene
 - (b) Bromobenzene
 - (c) Salicylaldehyde
 - (d) *p*-hydroxybenzaldehyde

- **17.** The best and latest technique for isolation,
 - purification and separation of organic compounds is
 - (a) crystallisation (b) distillation (NCERT)
 - (c) sublimation (d) chromatography
- **18.** The principle of column chromatography is (JEE Main 2019)
 - (a) differential absorption of the substances on the solid phase
 - (b) differential adsorption of the substances on the solid phase
 - (c) gravitational force
 - (d) capillary action
- **19.** Chromatography technique is used for the separation of

 - (a) small samples of mixture
 - (b) plant pigments
 - (c) dyestuff
 - (d) All of the above
- **20.** Adsorbent is made of ... in TLC.
 - (a) silica gel(b) alumina(c) Both (a) and (b)(d) None of these
- **21.** In paper chromatography
 - (a) mobile phase is liquid and stationary phase is solid(b) mobile phase is solid and stationary phase is liquid
 - (c) Both phases are liquids
 - (d) Both phases are solids
- **22.** A mixture of camphor and benzoic acid can be easily separated by
 - (a) sublimation
 - (b) extraction with solvent
 - (c) fractional crystallisation
 - (d) chemical method
- **23.** The presence of carbon in an organic compound is detected by heating it with
 - (a) sodium metal to convert it into NaCN
 - (b) CaO to convert it into CO which burns with a blue flame
 - (c) CuO to convert it into CO_2 which turns lime water milky
 - (d) Cu wire to give a bluish green flame
- 24. 0.5 g of hydrocarbon gave 0.9 g water on combustion. The percentage of carbon in the hydrocarbon is
 - (a) 60.6 (b) 28.8 (c) 80.0 (d) 68.6
- **25.** Lassaigne's test is used for the detection of
 - (a) carbon only
 - (b) hydrogen only
 - (c) oxygen only
 - (d) nitrogen, sulphur and halogens

- **26.** In Lassaigne's test, the organic compound is fused with a piece of sodium metal in order to
 - (a) increase the ionisation of the compound
 - (b) decrease the melting point of the compound
 - (c) increase the reactivity of the compound
 - (d) convert the covalent compound into a mixture of ionic compounds
- **27.** Nitrogen containing organic compound when fused with sodium forms
 - (a) sodium azide
 - (b) sodium cyanide
 - (c) sodamide
 - (d) sodium cyanate
- 28. In chromatography technique, the purification of compound is independent of (JEE Main 2021)
 - (a) mobility or flow of solvent system
 - (b) solubility of the compound
 - (c) length of the column or TLC plate
 - (d) physical state of the pure compound

Qualitative Analysis of Organic Compounds

29. The sodium extract of an organic compound on acidification with acetic acid and addition of lead acetate solution gives a black precipitate. The organic compound contains

(a) nitrogen	(b) halogen
(c) sulphur	(d) phosphorus

- **30.** Select the correct statement about the detection of element in the organic compounds.
 - (a) Sulphur present in the organic compound on fusion with sodium converts into $Na_2S_2O_3$
 - (b) FeCl_3 gives purple colour when added to the sodium fusion extract
 - (c) Sodium nitroprusside is used to detect the presence of sulphur
 - (d) All of the above
- **31.** In Lassaigne's solution, pink/violet colouration is produced when sodium nitroprusside solution is added. It indicates the presence of
 - (a) sulphur
 - (b) nitrogen(c) chlorine
 - (d) None of the above
 - (u) None of the above
- **32.** Red colour complex ion formed on adding $FeCl_3$ to sodium extract when N and S both are present in organic compound is
 - (a) $[Fe(CN)_6]^{4-}$ (b) $[Fe(CNS)]^{2+}$ (c) $[Fe(CNS)_2]^+$ (d) $[Fe(CN)_6]^{3-}$

33. Which of the organic compounds will give red colour in Lassaigne's test?

(a) NaCN
(b)
$$NH_2$$
—C— NH_2
(c) NH_2 —C— NH_2
(d) None of these

- 34. Which of the following sodium compound/compounds are formed when an organic compound containing both nitrogen and sulphur is fused with sodium?(a) Cyanide and sulphide (b) Thiocyanate(c) Sulphite and cyanide (d) Nitrate and sulphide
- 35. The sodium extract of an organic compound on treatment with FeSO₄ solution, FeCl₃ and HCl gives a red solution. The organic compound contains

 (a) both nitrogen and sulphur
 (b) nitrogen only
 (c) sulphur only
 (d) halogen
- **36.** The function of boiling sodium extract with conc. HNO_3 before testing for halogen is
 - (a) to make the solution acidic
 - (b) to make the solution clear
 - (c) to convert Fe^{2+} to Fe^{3+}
 - (d) to destroy $CN^{-} \mbox{ and } S^{2-} \mbox{ ions }$
- **37.** Copper wire test of halogens is known as

(a) Liebig's test	(b) Lassaigne's tes
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(c) Fusion test (d) Beilstein's test

- **38.** Which of the following statements is not applicable to Beilstein test?
 - (a) Green or bluish green flame is due to the formation of volatile cupric halides
 - (b) It does not tell us to which halogen is present in the organic compound
 - (c) It is a very sensitive test that can be easily performed
 - (d) It is a sure test for the presence of halogen
- **39.** During AgNO₃ test for detection of halogens, sodium extract is boiled with few drops of conc. HNO₃ to decompose

(a)	NaCN	(b)	Na ₂ S
(c)	Both (a) and (b) (d)	None of these

40. Detection of phosphorus in the compound can be done by its conversion into phosphate. Reagent to identify phosphate ion is

(a) sodium nitroprusside(b) ammonium molybdate(c) potassium ferrocyanide(d) potassium ferricyanide

41. Reagent, 1-naphthylamine and sulphanilic acid in acetic acid is used for the detection of (JEE Main 2021,) (a) N_2O (b) NO^{3-} (c) NO (d) NO^{2-} 42. Which of the following elements can't be detected by direct tests?(a) N (b) O (c) S (d) Br

Quantitative Analysis of Organic Compounds

- **43.** Carbon and hydrogen are estimated in organic compounds by
 - (a) Kjeldahl's method(b) Duma's method(c) Liebig's method(d) Carius method
- **44.** Duma's method involves the determination of nitrogen content in the organic compound in the form of
 - (a) NH_3 (b) N_2 (c) NaCN (d) $(NH_4)_2SO_4$
- **45.** In the estimation of nitrogen by Duma's method, 1.18 g of an organic compound gave 224 mL of N_2 at NTP. The percentage of nitrogen in the compound is
 - (a) 20.0 (b) 11.8 (c) 47.7 (d) 23.7
- **46.** In Kjeldahl's method for the estimation of nitrogen, the formula used to

(a) % of N =
$$\frac{1.4 V w}{N}$$
 (b) % of N = $\frac{1.4 V N}{w}$
(c) % of N = $\frac{V N w}{1.8}$ (d) % of N = $\frac{1.4 w N}{V}$

- **47.** Mark the incorrect statement for Kjeldahl's method of estimation of nitrogen.
 - (a) Nitrogen gas is collected over caustic potash solution
 - (b) Potassium sulphate is used as boiling point elevator of H_2SO_4
 - (c) Copper sulphate or mercury acts as a catalyst
 - (d) Nitrogen is quantitatively decomposed to give ammonium sulphate
- **48.** In kjeldahl's method of estimation of nitrogen, $CuSO_4$ acts as
 - (a) oxidising agent
 - (b) reducing agent
 - (c) catalytic agent
 - (d) hydrolysis agent
- 49. 29.5 mg of an organic compound containing nitrogen was digested according of Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralisation. The percentage of nitrogen in the compound is (AIEEE 2010)

 (a) 59.0
 (b) 47.4
 (c) 23.7
 (d) 29.5

50. In Carius method, 0.099 g organic compound gave 0.287 g AgCl. The percentage of chlorine in the compound will be

(a) 28.6	(b)	71.7
(c) 35.4	(d)	64.2

51. When 0.35 g of an organic compound is heated with HNO₃ and AgNO₃ in a Carius tube, it gives 0.70 g of silver chloride. The percentage of chlorine in the compound is
(a) 54.8%
(b) 49.47%

(a)	54.8%	(b)	49.47%
(c)	34.6%	(d)	25.85%

52. Which of the following methods is used to estimate iodine in the laboratory?

(a)	Duma's method	(b)	Liebig's method
(c)	Kjeldahl's method	(d)	Carius method

53. 0.197 g of an organic substance when heated with excess of strong nitric acid and silver nitrate gave 0.3525 g of silver iodide. The percentage of iodine

in the compound is		
(a) 84.6%	(b)	38.6%
(c) 96.68%	(d)	53.86%

- 54. How much of sulphur is present in an organic compound, if 0.53 g of the compound gave 1.158 g of BaSO₄ on analysis ?
 - (a) 10% (b) 15% (c) 20% (d) 30%
- **55.** In the estimation of sulphur in an organic compound, fuming nitric acid is used to convert sulphur into

(a) SO_2 (b) H_2S (c) H_2SO_3 (d) H_2SO_4

- **1.** Molecular mass of a volatile substance may be obtained by
 - (a) Beilstein method (b) Lassaigne method
 - (c) Victor Meyer's method (d) Liebig's method
- **2.** Incorrect statement is
 - (a) Aniline can be purified by steam distillation
 - (b) Beilstein test is not given by fluorine
 - (c) Kjeldahl's method is used for the estimation of sulphur
 - (d) Lassaigne's test is used in the qualitative detection of elements in organic compounds
- **3.** The most satisfactory method to separate sugars is to use
 - (a) fractional crystallisation (b) chromatography
 - (c) Benedict's reagent (d) Carius method

- **56.** Phosphorus is estimated as (a) Na_3PO_4 (b) P_2O_5 (c) P_2O_3 (d) $Mg_2P_2O_7$
- **57.** The simplest formula of a compound containing 50% of element *X* (at. wt. 10) and 50% of element *Y* (at. wt. 20) is

(a) XY (b) XY_2 (c) X_2Y (d) X_2Y_2

- **58.** A compound containing 80% C and 20% H is likely to be (a) C_6H_6 (b) C_2H_6 (c) C_2H_4 (d) C_2H_2
- **59.** The empirical formula of an acid is CH_2O_2 , the probable molecular formula of the acid may be (a) $C_2H_4O_2$ (b) $C_3H_6O_4$ (c) $C_2H_2O_4$ (d) CH_2O_2
- 60. 0.4 g of a silver salt of a monobasic organic acid gave 0.26 g pure silver on ignition. The molecular weight of the acid is (atomic weight of silver = 108) (a) 58 (b) 37 (c) 89 (d) 105
- 61. An organic compound contains 29.27% carbon, 5.69% hydrogen and 65.04% bromine. Its empirical formula is
 (a) C₃H₅Br
 (b) C₃H₃Br
 (c) C₂H₄Br₂
 (d) C₃H₇Br
- 62. The silver salt of a monobasic acid on ignition gave 60% of Ag. The molecular weight of the acid is
 (a) 37 (b) 57 (c) 73 (d) 88
- 63. 4 g of hydrocarbon on complete combustion gave 12.571 g of CO₂ and 5.143 g of water. What is the empirical formula of the hydrocarbon?
 (a) CH
 (b) C₂H₃
 (c) CH₂
 (d) CH₃

ROUND II Mixed Bag

- 4. The compound formed in the positive test for nitrogen with the Lassaigne's solution of an organic compound is (AIEEE 2004)
 - (a) $\operatorname{Fe}_4[\operatorname{Fe}(\operatorname{CN})_6]_3$
 - (b) $Na_3[Fe(CN)_6]$
 - (c) $Fe(CN)_3$
 - (d) $\operatorname{Na}_4[\operatorname{Fe}(\operatorname{CN})_5\operatorname{NOS}]$
- **5.** An organic compound having molecular mass 60 is found to contain C = 20%, H = 6.67% and N = 46.67%while rest is oxygen. On heating it gives NH_3 along with a solid residue. The solid residue gives violet colour with alkaline copper sulphate solution. The compound is (AIEEE 2005)

- 6. Percentage composition of an organic compound is as follows C = 10.06, H = 0.84, Cl = 89.10
 Which of the following corresponds to its molecular formula if the vapour density is 60.0?
 (a) CH₃Cl (b) CHCl₃ (c) CH₂Cl₂ (d) None of these
- 7. The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 M sulphuric acid. The excess of acid required 20 mL of 0.5 M sodium hydroxide solution for complete neutralisation. The organic compound is

 (a) acetamide
 (b) benzamide
 - (c) urea (d) thiourea
- **8.** Which of the following statement is correct?
 - (a) Impure glycerine can be purified by ordinary distillation
 - (b) Ethanol and water can be separated from each other completely by simple distillation method as they form azeotropic mixture
 - (c) Two solid organic substances are said to be different if their mixed melting point is depressed below the melting points of both of these
 - (d) Naphthalene can be separated from benzoic acid by sublimation
- 9. Which of the following statements is/are in correct?
 - (a) Liebig's method is used for the quantitative estimation of both C and H.
 - (b) Duma's method is used for the quantitative estimation of N in all nitrogen containing organic compounds.
 - (c) In Liebig's combustion method, ordinary CuO is used.
 - (d) Silver salt method is a chemical method for the determination of equivalent mass of organic acids.
- **10.** Which of the following statements is/are correct?
 - (a) When a Lassaigne's solution is heated with HNO_3 , cooled, and $AgNO_3$ solution is added, a yellow precipitate, partially soluble in NH_3 or NH_4OH , indicates the presence of iodine in organic compound.
 - (b) When (CH₃COO)₂Pb solution is added to the acidified Lassaigne's extract of an organic compound having S, a white precipitate of PbS is formed.
 - (c) An organic compound containing N, on heating with conc. H_2SO_4 gives $(NH_4)_2SO_4$ which liberates NH_3 on treatment with excess of NaOH.
 - (d) The molecular mass of a non-volatile organic compound is determined either by Duma's method or by Victor Meyer's method.
- **11.** Which of the following compounds produce a white precipitate of AgCl on warming with ethanolic silver nitrate solution?

(a)
$$CH_2 = CHCl$$
 (b) $O_2N - CH = CH - Cl$



- **12.** An organic compound of formula C_3H_7N was analysed for nitrogen by Duma's method. Calculate the volume of N_2 gas evolved at NTP from 2 g of substance.
 - (a) 405 mL (b) 342 mL (c) 392 mL (d) 100 mL
- **13.** A gaseous hydrocarbon has 85% carbon and vapour density of 28. The possible formula of the hydrocarbon will be
 - (a) C_3H_6 (b) C_2H_4 (c) C_2H_2 (d) C_4H_8
- 14. A chromatography column, packed with silica gel as stationary phase, was used to separate a mixture of compounds consisting of (A) benzanilide (B) aniline and (C) acetophenone. When the column is eluted with a mixture of solvents, hexane : ethyl acetate (20 : 80), the sequence of obtained compounds is (*JEE Main 2020*)
 (a) (C), (A) and (B) (b) (A), (B) and (C) (c) (B), (C) and (A) (d) (B), (A) and (C)
- 15. An organic compound having carbon, hydrogen and sulphur contains 4% of sulphur. The minimum molecular weight of the compound is
 (a) 500 (b) 800 (c) 400 (d) 100
- 16. When thiourea is heated with metallic sodium, the compound which can't be formed is
 (a) NaCNS (b) NaCN (c) Na₂SO₄ (d) Na₂S
- **17.** If a compound on analysis was found to contain C = 18.5%, H = 1.55%, Cl = 55.04% and O = 24.81%, then its empirical formula is (a) CH_2OCl (b) CH_2ClO_2 (c) $ClCH_2O$ (d) CHClO
- 18. An organic compound has carbon and hydrogen percentage in the ratio 6 : 1 and carbon and oxygen percentage in the ratio 3 : 4. The compound has the empirical formula
 (a) C₂H₆O
 (b) CHO₂
 (c) CH₄O
 (d) CH₂O
- 19. What is the molecular formula of a compound, its empirical formula is CH₂O and its molecular weight is 90?
 (a) C₃H₆O₃ (b) C₆H₆O₃ (c) C₄H₈O₄ (d) C₂H₆O₂
- 20. An organic compound contains C = 40%, H = 13.33% and N = 46.67%. Its empirical formula would be
 (a) CHN
 (b) C₂H₂N
 (c) C₃H₇N
 (d) CH₄N

21. The empirical formula of a compound is CH_2 . One mole of this compound has a mass of 42 g. Its molecular formula is

(a) C_2H_2	(b)	C_3H_6
(c) C ₃ H ₈	(d)	CH_4

- **22.** Simple distillation can be used to separate (a) a mixture of ethanol (bp 78°C) and water (bp 100°C)
 - (b) a mixture of benzene (bp 80°C) and toluene (bp 110°C)
 - (c) a mixture of ether (bp 35° C) and toluene (bp 110° C) (d) None of the above
- **23.** An organic compound is heated with CuO in a test tube. The evolved gases are allowed to pass into lime water which turns milky. The milkiness of lime is due to
 - (a) $CaSO_4$ and confirms the presence of S
 - (b) $CaCO_3$ and confirms the presence of C
 - (c) $CaSO_3$ and confirms the presence of C
 - (d) $CaCO_3$ and confirms the presence of S

24. Match the following :

Column I (Test / Method)	Column II (Reagent)
I. Lucas test	A. $C_6H_5SO_2Cl/aq.KOH$
II. Dumas method	B. HNO ₃ /AgNO ₃
III. Kjeldahl's method	C. CuO /CO $_2$
IV. Hinsberg test	D. Conc. HCl and $ZnCl_2$
	E. H ₂ SO ₄

Cod	\mathbf{les}			
	Ι	II	III	IV
(a)	D	С	В	Е
(b)	В	D	Е	А
(c)	D	С	Е	А
(d)	В	А	С	D

25. Organic compound ' $A' \longrightarrow$ Lassaigne's extract



II. H_2SO_4

Prussian blue coloured complex

The above Lassaigne's extract on treatment with

- Fe²⁺ does not give blood red colour because of the
- (a) absence of S in the organic compound
- (b) presence of halogen in the organic compound
- (c) dissociation of NaSCN into Na₂S and NaCN
- (d) conversion of NaSCN into HSCN
- **26.** A flask contains a mixture of isohexane and 3-methylpentane. One of the liquids boils at 63°C while the other boils at 60°C. What is the best way to separate the two liquids and which one will be distilled out first? (JEE Main 2020)
 - (a) Fractional distillation 3-methylpentane
 - (b) Fractional distillation, isohexane
 - (c) Simple distillation, 3-methylpentane
 - (d) Simple distillation, isohexane
- **27.** The correct match between Columns I and II is

	Column II (Separation method)
Ρ.	Sublimation
Q.	Recrystallisation
R.	Steam distillation
S.	Differential extraction
	P. Q. R. S.

(JEE Main 2020)	Codes			(JEE Main 2019)
	A B	С		
	(a) Q R	S		
	(b) Q R	Р		
	(c) S R	Р		
	(d) R P	S		

Round I

Answers

1. (b)	2. (c)	3. (d)	4. (d)	5. (a)	6. (d)	7. (c)	8. (b)	9. (c)	10. (d)
11. (c)	12. (d)	13. (a)	14. (c)	15. (a)	16. (d)	17. (d)	18. (b)	19. (d)	20. (c)
21. (c)	22. (d)	23. (c)	24. (c)	25. (d)	26. (d)	27. (b)	28. (d)	29. (c)	30. (c)
31. (a)	32. (b)	33. (b)	34. (b)	35. (a)	36. (d)	37. (d)	38. (d)	39. (c)	40. (b)
41. (d)	42. (b)	43. (c)	44. (b)	45. (d)	46. (b)	47. (a)	48. (c)	49. (c)	50. (b)
51. (b)	52. (d)	53. (c)	54. (d)	55. (d)	56. (d)	57. (c)	58. (b)	59. (d)	60. (a)
61. (d)	62. (c)	63. (c)							
Round II									
1. (c)	2. (c)	3. (b)	4. (a)	5. (b)	6. (b)	7. (c)	8. (c)	9. (c)	10. (c)
11. (b)	12. (c)	13. (d)	14. (a)	15. (b)	16. (c)	17. (d)	18. (d)	19. (a)	20. (d)
21. (b)	22. (c)	23. (b)	24. (c)	25. (c)	26. (b)	27. (a)			

Solutions

Round I

- **1.** Common salt is not soluble in alcohol but sugar is soluble in alcohol easily.
- **2.** Fractional crystallisation is used to purify organic solids which dissolve in a particular solvent, but their rate of solubility is slightly different.
- **3.** Sublimation is the process employed for those solids which convert directly into vapours on heating without converting into liquid phase like I₂.
- **7.** Distillation is applied to separate a solute from the solvent, if organic liquid is stable at its boiling point and contains a non-volatile impurity.
- **10.** The components of an azeotropic mixture are separated by special method, i.e. azeotropic distillation. The simple fraction which distills at 337.8 K is a ternary azeotrope consisting of water, some alcohol and benzene.
- **12.** Fractional distillation is used for the separation of crude petroleum into various fractions like coal tar, crude alcohol and petroleum.
- **13.** Organic compounds which are volatile in steam can be purified by steam distillation. It is based on the fact that vaporisation of organic liquid takes place at lower temperature than its boiling point.
- **14.** Glycerol can be separated from spent lye in soap industry by the distillation under reduced pressure because it decomposes near its boiling point.
- **15.** Dichloromethane, DCM or (CH_2Cl_2) is heavier (density = 1.3266 g cm^{-3}) than water (density = 1 g cm^{-3}). So, DCM and H_2O will stay as lower and upper layer respectively in the separating funnel (SF).
- **16.** The process of steam distillation is used for the separation and purification of liquids which are volatile in steam like nitrobenzene, bromobenzene, salicylaldehyde etc.
- 18. In column chromatography, separation of mixture of compounds (adsorbate) takes place over a column of solid adsorbent (silica gel and Al₂O₃) packed in a glass tube.

When an appropriate eluant (liquid) is allowed to flow down the column, the compounds present in the mixture get adsorbed to different extent on the adsorbent column and thus complete separation takes place.

Thus, column chromatography is based on the differential adsorption of the substance on the solid phase.

22. Camphor and benzoic acid both being sublimate and cannot be separated by sublimation. Chemical reagents are used to separate such mixtures.

24. % of
$$H = \frac{2}{18} \times \frac{\text{weight of } H_2O}{\text{weight of organic compound}} \times 100$$
$$= \frac{2}{18} \times \frac{0.9}{0.5} \times 100 = 20\%$$

- :. The percentage of carbon = 100 20 = 80%
- **27.** Organic compound containing nitrogen is fused with a small piece of sodium metal to form NaCN.

$$\begin{array}{ccc} Na + & \underbrace{C + N}_{From \ organic} & \longrightarrow & NaCN \end{array}$$

- **28.** In chromatography technique, the purification of a compound is independent of the physical state of the pure compound.
- **29.** The sulphur containing organic compounds when fused with sodium metal give Na_2S which react with lead acetate and forms black ppt. of PbS.

$$Na_2S + (CH_3COO)_2Pb \longrightarrow PbS + 2CH_3COONa$$

Black
ppt.

- **30.** Sulphur is present in the sodium extract in the form of sodium sulphide (Na₂S). FeCl₃ gives blood red colour with sodium extract having N and S both.
- **31.** $Na_2S + Na_2[Fe(CN)_5 NO] \longrightarrow Na_4[Fe(CN)_5 NOS]$ Sod. extract Sodium nitroprusside Pink/violet colour Thus, organic compound contains sulphur.
- **32.** When N and S both are present in the organic compound, a red colour complex ion $[Fe(CNS)]^{2+}$ is formed on adding $FeCl_3$ to sodium extract.

$$\begin{array}{ccc} {\rm NaCNS + FeCl}_3 & \longrightarrow & [{\rm Fe(SCN)}]{\rm Cl}_2 \ + {\rm NaCl} \\ & \\ {\rm Blood \ red \ colour} \end{array}$$

33. In the Lassaigne's test, if organic compound consists of both N and S then a red colour is obtained on adding

aqueous FeCl_3 to sodium extract. $\text{NH}_2 \longrightarrow \overset{\parallel}{\text{C}} \text{NH}_2$ contains both N and S hence, it will give red colour in Lassaigne test.

$$NaCNS + FeCl_3 \longrightarrow [Fe(SCN)]Cl_2 + NaCl$$

Blood red colour

34. When organic compound containing both nitrogen and sulphur is fused with sodium, sodium thiocyanate is formed.

$$Na + S + C + N \longrightarrow NaSCN$$

38. If organic compound gives blue or green colour at the tip of red hot copper wire, this indicates the presence of halogens in the compound. However, compounds like urea, thiourea etc., also give blue or green colour in this test even in the absence of halogens, thus, it is not a sure test for halogens.

40. Detection of phosphorus in the organic compound can be done by its conversion into phosphate. The ammonium molybdate is used to identify phosphate ion.

$$Na_2PO_4 + 3HNO_2 \longrightarrow H_2PO_4 + 3NaNO_4$$

$$\begin{array}{c} \mathrm{H_3PO_4+12(\mathrm{NH_4})_2\mathrm{MoO_4+21\mathrm{HNO_3}}} \xrightarrow{\Delta} \\ \mathrm{Ammonium} \\ \mathrm{molybdate} \\ (\mathrm{NH_4})_3 \,\mathrm{PO_4} \cdot 12\mathrm{MoO_3} + 21\mathrm{NH_4NO_3} + 12 \,\mathrm{H_2O} \\ \mathrm{Yellow \; ppt.} \end{array}$$

- **41.** For detection of NO²⁻, the following test is used. NO²⁻ + CH₃COOH \longrightarrow HNO₂
- **42.** Oxygen cannot be detected by direct test because oxygen is present in atmosphere and all tests are carried in atmosphere of oxygen.
- **43.** Carbon and hydrogen are estimated in organic compounds by Liebig's method.

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$

Percentage of carbon and hydrogen is calculated from the weights of $\rm CO_2$ and $\rm H_2O$ produced.

44. Duma's method involves the determination of nitrogen content in the organic compound in the form of N_2 .

$$\begin{split} & N_2 O + C u \longrightarrow N_2 + C u O \\ \% \text{ of } N = & \frac{28}{22400} \times \frac{\text{volume of } N_2 \text{ at } NTP}{\text{weight of compound}} \times 100 \end{split}$$

45. % of N =
$$\frac{28}{22400} \times \frac{\text{volume of N}_2 \text{ at NTP}}{\text{weight of compound}} \times 100$$

= $\frac{28}{22400} \times \frac{224}{1.18} \times 100 = \frac{28}{1.18} = 23.72\%$

- **48.** Kjeldahl's method is used for the estimation of nitrogen. The organic compound is heated with conc. H_2SO_4 in the presence of K_2SO_4 (used to raise boiling point of H_2SO_4) and $CuSO_4$ (used as catalyst) to convert all the nitrogen into $(NH_4)_2SO_4$.
- **49.** Weight of organic compound = 29.5 mg

$$\begin{array}{rcl} \mathrm{NH}_3 + \mathrm{HCl} &\longrightarrow \mathrm{NH}_4\mathrm{Cl} \\ \mathrm{HCl} &+ & \mathrm{NaOH} &\longrightarrow \mathrm{NaCl} + \mathrm{H}_2\mathrm{O} \\ \mathrm{(remaining)} &\stackrel{15 \times 0.1 \,\mathrm{M}}{_{of\,1.5 \,\mathrm{mmol}}} \\ \mathrm{Total \ millimole \ of \ HCl} = 2 \\ \mathrm{Millimole \ used \ by \ NH}_3 = 2 - 1.5 = 0.5 \\ \mathrm{Weight \ of \ NH}_3 = 0.5 \times 17 \ \mathrm{mg} = 8.5 \ \mathrm{mg} \\ \mathrm{Weight \ of \ nitrogen} = \frac{14}{17} \times 8.5 \ \mathrm{mg} = 7 \ \mathrm{mg} \\ \mathrm{\% \ of \ nitrogen} = \frac{7}{29.5} \times 100 = 23.7\% \\ \end{array}$$
50. % of chlorine = $\frac{35.5}{143.5} \times \frac{\mathrm{mass \ of \ AgCl}}{\mathrm{mass \ of \ the \ compound}} \times 100 \\ = \frac{35.5}{143.5} \times \frac{0.287}{0.099} \times 100 = 71.71\% \end{array}$

51. % of chlorine = $\frac{35.5}{143.5} \times \frac{\text{wt. of AgCl}}{\text{wt of organic compound}} \times 100$ = $\frac{35.5}{143.5} \times \frac{0.70}{0.35} \times 100$ = 49.47%

53. AgI = I
(108 + 127) = 127
Thus, percentage of iodine =
$$\frac{127}{235} \times \frac{0.3525}{0.197} \times 100$$

= 96.68%

56. Phosphorus is estimated as $Mg_2P_2O_7$.

$$P \xrightarrow{HNO_3} H_3PO_4$$

$$\begin{split} \mathrm{H_3PO_4} + \mathrm{Mg}^{2+} + \mathrm{NH_4OH} & \longrightarrow \mathrm{MgNH_4PO_4} \\ & 2\mathrm{MgNH_4PO_4} & \longrightarrow \mathrm{Mg_2P_2O_7} + \mathrm{H_2O} + 2\mathrm{NH_3} \\ \mathrm{\% \ of \ P} = & \frac{62 \times \mathrm{wt. \ of \ Mg_2P_2O_7 \times 100}}{222 \times w} \end{split}$$

57.	Atom	At. mass (a)	% (b)	$\frac{b}{a}$	Simplest ratio
	X	10	50	$\frac{50}{10} = 5$	2
	Y	20	50	$\frac{50}{20} = 2.5$	1

Hence, empirical formula = X_2Y

- **59.** Empirical formula of acid = CH_2O_2 We know that molecular formula = n (empirical formula) If n = 1, molecular formula = $(CH_2O_2)_1 = CH_2O_2$ If n = 2, molecular formula = $(CH_2O_2)_2 = C_2H_4O_4$ If n = 3, molecular formula = $(CH_2O_2)_3 = C_3H_6O_6$
 - Thus, the probable molecular formula = $\rm CH_2O_2$

60. Mass of silver salt = 0.4 g Mass of silver = 0.26 g

$$\frac{\text{Eq. mass of silver salt}}{\text{Eq. mass of Ag}} = \frac{\text{wt. of silver salt}}{\text{wt. of silver}}$$

Eq. mass of silver salt= $\frac{108 \times 0.4}{0.26}$ = 166

Eq. mass of acid = 166 - 108 = 58 g

1

61. C: H: Br =
$$\frac{29.27}{12}$$
 : $\frac{5.69}{1}$: $\frac{65.04}{80}$
= 2.43 : 5.69 : 0.813 = 3 : 7 :

So, empirical formula = C_3H_7Br

62.
$$\frac{E}{108} = \frac{100}{60}$$

Eq. wt. of the silver salt, $E = 108 \times \frac{100}{60} = 180$
 \therefore Eq. wt. of the acid $= E - 108 + 1 = 73$
63. % $C = \frac{12}{44} \times \frac{12.571}{4.0} \times 100 = 85.7$

% H =
$$\frac{2}{18} \times \frac{5.143}{4.0} \times 100 = 14.3$$

The mole ratio of C to H is $\frac{85.7}{12} : \frac{14.3}{1} = 7.14 : 14.3 = 1 : 2$
So, empirical formula = CH₂

Round II

1. Victor Meyer's method is applicable only for the determination of molecular mass of volatile substances.

6.	Atom	Atomic mass (a)	Percentage (b)	$\frac{b}{a} = x$	Ratio
	С	12	10.06	$\frac{10.06}{12} = 0.83$	1
	Н	1	0.84	$\frac{0.84}{1} = 0.84$	1
	Cl	35.5	89.10	$\frac{89.10}{35.5} = 2.50$	3

 $Empirical formula = CHCl_3$

Empirical formula mass = $12 + 1 + 106.5 = 119.5 \approx 120$

Molecular mass = $2 \times V$. D. = $2 \times 60 = 120$

Here, V.D. = Vapour density

 $n = \frac{\text{molar mass}}{\text{empirical formula mass}} = \frac{120}{120} = 1$

 $\label{eq:Molecular formula} \textbf{Molecular formula} = (\textbf{CHCl}_3)_1 = \textbf{CHCl}_3$

7. Let unreacted 0.1 M (0.2 N) $H_2SO_4 = V mL$ 20 mL of 0.5 M NaOH = V mL of 0.2 N H_2SO_4 20 × 0.5 = V × 0.2

$$V = \frac{20 \times 0.5}{0.2} = 50 \text{ mL}$$

Vol. of used,
$$H_2SO_4 = 100 - 50 = 50 \text{ mL}$$

% of $N = \frac{1.4 \text{ }NV}{1.4 \text{ }NV} = \frac{1.4 \times 0.2 \times 50}{1.4 \text{ }NV} = 46.67\%$

0.30

w

a)
$$CH_3CONH_2 = \frac{14 \times 100}{59} = 23.73\%$$

(b)
$$C_6H_5CONH_2 = \frac{14 \times 100}{121} = 11.57\%$$

(c)
$$\text{NH}_2\text{CONH}_2 = \frac{28 \times 100}{60} = 46.67\%$$

(d) $\text{NH}_2\text{CSNH}_2 = \frac{28 \times 100}{76} = 36.84\%$

8. Glycerine is purified by vacuum distillation. It boils with decomposition at 563 K but if pressure is lowered to 12 mm, it boils at 453 K without decomposition.

Naphthalene and benzoic acid both sublime thus cannot be separated by sublimation.

Other given statements are true.

- 9. For this method dry, CuO is used.
- **10.** Test given in (a) indicates the presence of Br.

(d) Victor Meyer's method is used to determine the molecular mass of volatile organic compound.Duma's method is used to calculate the percentage of nitrogen.

12. % of N in C₃H₇N =
$$\frac{14}{57} \times 100$$

Further % of N = $\frac{1}{8} \times \frac{V}{2}$
 $V = 392$ mL

13.

Symbol	Percent age	At. mass	Relative no. of atoms	Simplest ratio
С	85	12	$\frac{85}{12} = 7.08$	$\frac{7.08}{7.08} = 1$
Н	15	1	$\frac{15}{1} = 15$	$\frac{15}{7.08} = 2.11 = 2$

Empirical formula is CH₂

Mol. mass =
$$2 \times V.D. = 2 \times 28 = 56$$

mol. formula mass 56

Hence, molecular formula = $(CH_2)_n = (CH_2)_4 = C_4H_8$

14. In column chromatography, individual components of a mixture are separated by elution (washing with solvents).

In the given separation, the solvent used has greater polarity due to greater composition of polar solvent ethyl acetate (80%), and therefore, more polar component (having greater dipole moment) of mixture will have more R_f value and will get eluted faster. Dipole moment of components in mixture is in the order :



:. The sequence of obtained compounds is (C) > (A) > (B) **15.** As the minimum molecular weight must have at least one S atom.

$$S\% = \frac{\text{wt. of one S atom}}{\text{min. mol. wt.}} \times 100$$
$$4 = \frac{32}{\text{min mol wt}} \times 100$$
Minimum mol. wt. = $\frac{32 \times 100}{4} = 800$

16. The chemical formula of thiourea is NH₂CSNH₂ so here Na₂S, NaCN and NaCNS will be formed but not Na₂SO₄.

$$= \frac{6}{15} \times 100 : \frac{1}{15} \times 100 : \frac{8}{15} \times 100$$
$$= 40 : 6.67 : 53.3$$
$$= \frac{40}{12} : \frac{6.67}{1} : \frac{53.3}{16} = 1 : 2 : 1$$

So, empirical formula = CH_2O

19. Empirical formula = CH₂O Molecular weight = 90 Empirical formula weight of CH₂O = 12 + (1 × 2) + 16 = 30 $n = \frac{\text{molecular weight}}{\text{empirical formula weight}} = \frac{90}{30} = 3$ Molecular formula = (CH₂O)₃ = C₃H₆O₃ **21.** CH₂ = 12 + 2 = 14 and $n = \frac{42}{14} = 3$ mol Formula = (CH₂)₃ = C₃H₆.

23.
$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O$$

Milky
 $Ca(OH)_2 + CO_2 \longrightarrow CaCO_2 + H_2O$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2$$

Milky

- 24. I. Lucas test → Conc. HCl+ ZnCl₂ It is a solution of anhydrous zinc chloride in concentrated hydrochloric acid. This solution is used to classify alcohols of low molecular weight. Primary, secondary and tertiary alcohols are classified based on their reactivity with the Lucas reagent.
 - II. **Duma's method** \rightarrow CuO/CO₂

This method is based upon the fact that nitrogenous compound when heated with cupric oxide in an atmosphere of CO_2 , yield free nitrogen.

Traces of oxide of nitrogen, which may be formed in some cases, are reduced to elemental nitrogen by passing over heated copper spiral.

III. Kjeldahl's method $\,{\rightarrow}\, H_2\!SO_4$

This method is used for the quantitative determination of nitrogen containing organic

substances. In this method, consists of heating a sample at $360-410^{\circ}$ C with concentrated sulphuric acid (H₂SO₄), which decomposes the organic sample by oxidation to liberate the reduced nitrogen as ammonium sulphate.

IV. **Hinsberg test** \rightarrow C₆H₅SO₂Cl/aq. KOH

Hinsberg reagent is an alternative name for benzene sulphonyl chloride. This name is given for its use in the Hinsberg test for the detection and distinction of primary, secondary and tertiary amine in a given sample.

So, correct match is option (c).

The correct match is

 $I \to (D), II \to (C), III \to (E), IV \to (A).$

25. Lassaigne's extract gives violet colour complex, it clearly confirms the presence of sulphur. The formation of Prussian blue coloured complex confirms the presence of nitrogen.

If that Lassaigne's extract doesn't give red colour complex it means excess of Na metal caused dissociation of NaSCN into Na₂S and NaCN.

 $2Na + NaSCN \xrightarrow{\Delta} Na_2S + NaCN$

26. The boiling points of the given compounds are very close.

 \therefore Simple distillation can't be used.

Fractional distillation is only suitable to separate the two liquids.

Further, the liquid with lower boiling point distills out first. Since, 3-methyl pentane has a more symmetrical structure as compared to isohexane.

Therefore, it has a greater area of contact and better interaction between molecules. This accounts for the greater boiling point of 3-methyl pentane as compared to isohexane.



27. The correct option is $(A) \rightarrow (Q)$; $(B) \rightarrow (R)$; $(C) \rightarrow (S)$

- (A) H_2O and sugar mixture They do not react chemically. On heating, solubility of sugar in H_2O increases and on rapid cooling of saturated solution, sugar recrystallises (Q).
- (B) H_2O and aniline mixture Aniline is steam volatile but insoluble in H_2O . So, steam distillation (*R*) is employed for their separation.
- (C) H_2O and toluene mixture Toluene is steam non-volatile and also insoluble in H_2O . So, differential extraction method (S) can be used to separate them.