

CHAPTER - 14

PURIFICATION AND CHARACTERISATION OF ORGANIC COMPOUNDS

When an organic compound is extracted from a natural source or synthesised in the laboratory, first step is to purify it. The various methods used for the purification of organic compounds are as follows.

- 1) Crystallisation
- 2) Fractional crystallisation
- 3) Sublimation
- 4) Simple distillation
- 5) Fractional distillation
- 6) Vacuum distillation
- 7) Steam distillation
- 8) Solvent extraction
- 9) Chromatography

1. **Crystallisation** : It is based on the difference in solubilities of the compound and impurities in a given solvent. A saturated solution of impure organic substance is prepared in a suitable organic solvent at high temperature. It is filtered while hot to remove insoluble impurities. The clear solution is cooled when the solid organic compound separates out as fine crystals.

Eg : (1) Sugar mixed common salt can be purified with ethanol (2) Benzoic acid or phthalic acid mixed with naphthalene can be purified by hot water.

2. **Fractional crystallisation** : It is used for the separation of a mixture of two compounds which are soluble in the same solvent due to slight difference in their solubilities in the same solvent at suitable temperature. The hot saturated solution of the mixture is allowed to cool. The less soluble component crystallises out leaving behind the more soluble component

Eg : A mixture of KCl and KClO_3 can be separated by using cold and hot water.

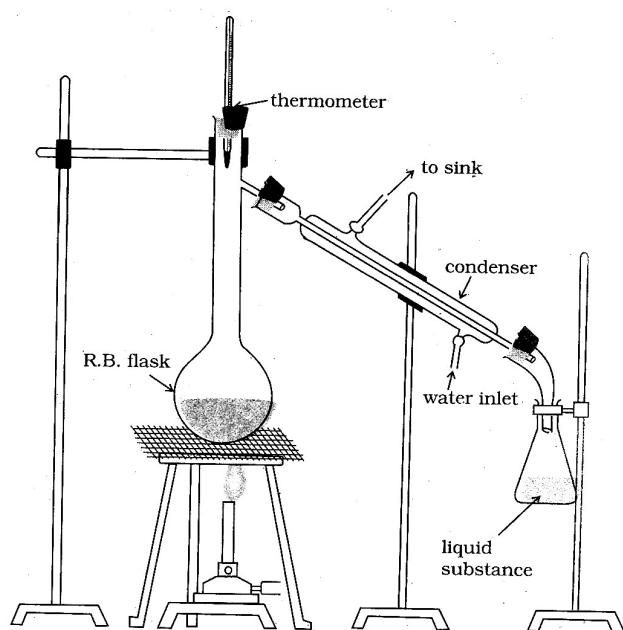
3. **Sublimation** : The process of conversion of a solid into the vapour state on heating without undergoing to the liquid state and vice-versa is called sublimation. A solid sublimes below its melting point. Only those substances whose vapour pressures become equal to the atmospheric pressure much before their respective melting point can be purified by this method. It is useful for the purification of such solids which sublime on heating and are associated with non-volatile impurities.

Eg : Benzoic acid, Camphor, Naphthalene, Anthracene, Phthalic anhydride, Ammonium chloride, Iodine, Anthraquinone, Indigo, Mercuric chloride (Corrosive sublimate), Dry ice etc.

4. **Simple distillation** : It is used to separate volatile liquids from non-volatile impurities and two liquids of their boiling points are largely different.

The process of converting the liquid into its vapour and condensing the vapours back to give the original liquid in the pure form is called distillation. In this method mixture of liquids is heated, the more volatile component distils over first leaving behind the less volatile component in the distillation flask.

Eg (1) A mixture of C_6H_{14} (b.p. 342 K) and Toluene (b.p. 384 K) (2) A mixture of benzene (b.p. 353 K) and Aniline (b.p. 457 K)

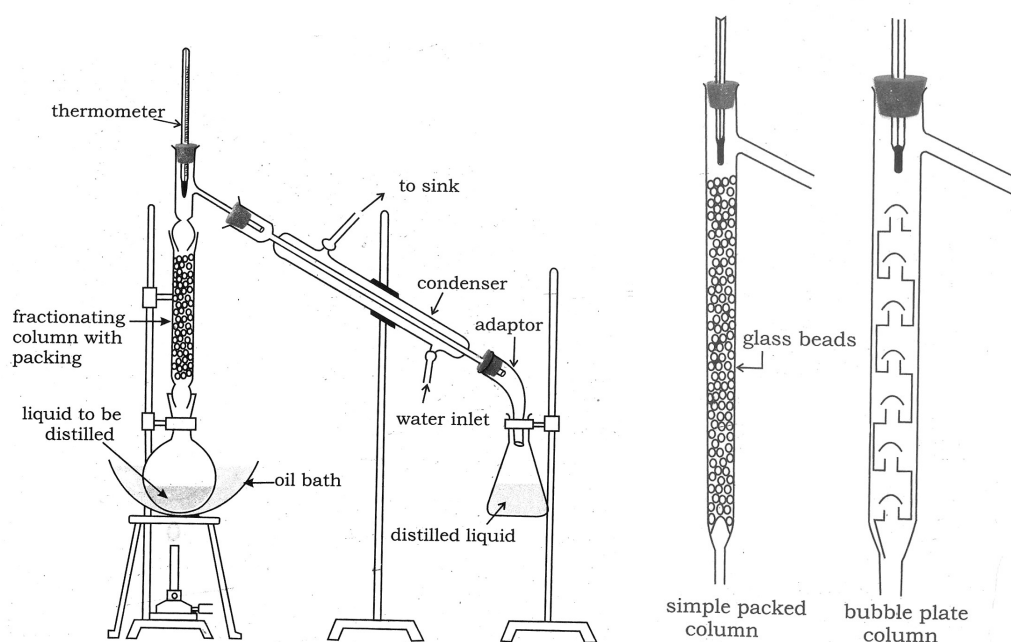


5. **Fractional distillation** : This method is used to separate and purify liquid mixtures having very close boiling points (ie differ by 10 –15 K). It is usually carried out with specially designed fractionating columns which provide large surface area for heat exchange between ascending vapours and descending liquid. As a result of distillation and condensation the vapours rising up become richer in the more volatile component and the liquid falling back into the flask becomes richer in the less volatile component. Thus the low boiling liquid distils first while the higher boiling liquid distils afterwards. After a series of successive distillations the remaining liquid in the distillation flask gets enriched in high boiling component. Each successive condensation and vapourisation unit in the fractionating column is called a theoretical plate.

Eg : (1) Crude oil can be purified by this method.

(2) Separation of heavy water from ordinary water

(3) A mixture of acetone (b.p. 329 K) and methanol (b.p. 338 K)



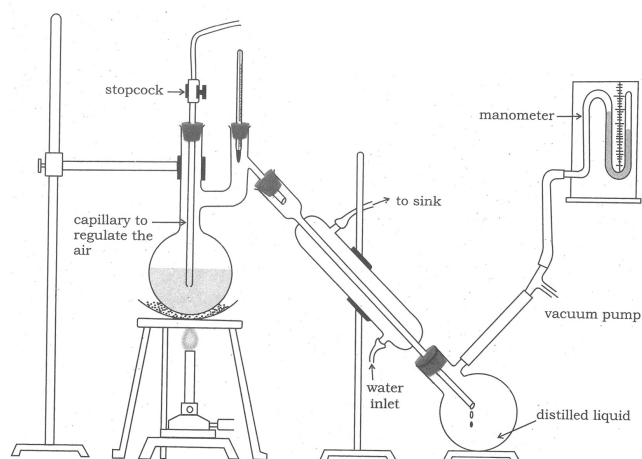
6. Vacuum distillation or distillation under reduced pressure

This method is used to purify liquids having high boiling point which get decomposed during direct heating. The principle of the method is that a liquid boils at a temperature when its vapour pressure becomes equal to the atmospheric pressure. The same liquid would boil at a lower temperature under reduced pressure. Since now the liquid boils at a lower temperature it does not undergo decomposition.

Eg : (1) Glycerol can be separated from spent-lye

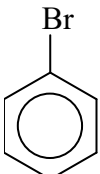
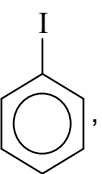
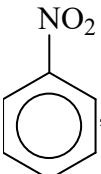
(2) Sugar can be separated from the juice of sugar can

(3) Concentration of H_2O_2 during its manufacture.

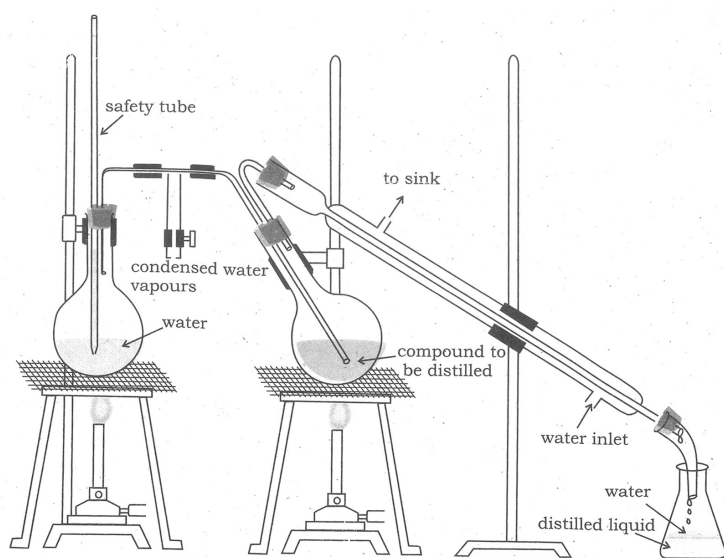


7. **Steam distillation** : This is used for the separation and purification of liquid mixtures which are insoluble in water, volatile in steam, possess a high vapour pressure, contain non-volatile impurities etc. In this method, steam from a steam generator is passed through a heated flask containing the liquid to be purified. The mixture of steam and the volatile organic compound is condensed and collected. The compound is separated from water by using a separating funnel. During this the liquid boils when the sum of vapour pressures due to organic liquid (P_1) and due to H_2O vapour (P_2) becomes equal to the atmospheric pressure P .

ie. $P = P_1 + P_2$. Since P_1 is lower than P , the organic liquid vapourises at lower temperature than its boiling point.

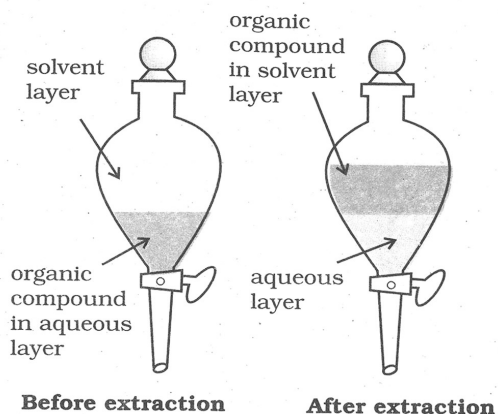
Eg : Aniline, , , , Turpentine oil, Eucalyptus oil etc. purified by this method. A

mixture of ortho isomers of nitrophenol, salicylic aldehyde, hydroxyacetone etc can be separated from their corresponding para isomers. Essential oils can also separated and purified by this method.



8. **Differential Extraction (Solvent extraction)** : When an organic compound is present in aqueous medium, it is separated by shaking with an organic solvent like ether in which it is more soluble. The organic compound is said to be extracted to the organic solvent. The organic layer containing the organic compound is separated using a separating funnel and the solvent is removed by evaporation or distillation.

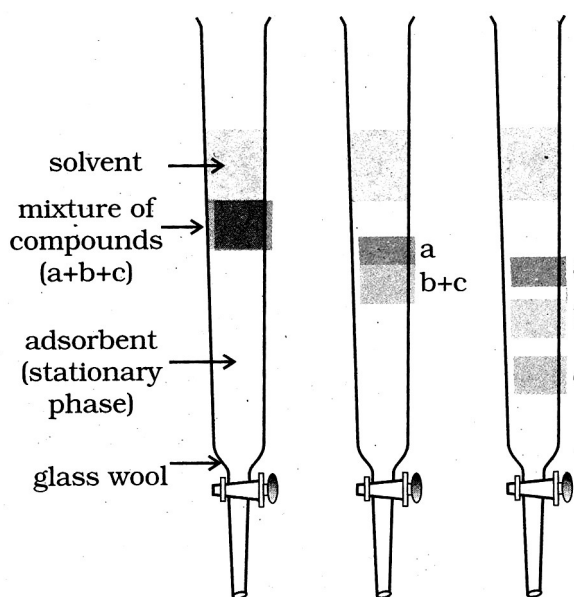
If the organic compound, is less soluble in the organic solvent, a very large quantity of solvent would be required to extract even for a very small amount of the substance. In that case continuous extraction method is used with the same solvent is repeatedly used.



9. Chromatography : It is a modern technique used for the isolation, separation, purification, identification and estimation of mixture of compounds on the basis of the difference in the rate of adsorption discovered by 'Tswett'. It involves two phases : one is stationary phase or fixed phase usually consist of Charcoal, Silica gel, Alumina, Cellulose, Starch powder etc while mobile or moving base is usually an organic solvent like acetic anhydride, CCl_4 , CHCl_3 , Benzene, Toluene etc. Depending upon the nature of stationary and the mobile phases, different types chromatographic techniques are used.

1. Adsorption chromatography : It includes **column chromatography** and thin layer chromatography (TLC)

In Column Chromatography involves the separation of a mixture over a column of adsorbent packed in a glass tube filled with a stop cock at the bottom. The mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube. A suitable eluent (solvent) is allowed to flow down the column slowly. Depending on the rate of adsorption, the most readily adsorbed substances are retained at the top and others come down to various distances in the column. By this way, the various components of the mixture can be separated.

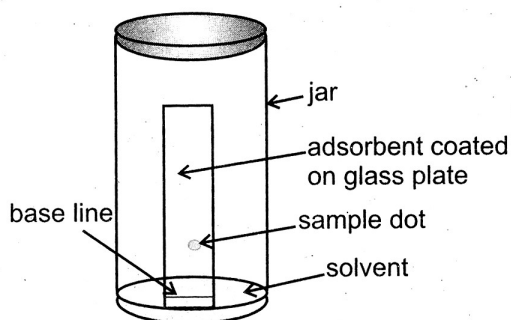


Thin Layer Chromatography (TLC) : In this method separation of a mixture of substances over a thin layer (about 0.2 mm) of an adsorbent (alumina) is spread over a glass plate of suitable size. The plate is known as thin layer chromatographic plate or chromaplate. The glass plate is then placed in a closed jar containing an eluent which rises up the plate which carries the solute (component) particles and get adsorbed on the basis of rate of adsorption. The relative adsorption is expressed in terms of Retention factor or retardation factor. (R_f value). It is defined as the ratio of the distance travelled by solute from the origin (base line) to the distance travelled by the solvent from the origin.

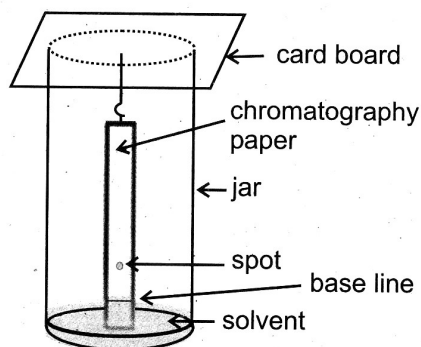
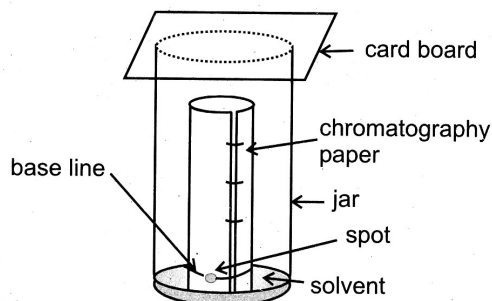
$$R_f = \frac{\text{Distance travelled by the solute from origin}}{\text{Distance travelled by the solvent from origin}}$$

The spots of coloured compounds are visible on TLC plate due to their original colour. But colourless compounds can be identified by the action of Iodine crystals or suitable organic reagents.

Eg : Amino acids can be detected by spraying the plate with ninhydrin solution which will develop a violet colour.



Partition chromatography: Paper chromatography is an example of partition chromatography. In this a special type chromatographic paper is used which contains water trapped, which acts as the stationary phase. A strip of chromatographic paper spotted at the base with the solution of the mixture is dissolved in suitable solvent, which acts as the moving phase. The chromatogram is suspended in a chromatographic chamber containing suitable solvent. The spots of the separated colourless compounds are identified by suitable reagents. Eg : Amino acids can be separated and identified by using ninhydrin reagent.



Elution : The process of removal of adsorbed substance from the surface of an adsorbent by using suitable organic solvent is called elution and the solvent used for that purpose is called eluent.

Purification of commercial benzene : Benzene obtained from coal tar contain 3-5% thiophene. Some their properties are same, it is difficult to remove thiophene from benzene by usual method. For the removal of trace impurities of thiophene from benzene, it is shaken with con. H_2SO_4 in a separating funnel during which thiophene 2-sulphonic acid is formed while benzene remain unreacted. The two layers are separated. The benzene layer is removed, washed with water to remove unreacted H_2SO_4 . It is dried over anhydrous CaCl_2 and finally distilled to get pure benzene.

Separation of mixture of compounds by chemical method

1. A mixture of carbohydrate and m-dinitrobenzene can be separated by shaking with ether, when m-dinitrobenzene dissolves leaving carbohydrate as the residue. Filtration and evaporation of ether from the filtrate gives m-dinitrobenzene.
2. A mixture of carboxylic acid can be separated form non-acidic compounds by shaking with NaHCO_3 solution when carboxylic dissolves to form sodium salts of acid while non-acidic compound remain insoluble. Filtration followed by acidification with dil.HCl gives free carboxylic acid.
3. A mixture of amines and non-basic compound can be separated by shaking with dil.HCl when amined dissolve to form corresponding hydrochlorides. While the non-basic compound remain insoluble. Filtration followed by treatment with NaOH gives free amine.
4. A mixture of urea and Naphthalene can be separated by shaking with H_2O when urea dissolves in water leaving naphthalene as the residue-Filtration and evaporation of water from the filtrate gives urea.
5. A mixture of phenol and non-phenolic compounds can be separated by shaking with NaOH solution when phenol dissolves to form sodium salt while non-phenolic compound remain insoluble.

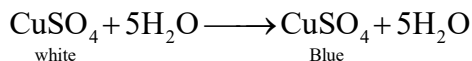
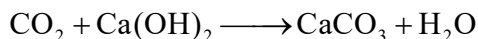
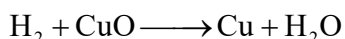
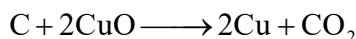
LAYER TEST FOR BROMINE AND IODINE

A little of the L.E is acidified with dil. HNO_3 or H_2SO_4 and then add 1 ml of CHCl_3 or CCl_4 . Now shake it regorously with Cl_2 water. If chloroform layer develop an orange colour, indicate the presence of bromine while of violet colour shows the presence of iodine.



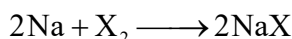
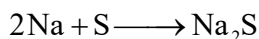
DETECTION OF ELEMENTS OR QUALITATIVE ANALYSIS

1. **Detection of carbon and hydrogen :** By Leibig's combustion method : A little of the organic compound contain carbon and hydrogen is strongly heated with dry cupric oxide in a hard glass tube fitted with a delivery tube, when carbon and hydrogen in the compound are oxidised by cupric oxide into CO_2 and H_2O respectively. CO_2 is passed through lime water turns milky due to the formation of CaCO_3 and water particles on the condensed on the inner wall of the test tube. The presence of water vapour can also be detected by passing through anhydrous CuSO_4 (white) which turns blue coloured due to the formation of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (blue vitriol). This indicate the presence of carbon and H_2 in the organic compound.



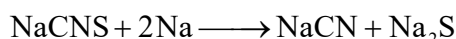
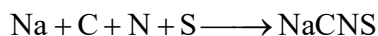
2. Detection of Nitrogen, Sulphur and Halogens:-

Preparation of sodium fusion extract : A little of the organic compound is fused with metallic sodium in an ignition tube or fusion tube. When the tube becomes red-hot it is phinged into china dish contian 10 ml distilled water. The mixture is stirred very well boiled and filtered. The filtrate is called sodium fusion extract.



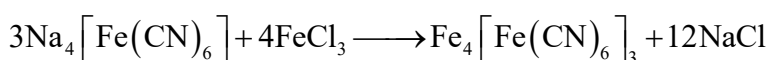
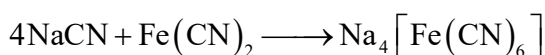
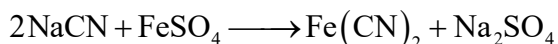
NOTE :

- Sodium metal should be slight excess otherwise in compounds containing nitrogen and sulphur together, sodium thiocyanate is formed which gives red colour with Fe^{3+} ions. With excess of sodium, the thiocyanate formed decomposes into cyanide and sulphide.



- Lithium is not used in Lassaigne's test since it reacts slowly and its compounds are covalent in nature
- Potassium cannot be used for the preparation of L.E. since it reacts violently and cannot be handled under normal condition.

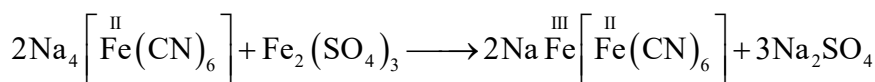
If nitrogen is present : A little of the L.E is boiled with freshly prepared ferrous sulphate solution and con. H_2SO_4 . The formation of prussian blue colour or green precipitate shows the presence of nitrogen in the organic compound. The blue colour is due to the formation of ferric ferrocyanide. The various steps involved are as follows.



NOTE:

- a. Instead of FeSO_4 , FeCl_3 can also be used to produce Fe^{3+} . Sometimes prussian blue is also written

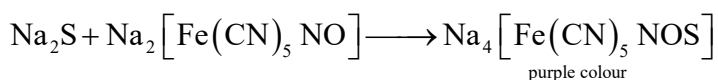
as $\text{Na}^{\text{III}}\text{Fe}^{\text{II}}\left[\text{Fe}^{\text{II}}(\text{CN})_6\right]$ due to the following reaction



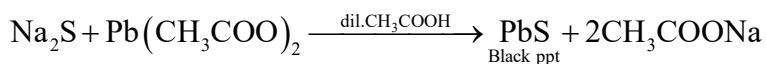
- b. A freshly prepared FeSO_4 is used in the L.E., because on keeping, FeSO_4 solution is oxidised to basic ferric sulphate by atmospheric oxygen. Since basic ferric sulphate is yellow, which interferes with light blue or green colouration.
- c. This test is not given by compounds which do not contain carbon atoms but contain nitrogen atoms.
Eg : NH_2OH , $\text{NH}_2\text{-NH}_2$, $\text{NH}_2\text{-NH}_2\text{-HCl}$, NH_4NO_3 etc. Cannot form NaCN during L.E. preparation
- d. This test is also not given by diazonium salts, CH_2N_2 (diazomethane), although they contain both carbon and nitrogen, because they decompose and lose N_2 gas.

If sulphur is present:-

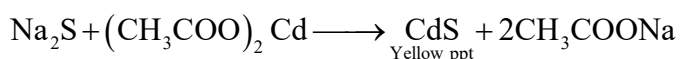
1. A little of the L.E. is treated with sodium nitro prusside solution. The formation of violet or purple colour indicates the presence of sulphur in the organic compound.



2. A little of the L.E. is acidified with acetic acid and lead acetate is added to it. The formation of a black ppt of PbS indicates presence of sulphur.



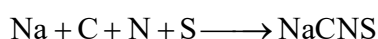
3. A little of the L.E. is acidified with $\text{dil. CH}_3\text{COOH}$ followed by the addition of cadmium acetate solution.



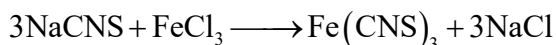
The formation of thick yellow ppt of cadmium sulphide indicates the presence of sulphur in the organic compound.

Note: For testing sulphur, L.E. is not acidified with dil. HCl or H_2SO_4 as white PbCl_2 or PbSO_4 will be formed, which will interfere the test.

If both nitrogen and sulphur are present: During L.E. preparation sodium thiocyanate is formed.



A little of the L.E. is treated with FeCl_3 solution. The formation of blood red colour due to $\text{Fe}(\text{CNS})_3$ formation indicates the presence of both nitrogen and sulphur in the organic compound.

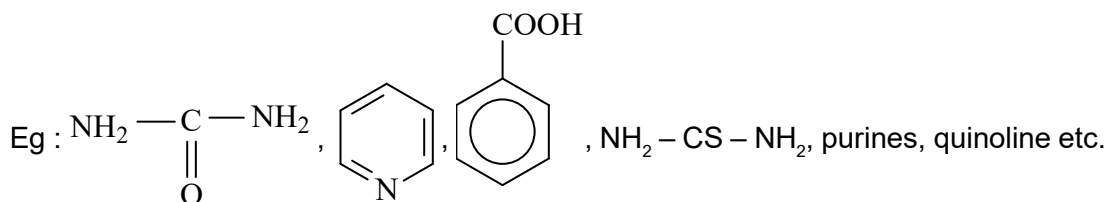


Test for Halogens: A little of the L.E is boiled with dil.HNO₃ followed by the addition of AgNO₃ solution. The formation of white curdy ppt of AgCl soluble in NH₄OH, a pale yellow ppt of AgBr partially soluble in NH₄OH or an yellow ppt of AgI insoluble in NH₄OH indicate the presence of Chlorine, Bromine or Iodine in the organic compound respectively.



The function of dil. HNO₃ is to decompose of NaCN or Na₂S formed during Lassaigne's test. These ions would otherwise interfere with AgNO₃ test for halogens. If these ions are not removed they would give a white ppt of AgCN or a black ppt of Ag₂S, which will interfere the colour of ppt of AgX formed.

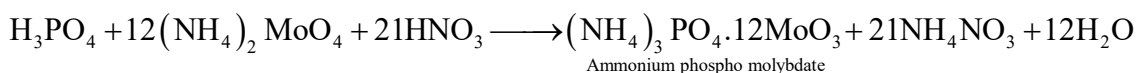
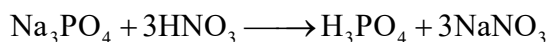
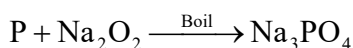
Beilsteins test : A copper wire is strongly heated on the bunsen flame. When it becomes red hot it is immersed in the organic compound containing halogen and heated in the flame. A green or blue colour due to the formation of a volatile copper halides confirms the presence of halogens. But it is not a reliable test for halogens as certain compounds which donot contain halogens also give positive test.



Again this test does not tell which halogen is present in the compound. Compound containing fluorine cannot give positive test because copper fluoride is non-volatile.

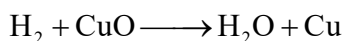
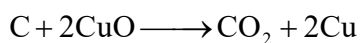
In the preparation of L.E., instead of sodium metal, mixture of sodium carbonate and zinc can be used. This is called Middleton's fusion method.

Detection of phosphorus : A little of the organic compound containing phosphorus is fused with sodium peroxide or with a fusion mixture (KNO₃ and Na₂CO₃). It is then extracted with water. During this phosphorus in the organic compound is converted into sodium phosphate Na₃(PO₄). This filtrate when boiled with con.HNO₃ and Ammonium molybdate solution form a thick yellow ppt of Ammonium phospho molybdate shows the presence of phosphorus in the organic compound.

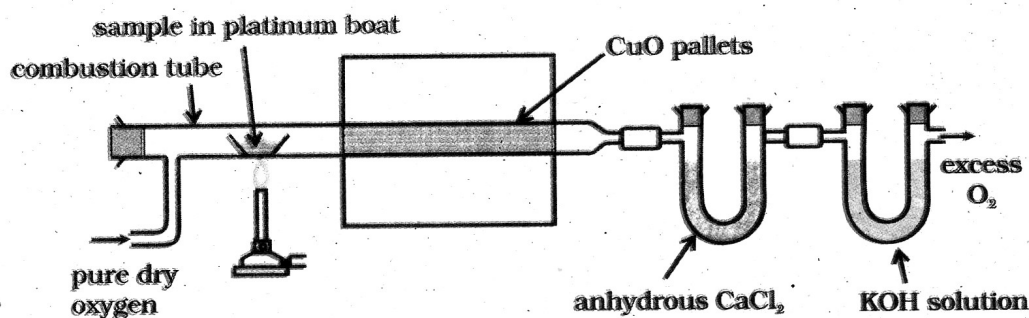


ESTIMATION OF ELEMENTS (QUANTITATIVE ANALYSIS)

- 1. Estimation of carbon and hydrogen** by Liebig's combustion method. A known wt of organic compound ('W'g) containing carbon and hydrogen is heated strongly with dry cupric oxide in a current of dry oxygen, when carbon is oxidised to CO₂ and H₂ into water.



The water thus produced is absorbed in anhydrous calcium chloride tube while CO_2 is absorbed in KOH solution and these tubes are weighed before and after the combustion. The increase in the mass of CaCl_2 tube gives the mass of water produced while increase in the mass of KOH tube gives the mass CO_2 produced. From the masses of CO_2 and H_2 , the percentages of carbon and hydrogen can be calculated.



Calculation:

Mass of CO_2 formed = 'a' g

Mass of H_2O formed = 'b' g

Weight of organic compound taken = 'W' g

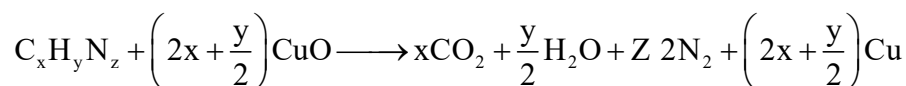
$$\therefore \% \text{ of carbon in 'a' g } \text{CO}_2 = \frac{12 \times a \times 100}{44 \times W}$$

$$\text{Similarly \% of hydrogen in 'b' g } \text{H}_2\text{O} = \frac{2 \times b \times 100}{18 \times W}$$

Note : KOH solution is used to absorb CO_2 gas because it is a strong base and can absorb CO_2 gas completely.

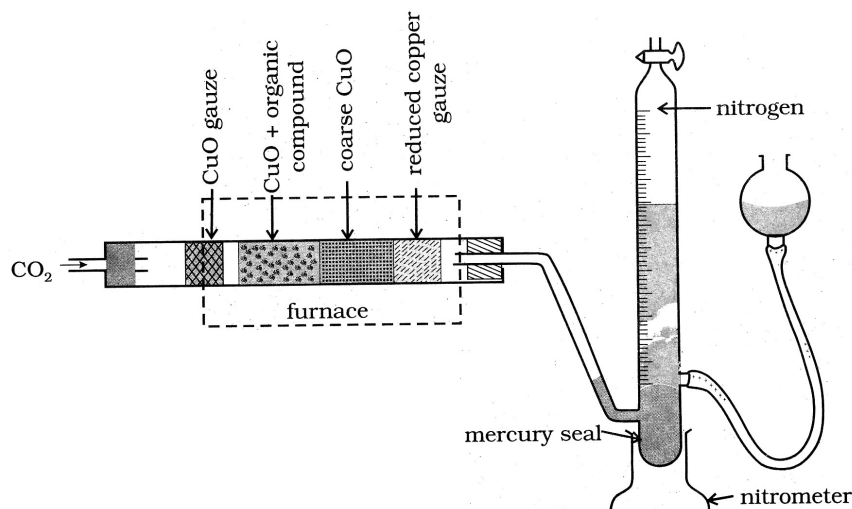
Estimation of Nitrogen by Dumas method

A known weight ('W'g) of nitrogenous organic compound is oxidised with dry cupric oxide in an atmosphere of CO_2 , when free N_2 oxides of nitrogen CO_2 and H_2O are formed.

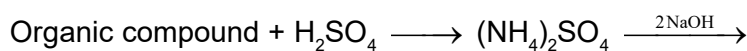
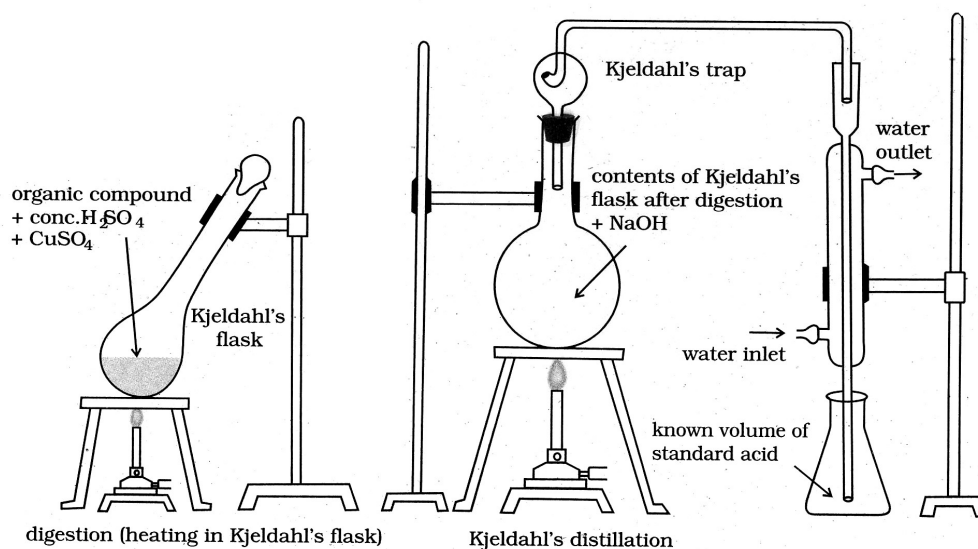


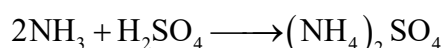
The oxides of nitrogen formed are reduced to nitrogen by passing the gaseous mixture over a heated copper wire gauge. The mixture of gases produced is passed through Schiff's nitrometer (contain 40% KOH solution) which absorb all gases except nitrogen. The nitrogen is collected in the upper part of the graduated tube and its volume is measured and reduced to STP volume.

$$\% \text{ of Nitrogen} = \frac{28 \times \text{Vol. of } \text{N}_2 \text{ at STP} \times 100}{22400 \times \text{Wt. of substance}}$$



Kjeldahl's method : A known mass of nitrogenous organic compound is heated with con. H_2SO_4 in presence of K_2SO_4 to raise the boiling point of H_2SO_4 and small of CuSO_4 , or Hg acts as a catalyst in a Kjeldahl's flask. During this, nitrogen in the organic compound is quantitatively converted into $(\text{NH}_4)_2\text{SO}_4$. It is then boiled with excess con. NaOH solution to liberate free NH_3 gas which is then absorbed in a standard excess known volume of acid like H_2SO_4 or HCl . The unreacted acid is then back titrated against NaOH using phenolphthalein indicator. From this, the volume of acid used up and hence the percentage of nitrogen in the organic compound can be calculated.





Let the weight of organic compound taken = 'W'g

Volume of H_2SO_4 of molarity 'M' = Vml

Volume of NaOH of molarity 'M' used for titration of excess of H_2SO_4 = V_1 ml

V_1 ml of NaOH of molarity M = $\frac{V_1}{2}$ ml of H_2SO_4 of molarity M

\therefore Volume of H_2SO_4 of molarity 'M' used = $\left(V - \frac{V_1}{2}\right)$ ml

$\left(V - \frac{V_1}{2}\right)$ ml of H_2SO_4 = $2\left(V - \frac{V_1}{2}\right)$ ml of NH_3

1000 ml of 1M NH_3 solution contain 17g NH_3 or 14g Nitrogen

$$\therefore \% \text{ of nitrogen} = \frac{14 \times M \times 2 \left(V - \frac{V_1}{2}\right) \times 100}{1000 \times W}$$

$$\text{OR } \% \text{ of nitrogen} = \frac{1.4 \times M \times 2 \left(V - \frac{V_1}{2}\right)}{W}$$

$$\text{OR } \% \text{ of nitrogen} = \frac{1.4 \times N \times V}{W}; \quad N = \text{Normality of } \text{H}_2\text{SO}_4$$

NOTE :

1. This method is not applicable to compounds containing nitrogen in the ring like, Pyridine, Quinoline, Isoquinoline, compounds containing NO_2 group and $-\text{N}=\text{N}-$ (azo groups). Since nitrogen in these compounds are not completely converted into $(\text{NH}_4)_2\text{SO}_4$.
2. It is a simpler and more convenient methods and is mainly used for estimating the percentage of nitrogen in food stuffs, soil, fertilizers and various agricultural products.

ESTIMATION OF SULPHUR BY

1. CARIUS METHOD:-

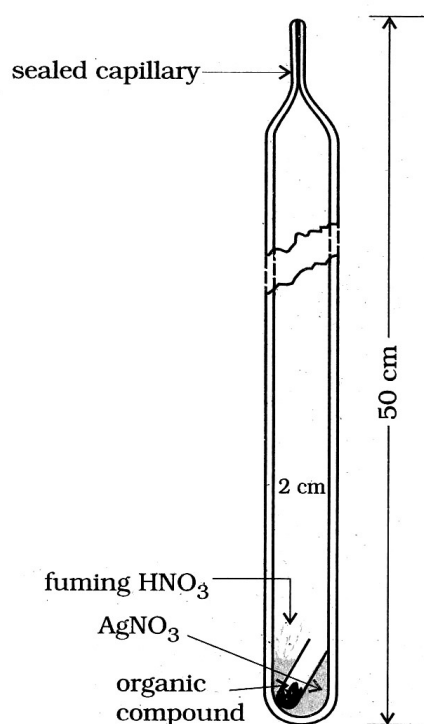
A known weight ('W' g) of organic compound is heated with fuming HNO_3 or sodium peroxide in a Carius tube when sulphur present in the organic compound is oxidised to H_2SO_4 . It is these precipitated as barium sulphate by adding excess of BaCl_2 solution. The precipitate is filtered, washed, dried, ignited and weighed (Gravimetry). From the weight of BaSO_4 the percentage of sulphur present in the organic compound can be calculated using the following relation.

Weight of organic compound take = 'W'g

Mass of BaSO_4 formed = 'a' g

Mass of 1 mole of BaSO_4 formed = 233 g

$$\therefore \% \text{ of sulphur in 'a'g } \text{BaSO}_4 = \frac{32 \times a \times 100}{233 \times W}$$



2. MESSENGER'S METHOD:-

In this method, a known weight of organic compound containing sulphur is oxidised with alk. KMnO_4 (Baeyer's reagent) in round bottom flask filled with a reflux condenser, when sulphur is oxidised to K_2SO_4 (solution form) which is precipitated as BaSO_4 by the addition of excess of BaCl_2 solution. Calculation is similar to those of Carius method.

ESTIMATION OF HALOGENS BY

1. CARIUS METHOD:-

A known weight ('W'g) of an organic compound is heated with fuming HNO_3 in presence of AgNO_3 solution in a Carius tube. Carbon and hydrogen in the organic compound are oxidised to CO_2 and H_2O . The halogen is converted into silver halide (AgX). Its weight is estimated gravimetrically. From the weight of AgX , the percentage halogen in the organic compound can be calculated.

Mass of organic compound taken = 'W'g

Mass of AgX formed = 'a'g

$$\therefore \% \text{ of Chlorine} = \frac{35.5 \times a \times 100}{143.5 \times W}$$

$$\therefore \% \text{ of Bromine} = \frac{80 \times a \times 100}{188 \times W}$$

$$\therefore \% \text{ of Iodine} = \frac{127 \times a \times 100}{235 \times W}$$

ESTIMATION OF HALOGEN BY SCHIFF'S AND PIRIA METHOD

In this method a known weight (Wg) of organic compound is heated strongly in a small platinum crucible with a mixture of lime and Na_2CO_3 cooled and dissolved in dil. HNO_3 in a beaker. This solution is filtered and the halide is precipitated with AgNO_3 solution. The percentage of halogen can be calculated as in Carius method.

ESTIMATION OF PHOSPHORUS BY CARIUS METHOD

A known weight of organic compound containing phosphorus ('W'g) is oxidised with fuming HNO_3 when phosphorus is oxidised to phosphoric acid. It is then precipitated as magnesium ammonium phosphate (MgNH_4PO_4) by the addition of magnesia mixture (MgCl_2 , NH_4OH and NH_4Cl). The precipitate MgNH_4PO_4 is filtered, washed, dried, ignited when it is decomposed to magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$). Its mass is determined and from this the percentage of phosphorus can be calculated.

Weight of organic compound taken = 'W'g

Weight of $\text{Mg}_2\text{P}_2\text{O}_7$ formed = 'a'g

Mass of one mole of $\text{Mg}_2\text{P}_2\text{O}_7$ = 222 g

$$\therefore \% \text{ of phosphorus} = \frac{62 \times a \times 100}{222 \times W}$$

Alternatively phosphoric acid is precipitated as Ammonium Phosphomolybdate

$[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$ by heating with con. HNO_3 and Ammonium molybdate solution. The yellow precipitate is filtered, washed, dried and weighed. From this weight the percentage of phosphorus can be calculated

$$\% \text{ of phosphorus} = \frac{31 \times \text{mass of Ammonium phosphomolybdate}}{1877 \times W}$$

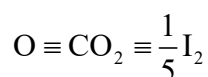
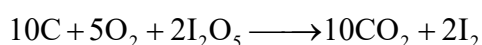
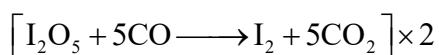
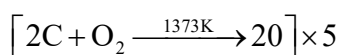
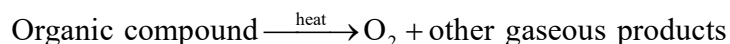
But this method will not give accurate result because of the colloidal nature of Ammonium Phosphomolybdate precipitate.

Estimation of oxygen: The percentage of oxygen in an organic compound is calculated by the difference method. eg : The percentage of all other elements present in the organic compounds are added and the sum is subtracted from 100

$\therefore \text{Percentage of oxygen} = 100 - \text{sum of percentages of all other elements}$
--

But oxygen can be directly estimated by **Aluise method** as follows.

A known mass of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products including oxygen is passed over red hot coke at 1373, when all the oxygen is converted into carbon monoxide. This mixture is then passed through warm I_2O_5 when carbon monoxide is oxidised to carbondioxide liberating iodine. The various reactions are

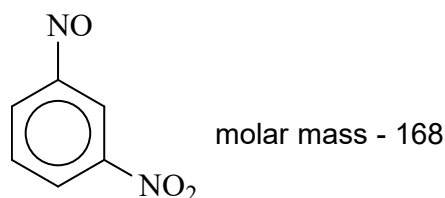
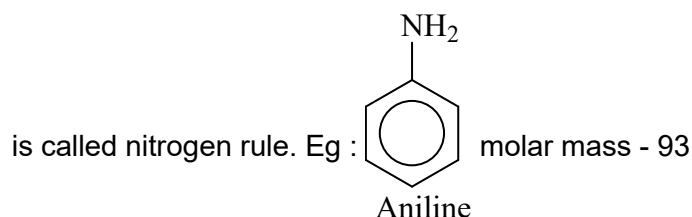


$$\therefore \% \text{ of oxygen} = \frac{16}{44} \times \frac{x}{w} \times 100$$

x = mass of CO_2 formed : w = mass of organic compound.

The elements like carbon, hydrogen and nitrogen present in an organic compound are determined by an automatic analyser called CHN elemental analyzer. It requires 1-3 mg of the compound and displays the percentages of C, H and N on a screen within a few minutes.

Nitrogen rule : All neutral compounds containing an odd number of nitrogen atoms (1, 3, 5 etc) have odd masses and those with even number of nitrogen atoms (2, 4, 6....) have even molar masses. This



Determinatio of molecular mass

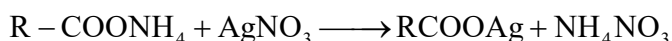
The molecular mass of the organic compounds can be determined by various methods as follows:

- Victor meyer's method :** It is used for the molar mass determination of volatile organic substance. In this method a known mass (wg) of volatile organic substance is vapourised in a Victor meyer's tube. The vapours formed displace an equal volume of air into a graduated tube and its volume is measured. This volume is converted to STP conditions.

$$\text{Molar mass } M = \frac{\text{Mass of the substance taken} \times 22400}{\text{Volume of organic vapour collected at STP}}$$

2. Silver salt method

It is used to determine the equivalent mass of organic acid from which molar mass can be calculated. The organic acid is treated with excess of NH_4OH , when ammonium salt of acid is formed and the unreacted ammonia is boiled off. The neutral solution is then treated with AgNO_3 solution. The precipitated silver salt is filtered, washed and dried.



A known mass (Wg) of silver salt is heated in a platinum crucible when metallic silver (xg) is obtained as residue and it is weighed. The eq. wt is calculated as follows.

$$\frac{\text{Eq. mass of silver salt}}{\text{Eq. mass of silver}} = \frac{W}{x}$$

$$\text{Eq. mass of silver salt} = \frac{W}{x} \times 108$$

$$\text{Eq. mass of silver salt} = E - 1 + 108 = E + 107$$

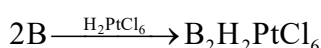
$$\text{ie } E + 107 = \frac{W}{x} \times 108$$

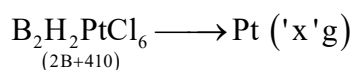
$$E = \left[\frac{W}{x} \times 108 - 107 \right]$$

$$\text{If 'n' be the basicity of the acid, then Molar mass of acid} = \left[\frac{W}{x} \times 108 - 107 \right] \times n$$

Platinic chloride method

It is used to determine the eq. wt of organic bases and from which their molar mass can be calculated. In this method organic bases are converted to insoluble chloro-platinate by reaction with H_2PtCl_6 (chloro platinic acid). A known wt of (wg) chloroplatinate salt is strongly heated in crucible to get platinum residue and its mass is determined. ('x'g). The eq. wt of base is calculated as follows.





Let 'E' be the equivalent mass of the base molar mass of the salt = $2E + 2 + 195 + 213 = 2E + 410$

$$\text{ie } \frac{2E + 410}{195} = \frac{w}{x}$$

$$410 + 2E = \frac{w}{x} \times 195 \text{ or } 2E = \frac{w}{x} \times 195 - 410$$

$$E = \frac{1}{2} \left[\frac{w}{x} \times 195 - 410 \right]$$

$$\text{Molar mass of the base} = \frac{1}{2} \left[\frac{w}{x} \times 195 - 40 \right] \times n$$

$$\boxed{\text{Molar mass of the base} = \frac{n}{2} \left[\frac{W}{x} \times 195 - 410 \right]}$$

Volumetric method for acids and bases:

In this method a known mass of acid is dissolved in specified quantity of water. It is then titrated against a standard solution of an alkali using phenolphthalein indicator. Knowing the volume of alkali, mass of the acid and normality of alkali eq: mass of acid can be calculated as follows:

$$\text{Eq: wt of the acid} = \frac{W \times 1000}{V \times N}$$

W = wt. of acid taken

V = Volume of alkali used

N = Normality of alkali

$$\boxed{\therefore \text{Molecular mass of acid} = \text{Equi. mass} \times \text{Basicity}}$$

Similarly molar masses of bases can be calculated.

Empirical Formula and Molecular formula

Empirical formula of a compound is defined as the simplest formula which represents simple relationship between the ratio of the various atoms of elements present in the molecules.

eg : The empirical formula of acetylene and benzene is CH. It expressed that simplest whole number ratio between carbon and hydrogen, present in one molecule of acetylene and benzene is 1 : 1.

Molecular formula of a compound is defined as the actual number of atoms of various elements present in the molecule of the substance.

Molecular formula = $n \times$ Empirical formula

$$n = \frac{\text{molar mass}}{\text{Empirical formula mass}}$$

Total mass = $2 \times$ vapour density

Molecular formula can be determined by an alternate method without determining empirical formula.

$$\text{Eg : Number of moles of element} = \frac{\% \text{ of element}}{100} \times \frac{\text{Molecular mass}}{\text{Atomic mass of element}}$$

Minimum molar mass

The molar mass of polymer, biomolecules like proteins, nucleic acid etc cannot be determined accurately. Hence to determine the molar mass of macromolecules, the concept of minimum molecular mass has been introduced. For that purpose it is assumed that it contain at least one atom of the least abundant element or monomer.

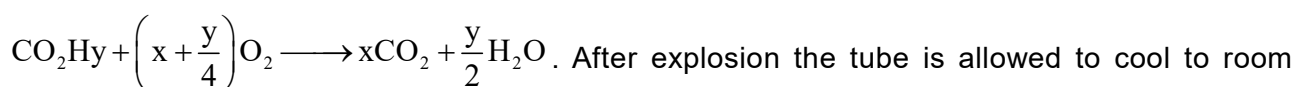
$$\therefore \% \text{ of that element} = \frac{\text{Atomic mass of that element} \times 100}{\text{Minimum molar mass}}$$

OR

$$\text{Minimum molar mass} = \frac{\text{Atomic mass of that element} \times 100}{\text{Percentage of that element}}$$

Determination of molecular formula of gaseous hydrocarbons by Eudiometry

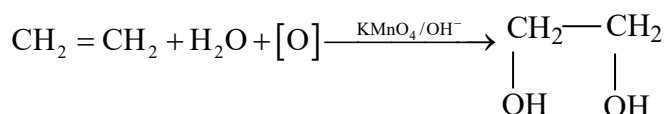
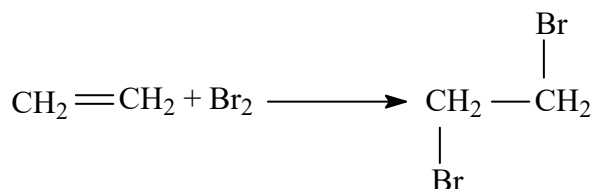
A known volume of hydrocarbon is taken in eudiometer tube and exploded with an excess of known volume of oxygen. The carbon and hydrogen of the hydrocarbon are oxidised to CO_2 and H_2O according to the following general reaction:



temperature. The volume of the gaseous mixture is recorded. The volume corresponds to unreacted oxygen and CO_2 . The volume of CO_2 is measured by passing through KOH solution and the gas left behind is the unreacted oxygen. Volume of oxygen used is then calculated by subtracting the volume of unreacted oxygen from the total volume of oxygen taken initially. Then the molecular formula of hydrocarbon can be evaluated by knowing the volumes of hydrocarbon taken, oxygen used and CO_2 produced.

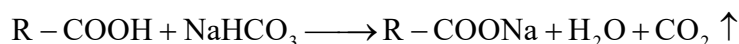
Detection of various functional groups

1. **Detection of unsaturation :** They will decolourise the purple colour of alkaline KMnO_4 (Baeyer's reagent) or Brown colour of Bromine water or Br_2 in CCl_4



2. **Detection of carboxylic group :**

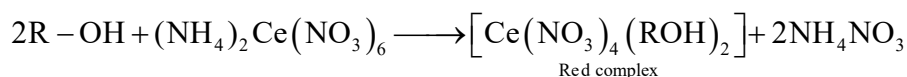
- 1) An aqueous solution of the compound turns blue litmus to red
- 2) It reacts with saturated aqueous solution of NaHCO_3 liberate brisk effervescence of CO_2 gas.



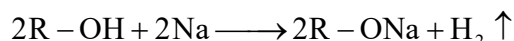
3. **Ester formation :** Acid when heated with ethanol in presence of $\text{con. H}_2\text{SO}_4$ gives a fruity smell due to the formation of an ester indicate the presence of carboxylic group.

Detection of alcoholic group

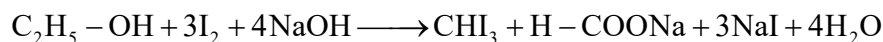
1. Add a freshly prepared ceric ammonium nitrate to the organic compound. A red colour indicates the presence of alcoholic group.



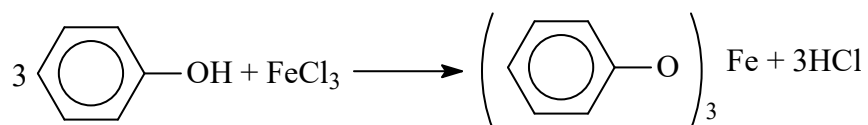
2. Alcohols react with sodium metal gives effervescence due to the liberation of H_2 gas



3. Iodoform test : When an aqueous of ethanol warmed with NaOH and I_2 powder on a water bath, a yellow oily compound having a characteristic smell is produced due to the formation of CHI_3 (iodoform)

**Detection of phenols:**

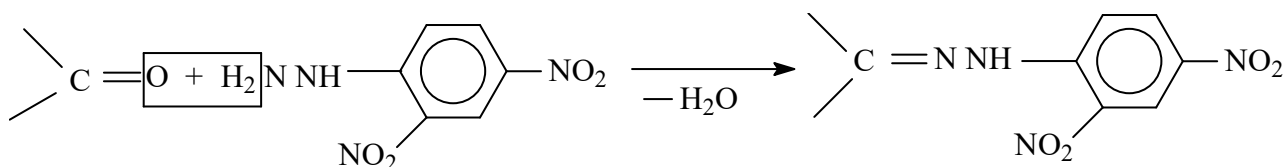
1. It turns blue litmus to red.
2. It gives green, blue or violet colour with neutral ferric chloride solution.



3. Lieberman's nitroso test : When phenol is heated with a crystal of NaNO_2 and con: H_2SO_4 . A deep green or blue solution is formed, which on dilution with H_2O changes to red. When it is made alkaline with NaOH , red colour changes to blue or green.

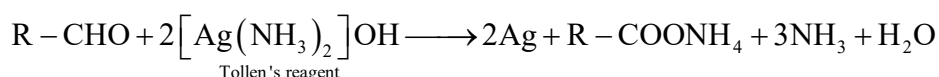
Detection of carbonyl compounds :

Both aldehyde and ketones react with Borche's reagent (Ethanolic solution of 2, 4-Dinitrophenyl hydrazine) form an orange red precipitate.



Test for aldehydes

1. Both aliphatic and aromatic aldehydes when warmed with Tollen's reagent (Ammoniacal AgNO_3 solution) form a grey black precipitate.



2. Fehling solution test : Only aliphatic aldehydes on warming with Fehling's solution (A mixture of alkaline CuSO_4 and sodium potassium tartarate (Rochelle salt)) gives red precipitate.

$\text{R}-\text{CHO} + \text{CuO} \longrightarrow \text{R}-\text{COOH} + \text{Cu}_2\text{O}$. Hence this test is used to distinguish between aliphatic and aromatic aldehydes.

Detection of primary amine :

Both aliphatic and aromatic 1° amines on heating with CHCl_3 and alcoholic KOH gives an unpleasant smell due to the formation of carbylamine (isocyanide).

