

27.

PRACTICAL ORGANIC CHEMISTRY

1. PURIFICATION

1.1 Introduction

Organic chemistry is based on carbon compounds either natural or synthetic. Such organic compounds are in a crude form. In order to observe the properties of them, a pure compound is necessary. Purity of the compound is required for their reactions. There are various methods of purification of organic compounds based on their physical and chemical properties such as adsorption, boiling point, sublime nature, etc.

Few of them are as follows:

- (a) Fractional Crystallization (b) Sublimation (c) Chromatography
- (d) Distillation (e) Differential Extraction

- (a) **Fractional crystallization:** Fractional crystallization is based on the solubility of a compound in a specific solvent. It is used when an organic compound is sparingly soluble in some solvent at room temperature but considerably soluble at higher temperature and impurity is highly soluble. Its solution can be heated dissolving the compound along with impurities and cooling it to form crystals of highly pure organic compound leaving impurities behind in the solution called mother liquor.

Examples:

1. p-Xylene
2. Benzoic acid- It is sparingly soluble in cold water but highly soluble in hot water.
3. Fructose

- (b) **Sublimation:** It is the property of a substance to change its state from a solid state to a vapour state without passing through a liquid state. Such compounds can be heated and separated from the impurity by separating its vapour by using the inverted funnel method.

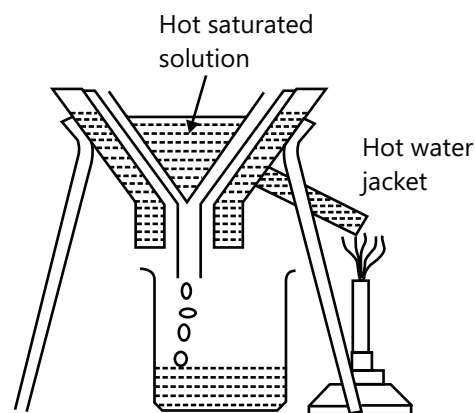


Figure 27.1: Hot Water funnel

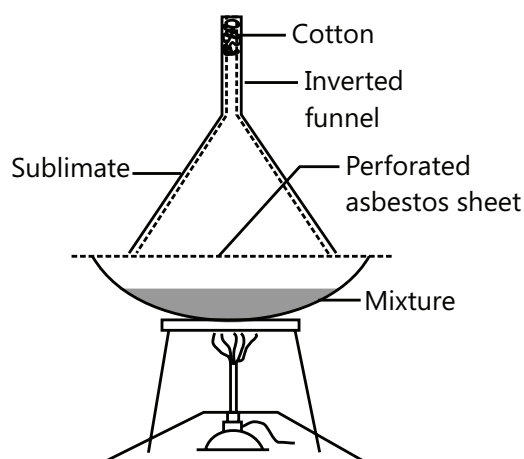


Figure 27.2: Sublimation

Example: Camphor, benzoic acid, anthracene.

Table 27.1: Melting Points

Substance	M.P.	Substance	M.P.
1,4-Dichlorobenzene	55	Benzoic acid	122
Naphthalene	82	Salicylic acid	159
1-Naphthol	96	Camphor	177
Acetanilide	114	Caffeine	235

(c) Chromatography: Chromatography is used for the separation of most of the compounds. There are two phases used in this technique namely stationary phase and mobile phase. Stationary phase is immobile throughout the process while mobile phase or eluent is a moving phase. Chromatography is based on its solubility in mobile phase as well as adsorption of the compound in stationary phase.

Terms involved in chromatography:

- (i) **R_f factor:** Retardation factor is used in identifying the product separated using paper or thin layer chromatography. R_f factor

is given as: $R_f = \frac{\text{Migration distance of substance}}{\text{Migration distance of solvent front}}$

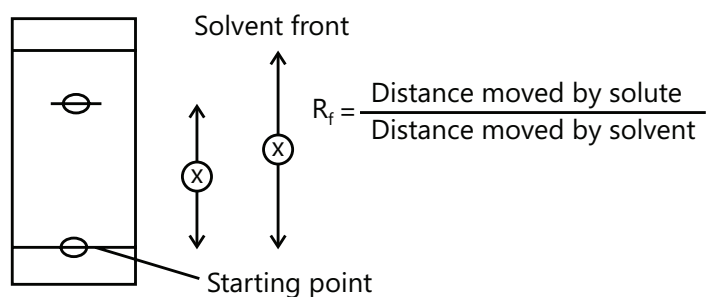


Figure 27.3: Chromatogram

In paper chromatography, if compounds are colourless, then ninhydrin spray is used to visualize the compounds in the form of various colours.

- (ii) **Stationary Phase:** The phase in chromatography which is stationary with respect to the components of a mixture is called stationary phase. In case of column chromatography, stationary phase adsorbs components at different heights.
- (iii) **Mobile Phase or Eluent:** The phase which moves along with components of a mixture is called a mobile phase or an eluent. Mobile phase determines R_f factor which is dependent on the solubility of the components in a given solvent or eluent.

The following are the different types of chromatography:

- **Column chromatography:** Column chromatography is a separation technique in which the stationary bed is within a tube. The particles of the solid stationary phase or the support coated with a liquid stationary phase may fill the whole inside volume of the tube (packed column) or be concentrated on or along the inside tube wall leaving an open, unrestricted path for the mobile phase in the middle part of the tube (open tubular column). Differences in rates of movement through the medium are calculated to different retention times of the sample. Silica gel is a commonly used stationary phase.
- **Paper chromatography:** Paper chromatography is a technique that involves placing a small dot or line of sample solution onto a strip of chromatography paper. The paper is placed in a jar containing a shallow layer of solvent and sealed. As the solvent rises through the paper, it meets the sample mixture, which starts to travel up the paper with the solvent.
- **Thin layer chromatography (TLC):** Thin layer chromatography (TLC) is a widely employed laboratory technique and is similar to paper chromatography. However, instead of using a stationary phase of paper, it involves a stationary phase of a thin layer of adsorbent like silica gel, alumina, or cellulose on a flat, inert substrate.

Example: Separation of vitamins.

- **Gas chromatography:** In this type if the stationary phase is a solid it is called solid gas chromatography. If the stationary phase is a high-boiling liquid deposit on a suitable support, it is called gas liquid chromatography. The mobile phase used is generally N_2 , He or Ar, which do not react with the sample to be separated out. Gas chromatography is based on solubility of different gases in their stationary phase. The least soluble constituent comes out first while the most soluble comes out at the end. Thus various components of a gaseous mixture are separated. Gas chromatogram is a graph of the detector response when a gas comes out vs time.

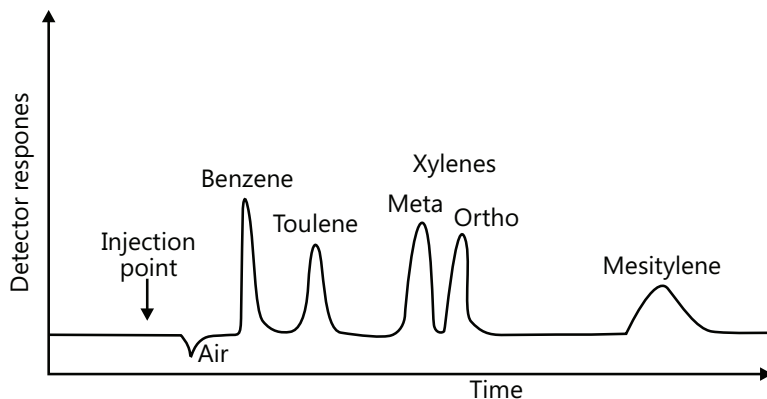


Figure 27.4: Plot of Detector response vs time

Example: Separation of amino acids.

- (d) **Distillation:** There are two types of distillations based on the difference between the boiling points of the organic compound and its impurity.
 - (i) **Simple distillation:** This method is used if there is sufficient difference in the boiling points of volatile liquids.

Example: a) Chloroform (CHCl_3) and aniline (PhNH_2) can be separated by simple distillation due to large difference in their boiling points.

b) ether (b.p. 308K) and toluene (b.p. 384K)

- (ii) **Fractional distillation:** This method is used to separate two volatile liquids when the difference in their boiling points is small. In such a case when one liquid starts boiling the other is also converted to vapour considerably. So, we get the vapours of both compounds. Hence, to avoid this fractionating column is used. Fractionating column opposes the vapour of one with higher boiling point and its vapour again condenses and goes to solution.

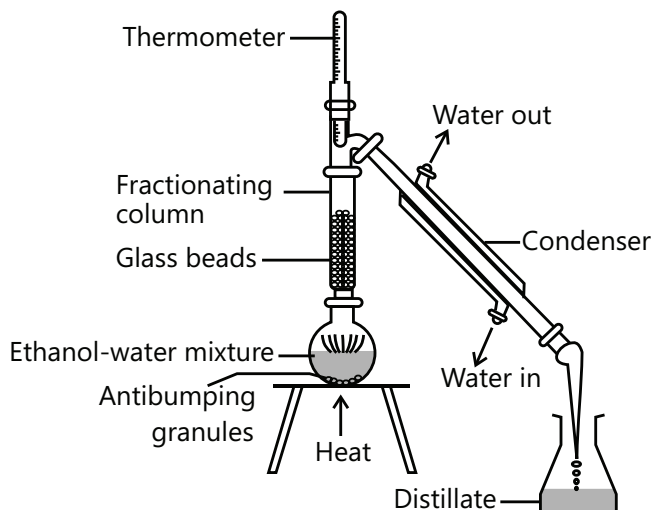


Figure 27.5: Distillation

Example: (a) Ethanol-water mixture, (b) Petroleum products are separated by fractional distillation, (c) Cyclohexane-toluene mixture, (d) Acetone (b.p. 330K) and methyl alcohol (b.p. 338K)

- (iii) **Steam distillation:** This method is used to separate the compounds which are steam volatile and are insoluble in water. In this method, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and vapour is condensed and collected in a receiver. Then the compound being insoluble in water can be separated easily.

Example: (a) Aniline-water mixture, (b) Isolation of citral, (c) Nitro benzene

- (iv) **Vacuum distillation:** The lowering of pressure on the surface of a liquid lowers its boiling point. As a result of this, a liquid can be boiled and distilled, without any decomposition, at temperature much below its normal boiling point.

Example: Distillation of crude oil in oil refineries, Glycerol.

- (v) **Azeotropic distillation:** Azeotropic mixture is a mixture having a constant boiling point. The constituents of this mixture cannot be separated by fractional distillation. So, in this method a third component is used in distillation. The process is based on the fact that dehydrating agents like C_6H_6 , CCl_4 , diethyl ether, etc. depress the partial pressure of one of the original components. As a result, the boiling point of that component is raised sufficiently and thus the other component distills over.

Example: Separation of ethanol and water.

- (e) **Differential extraction:** This method is based on the different solubilities of an organic compound in different solvents. If a compound is soluble in water but more soluble in an organic solvent, it is separated by shaking it with an organic solvent. As a result, the organic compound gets dissolved into a organic solvent which can be extracted from water.

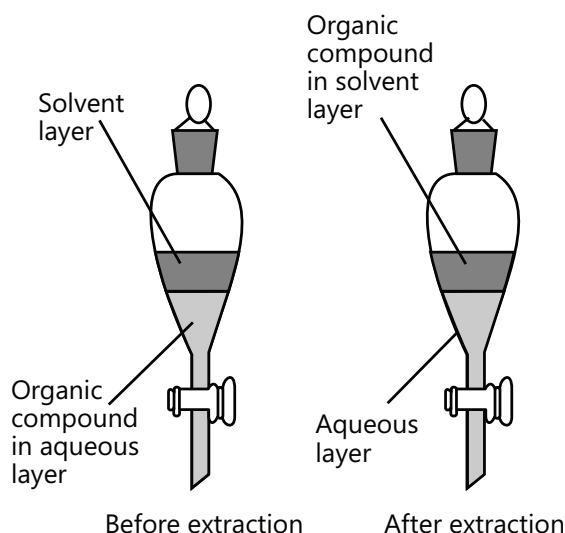


Figure 27.6: Separating Funnel

Example: (a) Iodine (I_2) can be purified as it is sparingly soluble in water but highly soluble in CCl_4 (b) Extraction of caffeine from tea

Illustration 1: Two volatile compounds differ in their boiling points by 20K, how will they be separated?

- What types of compound are purified by sublimation?
- How will I_2 be separated from KCl?
- How are o- and p-nitro phenols separated?
- How is aniline purified?
- How is a mixture of naphthalene and kerosene oil separated?

Sol: Fractional distillation.

- Substances whose vapour pressures become equal to the atmospheric pressure much below their b.p.
- Either by sublimation or by extraction with CCl_4 followed by evaporation.
- o-nitrophenol is steam volatile while p-nitro phenol is not due to intramolecular H-bonding. Hence, they are separated by steam distillation.
- Vacuum distillation or steam distillation.
- By simple distillation.

Illustration 2: p-nitrophenol and o-nitrophenol are separated by

- Crystallization
- Fractional crystallization
- Distillation
- Steam distillation

Sol: Steam distillation is used to separate the compounds which are steam volatile and are insoluble in water. This process effectively allows for distillation at lower temperatures.

2. QUALITATIVE ESTIMATION

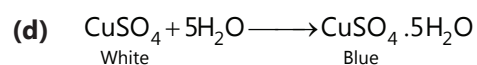
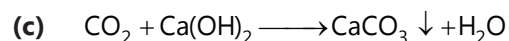
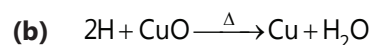
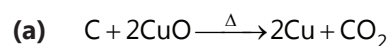
2.1 Introduction

Qualitative estimation is used in identifying elements in a compound. While judging the properties of a compound, it is necessary to find elements constituting it. Organic compounds contain mainly C and H; in addition to these they may contain O, N, S, halogens and P.

2.2 Detection of Elements

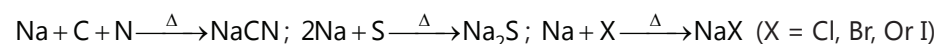
2.2.1 Detection of C and H

Many organic compounds burn with a sooty flame or char when strongly heated. C and H are detected by heating the compound with cupric oxide (CuO) in a dry test tube. They are oxidized to CO₂ and H₂O respectively. CO₂ turns lime water milky and H₂O turns anhydrous CuSO₄ blue.



2.2.2 Preparing Sodium Fusion Extract

Most of the organic compounds are covalent. So, it is not possible to detect elements in it due to a strong covalent bond. Therefore, it is necessary to convert them into ionic forms which can split easily in a polar medium. Sodium (Na) being strongly electropositive is used in this process by preparing sodium fusion extract. While preparing sodium fusion extract, the organic compound is strongly heated with clean sodium metal in a test tube fusing it with the sample. The fused sample is plunged into water, and a few tests are performed on the solution to identify elements in it. Following reactions occur:

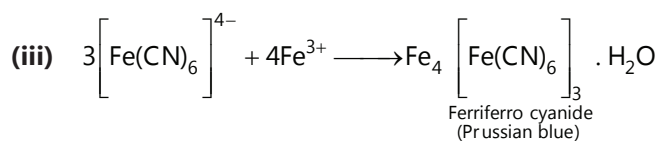
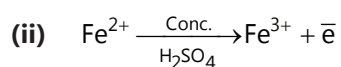
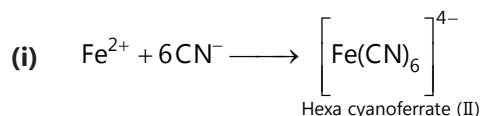


C, N, S and X come from organic compound.

2.2.3 Lassaighe's Test

N, S, halogens and phosphorous present in organic compound is detected by Lassaighe's test, after preparing sodium fusion extract.

- (a) **Test for nitrogen:** The sodium fusion extract is boiled with FeSO₄ and then acidified with Concentrated H₂SO₄. The appearance of Prussian blue colour confirms the presence of N. The following reaction occurs:



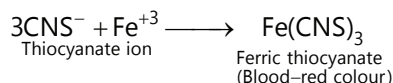
Exception:

1. This test is not given by compounds which do not contain C atoms but contain N atoms.

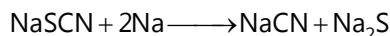
Example: NH_2NH_2 (hydrazine), NH_2OH (hydroxyl amine).

Reason: Since, these compounds do not contain carbon, in a sodium fusion extract, CN^- ion will not form and Prussian blue colour is not observed.

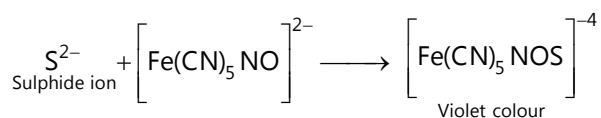
2. This test is also not given by diazonium salts although they contain both C and N elements, because the nitrogen in them is released due to strong heating while forming a sodium fusion extract.
3. If S is also present in organic compound along with C and N, this test gives a blood red colour.



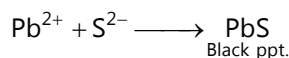
4. If fusion is carried out with excess of sodium, the fusion gives cyanide and sulphide giving usual tests.

**(b) Test for sulphur:**

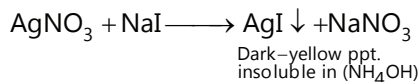
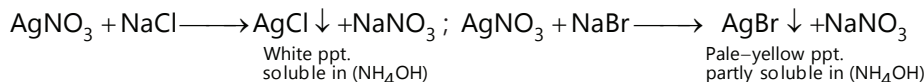
- (i) The sodium fusion extract is treated with sodium nitroprusside. Appearance of violet colour confirms the presence of S.



- (ii) The extract is treated with acetic acid and lead acetate is added to it. The appearance of black ppt. of lead sulphide confirms presence of S.

**(c) Test for halogens:**

- (i) Extract is acidified with HNO_3 and then treated with AgNO_3 . A white ppt. soluble in NH_4OH indicates the presence of Cl, a yellowish ppt. sparingly soluble in NH_4OH indicates presence of Br, and a yellow ppt. insoluble in NH_4OH shows presence of I.

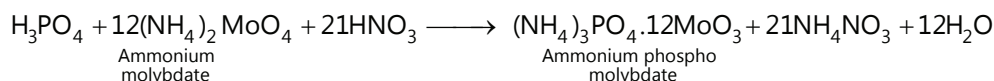


If N and S are also present in the compound, this reaction forms NaCN or Na_2S . These ions interfere with AgNO_3 test. If these ions are not removed they give white ppt. which will confuse it for AgCl .

- (ii) **Organic layer test:** Extract is treated with CS_2 and CCl_4 and then Cl_2 water is added to it. Then it is kept for some time. Appearance of orange colour in organic layer indicates the presence of Br, while a violet colour confirms iodine.



Exception: Urea (NH_2CONH_2) and thiourea (NH_2CSNH_2) do not contain halogens but still give this test.

$$\text{Na}_3\text{PO}_4 + 3\text{HNO}_3 \longrightarrow \text{H}_3\text{PO}_4 + 3\text{NaNO}_3$$


2.3 Detection of Organic Groups

1. **Lucas's reagent (ZnCl_2 ; conc. HCl):** This reagent converts alcohols into the corresponding alkyl chlorides. Zinc chloride (a Lewis acid) increases the reactivity of alcohols towards acid. The test depends on the rate of reaction of primary, secondary, and tertiary alcohols with the reagent at room temperature.

(ii) $R_2CHOH \rightarrow R_2CHCl + H_2O$ (1 hour or maybe longer)

To 1 mL of the alcohol in a small test tube add 6 mL of Lucas' reagent at room temperature. Close the tube with a cork, shake and allow to stand.

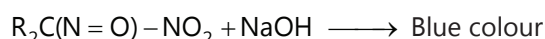
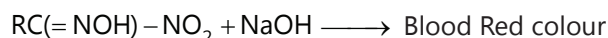
- **Primary alcohols** - The aqueous phase remains clear (except allyl alcohol - droplets after 7 minutes). No turbidity or cloudiness is observed.
- **Secondary alcohols** - Very slow reaction (~ 1 hour or maybe longer) when droplets of alkyl chloride may be seen. Turbidity or cloudiness is observed.
- **Tertiary alcohols** - Very fast reaction and droplets of the alkyl chloride formed almost immediately. Turbidity or cloudiness is observed.

(i) The given alcohol is first converted into its alkyl iodide by treating it with P & Iodine.

(ii) The alkyl iodide is then treated with silver nitrite (AgNO_2) to convert it into a corresponding nitro alkane.

(iii) The nitroalkane is then treated with nitrous acid (HNO_2), i.e., $\text{NaNO}_2 + \text{HCl}$.

(iv) The resulting solution is finally made alkaline with aqueous NaOH or KOH. If blood red colouration appears it is a primary alcohol. If blue colouration appears it is a secondary alcohol. If the solution remains colourless, indicates a tertiary alcohol.

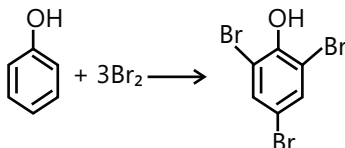


3. Iodoform test: Iodoform test is given by alcohols having $\left(\begin{array}{c} \text{CH}_3 - \text{C} - \text{OH} \\ | \\ \text{H} \end{array} \right)$ group. In Iodoform test, the

compound reacts with I_2 / NaOH reagent to give iodoform (CHI_3) which is pale yellow in colour. It is insoluble in water and has an antiseptic smell.

(b) Phenol detection

(i) Bromine water: Phenols are generally highly reactive towards electrophilic reagents and are readily brominated by bromine water. e.g.



Dissolve or suspend about 0.05 g of the compound in 2 mL of dilute hydrochloric acid and add bromine water dropwise until the bromine colour remains. A white precipitate of the bromophenol may form. Solid bromophenol derivatives can be used for the confirmation of the structure of a phenol.

(ii) Ferric chloride test: Most phenols react with iron (III) chloride to form coloured complexes. The colours vary - red, purple, blue or green - depending on various factors, e.g. the phenolic compound used, the solvent, concentration. Since some phenols do not give colours, a negative test must not be taken as significant without supporting information.

(c) Aldehyde detection

(i) Fehling's solution: Aldehydes reduce Fehling's solution to yellow or red copper (I) oxide.

Preparation of the reagent: Mix equal volumes of Fehling's solution I (aqueous alkaline potassium tartrate) and Fehling's solution II (copper sulphate solution).

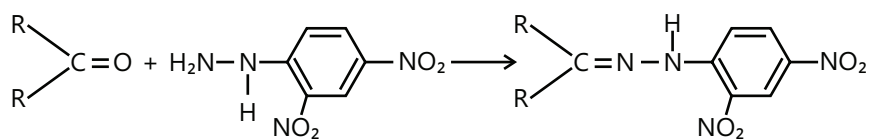
Exception: Only aliphatic aldehydes give this test. Aromatic aldehydes don't give this test.

(ii) Tollen's reagent (Ammoniacal silver nitrate solution): Aldehydes are readily oxidized to carboxylic acids and will reduce Tollen's reagent to produce a silver mirror on the inside of a clean test tube.

Exception: α -hydroxy ketones also give this test but other ketones do not. Hemiacetals and formic acid also give this test. But acetals do not.

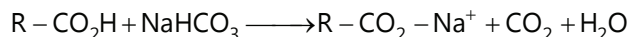
(d) Aldehyde or Ketone detection

(i) Brady's reagent (2,4-Dinitrophenylhydrazine): A test for the carbonyl group ($\text{C}=\text{O}$) in aldehydes and ketones. 2,4-Dinitrophenylhydrazine gives sparingly soluble yellow or red 2,4-dinitrophenylhydrazones with aldehydes and ketones.



$\text{R}, \text{R}' = \text{hydrogen or alkyl}$

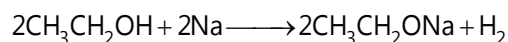
(ii) Iodoform Test: Iodoform test is given by simple methyl ketones and acetaldehyde only i.e. compounds having $(\text{CH}_3 - \text{C} = \text{O}-)$ group. In Iodoform test, the compound reacts with I_2 / NaOH reagent to give iodoform (CHI_3) which is pale yellow in colour. It is insoluble in water and has an antiseptic smell.

(e) Carboxylic acid: Test with 5% aq. NaHCO_3 

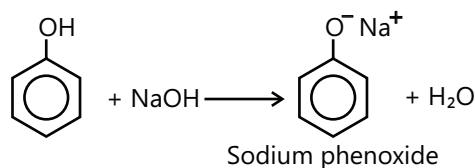
Sodium hydrogen carbonate reacts with carboxylic acids to give the sodium salt of the acid and liberates carbon dioxide. If the acid is insoluble in water and the reaction is sluggish, dissolve the acid in methanol and add carefully to a saturated sodium hydrogen carbonate solution, when a vigorous effervescence will be observed.

(f) Distinction between alcohol, phenol and carboxylic acid

(i) All alcohols react with sodium metal (Na) to evolve H_2 gas. But do not react with NaOH or NaHCO_3 .



(ii) All phenols react with sodium metal (Na) and NaOH. But do not react with NaHCO_3 .



(iii) All carboxylic acids react with sodium metal (Na), NaOH and NaHCO_3 .

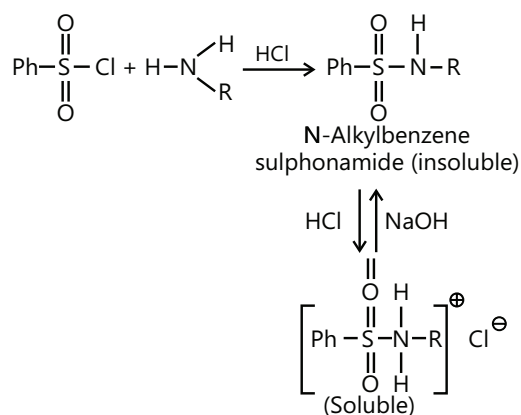
(g) Amines**(i) Reaction with nitrous acid:**

AMINE	REACTION
1° aliphatic	$\longrightarrow \text{N}_2$ evolved
$\text{RNH}_2 + \text{HNO}_2$	$\longrightarrow \text{ROH} + \text{N}_2 + \text{H}_2\text{O}$
1° aromatic	\longrightarrow Diazonium salt is formed.
$\text{ArNH}_2 + \text{HNO}_2$	$\longrightarrow \text{ArN} \equiv \text{N}^+$

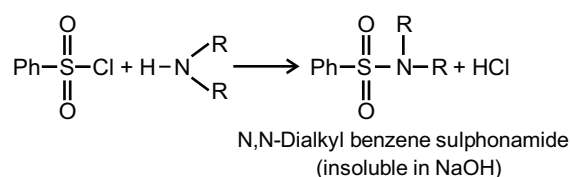
Add the cold diazonium solution and with swirling to a cold solution of 2-naphthol (0.2 g) in 5% NaOH solution (2mL). An orange-red azo dye is formed.

2° aliphatic	\longrightarrow Yellow oily nitrosamines are generally formed.
2° aromatic	$\longrightarrow \text{R}_2\text{NH} + \text{HNO}_2 \longrightarrow \text{R}_2\text{N} - \text{NO}$
3° aliphatic	\longrightarrow No visible reaction
3° aromatic	\longrightarrow Dialkylanilines yield green solid p-nitroso compounds (if p-position unsubstituted).

(ii) Hinsberg reaction: In this test amine is shaken well with Hinsberg reagent (benzene sulphonyl chloride) in the presence of aqueous alkali (either NaOH or KOH). A primary amine will form a soluble sulfonamide salt which precipitates after addition of diluted hydrochloric acid. A secondary amine in the same reaction will directly form an insoluble sulfonamide. A tertiary amine will not react with the sulfonamide but is insoluble. After adding a dilute acid this insoluble amine is converted to a soluble ammonium salt. In this way the reaction can distinguish between the three types of amines.

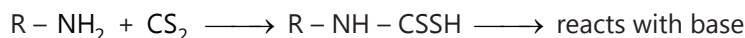


A precipitate which is an insoluble compound (which is insoluble in NaOH solution also) indicates 2° amines.



3° amines do not react with the reagent.

(iii) Reaction with Carbon disulphide (CS₂): Primary amine reacts with CS₂ and further reacts with base due to acidic hydrogen present on nitrogen.

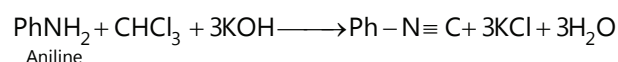


Secondary amine reacts with CS₂ but doesn't react with a base due to the absence of acidic hydrogen.



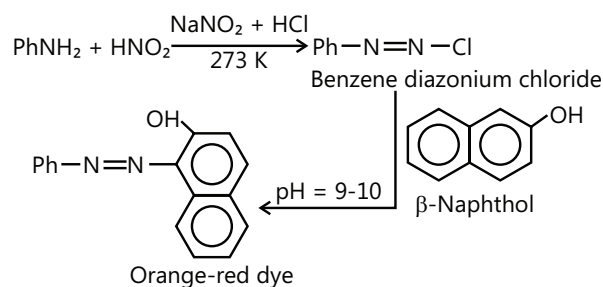
Tertiary amine do not react with CS₂.

(iv) Carbylamine test: 1° aliphatic and aromatic amines on heating with CHCl₃ and KOH give an offensive smell due to the formation of carbylamine.



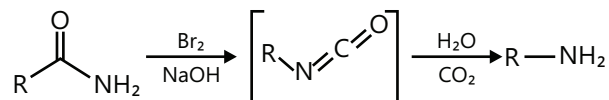
2° and 3° aliphatic and aromatic amines do not give this test.

(v) Azo-dye test: 1° aromatic amines on heating with NaNO₂ and HCl give stable diazonium salts which couple with alkaline solution of β-naphthol to give orange-red azo dye.



(h) Amides

- (i) Simple primary amides can be decomposed by boiling with alkali and thereby evolving ammonia which has pungent smell. E.g. $\text{CH}_3 - \text{CO} - \text{NH}_2 + \text{NaOH} \longrightarrow \text{CH}_3 - \text{CO}_2 - \text{Na}^+ + \text{NH}_3$
- (ii) **Hofmann rearrangement:** Amides show Hofmann rearrangement to form a primary amine when treated with $\text{Br}_2 / \text{NaOH}$



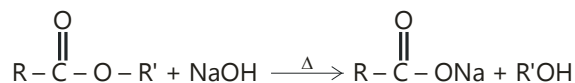
This test confirms presence of amide.

(i) Ester detection

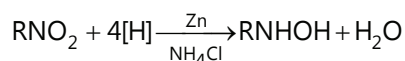
- (i) **Hydroxamic acid test:** $\text{R}-\text{CO}-\text{OR}' + \text{H}_2\text{N}-\text{OH} \longrightarrow \text{R}-\text{CO}-\text{NH}-\text{OH} + \text{R}'-\text{OH}$

Esters react with hydroxylamine in the presence of sodium hydroxide to form the sodium salt of the corresponding hydroxamic acid. On acidification and addition of ferric chloride the magenta-coloured iron (III) complex of the hydroxamic acid is formed.

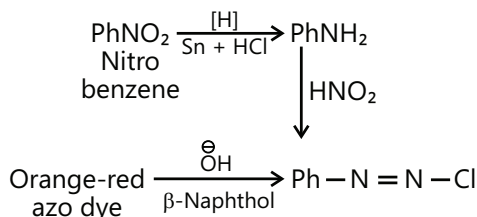
- (ii) **Hydrolysis test:** Esters undergo saponification reaction i.e. hydrolysed with NaOH . The compound is heated with NaOH with a small amount of phenolphthalein. The initial pink colour of the solution is discharged due to the formation of acid, since phenolphthalein shows pink colour in basic medium and is colourless in acidic medium.

**(j) Nitro group detection**

- (i) **Mulliken's test:** The nitro compound is dissolved in alcohol and is reduced with $\text{Zn}/\text{NH}_4\text{Cl}$ or CaCl_2 solution and Zn dust, and boiled. It is then filtered, cooled, and heated with ammoniacal AgNO_3 , white to grey and the black precipitate confirms the presence of nitro group.



- (ii) **Azo dye test:** Aromatic nitro compounds are first reduced to $-\text{NH}_2$ group with $\text{SnCl}_2 + \text{conc. HCl}$ which on reaction with nitrous acid forms diazonium salts. The stable diazonium salt forms orange red dye with alkaline solution of β -naphthol.

**(k) Sugars, Carbohydrates detection**

- (i) **Molisch's test:** This is a general test for carbohydrates. Dissolve 20 - 30 mg of the compound in 2 mL water and add 0.5 mL of the reagent (a 20% solution of 2-naphthol in ethanol). Pour 2 mL of concentrated sulphuric acid from a dropper carefully down the side of the tube so that the acid forms a layer beneath the aqueous solution without mixing with it. A red colouration, changing to dark purple forms at the interface.
- (ii) **Fehling's test:** This forms the reduction test of carbohydrates. Fehling's solution contains blue alkaline cupric hydroxide solution, heated with reducing sugars gets reduced to yellow or red cuprous oxide and is precipitated. Hence, formation of the yellow or brownish-red coloured precipitate helps in the detection of reducing sugars in the test solution.

(iii) **Osazone Test:** The ketoses and aldoses react with phenylhydrazine to produce a phenylhydrazone which further reacts with another two molecules of phenylhydrazine to yield osazone. Needle-shaped yellow osazone crystals are produced by glucose, fructose and mannose, whereas lactosazone produces mushroom shaped crystals. Crystals of different shapes will be shown by different osazones. Flower-shaped crystals are produced by maltose.

(l) Proteins

(i) **Ninhydrin test:** Amino acids also react with ninhydrin at pH = 4. The reduction product obtained from ninhydrin then reacts with NH_3 and excess ninhydrin to yield a blue colored substance. This test is given by only amino acids and proteins which contain free $-\text{NH}_2$ groups in their structure. Proline doesn't give this test due to absence of free $-\text{NH}_2$ group.

(ii) **Xanthoproteic test:** Some amino acids contain aromatic groups that are derivatives of benzene. These aromatic groups can undergo reactions that are characteristics of benzene and benzene derivatives. One such reaction is the nitration of a benzene ring with nitric acid. The amino acids that have activated benzene ring can readily undergo nitration. This nitration reaction, in the presence of activated benzene ring, forms yellow product.

Example: tyrosine, tryptophan, phenylalanine and glutamic acid.

(iii) **Millon's Test:** Millon's test is specific to phenol containing structures (tyrosine is the only common phenolic amino acid). Millon's reagent is concentrated HNO_3 , in which mercury is dissolved. As a result of the reaction a red precipitate or a red solution is considered as positive test. A yellow precipitate of HgO is NOT a positive reaction but usually indicates that the solution is too alkaline.

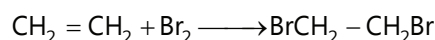
Example: tyrosine, phenylalanine, glycine and β -naphthol.

(iv) **Biuret Test:** The Biuret Test positively identifies the presence of proteins (not less than two Peptides). The reaction in this test involves the complex formation of the proteins with Cu^{2+} ions in a strongly alkaline solution.

Example: gelatin, casein and albumin.

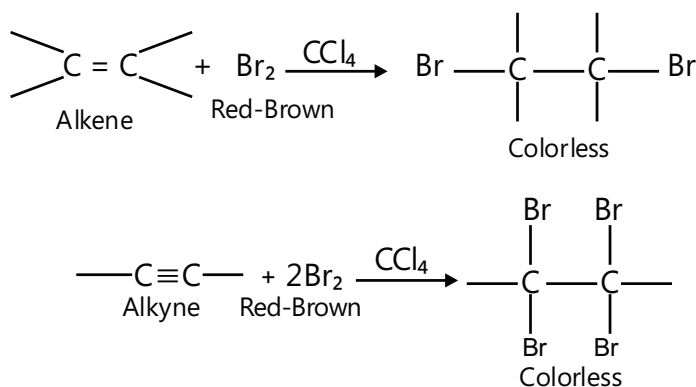
(m) Alkene and alkyne

(i) **Br_2 - water test:** The decoloration of a solution of bromine in water with dichloromethylene as catalyst is an analytical test for the presence of alkenes:

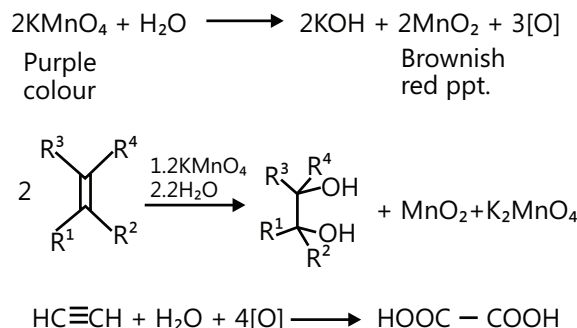


It is also used as a quantitative test of unsaturation.

(ii) **Bromine in CCl_4 :** Bromine will add to the carbon-carbon double bond of alkenes to produce dibromoalkanes and with alkynes to produce tetrabromoalkanes. When this reaction occurs, molecular bromine is consumed, and its characteristic dark redbrown color disappears if bromine is not added in excess. The rapid disappearance of the bromine color is a positive test for unsaturation.

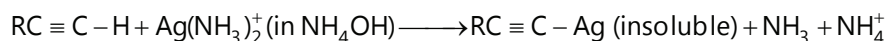


- (iii) **Baeyer's reagent: (Alkene only):** Baeyer's reagent is an alkaline solution of cold potassium permanganate, which is a powerful oxidant making this a redox reaction. Reaction with double or triple bonds ($-\text{C}=\text{C}-$ or $-\text{C}\equiv\text{C}-$) in an organic material causes the color to fade from purplish-pink to brown. It is a syn addition reaction.

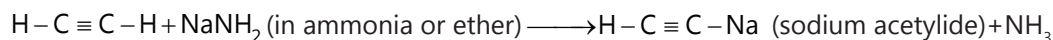


(n) Detection of terminal alkyne

- (i) **AgNO₃ in ammonia:** The reactions of alkynes with certain metal cations, e.g. Ag⁺ gives acetylides. Thus, few drops of diammine silver(I) hydroxide Ag(NH₃)₂OH reacts with terminal alkynes signaled by the formation of a silver white precipitate of the silver acetylide.



- (ii) **Acidic nature of terminal alkyne:** Terminal alkyne being acidic reacts with strong bases like NaNH₂ to form sodium acetylide.

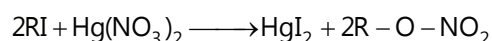
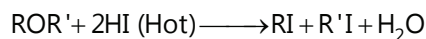


- (iii) **With Grignard reagent:** Terminal alkynes react with Grignard reagent to form alkanes.



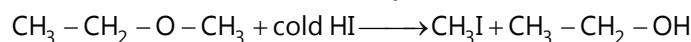
(o) Detection of alkoxy group

- (i) **Hot Hydroiodic Acid (HI) test:** The relatively unreactive C-O bonds in an ether can be cleaved by treatment with conc. HI to give two alkyl iodides and water. The alkyl iodides produced can react with mercuric nitrate, Hg(NO₃)₂, to give the orange-red coloured mercuric iodide (HgI₂).



Vermillion coloured

- (ii) **Cold HI Test:** When ether is treated with cold HI, the smaller alkyl group in ether forms iodide while bigger one forms alcohol in case of asymmetric ether.



MASTERJEE CONCEPTS

Exceptions:

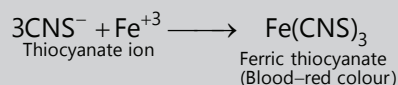
- Lassaigne's test is not given by compounds which do not contain C atoms but contain N atoms.

Example: NH₂NH₂ (hydrazine), NH₂OH (hydroxyl amine).

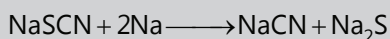
Reason: Since, these compounds do not contain carbon, in sodium fusion extract, CN⁻ ion will not form and Prussian blue colour is not observed.

MASTERJEE CONCEPTS

- This test is also not given by diazonium salts although they contain both C and N elements, because the nitrogen in them is released due to strong heating while forming sodium fusion extract.
- If S is also present in organic compound along with C and N, this test gives a blood red colour.



- If fusion is carried out with excess of sodium, the fusion gives cyanide and sulphide giving usual tests.



- In Beilstein's test, Urea (NH_2CONH_2) and thiourea (NH_2CSNH_2) do not contain halogens but still give the test.
- In detection of phosphorous using ammonium molybdate, if the organic compound contains arsenic (As), then it also gives this test forming ammonium arsenomolybdate forming canary yellow ppt.
- In Fehling's solution test, only aliphatic aldehydes give this test. Aromatic aldehydes don't give this test.
- In Tollen's reagent test, α -hydroxy ketones give this test but other ketones do not.
- All amino acids give ninhydrin test except Proline due to absence of free $-\text{NH}_2$ group.
- 2° and 3° amines do not give carbylamine test.

Nikhil Khandelwal (JEE 2009, AIR 94)

MASTERJEE CONCEPTS

- Lithium is not used in Lassaigne's test even being more electropositive than sodium because it reacts slowly and its compounds are covalent with less ionic nature. Potassium is not used because it reacts vigorously and cannot be handled properly.
- In the Lassaigne's test for nitrogen, if Fe^{3+} ions (with yellow colour) are in excess, it makes the blue colour of ferrocyanide to appear green.
- Tollen's test is also given by formic acid and hemiacetals. But acetals do not give this test.

Saurabh Gupta (JEE 2010, AIR 443)

Illustration 3: Lassaigne's test is not shown by diazonium salts and hydrazine (NH_2NH_2) even though they contain nitrogen. Why?

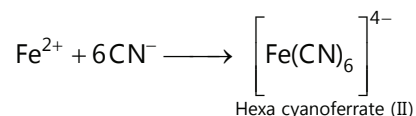
Sol: Lassaigne's test is not given by compounds which do not contain C atoms but contain N atoms. In case of diazonim salt the nitrogen is released due to strong heating while forming sodium fusion extract.

Diazonium salts usually lose N_2 on heating much before they react with fused Na metal. That is why they do not give the above test. Hydrazine does not have C atoms, so it does not form NaCN and hence does not give a positive test for N. In order to test the presence of N in such compounds, during fusion with Na, some charcoal or starch is added to supply C atoms. Under these conditions, NaCN is obtained and it will give a positive test.

Illustration 4: The Prussian blue colour obtained in the Lassaigne's test for nitrogen is due to the formation of

- (A) Iron (II) hexacyanoferrate (III) (B) Iron (III) hexacyanoferrate (II)
 (C) Iron (III) hexacyanoferrate(III) (D) Iron (II) hexacyanoferrate (II)
 (E) Sodium hexacyanoferrate (III)

Sol: (B) The Prussian blue colour obtained in the Lassaigne's test for nitrogen is due to the formation of



3. QUANTITATIVE ANALYSIS

Quantitative analysis of an organic compound includes the measurement of a quantity of an element in the compound. While determining molecular formula of an organic compound, it is necessary to know the percent quantity of every element present in it. There are various processes to determine this percentage based on that element.

- (a) **Liebig's combustion method:** A known mass of compound is heated with CuO. The carbon present is oxidized to CO_2 and hydrogen to H_2O . The CO_2 is absorbed in KOH solution, while H_2O vapours are absorbed in anhydrous CaCl_2 . So, change in their weights will give percentage of C and H.

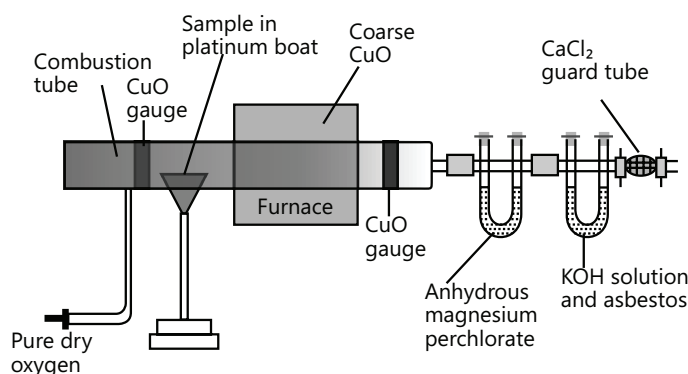


Figure 27.7: Combustion Tube

$$\text{Percentage of C} = \frac{12}{44} \times \frac{\text{Mass of } \text{CO}_2}{\text{Mass of compound}} \times 100;$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{\text{Mass of } \text{H}_2\text{O}}{\text{Mass of compound}} \times 100$$

- (b) **Carius Method:** The Carius halogen method in analytical chemistry is a method for the quantitative determination of halogens in chemical substances. A known mass of an organic compound is heated with fuming nitric acid (HNO_3) in the presence of silver nitrate (AgNO_3) contained in a hard glass tube known as carius tube, in a furnace. Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed. This chemical test works equally well for the determination of sulfur but without the addition of silver nitrate. The sulfuric acid intermediate formed after reaction of sulfur with fuming nitric acid forms insoluble barium sulfate on the addition of barium chloride.

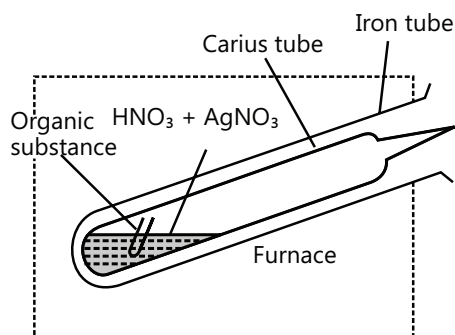


Figure 27.8: Carius Tube

$$(i) \text{ Percentage of X} = \frac{\text{Atomic mass of X}}{\text{Molecular mass of AgX}} \times \frac{\text{Mass of AgX} \times 100}{\text{Mass of compound}}$$

$$(ii) \text{ Percentage of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl} \times 100}{\text{Mass of compound}}$$

$$(iii) \text{ Percentage of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr} \times 100}{\text{Mass of compound}}$$

$$\text{Percentage of I} = \frac{127}{235} \times \frac{\text{Mass of AgI} \times 100}{\text{Mass of compound}}$$

(c) Estimation of sulphur: A known mass of compound is heated with fuming HNO_3 or sodium peroxide (Na_2O_2). In the presence of BaCl_2 solution in Carius tube. Sulphur is oxidized to H_2SO_4 and precipitated as BaSO_4 . It is filtered, dried and weighed.

$$\text{Percentage of S} = \frac{\text{Atomic mass of S}}{\text{Molecular mass of BaSO}_4} \times \frac{\text{Mass of BaSO}_4 \times 100}{\text{Mass of compound}} = \frac{32}{233} \times \frac{\text{Mass of BaSO}_4 \times 100}{\text{Mass of compound}}$$

(d) Estimation of phosphorous:

First Method: A known mass of compound is heated with fuming HNO_3 in Carius tube which converts phosphorous to H_3PO_4 (phosphoric acid). It is precipitated as ammonium phosphomolybdate $[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$ by adding NH_3 and ammonium molybdate. It is filtered, dried, and weighed.

$$\text{Percentage of P} = \frac{\text{Atomic mass of P}}{\text{Molecular mass of ammonium phospho molybdate}} \times$$

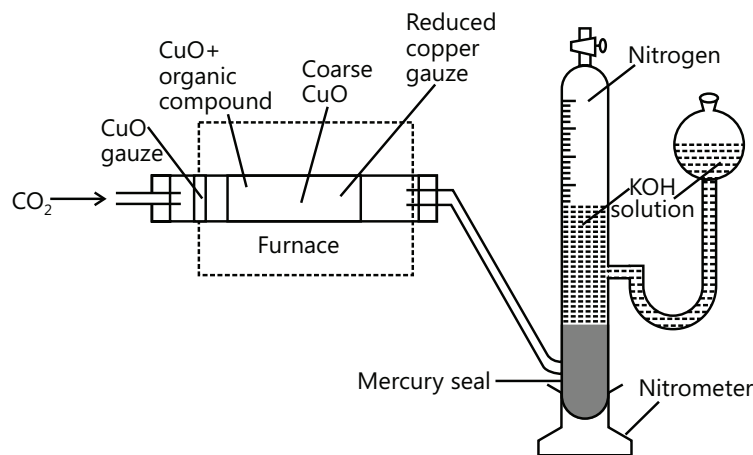
$$\frac{\text{Mass of ammonium phospho molybdate} \times 100}{\text{Mass of compound}} = \frac{31}{1877} \times \frac{\text{Mass of } (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \times 100}{\text{Mass of compound}}$$

Second Method (Carius method): A known mass of compound is heated with fuming HNO_3 or sodium peroxide in Carius tube which converts phosphorous to H_3PO_4 . Magnesia mixture ($\text{MgCl}_2 + \text{NH}_4\text{Cl}$) is then added, which gives the precipitate of magnesium ammonium phosphate MgNH_4PO_4 which on heating gives magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$), which is weighed.

$$\text{Percentage of P} = \frac{\text{Atomic mass of P}}{\text{Molecular mass of Mg}_2\text{P}_2\text{O}_7} \times \frac{\text{Mass of Mg}_2\text{P}_2\text{O}_7 \times 100}{\text{Mass of compound}} = \frac{62}{222} \times \frac{\text{Mass of Mg}_2\text{P}_2\text{O}_7 \times 100}{\text{Mass of compound}}$$

(e) Estimation of nitrogen:

- (i) **Dumas method:** A known mass of the organic compound is heated with cupric oxide in an atmosphere of carbon dioxide. The carbon and hydrogen in the compound are oxidized to carbon dioxide and water respectively, while nitrogen is set free. Any oxide of nitrogen produced during this process, is reduced back to free nitrogen by a heated copper gauze. The gaseous mixture consisting of CO_2 , H_2O and N_2 is collected over an aqueous solution of potassium hydroxide. All the gases except nitrogen are absorbed by the solution. The volume of gas (nitrogen) collected is measured. From the volume of nitrogen obtained the percentage of nitrogen in the compound is calculated.

**Figure 27.9:** Dumas Apparatus**Calculations**

Let, The mass of the organic compound taken be = W g; Volume of nitrogen collected = V_1 g

Atmospheric pressure = P mm Hg; Temperature at which gas is collected = T_1 K

Therefore, Pressure of the N_2 gas, $P_1 = (P - p)$ mm of Hg

$$\text{Volume of nitrogen at STP} = \frac{P_1 V_1 \times 273}{760 \times T_1} = V \text{ mL (Using } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{)}$$

$$\text{Mass of } V \text{ mL of nitrogen at STP} = \frac{28V}{22400} \text{ g (1 mol of } \text{N}_2 = 28 \text{ g} = 22400 \text{ mL)}$$

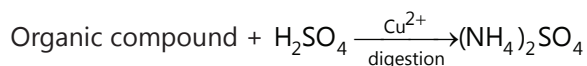
$$\text{Therefore, Percentage of nitrogen in the compound} = \frac{28V}{22400} \times \frac{100}{W}$$

- (ii) **Kjeldahl's method:** Kjeldahl's method is a faster method than Dumas' method. However, this method is used only for those organic compounds that are converted quantitatively to ammonium sulphate on heating strongly with concentrated sulphuric acid.

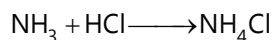
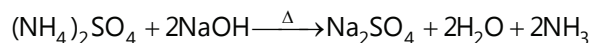
Kjeldahl's method cannot be used for the organic compounds,

1. Containing nitrogen in the ring, e.g., pyridine, quinoline etc.
2. Containing nitro ($-\text{NO}_2$) and diazo ($-\text{N}=\text{N}-$) groups.
3. Kjeldahl's method involves two steps:

- **Digestion:** A known mass (0.3 to 0.5 g) of the given organic compound is digested with concentrated H_2SO_4 in the presence of a small quantity of potassium sulphate and copper sulphate in a Kjeldahl's flask. Potassium sulphate raises the boiling point of sulphuric acid and copper sulphate catalyzes the digestion. In 3 to 4 hours, the organic compound is completely decomposed to form ammonium sulphate.



- **Distillation:** The digested reaction mixture, on cooling, is transferred to a round bottomed distillation flask, and distilled with a concentrated alkali solution (NaOH). Ammonia produced is absorbed in a known volume of HCl solution of a known strength.



The un-neutralised HCl is then back-titrated against a standard alkali. From the acid consumed, the amount of ammonia produced and hence the mass of nitrogen is calculated.

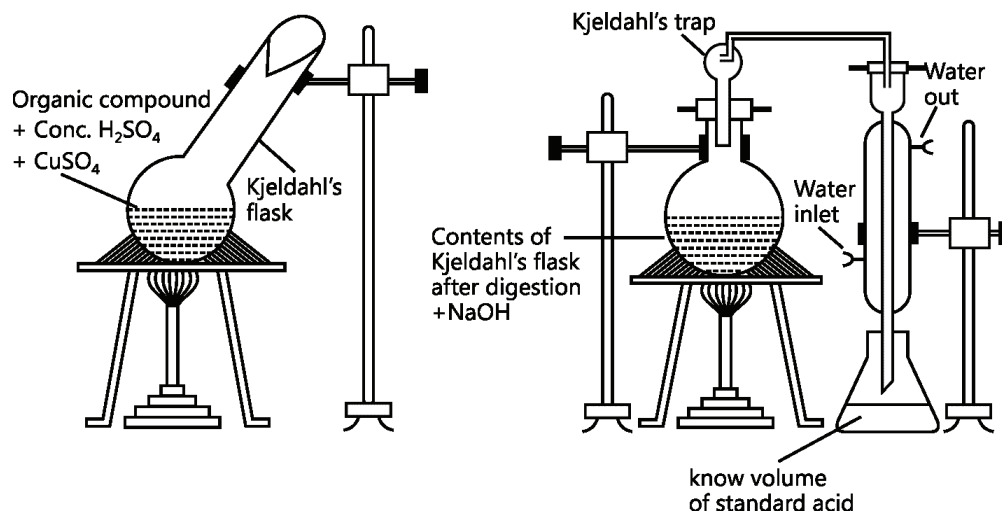


Figure 27.10: Kjeldahl's Method

Apparatus for the estimation of nitrogen by Kjeldahl's method

Calculation

Let, Mass of the organic compound = W g

Volume of the standard acid required for complete neutralization of the evolved ammonia = V mL; Normality of the standard solution of acid = N

From the law of equivalence (normality equation),

1000 mL of 1 N acid = 1000 mL of 1 N NH_3 = 17g NH_3 = 14g nitrogen

Then, V mL of N acid = V mL of NH_3

NV milli equivalent of acid = NV milli equivalent of ammonia

Therefore, Mass of nitrogen in the evolved ammonia = $\frac{14 \times N \times V}{1000}$ g

Then, Percentage of nitrogen in the sample = $\frac{14NV}{1000} \times \frac{100}{W} = \frac{1.4NV}{W}$

Percentage of nitrogen in the sample =

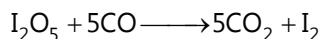
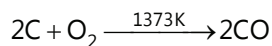
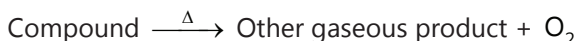
$$\frac{1.4 \times \text{Normality of HCl} \times \text{Volume of HCl used for complete neutralization of } \text{NH}_3}{\text{Mass of the compound taken}}$$

(f) Estimation of oxygen:

First Method: It is usually the difference between total percentage composition (100%) and sum of the percentage of all other elements.

Percentage of O = 100 – (Percentage of C + Percentage of H + Percentage of N +

Second Method (Aluise's method): A known mass of compound is decomposed by heating it in the presence of N_2 gas. The mixture of gaseous products containing O_2 is passed over red hot coke when all O_2 is converted into CO. This mixture is heated with I_2O_5 in which CO is converted into CO_2 liberating I_2 .



$$\text{Percentage of O} = \frac{\text{Molecular mass of } O_2}{\text{Molecular mass of } CO_2} \times \frac{\text{Mass of } CO_2 \times 100}{\text{Mass of compound}} = \frac{32}{44} \times \frac{\text{Mass of } CO_2 \times 100}{\text{Mass of compound}}$$

4. DETERMINATION OF EMPIRICAL FORMULAE AND MOLECULAR FORMULAE

The empirical formula of a chemical compound is a representation of the simplest whole number ratio between the elements comprising the compound. The molecular formula is the representation of the actual whole number ratio between the elements of the compound. This step by step tutorial shows how to calculate the empirical and molecular formulas for a compound.

Problem: A molecule with molecular weight of 180.18 g/mol is analysed and found to contain 40.00% carbon, 6.72% hydrogen and 53.28% oxygen. What are the empirical and molecular formulas of the molecule?

Solution: Finding the empirical and molecular formula is basically the reverse process used to calculate mass percent.

Step 1: Find the number of moles of each element in a sample of the molecule.

Our molecule contains 40.00% carbon, 6.72% hydrogen and 53.28% oxygen. This means a 100 gram sample contains:

40.00 grams of carbon (40.00% of 100 grams)

6.72 grams of hydrogen (6.72% of 100 grams)

53.28 grams of oxygen (53.28% of 100 grams)

Note: 100 grams is used for a sample size just to make the maths easier. Any sample size could be used, the ratios between the elements will remain the same.

Using these numbers we can find the number of moles of each element in the 100 gram sample. Divide the number of grams of each element in the sample by the atomic weight of the element (from the periodic table) to find the number of moles.

$$\text{moles C} = 40.00 \text{ g} \times 1 \text{ mol C} / 12.01 \text{ g/mol C} = 3.33 \text{ moles C}$$

$$\text{moles H} = 6.72 \text{ g} \times 1 \text{ mol H} / 1.01 \text{ g/mol H} = 6.65 \text{ moles H}$$

$$\text{moles O} = 53.28 \text{ g} \times 1 \text{ mol O} / 16.00 \text{ g/mol O} = 3.33 \text{ moles O}$$

Step 2: Find the ratios between the number of moles of each element.

Select the element with the largest number of moles in the sample. In this case, the 6.65 moles of hydrogen is the largest. Divide the number of moles of each element by the largest number.

$$\text{Simplest mole ratio between C and H: } 3.33 \text{ mol C} / 6.65 \text{ mol H} = 1 \text{ mol C} / 2 \text{ mol H}$$

The ratio is 1 mole C for every 2 moles H

$$\text{Simplest ratio between O and H: } 3.33 \text{ moles O} / 6.65 \text{ moles H} = 1 \text{ mol C} / 2 \text{ mol H}$$

The ratio between O and H is 1 mole O for every 2 moles of H

Step 3: Find the empirical formula.

We have all the information we need to write the empirical formula. For every 2 moles of hydrogen, there is one mole of carbon and one mole of oxygen. The empirical formula is CH_2O .

Step 4: Find the molecular weight of the empirical formula.

We can use the empirical formula to find the molecular formula using the molecular weight of the compound and the molecular weight of the empirical formula.

The empirical formula is CH_2O . The molecular weight is

$$\text{molecular weight of } \text{CH}_2\text{O} = (1 \times 12.01 \text{ g/mol}) + (2 \times 1.01 \text{ g/mol}) + (1 \times 16.00 \text{ g/mol})$$

$$\text{molecular weight of } \text{CH}_2\text{O} = (12.01 + 2.02 + 16.00) \text{ g/mol}$$

$$\text{molecular weight of } \text{CH}_2\text{O} = 30.03 \text{ g/mol}$$

Step 5: Find the number of empirical formula units in the molecular formula.

The molecular formula is a multiple of the empirical formula. We were given the molecular weight of the molecule, 180.18 g/mol. Divide this number by the molecular weight of the empirical formula to find the number of empirical formula units that make up the compound. Number of empirical formula units in compound = $180.18 \text{ g/mol} / 30.03 \text{ g/mol}$

$$\text{Number of empirical formula units in compound} = 6$$

Step 6: Find the molecular formula.

It takes six empirical formula units to make the compound, so multiply each number in the empirical formula by 6.

$$\text{molecular formula} = 6 \times \text{CH}_2\text{O}$$

$$\text{molecular formula} = \text{C}_{(1 \times 6)}\text{H}_{(2 \times 6)}\text{O}_{(1 \times 6)}$$

$$\text{molecular formula} = \text{C}_6\text{H}_{12}\text{O}_6$$

Sol: The empirical formula of the molecule is CH_2O .

The molecular formula of the compound is $\text{C}_6\text{H}_{12}\text{O}_6$.

MASTERJEE CONCEPTS**1. Leibig combustion method:** (Estimation of C and H)

$$\text{Percentage of C} = \frac{12}{44} \times \frac{\text{Mass of CO}_2}{\text{Mass of compound}} \times 100$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{\text{Mass of H}_2\text{O}}{\text{Mass of compound}} \times 100$$

2. Carius's method (Estimation of halogens):

$$\text{(i) Percentage of X} = \frac{\text{Atomic mass of X}}{\text{Molecular mass of AgX}} \times \frac{\text{Mass of AgX} \times 100}{\text{Mass of compound}}$$

$$\text{(ii) Percentage of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl} \times 100}{\text{Mass of compound}}$$

$$\text{(iii) Percentage of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr} \times 100}{\text{Mass of compound}}$$

MASTERJEE CONCEPTS

$$(iv) \text{ Percentage of I} = \frac{127}{235} \times \frac{\text{Mass of AgI} \times 100}{\text{Mass of compound}}$$

3. Estimation of sulphur:

$$\text{Percentage of S} = \frac{\text{Atomic mass of S}}{\text{Molecular mass of BaSO}_4} \times \frac{\text{Mass of BaSO}_4 \times 100}{\text{Mass of compound}} = \frac{32}{233} \times \frac{\text{Mass of BaSO}_4 \times 100}{\text{Mass of compound}}$$

4. Carius method (Estimation of phosphorous):

$$\text{Percentage of P} = \frac{\text{Atomic mass of P}}{\text{Molecular mass of Mg}_2\text{P}_2\text{O}_7} \times \frac{\text{Mass of Mg}_2\text{P}_2\text{O}_7 \times 100}{\text{Mass of compound}} = \frac{62}{222} \times \frac{\text{Mass of Mg}_2\text{P}_2\text{O}_7 \times 100}{\text{Mass of compound}}$$

5. Dumas's method (Estimation of nitrogen):

$$\text{Percentage of nitrogen in the compound} = \frac{28V}{22400} \times \frac{100}{W}$$

6. Kjeldahl's method (Estimation of nitrogen):

Percentage of nitrogen in the sample

$$= \frac{1.4 \times \text{Normality of HCl} \times \text{Volume of HCl used for complete neutralization of NH}_3}{\text{Mass of the compound taken}}$$

7. Estimation of oxygen in general:

Percentage of O = 100 – (Percentage of C + Percentage of H + Percentage of N +)

Molecular Formula = n × (Empirical formula)

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Illustration 6: 0.50 gm of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5 M H_2SO_4 . The residual acid requires 60 ml of M/2 NaOH solution. Find the percentage of nitrogen in the compound.

Sol: Percentage of nitrogen present in the given compound can be determined using Kjeldahl's method. We can use the following expression, this method makes use of titration of given compound with acid, and thus it involves neutralization reaction. From the volume of acid required for complete neutralization reaction percentage of nitrogen can be determined.

Percentage of nitrogen in the sample

$$= \frac{1.4 \times \text{Normality of HCl} \times \text{Volume of HCl used for complete neutralization of NH}_3}{\text{Mass of the compound taken}}$$

mEq. of acid = $50 \times 0.5 \times 2 = 50$; mEq. of base = $60 \times 0.5 \times 1 = 30$

Excess of acid used to neutralise ; $\text{NH}_3 = 50 - 30 = 20$ mEq

$$\text{Percentage of N}_2 = \frac{1.4 \times \text{mEq. of acid used}}{\text{Weight of compound}} = \frac{1.4 \times 20}{0.5} = 56.0\%$$

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Illustration 7:

- How is a mixture of two organic compounds separated, which have different solubilities in the same solvent?
- How is an organic liquid purified which decomposes below its boiling point?
- Why is sodium extract boiled with HNO_3 before testing for halogens?
- What type of organic compounds cannot be estimated by Kjeldahl's method?
- What does blood-red colouration during lassaingne's test indicate?
- What happens when AgNO_3 solution is added to bromo methane?

Sol: (a) By fractional crystallization.

(b) Distillation under reduced pressure i.e. vacuum distillation.

(c) To decompose NaCN or Na_2S present in the Lassaingne's extract, otherwise, these will produce white precipitate with AgNO_3 and thus interfere with the test of halogens.

(d) Compounds containing N in the ring and those compounds in which N atom is directly linked either to an oxygen atom or another N atom such as in azo ($-\text{N} = \text{N}-$) and nitro ($-\text{NO}_2$) compounds.

(e) It indicates the presence of both N and S.

(f) It would not give pale-yellow precipitate of AgBr because CH_3Br is a covalent compound and hence does not contain Br^- ion. To get the precipitate of AgBr , CH_3Br is treated with aqueous KOH to get CH_3OH and Br^- and then addition of AgNO_3 . It would now give the precipitate of AgBr partly soluble in NH_3 or NH_4OH .

Illustration 8: 'O' 1693 gm of a volatile substance when vapourised displaced 58.9 ml of air measured at 27°C and 746 mm pressure. Calculate the molar mass of the substance. (Aqueous tension at $27^\circ \text{C} = 26.7 \text{ mm Hg}$)

Sol: First calculate the volume of air displaced at STP condition by using the ideal gas equation. Now using the volume term calculate the molecular mass of the given compound.

Step I: To convert the volume at experimental condition to volume at STP.

$$P_1 = 746 - 26.7 = 719.3 \text{ mm} \quad P_2 = 760 \text{ mm}$$

$$V_1 = 58.9 \text{ ml} \quad V_2 = ?$$

$$T_1 = 273 + 27 = 300 \text{ K} \quad T_2 = 273 \text{ K}$$

Substituting these values in the gas equation.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}, \text{ we get } \frac{719.3 \text{ mm} \times 58.9 \text{ ml}}{300 \text{ K}} = \frac{760 \text{ mm} \times V_2 \text{ ml}}{273 \text{ K}}$$

$$\therefore V_2 = \frac{719.3 \text{ mm} \times 58.9 \text{ ml} \times 273 \text{ K}}{300 \text{ K} \times 760 \text{ mm}} = 50.73 \text{ ml}$$

$$\text{Molecular mass} = \frac{\text{Mass of substance} \times 22400}{\text{Volume of displaced air at STP}} = \frac{0.1693 \times 22400}{50.73} = 74.75 \text{ gm}$$

Illustration 9: 0.15 gm of an organic compound gave 0.12 gm of silver bromide by the Carius method. Find the percentage of bromide in the compound.

Sol: We are asked to find out the percentage of bromide in the compound. As we are provided with mass of given compound and mass of silver bromide produced by that compound by the carius method. So we can use the following expression Percentage of

$$\text{Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr}}{\text{Mass of compound}}$$

$$\text{Percentage of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr}}{\text{Mass of compound}} = \frac{80}{188} \times \frac{0.12}{0.15} \times 100 = 34.0\%$$

Illustration 10: 0.12 gm of an organic compound containing phosphorous gave 0.22 gm of $\text{Mg}_2\text{P}_2\text{O}_7$ by the usual analysis. Calculate the percentage of phosphorous in the compound.

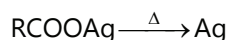
Sol: From the given data i.e mass of $\text{Mg}_2\text{P}_2\text{O}_7$ produced and mass of given compound percentage of phosphorous can be determined using following formula:

$$\text{Percentage of phosphorus} = \frac{62}{222} \times \frac{\text{Mass of } \text{Mg}_2\text{P}_2\text{O}_7}{\text{Mass of compound}} \times 100$$

$$\text{Percentage of phosphorus} = \frac{62}{222} \times \frac{\text{Mass of } \text{Mg}_2\text{P}_2\text{O}_7}{\text{Mass of compound}} \times 100 = \frac{62}{222} \times \frac{0.22}{0.12} \times 100 = 51.20\%$$

5. DETERMINATION OF MOLECULAR MASS

(a) Silver Salt Method For Carboxylic Acids: Most of the organic acids form sparingly soluble silver salts, which on ignition leave a residue of metallic silver. This forms the basis of the silver salt method for the determination of molecular mass of acids. The organic acid solution is neutralized with NH_4OH and heated to boil off excess NH_3 . It is then treated with excess of AgNO_3 solution and the precipitated silver salt is filtered, dried. A known mass of the dry silver salt is ignited in a crucible to a constant mass.



Let the equivalent weight of acid (RCOOH) be E .

The equivalent weight of $\text{RCOOAg} = E - 1 + 108 = (E + 107)$

Equivalent weight of $\text{Ag} = 108$; Weight of $\text{RCOOAg} = W$ gm

Weight of $\text{Ag} = w$ gm; 1 equivalent of $\text{RCOOAg} = 1$ equivalent of Ag

$$\frac{W}{E + 107} = \frac{w}{108} \therefore E = \left(\frac{W \times 108}{w} - 107 \right)$$

Molecular mass of an acid = $E \times n$ (basicity of an acid)

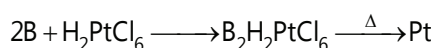
(b) Chloroplatinate or platinichloride method for organic bases: Organic bases form salts with HCl and the chloride give double salts with platinum chloride. Organic bases react with dibasic chloroplatinic acid (H_2PtCl_6) and form double salts and are called chloroplatinates or platinichlorides. These salts leave a residue of metallic platinum on ignition.

Equivalent weight of organic base = B

Mass or weight of chloroplatinic salt = W gm

Mass or weight of platinum = w gm

Equivalent weight of platinum = 195



Equivalent weight of $\text{B}_2\text{H}_2\text{PtCl}_6 = (2B + 2 + 195 + 35.5 \times 6) = 2B + 410$

$$1 \text{ equivalent of } B_2H_2PtCl_6 = 1 \text{ equivalent of Pt } \frac{W}{2B + 410} = \frac{w}{195} =$$

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

Molecular mass of the organic base = Equivalent mass \times Acidity = $B \times n$.

(c) Victor Meyer's method: This method is used for volatile organic compounds. A known mass of compound (W gm) is vapourised in an instrument called Victor Meyer tube. The vapours so obtained displace an equal amount of air into a graduated tube. The volume of vapours is measured and reduced to STP.

Let the volume of vapours at STP be V ml.

22400 ml of vapours are obtained from 1 mol of the compound.

V ml of vapours are obtained from $\frac{V \text{ ml}}{22400 \text{ ml}}$ mol of compound.

$$\text{Mole} = \frac{\text{Mass of the compound (W gm)}}{\text{Molecular mass of the compound (Mw)}} = \frac{W}{Mw}$$

$$\therefore \frac{W}{Mw} = \frac{V}{22400} \quad \therefore Mw = \frac{W \times 22400}{V} = \frac{\text{Mass of compound} \times 22400}{\text{Volume of vapours at STP}}$$

Illustration 10: 0.984 gm of the chloroplatinate of a diacid base gave 0.39 gm of platinum. Calculate the molecular mass of the base.

Sol: Mass of platinichloride taken = 0.984 gm; Mass of platinum left = 0.39 gm

To calculate the equivalent mass of base.

Let the equivalent mass of the base be B .

\therefore Molecular mass of the platininchloride ($B_2H_2PtCl_6$) = $2B + 410$.

$$\text{Now, } \frac{\text{Molecular mass of chloroplatinichloride}}{\text{Atomic mass of platinum}} = \frac{\text{Mass of platinichloride taken}}{\text{Mass of platinum left}}$$

$$\text{or } \frac{2B + 410}{195} = \frac{0.984}{0.39} \quad \text{or } B = \frac{1}{2} \left(\frac{0.984}{0.39} \times 195 - 410 \right) = 41$$

Thus, the equivalent mass of the base be 41.

To calculate the molecular mass of the base,

Acidity of base = 2.

Molecular mass of base = Equivalent mass of base \times acidity of base = $41 \times 2 = 82$

Thus, the molecular mass of base is 82.

Illustration 11: On analysis, 0.2 gm of a monobasic acid gave 0.505 gm of CO_2 and 0.0864 gm of H_2O . 0.305 gm of this acid required 25 ml of $N/10$ NaOH for complete neutralization. Find the molecular formula of this acid.

Sol: (a) Calculation of percentage composition

$$(i) \text{ Percentage of carbon} = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ produced}}{\text{Mass of substance taken}} \times 100 = \frac{12}{44} \times \frac{0.505}{0.2} \times 100 = 68.86\%$$

$$(ii) \text{ Percentage of Hydrogen} = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ produced}}{\text{Mass of substance taken}} \times 100 = \frac{2}{18} \times \frac{0.0864}{0.2} \times 100 = 4.8\%$$

(iii) Percentage of oxygen = $100 - (\text{Percentage of C} + \text{Percentage of H}) = 100 - (68.86 + 4.8) = 26.34\%$

(b) Calculation of empirical formula:

Element	Percentage	Atomic mass	Relative number of atoms	Simplest atomic ratio	Simplest whole number atomic ratio
Carbon	68.86	12	$\frac{68.86}{12} = 5.74$	$\frac{5.74}{1.65} = 3.48$	7
Hydrogen	4.80	1	$\frac{4.80}{1} = 4.80$	$\frac{4.80}{1.65} = 2.91$	6
Oxygen	26.34	16	$\frac{26.34}{16} = 1.65$	$\frac{1.65}{1.65} = 1.00$	2

Hence, the empirical formula of the compound is $\text{C}_7\text{H}_6\text{O}_2$.

(c) Calculation of molecular mass:

$$\text{mEq. Of NaOH} = 25 \times \frac{1}{10} = 2.5 \quad \text{mEq. Of acid} = 2.5$$

$$\text{Equivalent of acid} = 2.5 \times 10^{-3}$$

$$\text{Equivalent of acid} = E_w = \frac{\text{Weight}}{\text{Equivalent of acid}} = \frac{0.305}{2.5 \times 10^{-3}} = 122 \text{ gm of acid}$$

$$\text{Molecular weight of acid} = E_w \times n = 122 \times 1 = 122$$

(d) Calculation of molecular formula:

$$\text{Empirical formula } (\text{C}_7\text{H}_6\text{O}_2) \text{ mass of the compound} = (7 \times 12 + 6 \times 1 + 16 \times 2) = 122$$

$$\therefore n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{122}{122} = 1$$

$$\text{Thus, molecular formula of the compound} = n \times (\text{Empirical formula}) = 1 \times (\text{C}_7\text{H}_6\text{O}_2) = \text{C}_7\text{H}_6\text{O}_2$$

POINTS TO REMEMBER

- Distillation process is used for the purification of liquids which boil without decomposition and contain non-volatile impurities.
- Fractional distillation process is used to separate a mixture of two or more miscible liquids which have boiling points close to each other.
- Vacuum distillation is used for liquids which decompose at a temperature below their normal boiling points.
- Steam distillation is used for separation and purification of liquid which is appreciably volatile in steam, from non-volatile components of a mixture.
- Differential extraction method is used to separate a given organic compound present in aqueous solution by shaking with a suitable organic solvent in which the compound is more soluble than water.
- Chromatography is based on the difference in rates at which the components of a mixture are absorbed as a suitable adsorbent.
- Lassaigne's test is used for detection of nitrogen, halogen and sulphur.