UNIT

16

Purification and Characterisation of Carbon Compounds

SYLLABUS

Purification of carbon compounds : filtration, crystallization, sublimation, distillation, differential extraction and chromatography.

Qualitative analysis : detection of nitrogen, sulphur, phosphorus and halogens

Quantitative analysis : estimation of carbon, nitrogen, halogen, sulphur and phosphorus (basic principles only).

Determination of molecular mass : silver salt method, chloroplatinate salt method, use of mass spectrometer for determining accurate molecular mass (elementary idea only).

Calculation of empirical and molecular formulae.

16.1. Introduction

In unit 15, we have learnt that the properties of organic compounds can be correlated to their structures. In other words, a knowledge of the structures of compounds helps us to understand their chemistry. The determination of the structure of an organic compound, whether isolated from a natural source or prepared in the laboratory, involves the following steps :

(i) Purification of the compound

(ii) Qualitative analysis for determining the elements present

(iii) Quantitative analysis of elements detected under (ii)

(iv) Determination of molecular mass and molecular formulae

(v) Determination of structural formula by physiochemical and spectroscopic methods.

16.2. Purification of Organic Compounds

Compounds isolated from natural sources are seldom pure. They are generally mixed with other substances which also occur along with them. Similarly, the compounds prepared in the laboratory are also not pure since they are generally contaminated with other products that result from the side reactions. It, therefore, becomes essential to obtain the substance in the purest form in order to characterise it thoroughly. A large number of methods are available for the purification of substances. The choice of the method, however, depends upon the nature of the substance (whether solid or liquid) and the type of impurities present in it. Following are some of the important methods which are commonly employed for the purification of organic compounds :

(1) Filtration, (2) Crystallisation or Recrystallization, (3) Fractional crystallisation, (4) Sublimation, (5) Simple distillation, (6) Fractional distillation, (7) Distillation under reduced pressure, (8) Steam distillation, (9) Differential extraction, and (10) Chromatography.

The purity of the organic compound (purified by any one of the above methods) is finally checked by determining one or more of its physical constants. *Melting point, boiling point, refractive index etc. are used as the criteria of purity of organic compounds.* This is due to the reason that each pure compound has definite values of these physical constants. Besides these, in recent years, the purity of the organic compound is also checked by more sophisticated methods such as spectroscopic methods and different types of chromatography (TLC, GLC, HPLC etc.-discussed in sec 16.2.9).

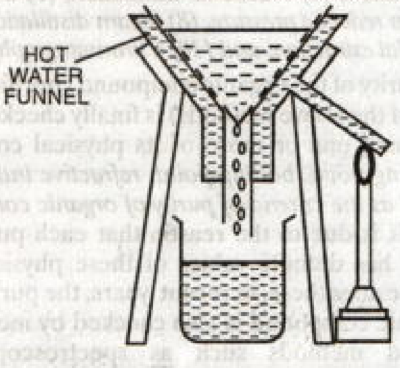
Let us now discuss the principle and brief procedure of each one of the above methods.

16.2.1. Filtration

The process of filtration is used to separate insoluble solid component of a mixture from the soluble component in a given solvent. For example, this technique can be used to separate a mixture of naphthalene and urea using water as solvent. Urea dissolves in water while naphthalene remains insoluble. Upon filtration, naphthalene remains on the filter paper while urea is recovered from the filtrate by evaporating water.

If the water soluble component of a mixture is appreciably soluble in hot water but only sparingly soluble in cold water, then to separate the mixture, filtration of a hot solution is required. This is carried out through a fluted filter paper (Fig. 16.1) to avoid crystallisation during filtration and also to remove suspended impurities. If the solution to be filtered is sufficiently large, then filtration is done through a *'hot water funnel'* (Fig. 16.2) to avoid formation of crystals in the funnel and its stem. The jacket of the hot water funnel keeps the solution hot in the glass funnel placed in it.

FIGURE 16.1. Fluted filter paper.



FILTERING THE SOLUTION OF THE SUBSTANCE USING HOT WATER FUNNEL TO PREVENT CRYSTALLISATION DURING FILTRATION

FIGURE 16.2. Filtration using hot water funnel.

For example, a mixture of anthracene and benzoic acid is separated by dissolving the mixture in hot water and filtering the hot solution. Benzoic acid dissolves is hot water but anthracene does not. Upon filtration, anthracene remains as a residue on the filter paper while benzoic acid crystallises from the filtrate on cooling.

Sometimes, the filtration is very slow and takes a long time. In such cases, filtration is carried out under reduced pressure using a Buchner funnel and water suction pump are shown in Fig. 16.3.

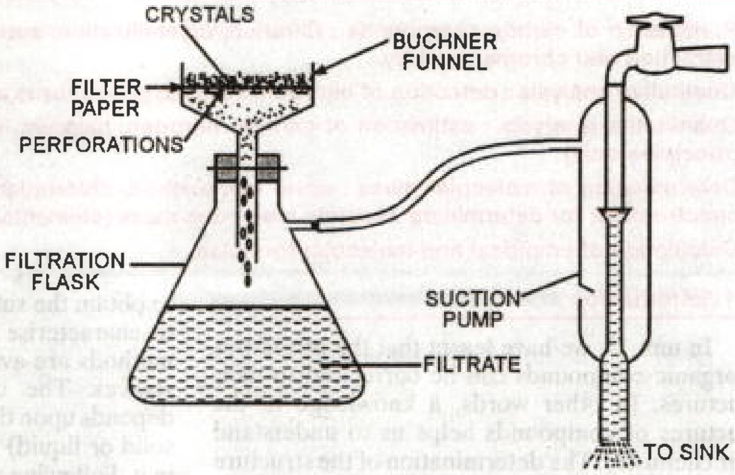


FIGURE 16.3. Quick filtration process using a Buchner funnel and a water suction pump.

16.2.2. Crystallisation or Recrystallisation

***Crystals are the purest form of a substance having definite geometrical shapes. The process by which an impure compound is converted into its crystals is known as* crystallisation.**

This is one of the most commonly used techniques for purification of solid organic compounds. It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. The impure compound is dissolved in a suitable solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to get nearly a saturated solution. When this saturated solution is cooled, crystals of pure substance will separate out which are removed by filtration. The filtrate, *i.e.*, mother liquor contains the impurities alongwith small quantity of the compound. If the compound is highly soluble in one solvent and too little soluble in another solvent, then crystallization can be carried out in a mixture of these solvents taken in a suitable ratio.

Coloured impurities if present are removed first by boiling the solution of the impure substance with activated charcoal for about 15-20 minutes. The charcoal is filtered out and the filtrate is allowed to cool when crystals of pure substance will separate out.

If the compound and the impurities have comparable solubilities, then repeated crystallizations may be necessary to purify the substance.

The main steps of this process are explained below :

(i) Choice of the solvent. A suitable solvent which fulfils the following conditions is selected for crystallization :

(*a*) *It should not react chemically with the impure substance.*

(*b*) *It should dissolve more of the substance upon heating than at room temperature so that the excess of the substance is thrown out upon cooling.*

(*c*) *Either the impurities should not dissolve at all in the solvent, or if they dissolve, they should be soluble to such an extent that they remain in the solution, i.e., in the mother liquor upon crystallisation.*

The various solvents which are commonly employed for crystallisation are water, alcohol, ether, chloroform, carbon tetrachloride, benzene, acetone, ethyl acetate, petroleum ether etc.

(ii) Preparation of the solution. The impure substance is finely powdered and then heated in a conical flask with a small quantity of the solvent which is just sufficient to dissolve whole of the substance on boiling.

(iii) Filtration of the solution. The hot solution obtained above is then filtered immediately either through fluted filter paper (Fig. 16.1) or through hot water funnel to avoid crystallization during filtration.

(iv) Crystallisation and separation of crystals. The dish containing the solution is then allowed to cool undisturbed when after some time crystals begin to separate out. If the crystals do not appear even after a long time, then it may be necessary to scratch the sides of the dish with a glass rod or to "*seed*" the substance with a small crystal of the same substance. This provides tiny fragments of glass or small particles of the pure substance as nuclei for crystallisation. *This process of inducing crystallisation by adding a crystal of the pure substance into its staurated solution is called* **seeding.**

When the crystallistaion is complete, the crystals are then separated from the mother liquor by filtration using a Buchner funnel and a water suction pump as shown in Fig. 16.3. The crystals left in the funnel are washed once or twice with a little of the cold solvent to remove adhering impurities, if any.

(v) Drying of crystals. The crystals are finally dried either in air or by placing them in a steam oven or an air oven.

Examples. For proper crystallisation, the choice of the solvent is very crucial. This is evident form the following two examples :

(*i*) *Crystallisation of sugar.* Suppose we have a sample of sugar containing an impurity of common salt (sodium chloride). This can be purified by shaking the impure solid with hot ethanol at 348 K. The sugar will dissolve whereas the common salt remains insoluble. The hot solution is filtered, concentrated and then allowed to cool when crystals of sugar will separate out. In this case, had water been used as a solvent, the purification of sugar would not have been possible since both sugar and common salt are readily soluble in water.

(*ii*) *Crystallisation of benzoic acid.* Suppose we have a mixture of benzoic acid and naphthalene. This mixture can be purified by treating the impure solid with hot water. Benzoic acid will dissolve while naphthalene remains insoluble. The hot solution is filtered and then allowed to cool when crystals of benzoic acid separate out. The crystals are separated by filtration and dried . Had benzene been used as a solvent, instead of water in this case, the purification of benzoic acid would not have been possible since both benzoic acid and naphthalene are quite soluble in benzene.

16.2.3. Fractional crystallisation

This method is used to separate and purify two or more compounds which have different solubilities in the same solvent. The process involves a series of repeated crystallisations as discussed below :

The mixture is dissolved in a suitable solvent in which the two components of the mixture have different solubilities. When a hot saturated solution of this mixture is allowed to cool, the less soluble substance crystallises out first while the more soluble substance remains in the solution. The crystals are then separated from the mother liquor as discussed above and the mother liquor is again concentrated and allowed to cool when the crystals of the second compound are obtained. By repeating this process, all the components of a mixture can be separated.

***The process of separation of different components of a mixture by repeated crystallisations is known as* fractional crytallisation.**

16.2.4. Sublimation

It involves the direct conversion of a solid into the gaseous state on heating without passing through the intervening liquid state and vice versa on cooling.

Only those substances whose vapour pressures become equal to the atmospheric pressure much before their respective melting points are capable of undergoing sublimation. *Such substances are called sublimable*. Since the number of such compounds is expected to be small, therefore, the process of sublimation is not of general application.

The process of sublimation is very useful in the purification of such solids which sublime on heating and are associated with non-volatile impurities.

The impure substance is taken in a china dish covered with a perforated filter paper over which an inverted funnel is placed. The stem of the funnel is plugged with a little cotton (Fig. 16.4). On heating the dish on a sand bath, vapours of the volatile solid rise up, pass through the holes in the filter paper and condense on the cooler walls of the funnel leaving behind the non-volatile impurities in the dish.

Camphor, naphthalene, anthracene benzoic acid, iodine etc. are purified by this process.

In case of organic compounds which are decomposed by heat, sublimation is done under reduced pressure.

16.2.5. Simple distillation

Liquids are generally purified by simple distillation.

Distillation involves conversion of a liquid into vapours by heating followed by condensation of the vapours thus produced by cooling.

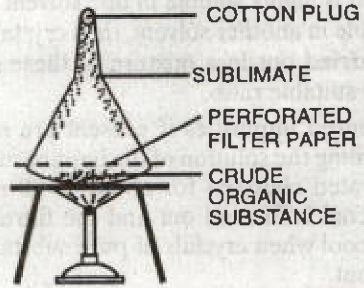


FIGURE 16.4. Sublimation.

The method is commonly used for those liquids which are sufficiently stable at their boiling points and which contain non-volatile impurities. For example, simple organic liquids such as benzene, ethanol, acetone, chloroform, carbon tetrachloride, toluene, xylenes, etc. can be purified by simple distillation.

Procedure. The apparatus used for simple distillation is shown in Fig. 16.5. When the flask is heated, the temperature rises gradually and the *liquid starts boiling when its vapour pressure becomes equal to the atmospheric pressure.* These vapours as they pass through the condenser are condensed.

Only the liquid which distils at a constant temperature is collected in a receiver. This gives us the pure liquid.

Purification of a mixture of liquids. Simple distillation can also be used for the separation and purification of a mixture of two or more miscible organic liquids provided their boiling points differ by 30 – 50 K. The separation is based upon the fact

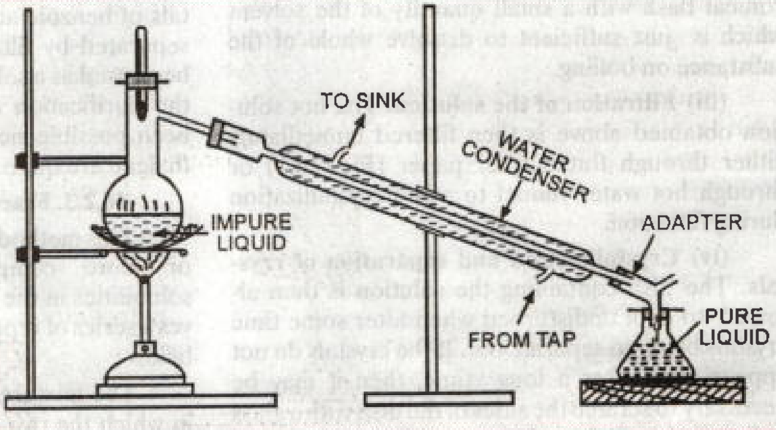


FIGURE 16.5. Apparatus for simple distillation

that at the b.p. of the more volatile liquid (low boiling) of the mixture, the vapours almost exclusively consist of the more volatile liquid. Likewise, at the b.p. of the less volatile liquid (high boiling), vapours almost entirely consist of the less volatile liquid since the more volatile liquid has already distilled over. *Thus, the separation of the liquid mixture into individual components can be achieved at their respective boiling points ; the more volatile component distils over first while the less volatile component distils over afterwards.* The non-volatile impurities and impurities of liquids having boiling points much higher than those of the two liquids separated above are, however, left in the distillation flask. This method can be used to separate :

(*a*) a mixture of ether (b.p. 308 K) and toluene (b.p. 384 K),

(*b*) a mixture of hexane (b.p. 342 K) and toluene (b.p. 384 K),

(*c*) a mixture of benzene (b.p. 353 K) or chlorofom (b.p. 334 K) and aniline (b.p. 457 K) and so on.

16.2.6. Fractional distillation

If the b.p.'s of the two liquids of the mixture are very close to one another *i.e.* differ by 10 K or so, the separation cannot be achieved by the simple distillation method as described above. *This is due to the reason that at the b.p. of the more volatile liquid of the mixture there will be sufficient vapours of the less volatile liquid as well. As a result, both the liquids of the mixture will distil together and the separation is denied.*

The separation of such a liquid mixture into individual components can, however, be achieved by *fractional distillation, which involves repeated distillations and condensations.* Fractional distillation is carried out using a *fractionating column*. It usually consists of a long glass tube with a wide bore either packed with glass beads, small stones, porcelain rings or coke, or blown into a number of spherical or pear-shaped bulbs. *The actual purpose of the fractionating column is to increase the cooling surface area and to provide hurdles or obstructions to the ascending vapours and descending liquid.* Some of the fractionating columns commonly employed in the laboratory are shown in Fig. 16.6.

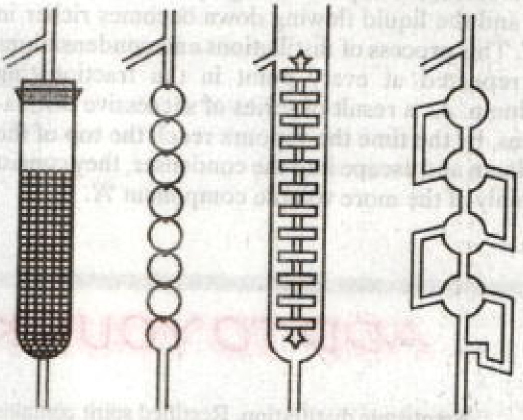


FIGURE 16.6. Various types of fractionating columns.

Procedure. The apparatus used for fractional distillation is shown in Fig. 16.7.

Suppose we have a mixture of two liquids 'A' and 'B' of which 'A' is more volatile than'B'. When

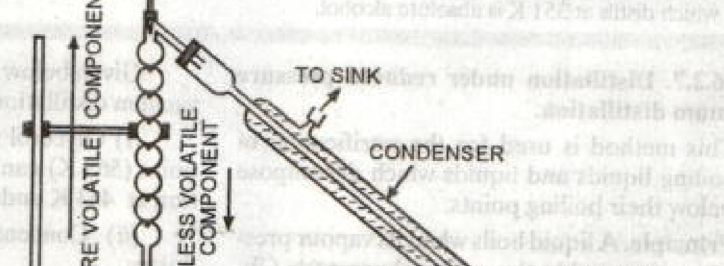


FIGURE 16.7. Apparatus for fractional distillation using a fractionating column.

such a liquid mixture is heated, the temperature rises slowly and mixture starts boiling. *The vapours formed mainly consist of the more volatile liquid 'A' with little of the less volatile liquid 'B'.* As these vapours travel up the fractionating column, the vapours of the less volatile liquid 'B' condense more readily than those of the more volatile liquid 'A'. Therefore, the vapours rising up become richer in 'A' and the liquid flowing down becomes richer in 'B'. This process of distillations and condensations is repeated at every point in the fractionating column. As a result of series of successive distillations, by the time the vapours reach the top of the column and escape into the condenser, they consist mainly of the more volatile component 'A'.

Similarly, after a series of successive distillations, the remaining liquid in the distillation flask gets enriched in higher boiling component. *Each successive condensation and vaporizationi is called* **theoretical plate.** Commercially, columns with hundreds of theoretical plates are available.

Applications. (*a*) One of the technological applications of fractional distillation is to separate crude oil in petroleum industry into various useful fractions such as gasoline, kerosene oil, diesel oil, luberating oil etc.

(*b*) Fractional distillation has also been used to separate acetone (b.p. 329 K) and methyl alcohol (b.p. 338 K) from *pyroligneous acid* obtained by destructive distillation of wood.

ADD TO YOUR KNOWLEDGE

Azeotropic distillation. Rectified spirit contains about 95% alcohol (b.p. 351 K) and 5% water (b.p. 373 K) but alcohol and water cannot be separated from this mixture even though their boiling points differ by 22 K. This is due to the reason that at this composition, alcohol and water form an **azeotrope** (*i.e.* constant boiling mixture) and thus both the components of the mixture distil together like a pure liquid. To remove water from such a mixture, a special method called **azeotropic distillation** is used. *Azeotropic distillation means fractional distillation using a suitable volatile solvent.* For example, in the present case, benzene is used.

Rectified spirit is mixed with a suitable amount of benzene and subjected to fractional distillation. The first fraction obtained at 331·8 K is a *ternary azeotrope* consisting of all the water, some alcohol and benzene (water 7·4%, benzene 74·1%, alcohol 18·5%). The second fraction is a *binary azeotrope* consisting of the remaining benzene and some alcohol (benzene 67·7%, alcohol 32·3%) which distils over at 341·2 K. The third fraction which distils at 351 K is absolute alcohol.

16.2.7. Distillation under reduced pressure or Vacuum distillation.

This method is used for the purification of high boiling liquids and liquids which decompose at or below their boiling points.

Principle. A liquid boils when its vapour pressure becomes equal to the external pressure. Obviously, the same liquid would boil at a lower temperature if the pressure acting on it is reduced. Since the liquid now boils at a lower temperature, its decomposition does not occur.

With the commonly used water suction pumps in the laboratory, a pressure of 10 – 20 mm Hg can be obtained. Under these conditions, the boiling points are reduced by about 100 degrees. However, with vacuum pumps, pressure of the order of 0.1 mm Hg can be easily obtained.

Apparatus. The apparatus used for vacuum distillation is shown in Fig. 16.8.

Given below are some of the examples where vacuum distillation has been used to purify liquids:

(*i*) Glycerol which decomposes at its boiling point (563 K) can be distilled without decomposition at 453 K under 12 mm Hg pressure.

(*ii*) Concentration of sugarcane in sugar industry.

16.2.8. Steam distillation

This is a convenient method for the separation and purification of organic compounds (solid or liquid) from non-volatile organic or inorganic impurities. This method is applicable to only those compounds which are *volatile in steam, insoluble in water, possess a vapour pressure of about 10 – 15 mm Hg at 373 K and contain non-volatile impurities*.

Steam distillation is particularly valuable when the substance to be purified boils above 373 K at 760 mm and decomposes at or below its

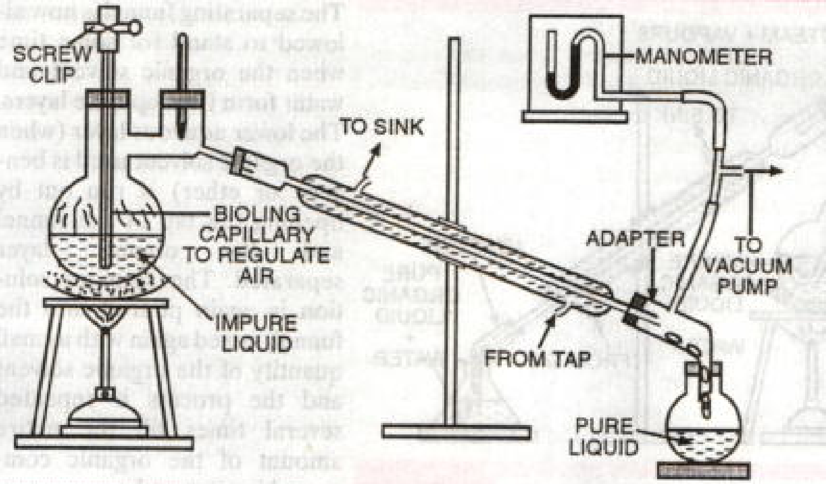


FIGURE 16.8. Distillation under reduced pressure.

boiling point. This is due to the fact that steam distillation makes the high-boiling substances to distil at low temperatures and hence avoids their decomposition. In this respect, steam distillation is comparable to vacuum distillation even though there is no reduction in the total pressure acting on the solution during the process of distillation.

Principle. In this method, a mixture of two immiscible liquids, *i.e.*, water and an organic liquid is heated. Each would exert its own vapour pressure independently of the other and the mixture will begin to boil at a temperature when the sum of the vapour pressures of the organic liquid (p_1) and that of water (p_2) becomes equal to the atmospheric pressure (p).

$$p = p_1 + p_2$$

Unless the vapour pressure of water or that of the organic liquid is zero, the temperature at which the mixture boils must be lower than the normal boiling point of both the organic liquid and the water. In other words, *the organic liquid boils at a temperature lower than its normal b.p. and hence the decomposition is avoided.*

Further, we know from Dalton's law that the partial pressures of different gases in a gaseous mixture are in the ratio of their relative number of moles. Therefore, the ratio of the number of moles of the organic liquid and water in the distillate must be in the ratio of their partial vapour pressures (in the boiling mixture), *i.e.*,

$$\frac{n_1}{n_2} = \frac{p_1}{p_2} \qquad \text{...}(i)$$

where n_1 and n_2 are the no. of moles and, p_1 and p_2 the partial pressures of the organic liquid and water respectively.

Let w_1 and w_2 be the respective masses of the organic liquid and water in the distillate. Then,

$$n_1 = \frac{w_1}{M}$$

where M is the molecular mass of the organic liquid

$$\text{and} \qquad n_2 = \frac{w_2}{18}$$

where 18 is the molecular mass of water.

Substituting the above values of n_1 and n_2 in equation (*i*) we get

$$\frac{w_1}{M} \times \frac{18}{w_2} = \frac{p_1}{p_2}$$

$$\text{or} \qquad \frac{w_1}{w_2} = \frac{p_1 \times M}{p_2 \times 18} \qquad \text{...}(ii)$$

Eq. (*ii*) gives the relative masses of the organic liquid and water in the distillate.

Consider the following examples for illustration :

(*i*) A mixture of nitrobenzene (*b.p.* 483 K) and water (*b.p.* 373 K) boils at 372.3 K during steam distillation. At this temperature, the vapour pressure of nitrobenzene (p_1) is 20 mm and that of water (p_2) is 740 mm. It follows from the equation (*i*) that the ratio of the no. of moles of nitrobenzene and water in the distillate must be 20/740 or 1 : 37 *i.e.* in the ratio of their respective vapour pressures.

(*ii*) A mixture of water (b.p. 373 K) and aniline (b.p. 457 K) boils at 371 K at 760 mm pressure in steam distillation. The vapour pressures of aniline and water at this temperature are 43 mm and 717 mm respectively.

Therefore, the ratio of the no. of moles of aniline and water in the distillate must be 43 : 717 *i.e.*, in the ratio of their respective vapour pressures.

Procedure. The apparatus used for steam distillation is shown in Fig. 16.9.

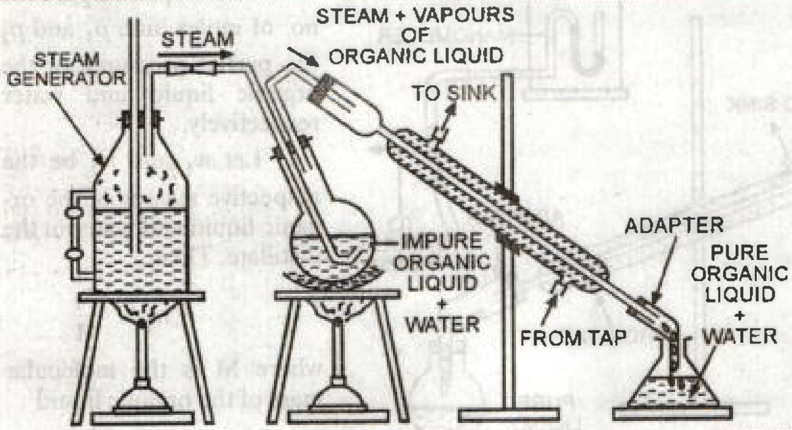


FIGURE 16.9. Apparatus for steam distillation.

The impure organic compound mixed with water is taken in a round bottomed flask and steam is passed. The mixture starts boiling when the combined vapour pressure becomes equal to the atmospheric pressure. At this temperature, steam mixed with vapours of the compound passes over to the condenser where they are condensed and collected in the receiver. The distillate contains the desired substance and water which can easily be separated with the help of a separating funnel.

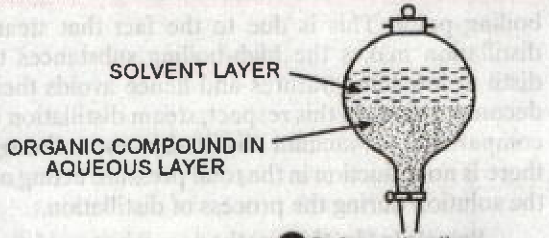
Some of the compounds which can be purified by this process are *o-nitrophenol, bromobenzene, aniline, nitrobenzene, essential oils, turpentine oil etc.*

16.2.9. Differential extraction

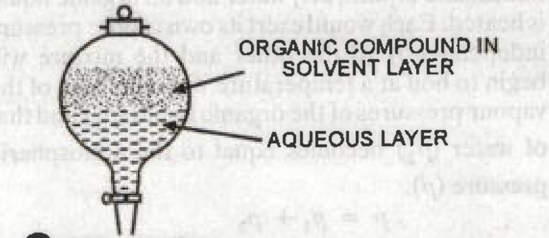
This method is used to recover organic compounds (solids or liquids) from their aqueous solutions.

The process essentially involves the shaking of the aqueous solution of the organic compound in a separating funnel with a suitable solvent which is immiscible with water but in which the organic compound is very highly soluble. Ether, benzene, chloroform, carbon tetrachloride are some of the solvents which are generally employed for extraction.

Procedure. The aqueous solution is mixed with a small quantity of the organic solvent in a separating funnel (Fig. 16.10). The funnel is stoppered and the contents are shaken thoroughly for sometimes when the organic solvent dissolves the organic compound present in the aqueous solution. The separating funnel is now allowed to stand for some time when the organic solvent and water form two separate layers. The lower aqueous layer (when the organic solvent used is benzene or ether) is run out by opening the tap of the funnel and the organic layer separated. The aqueous solution is again poured into the funnel, mixed again with a small quantity of the organic solvent and the process is repeated several times till the entire amount of the organic compound is extracted.



ⓐ Before extraction



ⓑ After extraction

FIGURE 16.10. Differential extraction.

The organic layers from all the steps are taken in a distillation flask. The organic solvent is distilled off leaving the organic compound in the distillation flask.

The efficiency of the process of extraction depends upon the number of times the extraction is repeated. It has been found that *with a given amount of the solvent, larger the number of extractions, greater is the amount of the material extracted.*

This method is normally applicable to nonvolatile compounds. For example, benzoic acid can be extracted from its water solution using benzene.

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Soxhlet extractor. If the organic compound is less soluble in the organic solvent, a very large quantity of the solvent would be required to extract even a very small quantity of the compound. In such cases, the technique of **continuous extraction** is employed. In this process, the same solvent is repeatedly used for extraction of the compound. The most commonly used apparatus for this process is called **Soxhlet extractor** (Fig. 16.11).

The powdered material to be extracted is placed in thimble tube 'A' made up of stout filter paper and a suitable solvent such as ether, alcohol, chloroform etc. is taken in the flask B. The length of the thimble tube 'A' is a little more than that of the siphon tube 'S'. On heating vapours of the solvent rise up and condense in the condenser. The condensed solvent falls in the thimble A, dissolves the organic compound and filters out into the space between the thimble and the glass cylinder C. When the level of the liquid in thimble A reaches up to the top in siphon tube S, the solution flows through the siphon 'S' back into the flask B which is being heated continuously. The solvent once again gets vapourised leaving the extracted substance in the flask. In this way, a continuous stream of pure solvent falls in the thimble T, extracts the soluble substance and returns to the flask. At the end of the extraction, the solvent in the boiling flask is distilled off, leaving the organic substance behind.

Soxhlet extractor is commonly used for extraction of oils and flavouring agent vanillin from (vanilla beans) from flowers and seeds and alkaloids from plants.

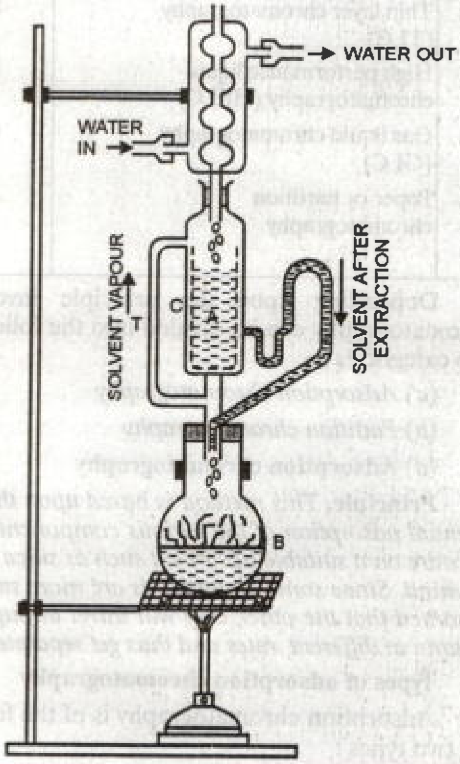

FIGURE 16.11. Continuous differential extraction of a less soluble component in a solvent by Soxhlet extractor.

16.2.10. Chromatography

Chromatography is the most modern and versatile method used for the separation, purification and testing the purity of organic compounds. This method was first discovered by *Tswett*, a Russian botanist, in 1906. The name chromatography was originally derived from the Greek word *chroma* meaning colour and *graphy* for writing because the method was first used for the separation of coloured substances (plant pigments) into individual components. Now this method is widely used for *separation, purification, identification* and *characterisation* of the components of a mixture, whether *coloured* or *colourless*.

Chromatography is essentially a physical method of separation. It is defined as follows :

The technique of separating the components of a mixture in which separation is achieved by the differential movement of individual components through a stationary phase under the influence of a mobile phase.

Types of chromatography. The stationary phase can be either a *solid* or tightly bound *liquid* on a solid support while the mobile phase can be either a *liquid* or a *gas*. Depending upon the nature of the stationary and the mobile phases, the different types of chromatographic techniques commonly used are given in Table 16.1.

TABLE 16.1. Some common types of chromatography

Sr. No.	TYPE OF CHROMATOGRAPHY	MOBILE/STATIONARY PHASE	USES
1.	Adsorption or Column chromatography	Liquid/Solid	Large scale separations
2.	Thin layer chromatography (TLC)	Liquid/Solid	Qualitative analysis (identification and characterization of organic compounds).
3.	High performance liquid chromatography (HPLC)	Liquid/Solid	Qualitative and quantitative analysis
4.	Gas liquid chromatography (GLC)	Gas/Liquid	Qualitative and quantitative analysis.
5.	Paper or partition chromatography	Liquid/Liquid	Qualitative and quantitative analysis of polar organic compounds (sugars, α-amino acids) and inorganic compounds.

Depending upon the principle involved, chromatography can be divided into the following two categories :

(*a*) *Adsorption chromatography*

(*b*) *Partition chromatography*

(*a*) Adsorption chromatography

Principle. *This method is based upon the differential adsorption of the various components of a mixture on a suitable adsorbent such as silica gel or alumina. Since some compounds are more strongly adsorbed that the other, they will travel through the column at different rates and thus get separated.*

Types of adsorption chromatography

Adsorption chromatography is of the following two types :

(*i*) Column chromatography

(*ii*) Thin layer chromatography.

(i) Column chromatography. Column chromatography is the simplest of all the chromatographic techniques and is widely used. The whole process is carried out in a long glass column provided with a stop-cock at the bottom. The various steps involved in this process are :

(*i*) *Preparation of the Column.* A plug of cotton or glass wool is placed at the bottom (Fig. 16.12) of a clean and dry glass column. Above this, a thin layer of acid-washed sand is placed to support the adsorbent. A suitable adsorbent such as alumina (Al_2O_3), silica gel, magnesium oxide, starch, charcoal etc. is made into slurry with a suitable solvent

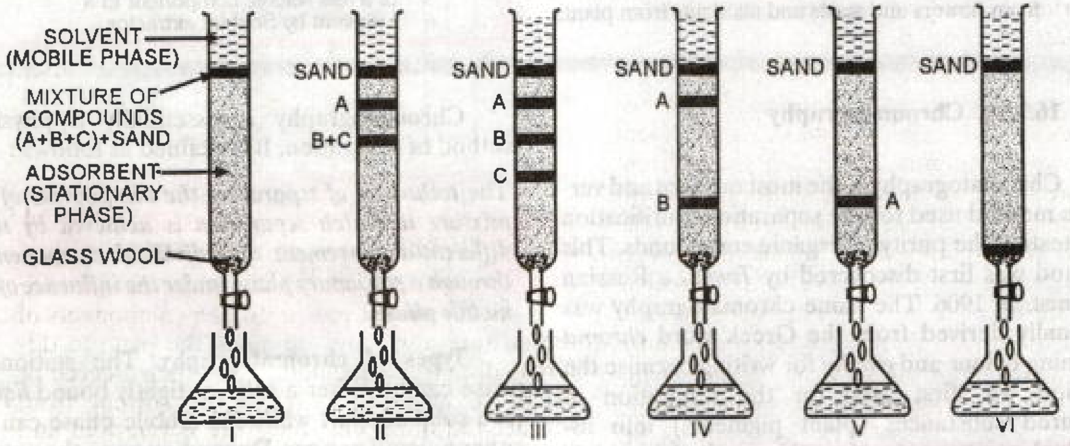

FIGURE 16.12. Column chromatography - stages I, II, III, IV, V and VI represent the progressive separation of the mixture into three individual components.

(preferably non-polar) such as hexane or petroleum ether. The slurry is then carefully packed in the column by gentle tapping so that no air bubble is entraped in the column. This constitutes the *stationary phase.*

(ii) Adsorption. The mixture to be separated (or the impure compound to be purified) is dissolved in a minimum volume of a suitable highly polar solvent* and applied on the top of the column of the adsorbent with the help of a dropper or a microsyringe. As the solution travels down, the mixture is adsorbed in a narrow band. A thin layer of acid- washed sand is again placed at the top of the column followed by a loose plug of cotton or wool. The sand layer prevents the column from being disturbed during the addition of solvent from time to time.

After the application of the sample, a little amount of the solvent is placed over the sand layer and the column is allowed to stand for about 15–20 minutes as shown in stage I (Fig. 16.12). During this period, the various components of the mixture (say A, B and C) are adsorbed to different extents depending upon their polarity (say A > B > C) within a narrow band. *Thus, within the narrow band,* **component A** *is strongly adsorbed* **component B** *is moderately adsorbed while* **component C** *is weakly adsorbed.*

(iii) Elution. It is the proccess of extraction of the adsorbed components from the adsorbent with the help of solvents of increasing polarity. The solvents usually employed in the increasing order of polarity are petroleum ether, carbon tetrachloride, benzene, chloroform, diethyl ether, ethyl acetate, acetone, alcohol etc.

A solvent or a mixture of solvents which is used to extract the column constitutes the *mobile phase* and is usually called an *eluent*. As the eluent passes down the column, it dissolves the different compounds. *The least strongly adsorbed component of the mixture i.e.* component C is eluted first by the least polar solvent *followed by moderately strongly adsorbed component B by solvent of intermediate polarity while the most strongly adsorbed component A is eluted last of all by the solvents of higher polarity.*

In this way, the various components of the mixture can be separated into different fractions. Distillation or evaporation of the solvent from different fractions gives the various components of the mixture in pure form.

This technique is being widely used throughout the world for the purification of different substances and the separation of mixtures. For example, a mixture of naphthalene (hydrocarbon) and benzophenone (ketone) can be separated over a column of alumina and by using petroleum ether containing benzene as eluent. Naphthalene being less polar is weakly adsorbed while benzophenone being more polar is strongly adsorbed over the column. Elution of the column will first elute naphthalene and then benzophenone.

(ii) Thin layer chromatography (TLC). It is another type of adsorption chromatography in which separation of the components of a mixture is achieved over a thin layer of an adsorbent. A thin layer (0·2 mm thick) of an adsorbent such as silica gel or alumina) is spread over a plastic or glass plate of suitable size.

A suitable TLC plate is taken and two pencil lines are drawn across the width of the plate about 1 cm from each end. The lower pencil line is called the *starting line* while the upper line is called the *finish line* or *solvent front.*

A solution of the mixture to be separated is applied as a small spot with the help of a capillary on the starting line. The plate is then placed in a closed jar containing a suitable solvent (Fig. 16.13).

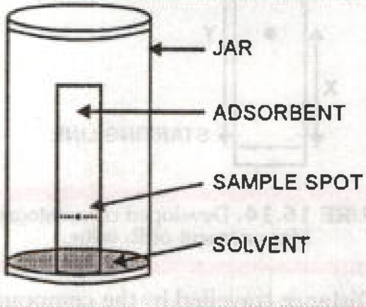

FIGURE 16.13. TLC chromatograph being developed.

As the solvent moves up, the components of the mixture also move up along the plate to different distances depending upon their degree or extent of adsorption. When the solvent front reaches the finish line, the plate is removed and then dried in air.

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*If a less polar or a non-polar solvent is used for dissolving the mixture, it will require a large volume of the solvent and in that case, it will be difficult to get the mixture adsorbed on the column in a narrow band which is an essential criterion for optimum separation.

The spots of coloured components are visible on TLC plate due to their original colour. The spots of the colourless components which are invisible to the eye can be observed using the following *visualization methods*.

(i) Ultraviolet light. Organic compounds which fluoresce can be detected by placing the plate under UV lamp having light of 254 nm. Since all organic compounds do not produce fluorescence under UV light, this method is not of general applicability.

(ii) Iodine vapours. This is the most commonly used detection reagent. The developed TLC plate is placed in a covered jar containing a few crystals of iodine. Spots of compounds which adsorb iodine will show up as brown spots.

(iii) Chemical methods. Sometimes a suitable chemical reagent may be sprayed on the plate. For example, amino acids can be detected by spraying the plate with ninhydrin solution. Similarly, aldehdyes/ketones can be detected by sparying the plate with the solution of 2, 4-dinitrophehylhydrazine.

The various components on the developed TLC plate are identified through their retention factor, ***i.e.***, **R_f values (Fig. 16.14). It is defined as**

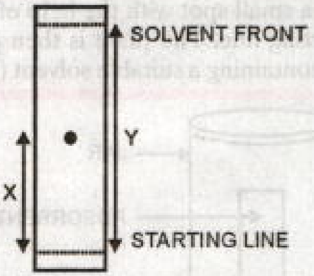


FIGURE 16.14. Developed chromatogram–Measurement of R_f value.

$$R_f = \frac{\text{Distance travelled by the compound (X)}}{\text{Distance travelled by the solvent front (Y)}}.$$

Since the solvent front always moves faster on the TLC plate than the compounds, R_f values are usually expressed as a decimal fraction.

(b) Partition chromatography. We have discussed above that column chromatography or TLC is a *liquid/solid chromatography i.e.*, the mobile phase is a liquid while the stationary phase is a solid. In contrast, partition chromatography is a liquid/liquid chromatography in which both the mobile phase and the stationary phase are liquids.

Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper called chromatographic paper is used. *Although paper consists mainly of cellulose, the* **stationary phase** *in paper chromatography is not the cellulose but the water which is adsorbed or chemically bound to it. The* **mobile phase** *is another liquid which is usually a mixture of two or three solvents with water as one of the components.*

Principle. Paper chromatography works on the principle of **partition** ***i.e.***, *it is based upon continuous differential partitioning (or distribution) of the various components of the mixture between the stationary and the mobile phases.*

Process. A suitable chromatographic paper is selected and a starting line is drawn across the width of the paper at about 1 or 2 cm from the bottom. A spot of the mixture of components to be separated is applied on the starting line with the help of a fine capillary or syringe. The chromatographic paper is then suspended in a suitable solvent mixture (Fig. 16.15*a*).

The solvent rises up the paper by capillary action and flows over the spot. The different components of the mixture travel through different distances depending upon their solubility in or partitioning between the stationary and the mobile phases. When the solvent reaches the top end of the paper, the paper is taken out and allowed to dry. *The paper strip so developed is called the* **chromatogram.** The spots of the separated coloured compounds are visible at different heights from the starting line and are identified by their R_f values as discussed under TLC. The spots of the colourless compounds may, however, be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under TLC.

The type of chromatography discussed above is called **ascending paper chromatography.** Alternatively, the paper can be folded into a cyclinder and the two ends dipped together as shown in Fig. 16.15*b*. This is also sometimes called as **circular chromatography.**

There is yet another type of paper chromatography called **descending paper chromatography.** In this type, the solvent is kept in a trough at the top of the chamber, spotted end of the paper is dipped in it, and the solvent is allowed to flow down by capillary action and gravity. In this type, solvent flow is rapid and hence the process is less time consuming than the ascending method.

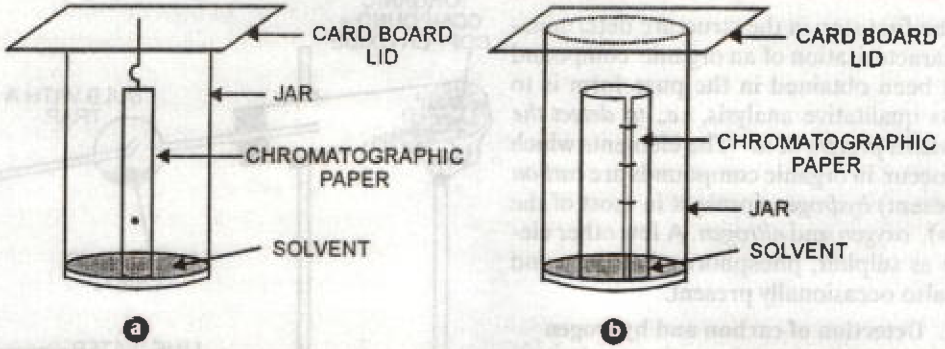


FIGURE 16.15. Apparatus for ascending chromatography.

Uses. Paper chromatography is especially used for separation of sugars and amino acids.

ADD TO YOUR KNOWLEDGE

Chemical methods of Separation

Apart from the physical methods discussed above, it is sometimes more convenient to separate the components of a mixture by chemical methods based upon their solubility in certain solvents and typical reactions of the functional groups present in them. The following solvents and reagents are commonly used :

(i) Water. If one of the components of a binary mixture is highly soluble in H_2O while the other is practically insoluble, then H_2O can be used for their separation. For example, urea and naphthene can be separated by just shaking the mixture with H_2O when urea dissolves leaving naphthalene as the residue. Filtration and evaporation of H_2O from the filtrate gives urea.

(ii) Ether. It is specifically used only for the separation of carbohydrates from other organic compounds which are soluble in ether. Carbohydrates are highly polar due to the presence of a number of OH groups and hence are practically insoluble in ether. For example, a mixture of glucose or sucrose and *m*- dinitrobenzene can be separated by just shaking with ether when *m*-dinitrobenzene dissolves leaving carbohydrate as the residue. Filtration and evaporation of ether from the filtrate gives *m*-dinitrobenzene.

(iii) Sodium bicarbonate. Water insoluble carboxylic acids can be separated from non-acidic compounds simply by shaking with a 5% aqueous solution of $NaHCO_3$ when carboxylic acids dissolve as their corresponding sodium salts while non-acidic compounds remain insoluble. Filtration followed by acidification of the filtrate with dil. HCl solution gives the desired carboxylic acid.

(iv) Hydrochloric acid. Water insoluble amines can be separated from non-basic compounds simply by shaking with dil. HCl when amines dissolve as their corresponding hydrochlorides while the non-basic compounds remain insoluble. Filtration followed by basification of the filtrate with dil. NaOH solution gives the desired amine.

(v) Sodium hydroxide. Water insoluble phenols can be separated from non-phenolic compounds simply by shaking with a 5% aqueous solution of NaOH when the phenols dissolve as their corresponding sodium salts while non-phenolic compounds remain insoluble. Filtration followed by acidification of the filtrate with dil. HCl gives the required phenol.

16.3. Qualitative Analysis

The first step in the structure determination and characterisation of an organic compound after it has been obtained in the pure form is to carry out its qualitative analysis, *i.e., to detect the various elements present in it.* The elements which commonly occur in organic compounds are *carbon* (always present) *hydrogen* (present in most of the compounds), *oxygen* and *nitrogen*. A few other elements such as sulphur, phosphorus, halogens and metals are also occasionally present.

16.3.1. Detection of carbon and hydrogen

Principle. The presence of carbon and hydrogen, in an organic compound, is detected by heating the given compound with dry cupric oxide in a hard glass test tube when *carbon present is oxidised to carbon dioxide and hydrogen is oxidised to water :*

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

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

Carbon dioxide turns lime water *milky* while water condenses on the cooler parts of the test tube and turns anhydrous copper sulphate *blue*.

$$\underset{\text{Lime water}}{Ca(OH)_2} + CO_2 \longrightarrow \underset{(Milkiness)}{CaCO_3} + H_2O$$

$$\underset{(White)}{CuSO_4} + 5H_2O \longrightarrow \underset{(Blue)}{CuSO_4.5H_2O}$$

Procedure. In actual practice, a small quantity of the pure and dry compound is mixted with nearly five to six times its weight of dry and pure cupric oxide powder. The intimate mixture is strongly heated in a hard glass test tube fitted with a delivery tube having a bulb in the centre as shown in Fig. 16.16. The other end of the delivery tube is dipped in lime water taken in a test tube.

The bulb in the delivery tube is packed with anhydrous copper sulphate supported over glass wool. On heating, the carbon is oxidised to CO_2 which turns lime water milky and hydrogen is oxidised to water which turns anhydrous copper sulphate blue.

Modifications. (*i*) If the organic substance is a *volatile liquid* or a *gas,* the vapours of the compound are passed through heated cupric oxide taken in a hard glass test tube and gases evolved are tested for CO_2 and H_2O vapours as described above.

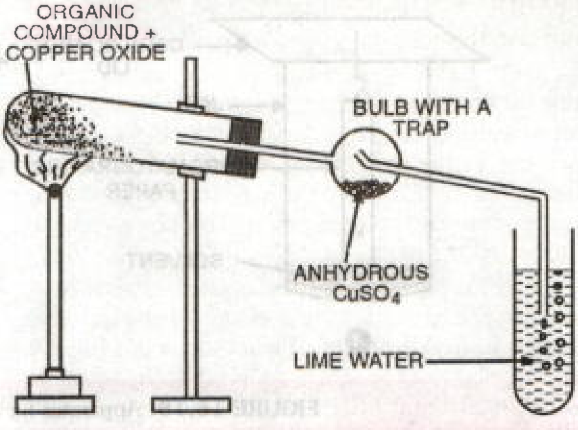


FIGURE 16.16. Detection of Carbon and Hydrogen.

(*ii*) If the organic compound also contains *sulphur* besides carbon and hydrogen, the method is slightly modified. This is due to the fact that sulphur is oxidised to sulphur dioxide which also turns lime water milky due to the formation of insoluble calcium sulphite.

$$4CuO + S \xrightarrow{\Delta} 2Cu_2O + SO_2$$

$$Ca(OH)_2 + SO_2 \longrightarrow \underset{(Milkiness)}{CaSO_3} + H_2O$$

In such a case, the outcoming gases are first passed through an acidified solution of potassium dichromate which absorbs sulphur dioxide and turns it green, and then through lime water.

16.3.2. Detection of nitrogen

The presence of nitrogen is detected by the following tests :

(1) Dry heating test. If the organic compound containing nitrogen is heated strongly, it gives a smell of burning hair or feather.

Limitation. This test is, however, not reliable since many compounds containing nitrogen do not give this test.

(2) Soda lime test. A pinch of the organic compound is heated strongly in a dry test tube with soda lime (NaOH + CaO). A smell of ammonia indicates the presence of nitrogen.

$$\underset{\text{Urea}}{NH_2CONH_2} + 2NaOH \xrightarrow[\Delta]{CaO} 2NH_3 + Na_2CO_3$$

Limitation. This test is also not reliable since many organic compounds containing nitrogen such as **nitro** ($-NO_2$), azo ($-N=N-$) groups etc. do not give this test.

(3) Lassaigne's test. This is the most reliable test for detecting nitrogen, silphur and halogens in an organic compound. In this test, the elements present in the organic compound are converted from covalent form into the ionic form by fusing the compound with sodium metal. This test is carried out as follows :

(*i*) Preparation of the Lassaigne's extract. A small piece of freshly cut sodium (of the size of a pea) is heated gently in a fusion tube till it forms a *shining globule*. The tube is removed from the flame and a small amount of the organic compound (50–60 mg) is added and the tube heated strongly till it becomes red hot (2–3 minutes). The hot tube is then plunged into a china dish containing 10–15 ml of distilled water. The contents of the china dish are boiled for a few minutes, cooled and then filtered. The filtrate is called *Lassaigne's extract* or *sodium fusion extract.*

(*ii*) Test for nitrogen. The Lassaigne's extract is usually alkaline since the excess of sodium reacts with water to produce sodium hydroxide. If not, it is made alkaline by adding a few drops of a dilute solution of sodium hydroxide. To a part of this alkaline solution is added a few drops of a freshly prepared solution of ferrous sulphate. The contents are warmed a little, cooled and then acidified with dil. H_2SO_4. *Appearance of a green or blue colouration indicates the presence of nitrogen. However, appearance of blood red colour indicates the presence of both nitrogen and sulphur.*

Chemistry of the test. During fusion, carbon and nitrogen of the organic compound combine to form sodium cyanide.

$$Na + \underset{\text{(From organic compound)}}{C + N} \xrightarrow{\Delta} NaCN$$

On heating the filtrate with ferrous sulphate solution, sodium ferrocyanide, *i.e.*, sodium hexacyanoferrate (II) is formed and at the same time some ferrous (Fe^{2+}) ions are oxidised to ferric (Fe^{3+}) ions. These Fe^{3+} ions then react with sodium hexacyanoferrate (II) to produce iron (III) hexacyanoferrate (II) or ferriferrocyanide which is prussion blue in colour.

$$2NaCN + FeSO_4 \longrightarrow Na_2SO_4 + Fe(CN)_2$$

$$Fe(CN)_2 + 4NaCN \longrightarrow \underset{\text{Sodium hexacyanoferrate (II)}}{Na_4[Fe(CN)_6]}$$

$$3Na_4[Fe(CN)_6] + 4Fe^{3+} \longrightarrow \underset{\substack{\text{Iron (III) hexacyanoferrate (II)} \\ \textit{(Prussian blue)}}}{Fe_4[Fe(CN)_6]_3} + 12Na^+$$

If nitrogen and sulphur both are present in the organic compound, they may combine during fusion to form sodium thiocyanate (sulphocyanide) due to *insufficient sodium*. This when heated with ferrous sulphate produces a blood red colouration due to ferric thiocyanate (or sulphocyanide) by reaction with ferric ions formed by oxidation of ferrous ions.

$$Na + C + S + N \xrightarrow{\Delta} \underset{\text{Sod. thiocyanate}}{NaSCN}$$

$$Fe^{3+} + 3NaSCN \longrightarrow \underset{\substack{\text{Ferric thiocyanate} \\ \textit{(Blood red colouration)}}}{Fe(SCN)_3} + 3Na^+$$

But the absence of blood red colouration does not necessarily mean that sulphur is absent. This is due to the reason that in presence of excess of sodium metal, sodium thiocyanate decomposes to form sodium cyanide and sodium sulphide.

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

16.3.3. Detection of halogens

The presence of halogens in an organic compound is detected by the following tests :

(1) Beilstein test. It is a very simple and sensitive test for the detection of halogens in an organic compound. In this test, a clean and stout copper wire is heated in the non-luminous flame of the Bunsen burner until it ceases to impart any green or bluish green colour to the flame. The heated end is then dipped in the organic compound and again introduced into the Bunsen flame. *The appearance of a green or bluish green flame due to the formation of volatile cupric halides indicates the presence of halogens in the organic compound.*

Limitations. (*i*) Organic compounds like urea, thiourea, etc. which do not contain halogens also give this test due to the formation of volatile cupric cyanide.

(*ii*) It does not tell also as to which halogen (chlorine, bromine, or iodine) is actually present in the organic compound.

(2) Lassaigne's test. It is a very reliable test for the detection of halogens in an organic compound. It involves the following steps :

(i) Preparation of the Lassaigne's extract. A pinch of the organic compound is fused with a small piece of freshly cut sodium in a fusion tube to prepare the sodium fusion extract in the manner described under detection of nitrogen. During fusion, the halogens present in the organic compound are converted into the corresponding sodium halides.

$$Na + \underset{\text{(From organic compound)}}{X} \xrightarrow{\Delta} NaX \ (X = Cl, Br \text{ or } I)$$

(ii) Test for halogens. A part of the Lassaigne's extract is boiled with dil. HNO_3 and cooled. A few drops of silver nitrate solution are then added.

(a) A white precipitate soluble in ammonia and insoluble in dil. HNO_3 indicates the presence of chlorine,

$$NaCl + AgNO_3 \longrightarrow \underset{\text{(White ppt.)}}{AgCl} + NaNO_3$$

(b) A pale yellow precipitate partially soluble in ammonia indicates the presence of bromine.

$$NaBr + AgNO_3 \longrightarrow \underset{\text{(Pale yellow ppt.)}}{AgBr} + NaNO_3$$

(c) A yellow precipitate insoluble in ammonia indicates the presence of iodine.

$$NaI + AgNO_3 \longrightarrow \underset{\text{(yellow ppt.)}}{AgI} + NaNO_3$$

Function of nitric acid. If the organic compound also contains nitrogen or sulphur, the Lassaigne's extract on boiling with dil. HNO_3 decomposes sodium cyanide or sodium sulphide formed during fusion.

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN \uparrow$$

$$Na_2S + 2HNO_3 \longrightarrow 2NaNO_3 + H_2S \uparrow$$

If cyanide and sulphide ions are not decomposed, they will react with silver nitrate and hence will interfere with the test.

$$NaCN + AgNO_3 \longrightarrow \underset{\substack{\text{Silver cyanide} \\ \text{(White ppt.)}}}{AgCN} + NaNO_3$$

$$Na_2S + 2AgNO_3 \longrightarrow \underset{\substack{\text{Silver sulphide} \\ \text{(Black ppt.)}}}{Ag_2S} + 2NaNO_3$$

(3) Carbon disulphide test for Bromine and Iodine. A small portion of the Laissaigne's extract is boiled with dil. H_2SO_4 to decompose sodium cyanide and sodium sulphide. The solution is then cooled and a few cm^3 of freshy prepared chlorine water and carbon disulphide or carbon tetrachloride are added. The solution is vigorously shaken and allowed to stand when :

(i) an orange colour in CS_2 or CCl_4 layer indicates the presence of bromine.

(ii) a violet colour in CS_2 or CCl_4 layer indicates the presence of iodine.

Theory of the test. This is due to the reason that chlorine displaces bromine and iodine from their corresponding halides. The halogen thus liberated dissolves in CS_2 or CCl_4 to produce the specific colour.

$$2NaBr + Cl_2 \longrightarrow 2NaCl + \underset{\substack{\text{(Dissolves in } CS_2 \text{ or} \\ CCl_4 \text{ to give orange colour)}}}{Br_2}$$

$$2NaI + Cl_2 \longrightarrow 2NaCl + \underset{\substack{\text{(Dissolves in } CS_2 \text{ or} \\ CCl_4 \text{ to give violet colour)}}}{I_2}$$

16.3.4. Detection of sulphur

The presence of sulphur in the organic compound is detected by the following tests :

(1) Lassaigne's test. If sulphur is present in the organic compound then on fusion with sodium metal, sodium sulphide is formed.

$$2Na + S \xrightarrow{\Delta} Na_2S$$

Then the following tests are performed with the Lassaigne's extract to detect the presence of sulphur :

(i) Sodium nitroprusside test. A small portion of the Lassaigne's filtrate is treated with a few drops of sodium nitroprusside solution when a *violet colouration* is obtained. This colour slowly fades on standing.

$$Na_2S + \underset{\text{Sodium nitroprusside}}{Na_2[Fe(CN)_5(NO)]} \longrightarrow \underset{\text{(Violet colour)}}{Na_4[Fe(CN)_5(NOS)]}$$

(ii) Lead acetate test. Another portion of Lassaigne's filtrate is acidified with dilute acetic acid and a few drops of lead acetate solution are added to it. *Formation of black precipitate of lead sulphide indicates the presence of sulphur in the given compound.*

$$Na_2S + \underset{\text{Lead acetate}}{(CH_3COO)_2Pb} \longrightarrow \underset{\text{(Black ppt.)}}{PbS} + 2CH_3COONa$$

(2) Oxidation test. The given compound is fused with a mixture of potassium nitrate and sodium carbonate. If sulphur is present, it gets oxidised to sulphate :

$$KNO_3 \xrightarrow{\Delta} KNO_2 + [O]$$

$$Na_2CO_3 + S + 3[O] \xrightarrow{\Delta} Na_2SO_4 + CO_2$$

The fused mass is then extracted with water and filtered. The filtrate is acidified with dilute hydrochloric acid and treated with barium chloride solution when a *white precipitate insoluble in acids is obtained.*

$$Na_2SO_4 + BaCl_2 \longrightarrow 2NaCl + \underset{\text{(White ppt.)}}{BaSO_4}$$

16.3.5. Detection of phosphorus

Phosphorus is detected by fusing the organic compound with an oxidising agent, *i.e.*, sodium peroxide when phosphorus is oxidised to sodium phosphate.

$$5Na_2O_2 + \underset{\substack{\text{(From organic}\\ \text{compound)}}}{2P} \xrightarrow{\Delta} 2Na_3PO_4 + 2Na_2O$$

The fused mass is extracted with water. The aqueous solution is boiled with conc. HNO_3 and then ammonium molybdate solution is added. *The appearance of a yellow precipitate or colouration due to the formation of ammonium phosphomolybdate indicates the presence of phosphorus.*

$$Na_3PO_4 + 3HNO_3 \xrightarrow{\Delta} H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + \underset{\text{Amm. molybdate.}}{12(NH_4)_2MoO_4} + 21HNO_3 \xrightarrow{\Delta}$$

$$\underset{\substack{\text{Amm. phosphomolybdate}\\ \text{(Yellow ppt.)}}}{(NH_4)_3PO_4 \cdot 12MoO_3} + 21\,NH_4NO_3 + 12H_2O$$

16.3.6. Detection of oxygen

There are no direct tests available for the detection of oxygen in an organic compound. However, its presence can be detected indirectly by any one of the following methods :

(*i*) The compound is tested for the presence of oxygen containing functional group such as $-OH$, $-CHO$, $-COOH$, $-NO_2$ etc. *The presence of any one of these groups in the compound, in turn, confirms the presence of oxygen in it.*

(*ii*) *If the sum of the percentages of various elements present in the given compound, as determined by known methods, comes out to be less than hundred, the presence of oxygen is indicated and the difference is taken to be equal to the percentage of oxygen in the given compound.*

16.4. Quantitative Analysis

After detecting various elements present in a compound, the next step is to determine the percentage of each element. This is called *quantitative analysis*. We shall now discuss the principles involved in the estimation (quantitative determination) of various elements usally present in an organic compound.

16.4.1. Estimation of carbon and hydrogen

Principle. A known mass of the organic compound is heated strongly with excess of dry copper oxide in a current of dry air or oxygen (*free from carbon dioxide*). Under these conditions, carbon present in the organic compound is oxidised to carbon dioxide and hydrogen is oxidised to water.

$$\text{C (from organic compond)} + 2CuO \xrightarrow{\Delta} CO_2 + 2Cu$$

$$\text{2H (from organic compound)} + CuO \xrightarrow{\Delta} H_2O + Cu$$

The water thus produced is absorbed in a U-tube containing anhydrous calcium chloride or anhydrous magnesium perchlorate while CO_2 produced is absorbed in another U-tube containing a strong solution of KOH or *ascarite* (NaOH + CaO). The tubes are weighed before and after the combustion. The *increase in the mass of $CaCl_2$ or $Mg(ClO_4)_2$ U-tube gives the mass of water produced while increase in the mass of KOH or ascarite U-tube gives the mass of CO_2 produced.*

The apparatus used for estimation of carbon and hydrogen is shown in Fig. 16.17.

From the masses of carbon dioxide and water formed, the percentage of carbon and hydrogen can be easily calculated.

Calculations : Let the mass of the substance taken = *w g*

Mass of CO_2 formed = *x* g

Mass of water formed = *y* g

Percentage of Carbon

One mole of CO_2 contains one gram atom of C.

i.e. $(12 + 2 \times 16) = 44\,g\ CO_2$ contain carbon $= 12\ g$

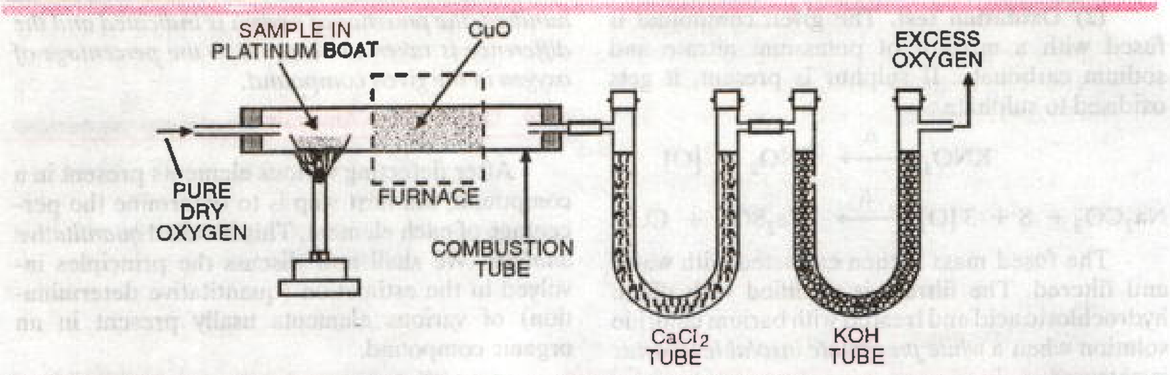


FIGURE 16.17. Apparatus for estimation of Carbon and Hydrogen.

$\therefore$ x g CO_2 will contain carbon $= \frac{12}{44} \times x$ g

This is the mass of carbon present in w g of the compound.

$\therefore$ % age of carbon in the compound

$$= \frac{12}{44} \times x \times \frac{100}{w}$$

i.e. Percentage of carbon

$$= \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

Percentage of Hydrogen

One mole of H_2O contains 2 gram atoms of hydrogen.

i.e. $(2 \times 1 + 16) = 18$ g of H_2O contain hydrogen $= 2$ g

$\therefore y$ g H_2O will contain hydrogen $= \frac{2}{18} \times y$ g

This is the mass of hydrogen present in w g of the compound.

$\therefore$ % age of hydrogen in the compound

$$= \frac{2}{18} \times y \times \frac{100}{w}$$

i.e. Percentage of hydrogen

$$= \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{\text{Mass of substance taken}} \times 100$$

Modifications under specific conditions. Liebeg's method as described above is suitable in case of organic compounds containing C, H and O only. If, however, the organic compound contains one or more of the elements like N, S and halogens also, the method is modified as under :

(*i*) **Substances containing nitrogen.** Under the conditions of combustion, nitrogen, if present, in the organic compound is oxidised to oxides of nitrogen (NO, NO_2 etc.) which are also absorbed in KOH solution. In such cases, a reduced copper gauze is placed near the exit end of the tube (as shown in Fig. 16.18) which reduces oxides of nitrogen back to N_2 gas.

$$2\,Cu + 2\,NO \xrightarrow{\text{Heat}} 2\,CuO + N_2$$
$$4\,Cu + 2\,NO_2 \longrightarrow 4\,CuO + N_2$$

(*ii*) **Substances containing halogens.** Halogens, if present, in the organic compound are converted into cupric halides which themselves decompose to form free halogens. These halogens and volatile cupric halides also get dissolved in KOH solution. In such cases, a roll of bright silver gauze is placed near the exit end of the combustion tube. Silver gauze decomposes volatile cupric halides forming non-volatile silver halides. Halogens also combine with silver giving silver halides.

$$CuX_2 + 2\,Ag \longrightarrow 2\,AgX + Cu$$
$$X_2 + 2\,Ag \longrightarrow 2\,AgX$$

(*iii*) **Substances containing sulphur or sulphur and halogens.** Under the conditions of combustion, sulphur, if present in the organic compound is oxidised to SO_2 which will also be absorbed in KOH solution. In such cases, either an additional layer of fused lead chromate is placed after the CuO layer or CuO layer is replaced by fused lead chromate layer. At high temperatures, lead chromate decomposes to give O_2 which oxidises C and H of the organic compound to CO_2 and H_2O respectively.

$$4\,PbCrO_4 \xrightarrow{\Delta} 4\,PbO + 2\,Cr_2O_3 + 3\,O_2$$

SO_2 and halogens produced during combustion react with lead chromate to form non-volatile lead sulphate and lead halides which are retained in the combustion tube.

$$4\,PbCrO_4 + 4\,SO_2 \xrightarrow{\Delta} 4\,PbSO_4 + 2\,Cr_2O_3 + O_2$$
$$4\,PbCrO_4 + 4\,X_2 \xrightarrow{\Delta} 4\,PbX_2 + 2\,Cr_2O_3 + O_2$$

Besides, S and halogens, $PbCrO_4$ is also useful for phosphorus containing compounds. This is because oxides of phosphorus produced during combustion also react with lead chromate to form non-volatile lead phosphate.

$$12\,PbCrO_4 + 4\,P_2O_5 \xrightarrow{\Delta} 4\,Pb_3(PO_4)_2 + 6\,Cr_2O_3 + 9\,O_2$$

EXAMPLE 16.1. *On complete combustion, 0·246 g of an organic compound gave 0·198 g of carbon dioxide and 0·1014 g of water. Determine the percentage composition of carbon and hydrogen in the compound.* (N.C.E.R.T.)

Solution. Here, mass of the organic substance taken = 0.246 g

Mass of CO_2 formed = 0.198 g

Mass of H_2O formed = 0.1014 g

(i) Percentage of Carbon.

One mole of CO_2 contains one gram atom of carbon.

i.e. 44 g of CO_2 contain carbon = 12 g

∴ 0·4950 g CO_2 will contain carbon

$$= \frac{12}{44} \times 0 \cdot 198 \text{ g}$$

This is the mass of carbon present in 0·246 g of the compound.

∴ % age of carbon in the compound

$$= \frac{12}{44} \times 0 \cdot 198 \times \frac{100}{0 \cdot 246} = \mathbf{21 \cdot 95}$$

***(ii)* Percentage of Hydrogen**

One mole of H_2O contains two gram atoms of hydrogen.

i.e. 18 g of H_2O contain hydrogen = 2 g

∴ 0·1014 g H_2O will contain hydrogen

$$= \frac{2}{18} \times 0 \cdot 1014$$

This is the mass of hydrogen present in 0·2475 g of the compound.

∴ %age of hydrogen in the compound

$$= \frac{2}{18} \times 0 \cdot 1014 \times \frac{100}{0 \cdot 246} = \mathbf{4 \cdot 58}$$

EXAMPLE 16.2. *An organic compound contains 69% carbon and 4·8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0·20 g of this substance is subjected to complete combustion.* **(N.C.E.R.T.)**

Solution. We know that,

$$\%C = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

Substituting the values of %C and mass of the substance taken, we have,

$$69 = \frac{12}{44} \times \frac{\text{mass of } CO_2 \text{ formed}}{0 \cdot 2 \text{ g}} \times 100$$

$$\text{or Mass of } CO_2 \text{ formed} = \frac{69 \times 44 \times 0 \cdot 2}{12 \times 100}$$

$$= 0 \cdot 506 \text{ g}$$

Similarly,

$$\% H = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{\text{Mass of substance taken}} \times 100$$

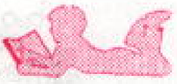
Substituting the values of % of H and mass of the substaken taken, we have,

$$4 \cdot 8 = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{0 \cdot 2} \times 100$$

$$\text{or Mass of } H_2O \text{ formed} = \frac{4 \cdot 8 \times 18 \times 0 \cdot 2}{2 \times 100}$$

$$= \mathbf{0 \cdot 0864 \text{ g.}}$$

PROBLEMS FOR PRACTICE



1. 0.6723 g of an organic compound gave on combustion 1.530 g of carbon dioxide and 0.625 g of water. Find the percentage of carbon and hydrogen in the compound. [Ans. **C = 62.07%, H = 10.33%]**
2. 0.465 g of an organic substance gave on combustion 1.32 g of CO_2 and 0.315g of H_2O. Calculate the percentage of carbon and hydrogen in the compound. [Ans. **C = 77.42%, H = 7.53%]**
3. 0.2475 g of an organic substance gave on combustion 0.495 g of CO_2 and 0.2025 g of H_2O. Calculate the percentage of carbon and hydrogen in it. [Ans. **C = 54·54%, H = 9·09%]**

16.4.2. Estimation of nitrogen

The two most commonly used methods for the estimation of nitrogen in an organic compound are :

(1) Duma's method (2) Kjeldahl's method.

(1) Duma's method. This method is applicable to all organic compounds containing nitrogen and is briefly discussed below :

Principle. A known mass of the organic substance is heated with excess of copper oxide in an atmosphere of CO_2. Carbon, hydrogen and sulphur (if present) are oxidised to CO_2, H_2O and SO_2 while nitrogen gas is set free. Any oxide of nitrogen that may be formed is reduced back to free nitrogen by passing over a hot reduced copper gauze.

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

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

$$\text{Nitrogen} + CuO \xrightarrow{\Delta} N_2$$

$$+ \text{ a small amount of oxides of nitrogen}$$

$$\text{Oxides of nitrogen} + Cu \xrightarrow{\Delta} CuO + N_2$$

If the organic compound having nitrogen is assumed to have $C_xH_yN_z$ as the molecular formula then the combined combustion equation may be written as

$$C_xH_yN_z + (2x + y/2)\,CuO \xrightarrow{\Delta}$$

$$xCO_2 + y/2\,H_2O + z/2\,N_2 + (2x + y/2)\,Cu$$

The nitrogen thus formed is *collected over conc. KOH solution* which absorbs all other gases *i.e.* CO_2, H_2O vapours, SO_2 etc. The volume of nitrogen collected is thus noted and from this the percentage of nitrogen can be calculated.

Apparatus. The apparatus used for estimation of nitrogen by Duma's method is shown in Fig. 16.18.

It consists of three parts : (*a*) *carbon dioxide generator* (*b*) *combustion tube and* (*c*) *Schiff's nitrometer.*

(*a*) **Carbon dioxide generator** (not shown in the Fig. 16.18). CO_2 needed for the purpose is produced by heating either sodium bicarbonate or magnesium carbonate. The gas is perfectly dried by bubbling through conc. H_2SO_4 before passing it through the combustion tube.

(*b*) **Combustion tube.** It is a hard glass test tube about 90 cm long and about 2 cm in diameter. It is packed with (*i*) a roll of oxidised copper gauze which prevents *backward diffusion of gases produced during combustion*, (*ii*) an accurately weighed quantity of the substance mixed with excess of cupric oxide, (*iii*) coarse CuO that fills nearly half of the combustion tube and (*iv*) a reduced copper gauze which helps to reduce any oxides of nitrogen formed during combustion back to nitrogen gas.

(*c*) **Schiff's nitrometer.** It consists of a long graduated tube having a resevoir and a tap at the upper end. It contains about 40% KOH solution. It also has a mercury seal at the bottom which *prevents KOH solution from being sucked back into the combustion tube.*

Both CO_2 and H_2O produced during combustion are absorbed by KOH solution white N_2 is collected over it. The volume of N_2 is measured after careful levelling (by making the level of KOH in the nitrometer tube and reservoir the same).

Modifications under specific conditions. If the organic compound, in addition to C, H, O and N also contains S or halogens, the layer of coarse. CuO in the combustion tube is replaced by fused $PbCrO_4$ as discussed under Liebig's method.

Calculations :

Suppose the mass of the substance taken $= w$ g

Volume of N_2 collected $= V\ cm^3$

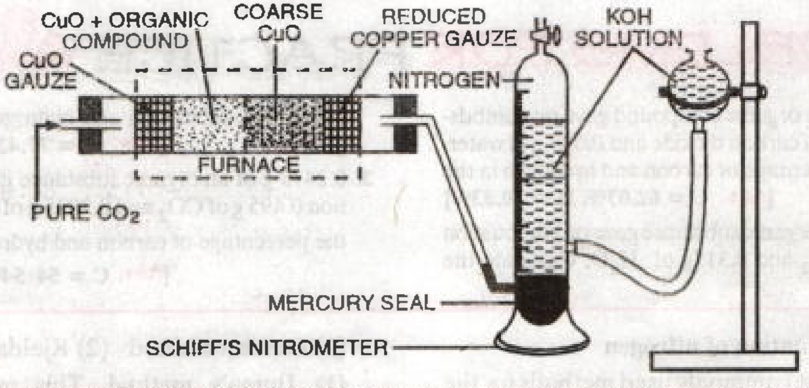


FIGURE 16.18. Apparatus for the estimation of Nitrogen by Duma's Method.

Atmospheric pressure (read from barometer) = P mm

Room temperature = t°C

Aqueous tension at t°C (from tables) = p mm

∴ Pressure of the dry N_2 gas = $(P - p)$ mm

Step 1. ***Conversion of the volume at experimental conditions to the volume at STP.***

Experimental values	*At STP*
$P_1 = (P - p)$ mm	$P_2 = 760$ mm
$V_1 = V$ cm^3	$V_2 = ?$
$T_1 = (273 + t)$ K	$T_2 = 273$ K

Applying the relation :

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

The value of V_2 can be calculated.

Step 2. *Conversion of volume at STP or NTP into mass.* According to the definition of Gram Molecular Volume (GMV),

22400 cm^3 of N_2 gas at STP weigh equal to its molecular weight expressed in grams, *i.e.*, = 28g

∴ V_2 cm^3 of N_2 gas at STP will weigh

$$= \frac{28}{22400} V_2 \text{ g}$$

Step 3. *Calculation of % age of N.*

This is the mass of nitrogen present in w g of the substance.

∴ % age of Nitrogen in the compound

$$= \frac{28}{22400} \times V_2 \times \frac{100}{w}$$

Percentage of Nitrogen

$$= \frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at STP}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{\text{Mass of } N_2 \text{ at STP}}{\text{Mass of the substance taken}} \times 100$$

EXAMPLE 16.3. *0.30 g of an organic compound gave 50 cm^3 of nitrogen collected at 300 K and 715 mm pressure in Duma's method. Calculate the percentage of nitrogen in the compound (vapour pressure of water or aqueous tension of water at 300 K is 15 mm).* **(N.C.E.R.T.)**

Solution. Here, mass of the substance taken = 0.30 g

Volume of nitrogen collected = 50 cm^3

Atmospheric pressure = 715 mm Hg

Room temperature = 300 K

Vapour pressure of water at 300 K = 15 mm

∴ Actual pressure of the gas (dry gas)

= 715 – 15

= 700 mm Hg

Step 1. ***To convert the volume at experimental conditions to volume at STP.***

Exptl. conditions	*At STP*
$P_1 = 700$ mm	$P_2 = 760$ mm
$V_1 = 50$ cm^3	$V_2 = ?$
$T_1 = 300$ K	$T_2 = 273$ K

Substituting these values in the gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}, \text{ we get}$$

$$\frac{700 \text{ mm} \times 50 \text{ cm}^3}{300 \text{ K}} = \frac{760 \text{ mm} \times V_2 \text{ cm}^3}{273 \text{ K}}$$

$$\text{or} \quad V_2 = \frac{273 \times 700 \times 50}{300 \times 760}$$

$$= 41 \cdot 9 \text{ cm}^3$$

Step 2. ***To convert the volume at STP into mass.***

According to the definition of GMV,

22400 cm^3 of nitrogen at STP weigh = 28 g

∴ 41·9 cm^3 of nitrogen at STP will weigh

$$= \frac{28 \times 41 \cdot 9}{22400} \text{ g}$$

Step 3. ***To calculate the percentage of nitrogen.***

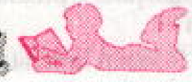
Percentage of nitrogen

$$= \frac{\text{Mass of } N_2 \text{ at STP}}{\text{Mass of the substance taken}} \times 100$$

$$= \frac{28 \times 41 \cdot 9 \times 100}{22400 \times 0 \cdot 3}$$

$$= 17 \cdot 46$$

PROBLEMS FOR PRACTICE



1. 0.2046 g of an organic compound gave 30.4 cm^3 of moist nitrogen measured at 288 K and 732.7 mm pressure. Calculate the percentage of nitrogen in the substance (Aqueous tension at 288 K is 12.7 mm). [Ans. 16.68%]
2. 0.27 g of an organic compound gave on combustion 0.396 g of CO_2 and 0.216 g of H_2O. 0.36 g of the same substance gave 48.88 cm^3 of N_2 at 290 K and 740 mm pressure. Calculate the percentage composition of the compound. [Ans. C = 40%, H = 8.89%, N = 15.56% and O = 35.55%]

(2) Kjeldahl's method. This is a more convenient and simpler method for the estimation of nitrogen and is largely used for the estimation of nitrogen in fertilizers, food stuffs, drugs etc. The method is, however, not applicable to compounds containing nitrogen in the ring (*e.g.*, pyridine, quinoline etc.) and compounds containing nitrogen directly linked to oxygen atom (*e.g.* NO_2) or another nitrogen atom *i.e.* azo ($-N=N-$) compounds.

The apparatus used for the estimation of nitrogen by Kjeldahl's method is shown in Fig. 16.19.

Principle. A known mass of the organic compound is digested (heated) with conc. H_2SO_4 in presence of potassium sulphate and a little copper sulphate or mercury in a long-necked flask called *Kjeldahl's flask* (Fig. 16.19a). Potassium sulphate raises the boiling point of H_2SO_4 and thus ensures complete reaction while copper sulphate or mercury catalyses the reaction.

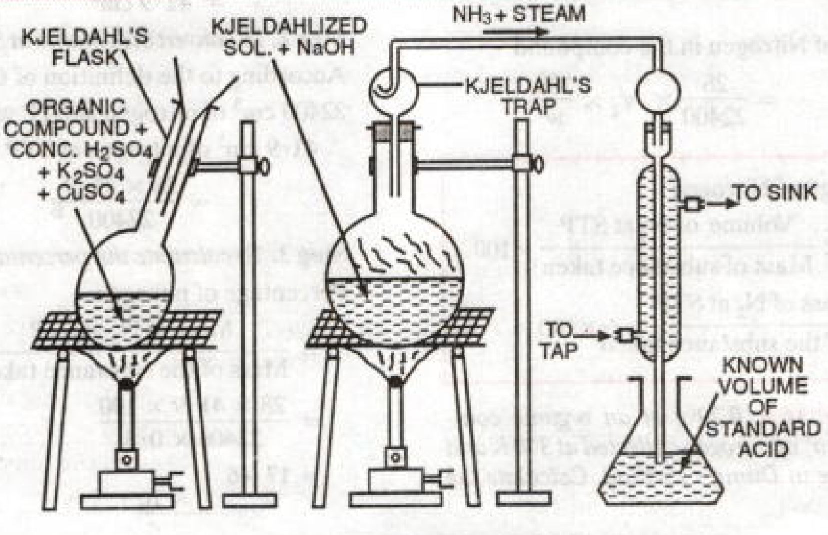
As a result of digestion, the nitrogen present in the organic compound is quantitatively converted into ammonium sulphate. Ammonium sulphate thus obtained is boiled with excess of NaOH solution (Fig. 16.19b) to liberate ammonia gas which is then absorbed in a known excess of a standard acid such as H_2SO_4 or HCl.

$$\text{N(from compound)} + \text{Conc. } H_2SO_4 \xrightarrow{\Delta} (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + 2NaOH \xrightarrow{\Delta} Na_2SO_4 + 2H_2O + 2NH_3$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

The volume of the acid left unused is found by titration against a standard alkali solution.



ⓐ Digestion (heating in Kjeldahl's flask) ⓑ Kjeldahl's distillation

FIGURE 16.19. Apparatus for estimation of nitrogen by Kjeldahl's method.

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

From this, the volume of the acid used up (or the volume of the ammonia evolved) and hence the percentage of nitrogen in the organic compound can be calculated.

Calculations :

Let the mass of organic substance taken = w g

Volume of H_2SO_4 taken = V cm^3 of M_1 molarity

Volume of NaOH used for titration of excess of H_2SO_4 = v cm^3 of M_1 molarity

Applying molarity equation,

$$n_b M_b V_b = n_a M_a V_a$$

where n_b, M_b and V_b are the acidity, molarity and volume of NaOH used while n_a, M_a and V_a are the basicity, molarity and volume of acid used.

$$\therefore 1 \times v \times M_1 \text{ (NaOH)} = 2 \times M_1 \times V_a \text{ } (H_2SO_4)$$

or $V_a = v/2$ ($\because$ basicity of $H_2SO_4 = 2$)

i.e., Volume of H_2SO_4 left unused $= v/2$ cm^3 of M_1 molarity.

$\therefore$ Volume of H_2SO_4 used up by NH_3 $= (V - v/2)$ cm^3 of M_1 H_2SO_4

But $(V - v/2)$ cm^3 of M_1 H_2SO_4 $\equiv 2(V - v/2)$ cm^3 of M_1 NH_3

($\because$ 1 mole of H_2SO_4 neutralises two moles of NH_3)

Now 1000 cm^3 of 1 M NH_3 solution contain NH_3 = 17 g or N = 14 g

$\therefore$ $2(V - v/2)$ cm^3 of M_1 NH_3 will contain

$$N = \frac{14}{1000} \times 2(V - v/2) \times M_1 \text{ g}$$

This is the mass of nitrogen present in w g of the substance

$$\therefore \%\text{age N} = \frac{14 \times M_1 \times 2(V - v/2)}{1000} \times \frac{100}{w}$$

$$= \frac{1.4 \times M_1 \times 2(V - v/2)}{w}$$

$$\boxed{\text{or } \%\text{age N} = \frac{1.4 \times \text{Molarity of } H_2SO_4 \times \text{twice the vol of } H_2SO_4 \text{ used}}{\text{Mass of the substance taken}}}$$

In general,

$$\boxed{\%\text{age of Nitrogen} = \frac{1.4 \times \text{Molarity of acid} \times \text{Basicity of acid} \times \text{Vol. of the acid used}}{\text{Mass of the substance taken}}}$$

If however, the acid used is monobasic (*i.e.* basicity = 1), the above equation reduces to

$$\boxed{\begin{aligned}\%\text{ age of Nitrogen} &= \frac{1.4 \times \text{Molarity of acid} \times \text{Vol. of acid used}}{\text{Mass of the substance taken}}\\ &= \frac{1.4 \times \text{Normality of acid} \times \text{Vol. of acid used}}{\text{Mass of the substance taken}}\\ &(\because \text{for monobasic acids, molarity = normality})\end{aligned}}$$

EXAMPLE 16.4. *During nitrogen estimation present in an organic compound by Kjeldhal's method, the ammonia evolved from 0·5 g of the compound in Kjeldahl's estimation of nitrogen neutralized 10 ml of 1 M H_2SO_4. Find the percentage of nitrogen in the compound.* (N.C.E.R.T.)

Solution. Volume of H_2SO_4 used = 10 ml of 1 M H_2SO_4

Now $H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$

Now 1 mole of H_2SO_4 reacts with 2 moles of NH_3.

$\therefore$ 10 ml of 1 M H_2SO_4 $\equiv$ 20 ml of 1 M NH_3

Now 1000 ml of 1 M NH_3 contains N = 14 g

$\therefore$ 20 ml of 1 M NH_3 will contain N

$$= \frac{14}{1000} \times 20$$

But this amount of nitrogen is present in 0·5 g of the organic compound.

$\therefore$ Percentage of nitrogen

$$= \frac{14 \times 20}{1000} \times \frac{100}{0.5} = 56.0.$$

Alternatively, %age of M

$$= \frac{1.4 \times \text{Vol. of acid used} \times \text{Basicity of acid} \times \text{Molarity of acid}}{\text{Mass of the substance taken}}$$

$$= \frac{1.4 \times 10 \times 2 \times 1}{0.5} = 56.0$$

EXAMPLE 16.5. *0.50 g 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 required 60 ml of 0·5 M NaOH solution. Find the percentage of nitrogen in the compound. (N.C.E.R.T.)

Solution. Step 1. *To determine the volume of H_2SO_4 used.*

Volume of acid taken = 50 ml of 0·5 M H_2SO_4 = 25 ml of 1 M H_2SO_4

Volume of alkali used for neutralization of excess acid = 60 ml of 0·5 M NaOH

= 30 ml of 1 M NaOH.

Now 1 mole of H_2SO_4 neutralizes 2 moles of NaOH (*i.e.* $H_2SO_4 + 2\,NaOH \longrightarrow Na_2SO_4 + 2\,H_2O$)

∴ 30 ml of 1 M NaOH = 15 ml of 1 M H_2SO_4

∴ Volume of acid used by ammonia

= 25 − 15 = 10 ml

Step 2. *To determine percentage of nitrogen.*

Again 1 mole of H_2SO_4 neutralizes 2 moles of NH_3

∴ 10 ml of 1 M H_2SO_4 ≡ 20 ml of 1 M NH_3

But 1000 ml of 1 M NH_3 contain nitrogen = 14 g

∴ 20 ml of 1 M NH_3 will contain nitrogen

$$= \frac{14}{1000} \times 20 \text{ g}$$

But this much amount of nitrogen is present in 0·5 g of the organic compound.

∴ Percentage of nitrogen

$$= \frac{14}{1000} \times \frac{20}{0\cdot 5} \times 100 = 56\cdot 0.$$

PROBLEMS FOR PRACTICE

1. 0.2 g of an organic compound on Kjeldahl's analysis gave enough ammonia to just neutralize 20 cm^3 of 0.1 N H_2SO_4. Calculate the percentage of nitrogen in the compound. **[Ans. 14%]**
2. 0.4422 g of an organic compound was Kjeldahlised and ammonia evolved was absorbed in 50 ml cm^3 of semi-molar (0·5 M) H_2SO_4. The residual acid required 131 ml of 0.25 M NaOH. Determine the percentage of nitrogen in the compound. **[Ans. 54.61%]**
3. Ammonia obtained from 0.4 g of an organic substance by Kjeldahl's method was absorbed in 30 cm^3 of 0·25 M H_2SO_4. The excess of the acid was neutralized by the addition of 30 cm^3 of 0·2 M NaOH. Calculate the percentage of nitrogen in the substance. **[Ans. 31.5%]**

16.4.3. Estimation of halogens (Carius method)

Principle. A known mass of the organic substance is heated with fuming nitric acid and a few crystals of silver nitrate in a sealed hard glass tube (about 2 cm wide 50 cm long) called *Carius tube* in a furnace, (Fig. 16.20).

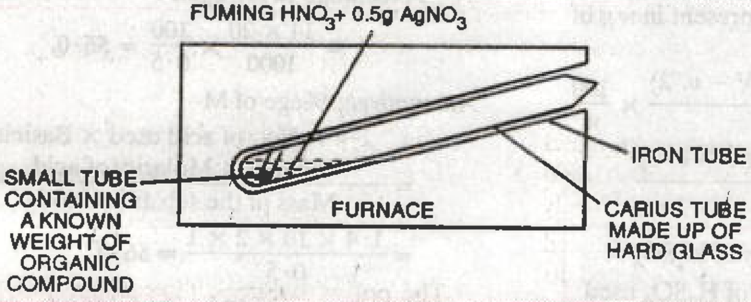


FIGURE 16.20. A Carius tube for estimation of Halogens.

Under the conditions, carbon and hydrogen are oxidised to carbon dioxide and water respectively while halogen is converted into silver halide. The precipitates of silver halide are filtered, washed, dried and weighed. Knowing the mass of the substance taken and the mass of the precipitate formed, the percentage of halogen is calculated as follows :

Calculations :

Let the mass of the substance taken = *w* g

and the mass of the silver halide (AgX) formed = *x* g

Now, 1 mole of AgX contains 1 gram atom of X(X = Cl, Br or I)

i.e. (108 + At. mass of X) g of AgX contain X

= (At. mass of X) g

∴ x g of AgX contain X

$$= \frac{\text{At. mass of X}}{108 + \text{At. mass of X}} \times x\,g$$

This is the mass of the halogen (X) present in w g of the substance.

∴ % age of halogen in the compound

$$= \frac{\text{At. mass of X}}{108 + \text{At. mass of X}} \times x \times \frac{100}{w}$$

Thus,

(*a*) *For chlorine*, as the atomic mass of chlorine = 35·5 amu

∴ % age of chlorine in the compound

$$= \frac{35\cdot5\,x}{108 + 35\cdot5} \times \frac{100}{w} = \frac{35\cdot5\,x}{143\cdot5} \times \frac{100}{w}$$

or %age of chlorine

$$= \frac{35\cdot5}{143\cdot5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of substance taken}} \times 100$$

(*b*) *For bromine,* as atomic mass of bromine = 80 amu

∴ % age of bromine in the compound

$$= \frac{80\,x}{108 + 80} \times \frac{100}{w} = \frac{80\,x}{188} \times \frac{100}{w}$$

or %age of bromine

$$= \frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of substance taken}} \times 100$$

(*c*) *For iodine*, as atomic mass of iodine = 127 amu

∴ %age of iodine in the compound

$$= \frac{127\,x}{108 + 127} \times \frac{100}{w} = \frac{127\,x}{235} \times \frac{100}{w}$$

or %age of iodine

$$= \frac{127}{235} \times \frac{\text{Mass of AgI formed}}{\text{Mass of substance taken}} \times 100$$

EXAMPLE 16.6. *0·15 g of an organic compound gave 0·12 g of silver bromide by the Carius method. Find out the percentage of bromine in the compound.* **(N.C.E.R.T.)**

Solution. Here, the mass of the substance taken = 0·15 g

Mass of AgBr formed = 0·12 g

Now 1 mole of AgBr ≡ 1 g atom of Br

or (108 + 88) = 188 g of AgBr ≡ 80 g of Br

∴ 188 of AgBr contain bromine = 80 g

∴ 0·12 g of AgBr will contain bromine

$$= \frac{80}{188} \times 0\cdot12$$

But this much amount of bromine is present in 0·15 g of the organic compound.

$$\therefore \text{ Percentage of bromine} = \frac{80 \times 0\cdot12 \times 100}{188 \times 0\cdot15} = 34\cdot04.$$

PROBLEMS FOR PRACTICE

1. 0.189 g of an organic substance gave in a Carius determination 0.287 g of silver chloride. What is the percentage of chlorine in the given compound ? **[Ans. 37.57%]**

2. 0.301 g of an organic compound gave 0.282 g of silver bromide by a halogen estimation method. Find the percentage of bromine in the compound. **[Ans. 39.87%]**

16.4.4. Estimation of sulphur (Carius method)

Principle. A known mass of the substance is heated with sodium peroxide or fuming nitric acid in a sealed tube (*Carius tube*). Carbon and hydrogen are oxidised to CO_2 and H_2O respectively while sulphur present in the compound is oxidised to sulphuric acid which is then precipitated as barium sulphate by adding excess of barium chloride solution.

$$C + 2O \text{ (from } HNO_3) \xrightarrow{\Delta} CO_2$$

$$2H + O \text{ (from } HNO_3) \xrightarrow{\Delta} H_2O$$

$$S + H_2O + 3O \text{ (from } HNO_3) \xrightarrow{\Delta} H_2SO_4$$

$$H_2SO_4 + BaCl_2 \longrightarrow \underset{\textit{(White ppt.)}}{BaSO_4} + 2HCl$$

The ppt. of $BaSO_4$ is filtered, washed, dried and weighed. Knowing the mass of the substance taken and the mass of $BaSO_4$ ppt. formed, the percentage of sulphur can be calculated.

Calculations :

Let the mass of the substance taken $= w$ g

Mass of $BaSO_4$ ppt. formed $= x$ g

Now, 1 mole of $BaSO_4$ contains 1 gram atom of S

i.e., $(137 + 32 + 64) = 233$ g of $BaSO_4$ contain sulphur = 32 g

$\therefore$ x g of $BaSO_4$ will contain sulphur $= \dfrac{32}{233} \times x$ g

This is the mass of sulphur present in w g of the substance.

$\therefore$ % age of sulphur present in the compound

$$= \frac{32\,x}{233} \times \frac{100}{w}$$

$$\boxed{\therefore \text{ \% age of sulphur} = \frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \text{ formed}}{\text{Mass of substance taken}} \times 100}$$

ADD TO YOUR KNOWLEDGE

Messenger's method is used for estimation of sulphur. In this method, the organic compound is heated with alkaline $KMnO_4$ solution when sulphur present in the organic compound is oxidised to K_2SO_4 which is then estimated as $BaSO_4$.

EXAMPLE 16.7. *In sulphur estimation, 0·157 g of an organic compound gave 0·4813 g of barium sulphate. What is the percentage of sulphur in the compound ?* **(N.C.E.R.T.)**

Solution. Here, mass of the substance taken = 0·157 g

Mass of $BaSO_4$ ppt. formed = 0·4813 g

Now, 1 mole of $BaSO_4$ $\equiv$ 1 g atom of S

or $(137+32+64) = 233$ g of $BaSO_4 \equiv 32$ g of S

i.e. 233 g of $BaSO_4$ contain sulphur = 32 g

$\therefore$ 0·4813 g of $BaSO_4$ will contain sulphur

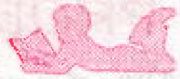
$$= \frac{32}{233} \times 0{\cdot}4813 \text{ g}$$

$\therefore$ % age of sulphur in the compound

$$= \frac{32}{233} \times 0{\cdot}4813 \times \frac{100}{0{\cdot}157}$$

$$= \mathbf{42{\cdot}10}$$

PROBLEMS FOR PRACTICE



1. 0.2175 g of the substance gave 0.5825 g of $BaSO_4$ by Carius method. Calculate the percentage of sulphur. **[Ans. 36.78%]**

2. 0.16 g of an organic substance was heated in Carius tube and the sulphuric acid formed was precipitated as $BaSO_4$ with $BaCl_2$. The weight of the dry $BaSO_4$ was 0.35 g. Find the percentage of sulphur. **[Ans. 30.04%]**

3. 0·2595 g of an organic substance, when treated by Carius method, gave 0·25 g of $BaSO_4$. Calculate the percentage of sulphur in the compound. **[Ans. 13·23%]**

16.4.5. Estimation of phosphorus

Principle. A known mass of the organic compound is heated with fuming nitric acid in a sealed tube (*Carius tube*). Under these conditions, carbon and hydrogen are oxidised to CO_2 and H_2O respectively while phosphorus present in the organic compound is oxidised to phosphoric acid which is precipitated as as ammonium phosphomolybdate by heating it with conc. HNO_3 and then adding ammonium molybdate

$$C + 2O\ (\text{from } HNO_3) \xrightarrow{\Delta} CO_2$$

$$2H + O\ (\text{from } HNO_3) \xrightarrow{\Delta} H_2O$$

$$2P + 5O \text{ (from } HNO_3) \xrightarrow{\Delta} P_2O_5$$

$$P_2O_5 + 3H_2O \xrightarrow{\Delta} \underset{\text{Phosphoric acid}}{2H_3PO_4}$$

$$H_3PO_4 + 12\underset{\text{Amm. molybdate}}{(NH_4)_2MoO_4} + 21\,HNO_3 \xrightarrow{\Delta}$$

$$\underset{\substack{\text{Amm. phosphomolybdate}\\(\textit{Yellow ppt.})}}{(NH_4)_3PO_4 \,.\, 12\,MoO_3} + 21\,NH_4NO_3 + 12\,H_2O$$

The precipitates of amm. phosphomolybdate thus formed are filtered, washed, dried and weighed.

Alternatively phosphoric acid is precipitated as magnesium ammonium phosphate by adding magnesia mixture (a solution containing magnesium chloride, ammonium chloride and ammonia).

$$MgCl_2 + NH_4Cl + H_3PO_4 \xrightarrow{\Delta}$$

$$\underset{\substack{\text{Mag. amm. phosphate}\\(\textit{White ppt.})}}{MgNH_4PO_4} + 3HCl$$

The precipitates of magnesium ammonium phosphate are filtered, washed, dried and then ignited.

$$2MgNH_4PO_4 \xrightarrow{\Delta} \underset{\text{Mag. pyrophosphate}}{Mg_2P_2O_7} + 2NH_3 + H_2O$$

The magnesium pyrophosphate thus formed is weighed. Knowing the mass of the organic compound taken and the mass of ammonium phosphomolybdate or magnesium pyrophosphate formed, the percentage of phosphorus can be easily calculated.

Calculations. If phosphorus is estimated as $(NH_4)_3PO_4 \,.\, 12\,MoO_3$. Let the mass of the organic compound taken = w g

Mass of amm. phosphomolybdate formed = x g

Now 1 mole of $(NH_4)_3PO_4 \,.\, 12\,MoO_3$ contains one gram atom of P *i.e.*

$$3 \times (14 + 4) + 31 + 4 \times 16 + 12\,(96 + 3 \times 16)$$

$= 1877$ g of $(NH_4)_3PO_4 \,.\, 12\,MoO_3$ contain P $= 31$ g

$\therefore$ x g of $(NH_4)_3PO_4 \,.\, 12\,MoO_3$ will contain P

$$= \frac{31 \times x}{1877}\,g$$

This is the mass of P present in w g of the compound

$$\therefore \quad \%\text{age of P} = \frac{31 \times x}{1877} \times \frac{100}{w}$$

$$\boxed{\text{or \%age of P} = \frac{31}{1877} \times \frac{\text{Mass of amm. phosphomolybdate}}{\text{Mass of substance taken}} \times 100}$$

Alternatively if phosphorus is estimated as $Mg_2P_2O_7$.

Mass of $Mg_2P_2O_7$ formed $= x$ g

Now, 1 mole of $Mg_2P_2O_7$ contains two gram atoms of P

i.e. $(24 \times 2 + 31 \times 2 + 16 \times 7) = 222$ g of $Mg_2P_2O_7$ contain phosphorus $= 62$ g

$\therefore$ x g of $Mg_2P_2O_7$ will contain phosphorus

$$= \frac{62\,x}{222}\,g$$

This is the mass of phosphorus present in w g of the compound.

i.e., %age of phosphorus present in the compound $= \dfrac{62\,x}{222} \times \dfrac{100}{w}$

$$\boxed{\therefore\ \%\,\text{age of phosphorus} = \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7 \text{ formed}}{\text{Mass of substance taken}} \times 100}$$

EXAMPLE 16.8. *0·12 g of an organic compound containing phosphorus gave 0·22 g of $Mg_2P_2O_7$ by the usual analysis. Calculate the percentage of phosphorus in the compound.*

Solution. Here, the mass of the compound taken = 0·12 g

Mass of $Mg_2P_2O_7$ formed = 0·22 g

Now 1 mole of $Mg_2P_2O_7 \equiv 2$ g atoms of P

or $(2 \times 24 + 2 \times 31 + 16 \times 7)$

$= 222$ g of $Mg_2P_2O_7 \equiv 62$ g of P

i.e., 222 g of $Mg_2P_2O_7$ contain phosphorus $= 62$ g

$\therefore$ 0·22 g of $Mg_2P_2O_7$ will contain phosphorus

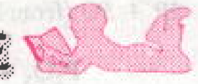
$$= \frac{62}{222} \times 0{\cdot}22\,g$$

But this is the amount of phosphorus present in 0·12 g of the organic compound.

$\therefore$ Percentage of phosphorus

$$= \frac{62}{222} \times \frac{0{\cdot}22}{0{\cdot}12} \times 100 = 51{\cdot}20$$

PROBLEMS FOR PRACTICE



1. 0.092 g of an organic compound containing phosphorus gave 0·111 g of $Mg_2P_2O_7$ by usual analysis. Calculate the percentage of phosphorus in the organic compound. [Ans. 33.7%]

2. 0.40 g of an organic compound containing phosphorus gave 0.555 g of $Mg_2P_2O_7$ by usual analysis. Calculate the percentage of phosphorus in the organic compound. [Ans. 38.75%]

16.4.6. Estimation of oxygen

The percentage of oxygen in an organic compound is usually calculated by the *difference method*. For this, the percentages of all other elements present in the organic compound are added and the sum is subtracted from 100.

Percentage of Oxygen = 100 – (Sum of the percentages of all other elements)

However oxygen can be directly estimated 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 thus formed is passed over red hot coke at 1373 K. When all the oxygen is converted into carbon monoxide. This mixture is then passed through warm iodine pentoxide (I_2O_5) when carbon monoxide is oxidised to carbon dioxide liberating iodine. The various reactions involved are :

$$\text{Compound} \xrightarrow{\text{heat}} O_2 + \text{other gaseous products}$$

$$2\,C + O_2 \xrightarrow{1373\text{ K}} 2\,CO] \times 5$$

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

$$5\,O_2 + 10\,C + 2\,I_2O_5 \longrightarrow 10\,CO_2 + 2\,I_2$$

$$\text{or} \quad 5\,O_2 \equiv 10\,CO_2 \equiv 2\,I_2$$

$$\text{or} \quad O \equiv CO_2 \equiv 1/5\,I_2 \qquad ...(i)$$

By knowing the mass of iodine liberated or CO_2 formed, the percentage of oxygen in the organic compound can be calculated easily.

Calculations. Let the mass of the organic compound taken = w g.

and mass of CO_2 formed = x g

From Eq. (*i*), it is evident that 1 *g* atom of O present in the organic compound produces one mole of CO_2

i.e., 44 *g* of CO_2 contain O = 16 g

$$\therefore\ x \text{ g of } CO_2 \text{ will contain } O = \frac{16}{44} \times x\,g$$

$$= \frac{16}{44} \times x\,g$$

This is the mass of oxygen present in *w* g of the organic compound.

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

or Percentage of oxygen

$$= \frac{16}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of substance taken}} \times 100$$

These days, the elements carbon, hydrogen and nitrogen present in an organic compound are determined by an automatic analyser called **CHN elemental analyzer.** This analyzer requires 1 – 3 mg of the compound and displays the values on a screen within a few minutes. These results are generally accurate within ±0·03% error. A detailed discussion of such methods is beyond the scope of this book.

16.5. Determination of Molecular Mass

After the percentages of the various elements present in an organic compound have been determined, the next step in finding out the molecular formula of the compound, is to determine its molecular mass of the compound depending upon its nature. The methods commonly empoyed for determining the molecular mass are as follows :

1. **Silver salt method for organic acids.**
2. **Chloroplatinate salt method for organic bases (amines).**
3. **Volumetric method.**
4. **Victor-Meyer's method for volatile liquids.**
5. **Freezing point depression or boiling point elevation method.**
6. **Mass spectrometry.**

We shall briefly discuss here the principles of silver salt method, chloroplatinate salt method, volumetric method Victor-Meyer's method and mass spectrometry.

16.5.1. Gravimetric or Silver salt method for the determination of Molecular Mass of Organic Acids.

Principle. This method is based upon the fact that most of the organic acids form insoluble silver salts which upon ignition give metallic silver as residue. Knowing the mass of the silver salt taken and the mass of silver left as residue, the molecular mass of the acid can be determined as discussed below :

Procedure. The acid is neutralized by adding NH_4OH solution. The excess of NH_3 is then boiled off. The solution of the ammonium salt of the acid thus obtained is treated with excess of silver nitrate solution when silver salt of the acid gets precipitated. This is filtred, washed and dried.

A known mass of the dried silver salt is then carefully ignited in a porcelain or platinum crucible when metallic silver is obtained.

If RCOOH represents the organic acid, the various reactions involved are :

$$RCOOH + NH_4OH \longrightarrow \underset{\text{Ammonium salt}}{RCOONH_4} + H_2O$$

$$RCOONH_4 + AgNO_3 \longrightarrow \underset{\text{Silver salt}}{RCOOAg} + NH_4NO_3$$

$$RCOOAg\,(s) \xrightarrow{\text{Ignited}} Ag\,(s) + CO_2\,(g) + H_2O\,(g)$$

Calculations. Let the mass of the silver salt taken $= w$ g

and the mass of silver left as residue $= x$ g

(a) For monocarboxylic acids

Step 1. *To calculate the molar mass of the silver salt.*

$$\underset{w\,g}{RCOOAg} \xrightarrow{\Delta} \underset{x\,g}{Ag}$$

x g of silver is obtained from silver salt $= w$ g

$\therefore$ 108 g of silver will be obtained from silver salt $= \frac{w}{x} \times 108$ g

This gives us the molar mass of the silver salt of the monocarboxylic acid.

Step 2. *To calculate the molar mass of the acid.*

Now, RCOOH = RCOOAg − Ag + H

$\therefore$ Molar mass of RCOOH

= Molar mass of RCOOAg − At. mass of Ag + At. mass of H

$\therefore$ Molar mass of monocarboxylic acid

$$= \left(\frac{w}{x} \times 108\right) - 108 + 1$$

$$= \left(\frac{w}{x} \times 108\right) - 107$$

(b) For polycarboxylic acids.

Step 1. *To determine the molar mass of the silver salt.*

Let the polycarboxylic acid be represented as $R(COOH)_n$ where n is the basicity of the acid. Thus,

$$\underset{\text{Organic acid}}{R(COOH)_n} \xrightarrow[(ii)\ AgNO_3]{(i)\ NH_4OH} \underset{w\,g}{\underset{\text{Silver salt}}{R\,(COOAg)_n}} \xrightarrow{\text{Ignite}} \underset{x\,g}{n\,Ag}$$

Here 1 mole of polycarboxylic acid or 1 mole of its silver salt gives n gram atoms *i.e.* $n \times 108$ g of Ag

Now x g of Ag is obtained from silver salt $= w$ g

$\therefore n \times 108$ g of Ag will be obtained from silver salt $= n\left(\frac{w}{x} \times 108\right)$ g

This gives us the molar mass of the silver salt of the polycarboxylic acid.

Step 2. *To calculate the molar mass of the acid.* In other words, molar mass of polycarboxylic acid

= (Molar mass of silver salt) − (n × At. mass of Ag) − (n × At. mass of H)

$$= n\left[\frac{w}{x} \times 108\right] - 108 \times n + 1 \times n$$

$$= n\left[\left(\frac{w}{x} \times 108\right) - 107\right] \text{ g mol}^{-1}.$$

EXAMPLE 16.9. ***A sample of 0·46 g of the silver salt of a dibasic acid gave a residue of 0·324 g of silver on ignition. Determine the molecular mass of the acid.*** **(N.C.E.R.T.)**

Solution. Mass of silver salt taken (w) = 0·46 g

Mass of silver left (x) = 0·324 g

Basicity of the acid (n) = 2

Now molar mass fo the polycarboxylic acid of basicity $n = n\left[\left(\frac{w}{x} \times 108\right) - 107\right]$

Substituting the values of w, x and n, we have

Molar mass of acid

$$= 2\times\left[\left(\frac{0\cdot46}{0\cdot324}\times108\right)-107\right]$$

$$= 2\times46\cdot333$$

$$= 92\cdot67\ \text{g mol}^{-1}$$

∴ Molecular mass of the acid $= 92\cdot67\ u$

PROBLEMS FOR PRACTICE

1. The silver salt of a monobasic organic acid on ignition gave 60% of silver. Calculate the molecular mass of the acid. [Ans. 73]
2. The silver salt of a dibasic organic acid contains 71·1% silver. Calculate the molecular mass of the acid. [Ans. 89·78]
3. 0·607 g of silver salt of a tribasic acid on combustion deposited 0·370 g of pure silver. Calculate the molecular mass of the acid. [Ans. 210·0]
4. 0·76 g of the silver salt of a dibasic acid was ignited, it gave 0·54 g of pure silver. Determine the molecular mass of the acid. [Ans. 90]

16.5.2. Gravimetric or Chloroplatinate method for the determination of Molecular Mass of Organic Bases.

Principle. This method is based upon the fact that most of the organic bases *i.e.* amines react with chloroplatinic acid (H_2PtCl_6) to form insoluble salts called *platinichlorides* or *chloroplatinates* of the general formula $B_2H_2PtCl_6$ where B is the monoacidic amine. On heating, these salts decompose to yield metallic platinum.

$$2\,RNH_2 + H_2PtCl_6 \longrightarrow (RNH_3)_2PtCl_6$$

$$(RNH_3)_2PtCl_6\,(s) \xrightarrow{\text{Ignition}} Pt\,(s)$$

In case of diacidic amine B, the general formula of the chloroplatinate formed with H_2PtCl_6 will be $B_2(H_2PtCl_6)_2$ and with triacidic amine it would be $B_2(H_2PtCl_6)_3$ and in case of amine of acidity n, it would be $B_2(H_2PtCl_6)_n$.

Calculations. Let the mass of chloroplatinate taken $= w$ g

and mass of metallic platinum formed $= x$ g

$$\text{Now}\quad B_2H_2PtCl_6 \xrightarrow{\text{Ignition}} Pt$$

That is one gram atom of Pt, *i.e.*, 195 g will be obtained from 1 gram mole of chloroplatinate salt ($B_2H_2PtCl_6$) of monoacidic base.

Now x g of Pt are obtained from chloroplatinate $= w$ g

∴ 195 g of Pt will be obtained from chloroplatinate $= \frac{w}{x}\times195\,g$

In other words, the molar mass of chloroplatinate salt of monoacidic base,

$$[B_2(H_2PtCl_6)] = \frac{w}{x}\times195 \quad ...(i)$$

Similarly, we can derive that molar mass of diacidic base,

$$[B_2(H_2PtCl_6)_2] = \frac{w}{x}\times195\times2 \quad ...(ii)$$

and molar mass of polyacidic base,

$$[B_2(H_2PtCl_6)_n] = \frac{w}{x}\times195\times n \quad ...(iii)$$

If B is the molar mass of monoacidic base, then the molar mass of chloroplatinate salt of monoacidic base $B_2(H_2PtCl_6)$

$$= 2\,B + 2\times1 + 195 + 6\times35\cdot5$$

$$= 2\,B + 410 \quad ...(iv)$$

Equating the molar mass of chloroplatinate of monoacidic base from Eq. (*i*) and Eq. (*iv*), we have,

$$2\,B + 410 = \frac{w}{x}\times195$$

$$\text{or}\qquad B = \frac{1}{2}\left[\frac{w}{x}\times195 - 410\right]$$

This gives us the molar mass of monoacidic base (B).

Working on similar lines we can derive that the molar mass of a polyacidic base of acidity n

$$= \frac{1}{2}\left[\frac{w}{x}\times195 - 410\right]\times n\ \text{g mol}^{-1}$$

EXAMPLE 16.10. *A sample of 0·400 g of the chloroplatinate of a monoacidic base on ignition left 0·125 g of platinum. What is the molecular mass of the base ?* (N.C.E.R.T.)

Solution. Let B be the molar mass of monoacidic base B, therefore, molar mass of its chloroplatinate salt *i.e.*, $[B_2(H_2PtCl_6)] = 2\,B + 410$ ...(*i*)

Mass of chloroplatinate taken $= 0\cdot400$ g

Mass of platinum left as residue $= 0\cdot125$ g

Now $0\cdot125$ g of Pt are obtained from chloroplatinate $= 0\cdot40$ g

$\therefore$ 195 g of Pt will be obtained from chloroplatinate $= \dfrac{0\cdot40}{0\cdot125} \times 195$ g

Thus, the molar mass of chloroplatinate

$$= \frac{0\cdot40}{0\cdot125} \times 195 \text{ g} \quad ...(ii)$$

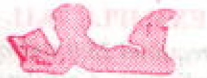
Equating the values of molar mass of chloroplatinate from Eq. (*i*) and Eq. (*ii*), we have,

$$2\,B + 410 = \frac{0\cdot40}{0\cdot125} \times 195$$

or $$B = \frac{1}{2}\left[\frac{0\cdot40}{0\cdot125} \times 195 - 410\right] = 107 \text{ g mol}^{-1}$$

Thus, molecular mass of the base = 107 u.

PROBLEMS FOR PRACTICE



1. $0\cdot30$ g of the chloroplatinate of a monoacidic base gave $0\cdot09375$ g of platinum on ignition. Find out the molecular mass of the base. [Ans. 107]
2. The chloroplatinate of a diacid base contains 39% of platinum. Calculate the molecular mass of the base. [Ans. 90]
3. $0\cdot532$ g of the chloroplatinate of a diacid base gave $0\cdot195$ g of platinum on ignition. Calculate the molecular mass of the base. [Ans. 122]
4. $0\cdot984$ g of the chloroplatinate of a diacid base gave $0\cdot39$ g of platinum. Calculate the molecular mass of the base. [Ans. 82]

16.5.3. Volumetric method for acids and bases.

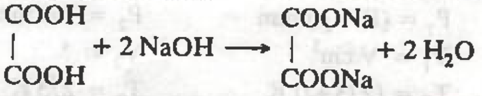
Principle. This method is based upon the principle that acids and bases always react in the ratio fo their stoichromatic coefficients appearing in the balanced chemical reaction of the given acid-base reaction. Knowing the mass of the acid which neutralizes one mole of base, and the basicity of acid, we can calculate the molecular mass of the acid, *i.e.*,

Molar mass of the acid = Mass of acid neutralized by one mole of base × Basicity of the acid

Similarly,

Molar mass of the base = Mass of base neutralized by one mole of acid × Acidity of the base

The acidity of the base is, in fact, the stoichiometric coefficient of the acid and basicity of the acid is the stoichiometric coefficient of the base appearing in the balanced chemical equation for the acid-base reaction. These are always whole numbers. For example,



$$\begin{array}{c}\text{COOH}\\ |\\ \text{COOH}\end{array} + 2\,\text{NaOH} \longrightarrow \begin{array}{c}\text{COONa}\\ |\\ \text{COONa}\end{array} + 2\,H_2O$$

Here, one mole of the acid neutralizes two moles of the base, therefore, basicity of oxalic acid is 2 while acidity of NaOH is 1.

A. For acids

Procedure. A known mass of the acid is dissolved in a suitable solvent (usually water) and the solution is titrated against a standard alkali solution (usually NaOH) using phenolphthalein as indicator.

Calculations : Suppose the mass of the acid taken = *w* g

Molarity of the NaOH soln. used = M/*x*

Volume of NaOH used for complete neutralization of the acid soln. = v cm^3

Now, v cm^3 of M/x NaOH neutralizes acid $= w$ g

$\therefore$ 1000 cm^3 of 1 M NaOH will neutralize acid

$$= \frac{w}{v} \times 1000 \times x \text{ g}$$

But 1000 cm^3 of 1 M NaOH solution, according to the definition of molar solution, contains one gram mole of NaOH.

$\therefore$ Mass of the acid neutralized by one mole of NaOH $= \dfrac{w}{v} \times 1000 \times x$ g

If n is the basicity of the acid, then, 1 mole of acid will neutralize n moles of NaOH. In other words, molecular mass of the acid

= Mass of the acid neutralized by 1 mole of the NaOH × basicity of the acid

$$= \frac{w}{v} \times 1000 \times x \times n$$

B. For bases

Procedure. A known mass of the base is dissolved in a suitable solvent and the solution titrated against a standard monobasic acid (say HCl) solution using a suitable indicator. The molar mass of the acid is calculated in the same way as described above. Knowing the acidity of the base, its molar mass can be calculated :

Molar mass of the base = Mass of the base neutralized by one mole of HCl × acidity of the base

EXAMPLE 16.11. ***0.16 g of a dibasic organic acid required 25.0 cm³ of M/10 NaOH for complete neutralization. Calculate its molecular mass.***

Solution. **Here, the mass of the acid taken = 0.16 g**

Volume of M/10 NaOH used for complete neutralization of the acid = 25.0 cm³

i.e. 25.0 cm³ of M/10 NaOH neutralize acid = 0·16 g

∴ 1000 cm³ of 1 M NaOH will neutralize acid

$$= \frac{0\cdot16}{25\cdot0} \times 1000 \times 10 \text{ g} = 64 \text{ g}$$

But 1000 cm³ of 1 M NaOH contains one gram mole of NaOH.

∴ Mass of the acid neutralized by one mole of NaOH = 64 g

But basicity of acid (n) 2

∴ Molar mass of the acid = Mass of the acid neutralized by 1 mole of NaOH × Basicity of the acid = 64 × 2 = **128**

PROBLEMS FOR PRACTICE

1. 0·075 g of a monobasic acid requires 10 cm³ of M/12 NaOH for complete neutralization. Calculate the molecular mass of the acid. **[Ans. 90]**
2. 7·5 g of a diabasic acid are dissolved per litre of the given solution. 20 cm³ of this acid solution required 25 cm³ of M/15 NaOH solution for complete neutralization. Calculate the equivalent mass and molecular mass of the acid. **[Ans. 90 and 180]**

16.5.4. Victor-Meyer's method* for determination of Molecular Mass of Volatile Liquids

It is a convenient method for the determination of molecular masses of volatile substances. It works on the following principle :

Principle. A known mass of a volatile substance is heated in a Victor Meyer's tube (Fig. 16.21). As a result, the substance changes into vapours. The vapours, in turn, displace an equal volume of air which is collected over water. The volume of air thus collected is measured at laboratory temperature and pressure. This volume is then converted into volume at STP by applying the general gas equation,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

From the mass of the organic compound taken and the volume of air displaced at STP, the mass of the substance which will displace 22.4 litres of air at STP is calculated. This gives us the molecular mass of the substance.

Apparatus. The apparatus used is shown in Fig. 16.23. It consists of the following main parts :

(i) An inner Victor Meyer's tube (A) having the side tube (S).

(ii) an outer copper jacket (J) *(iii) A graduated cylinder (G), and* *(iv) Hofmann's bottle (H).*

Calculations : Suppose the mass of the substance taken = w g

Volume of air displaced = V cm³

Experimental pressure (read from the barometer) = P mm

Room temperature = t°C

Aq. tension at t°C (read from tables) = p mm

∴ Pressure of the dry air = (P − p) mm

Ist step. *To convert the volume at the experimental conditions to the volume at STP.*

Exptl. conditions	*At STP*
$P_1 = (P - p)$ mm	$P_2 = 760$ mm
$V_1 = V$ cm³	$V_2 = ?$
$T_1 = (273 + t)$ K	$T_2 = 273$ K

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*Not included in the CBSE Syllabus.

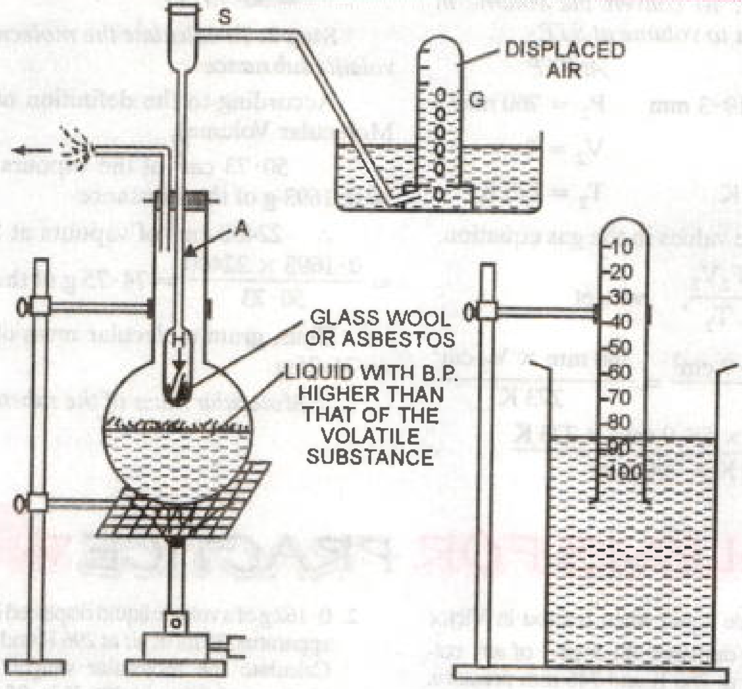

FIGURE 16.21. Victor Meyer's Apparatus.

Now, $\dfrac{P_1 \times V_1}{T_1} = \dfrac{P_2 \times V_2}{T_2}$

or $\dfrac{(P-p) \times V}{(273+t)} = \dfrac{760 \times V_2}{273}$

So 'V_2' can be calculated.

Here, volume of air displaced at STP

= Volume of liquid vapours = V_2 cm^3

2nd step. *To calculate the molecular mass.*

V_2 cm^3 of the vapours at STP are obtained from *w* g of the substance.

∴ 22400 cm^3 of the vapours at STP will be obtained from $= \dfrac{w}{V_2} \times 22400$ g of the substance

But 22400 cm^3 is the volume occupied by gram molecular mass of the volatile liquid at STP.

∴ Gram molecular mass $= \dfrac{w}{V_2} \times 22400$ g

or Molecular mass of the substance

$$= \frac{w}{V_2} \times 22400$$

i.e. Molecular mass

$$= \frac{\text{Mass of the substance taken}}{\text{Vol. of displaced air at STP}} \times 22400$$

Alternatively,

Vapour Density (V.D.) of the substance

$$= \frac{\text{Mass of } V_2 \text{ cm}^3 \text{ of vapours at STP}}{\text{Mass of } V_2 \text{ cm}^3 \text{ of hydrogen at STP}}$$

$$= \frac{w}{V_2 \times 0{\cdot}00009} \text{ (approx.)}$$

(∵ weight of 1 cm^3 of H_2 at STP = 0·00009 g or accurately = 2/22400)

or V.D. $= \dfrac{w}{V_2 \times 2/22400} = \dfrac{w \times 22400}{V_2 \times 2}$ (accurately)

Since molecular mass = 2 × V.D., so molecular mass can be calculated.

EXAMPLE 16.12. *0·1693 g of a volatile substance when vaporized displaced 58·9 cm³ of air measured at 27°C and 746 mm pressure. Calculate the molecular mass of the substance (Aqueous tension at 27°C = 26·7 mm Hg).*

Solution. Step 1. *To convert the volume at experimental conditions to volume at STP.*

Exptl. Conditions	*At STP*
$P_1 = 746 - 26 \cdot 7 = 719 \cdot 3$ mm	$P_2 = 760$ mm
$V_1 = 58 \cdot 9 \text{ cm}^3$	$V_2 = ?$
$T_1 = 273 + 27 = 300$ K	$T_2 = 273$ K

Substituting these values in the gas equation,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}, \quad \text{we get}$$

$$\frac{719 \cdot 3 \text{ mm} \times 58 \cdot 9 \text{ cm}^3}{300 \text{ K}} = \frac{760 \text{ mm} \times V_2 \text{ cm}^3}{273 \text{ K}}$$

$$V_2 = \frac{719 \cdot 3 \text{ mm} \times 58 \cdot 9 \text{ cm}^3 \times 273 \text{ K}}{300 \text{ K} \times 760 \text{ mm}}$$

$$= 50 \cdot 73 \text{ cm}^3$$

Step 2. ***To calculate the molecular mass of the volatile substance***

According to the definition of GMV (Gram Molecular Volume),

$50 \cdot 73 \text{ cm}^3$ of the vapours at STP weight $= 0 \cdot 1693$ g of the substance

$\therefore$ 22400 cm^3 of vapours at STP will weigh

$$= \frac{0 \cdot 1693 \times 22400}{50 \cdot 73} = 74 \cdot 75 \text{ g of the substance}$$

Thus, gram molecular mass of the substance $= 74 \cdot 75$ g

$\therefore$ *Molecular mass of the substance* = **74·75**

PROBLEMS FOR PRACTICE

1. $0 \cdot 150$ g of a volatile liquid when treated in Victor Meyer's apparatus displaced $40 \cdot 5 \text{ cm}^3$ of air collected over water at 288 K and 746 mm pressure. Calculate the molecular weight of the liquid (Aqueous tension at 288 K = $13 \cdot 7$ mm) **[Ans. 90·8]**

2. $0 \cdot 162$ g of a volatile liquid displaced in a Victor Meyer's apparatus, 35 ml of air at 296 K and 745 mm pressure. Calculate the molecular weight of the substance (Aqueous tension at 296 K is 25 mm and 1 ml of hydrogen at NTP weighs $0 \cdot 00009$ g). **[Ans. 118·6]**

16.5.5. Modern Methods of Structure Elucidation

During the last three decades, there has been a tremendous progress in the development of scientific instruments. Through their use, the complete structure of any unknown compound can be elucidated within a few days.

Among the most prominent spectroscopic techniques used are ultraviolet-visible (UV-Vis) infrared (IR), nuclear magnetic resonance (NMR) spectroscopy and mass spectrometry. A molecule absorbs a specific amount of energy in discrete units corresponding to radiations of specific frequency or wavelength. The energy thus absorbed by the molecule may cause electronic transitions (UV-Vis), vibrational and rotational energy changes (IR, Raman), nuclear magnetic transitions (NMR) or ionization or fragmentation of molecules (mass spectrometry).

The electronic absorptions occur in the ultraviolet region (UV region : 200-400 nm and visible region, 400-800 nm) vibrational in the infrared (4000-650 cm^{-1}) and rotational in the far infrared and microwave regions. The molecular mass and molecular formula of an organic compound can be easily determined by mass spectrometry. The nature of functional groups, present in an organic compound are determined by a combination of UV and IR spectroscopic methods. For example, conjugation, aldehydes, ketones and aromatic compounds are best detected by UV while all other functional groups such as double bond, triple bond, carbonyl groups (aldehydes, ketones, esters, amides, acid chlorides, anhydrides etc.), hydroxyl and nitriles are detected by IR spectroscopy.

NMR involves nuclear transitions of certain atoms such as ${}^{1}_{1}\text{H}$, ${}^{13}_{6}\text{C}$ etc. Proton (${}^{1}_{1}\text{H}$) NMR can distinguish H-atoms attached to different atoms and in different electronic environments. For example, protons present in CH_3-Cl and $H_2C = C <$ give different signals in NMR specterum. Thus NMR gives wealth of information about the structures of organic compounds. Some other techniques which have been used for structure elucidation are emission, fluorescence and phosphorescence spectroscopy. The three-dimensional structure of the molecule including bond lengths and bond angles is finally determined through **X-ray diffraction**. These modern methods of structure elucidation require only a small amount of the compound as compared to the classical methods discussed in this unit. Further, all these methods have made the structure determination a much simpler task than what it used to be a few decades ago. A detailed discussion and application of these methods is beyond the scope of this book. However, the use of mass spectrometry to determine the accurate molecular masses and molecular formulae of organic compounds is briefly discussed below :

16.5.5.1. Determination of Accurate Molecular Mass – Mass Spectrometer.

A mass spectrometer is an instrument used to determine accurate molecular masses and molecular formulae of organic substances. It also gives valuable information about the molecular structure of the organic compound.

Basic Principle. In the mass spectrometer (Fig. 16.22), a very small amount of the substance (1-2 mg) is vaporized and bombarded with a beam of high-energy electrons (usually 70 eV). As a result of this bombardment, some of the molecules lose an electron and get ionized to produce a positively charged* radical cation called the *molecular ion or the parent ion.*

$$\underset{\text{Molecule}}{M} + \underset{\text{High energy electron}}{e^-} \longrightarrow \underset{\text{Molecular ion}}{M^{+\cdot}} + 2e^-$$

Since the electron beam is highly energetic (70 eV, ~ 67500 kJ mol^{-1}), it not only produces the molecular ions but also imparts them (molecular ions) with considerable *surplus energy.* Not all the molecular ions will have the same amount of energy but most of them will have surplus energy far greater than that required to break covalent bonds (210 – 420 kJ mol^{-1}). Therefore, soon after their formation, most of the molecular ions will break up (or fragment) into smaller ions called the *fragment or the daughter ions.* The molecular ion may fragment either

(*i*) *by producing a radical and a cation, i.e.,*

$$\overset{+}{M^{\cdot}} \longrightarrow \underset{\text{Fragment ion}}{m_1^+} + \underset{\text{Radical}}{\dot{m}_2}$$

(*ii*) *by producing a neutral molecule and another radical cation, i.e.*

$$\overset{+}{M^{\cdot}} \longrightarrow \underset{\text{Fragment radical ion}}{m_1^{+\cdot}} + \underset{\text{Neutral molecule}}{m_2}$$

The molecular ion, the fragment ions and the fragment radical ions are then separated according to their mass to charge (*m*/*z*) ratio. Since for most of the ions, the charge is + 1 (*singly charged ions*)**, *m*/*z* is simply the mass of the ion.

For separating the positive ions according to their *m*/*z* ratio, the mixture of ions is passed between a series of negatively charged metal plates (called accelerators) which accelerate them to high speeds. From the accelerator, the ions reach the electrostatic analyser. The electric field of the analyser makes the ions to move in curved paths and finally directs them to region of high magnetic field. Here the ions move in circular paths. The path they take depends upon their *m*/*z* ratio.

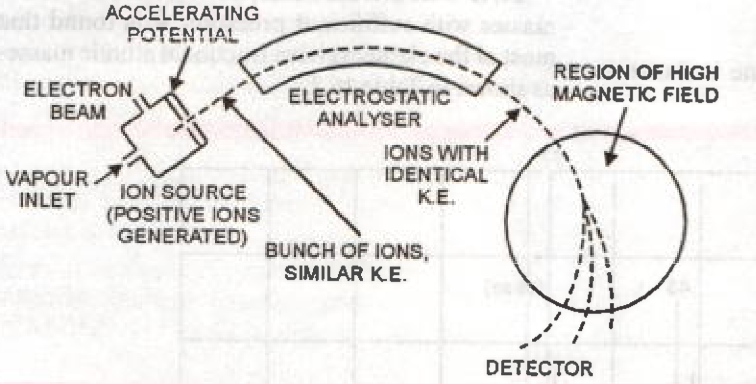

FIGURE 16.22. Mass spectrometer. An organic compound is split iont small positively charged fragement ions the analyzer separates the fragmentions according to their m/g ration the detector measures the relative aboundance of ions.

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*Alternatively, the molecule may accept an electron to produce a radical anion.

$$M + e^- \longrightarrow \underset{\text{Radical anion}}{M^{\cdot -}}$$

This process is less probable by a factor of 10^2 and hence only positively charged ions are formed.

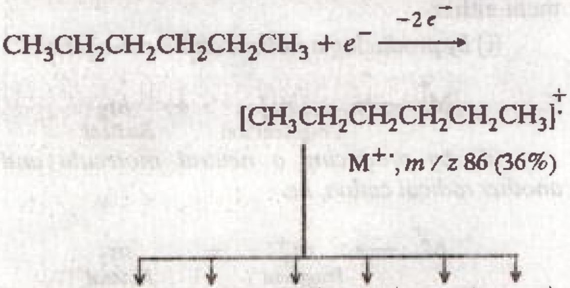
**Doubly charged ions are also occasionally formed. These are deflected (by the magnetic field) much more than the singly charged ions of the same mass and hence appear in the mass spectrum at the same value as singly charged ions of half the mass, since $2m/2z = m/z$.

The ions thus separated are made to fall on a detector which produces a signal for each value of *m/z*. The intensity of each signal represents the relative abundance of the ion producing the signal.

The detector input is amplified and transmitted to a recorder which traces out a *plot showing the relative abundance of the various ions along the Y-axis and their m/z values along the X-axis. This plot is called the* **mass spectrum.**

It is interesting to note that neutral molecules and free radicals formed during fragmentation cannot be detected in the mass spectrometer.

The entire process of fragmentation can be illustrated by taking the example of *n*-hexane.



$$CH_3CH_2CH_2CH_2CH_2CH_3 + e^- \xrightarrow{-2e^-} [CH_3CH_2CH_2CH_2CH_2CH_3]^{+\cdot}$$

$M^{+\cdot}$, m/z 86 (36%)

Fragment ion	$C_5H_{11}^+$	$C_4H_9^+$	$C_3H_7^+$	$C_3H_5^+$	$C_2H_5^+$	$C_2H_3^+$
(m/z)	71	57	43	41	29	27
Relative abundance or Intensity	3·6	100	72·5	55·6	36·2	22·5

The mass spectrum of n-hexane is shown in Fig. 16.23.

The highest peak in the spectrum (*i.e.*, *m/z* = 57 in the spectrum of hexane) is called the **base peak** and its intensity is taken to be 100 and the intensities of the other peaks are expressed relative to it. A common mass spectrometer can resolve mass peaks to the nearest whole number (unit resolution) upto a mass number of about 500. A high resolution mass spectrometer can, however, resolve mass peaks differing by 0·001 atomic mass unit.

16.5.5.2. Precise Atomic Masses

It may be noted here that the value of the mass of any ion appearing in a mass spectrum is its *true mass and not its molecular weight obtained through the use of chemical atomic weights.* The chemical scale of atomic weights is based on averages of the weights of all the isotopes of a given element. The mass spectrometer can distinguish between masses of particles having the most common isotopes of the elements and particles bearing heavier isotopes. Consequently, the masses which are observed for molecular ions are the masses of the molecules in which every atom is present in its most common isotope.

In routine chemical calculations, we usually use integral atomic weights, *i.e.*, H = 1, C = 12, N = 14, O = 16 etc. However, if we determine atomic masses with suffificient precision, it is found that most of the elements have fractional atomic masses as shown in Table 16.2.

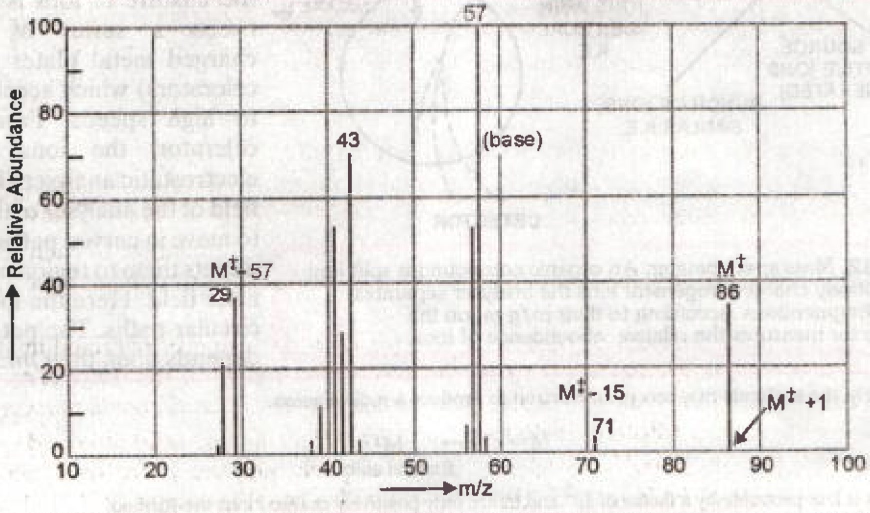


FIGURE 16.23. Mass spcetrum of *n*-hexane.

TABLE 16.2. Precise masses of some common elements

Element	Atomic Weight	Nuclide	Mass
Hydrogen	1·00797	^{1}H	1·00783
		^{2}H	2·001410
Carbon	12·01115	^{12}C	12·0000
		^{13}C	13·00336
Nitrogen	14·0067	^{14}N	14·0031
		^{15}N	15·0001
Oxygen	15·9994	^{16}O	15·9949
		^{17}O	16·9991
		^{18}O	17·9992
Sulphur	32·064	^{32}S	31·9732
		^{33}S	32·9715
		^{34}S	33·9679
Chlorine	35·435	^{35}Cl	34·9689
		^{37}Cl	36·9659

16.5.5.3. Molecular mass from the Molecular ion

The mass of the molecular ion peak gives the molecular mass of the compound. In majority of the organic compounds, the most abundant ion amongst the cluster of ions appearing in the high mass region of the spectrum gives the molecular mass of the organic compound. For example, in the mass spectrum of *n*-hexane (Fig. 16.18) the most abundant ion amongst the cluster of ions in the high mass region is at *m/z* 86. Hence molecular mass of *n*-hexane is 86 amu.

With low resolution mass spectrometers only integral molecular mass of the substance can be determined but with high resolution mass spectrometers it is possible to determine the accurate molecular mass of the substance upto five decimal places.

16.5.5.4. Molecular formulae from Precise molecular mass

It has been stated above that high resolution mass spectrometer can be used to determine accurate molecular masses upto five decimal places. With the help of these precise molecular masses, it is possible to find out the exact molecular formula of the compound. For example, a substance with a molecular weight of 60 may be C_3H_8O, $C_2H_8N_2$, $C_2H_4O_2$ or CH_4N_2O with help of Table 16.2, we can find out the precise masses of these species as follows :

$$C_3H_8O : 3 \times 12 + 8 \times 1\cdot00783 + 15\cdot9949 = 60\cdot05774$$

$$C_2H_8N_2 : 2 \times 12 + 8 \times 1\cdot00783 + 2 \times 14\cdot0031 = 60\cdot06884$$

$$C_2H_4O_2 : 2 \times 12 + 4 \times 1\cdot00783 + 2 \times 15\cdot9949 = 60\cdot02112$$

$$CH_4N_2O : 1 \times 12 + 4 \times 1\cdot00783 + 2 \times 14\cdot0031 + 15\cdot9949 = 60\cdot3242$$

If the high resolution mass spectrum of the given unknown compound shows the molecular ion at *m/z* 60·058, then certainly the unknown compound is C_3H_8O. In case it shows the molecular ion at *m/z* 60·021, it must be $C_2H_4O_2$ so on and so forth.

16.6. Empirical and Molecular Formulae

After finding out the elements present, their percentage composition and the molecular mass, the next step is to establish the formula of the compound.

Empirical Formula. ***It is defined as that formula of a substance which gives the simplest whole number ratio between the atoms of the various elements present in one molecule of the substance.***

It may be exphasised here that the empirical formula does not give the actual number of the atoms present in a molecule of the substance but it gives only the relative number of atoms. For example, the empirical formula of glucose is CH_2O which tells that the ratio between the various atoms is $C : H : O = 1 : 2 : 1$, which is the simplest ratio. However, the actual number of atoms present in a molecule of glucose are 6 carbon, 12 hydrogen and 6 oxygen atoms.

Calculation of Empirical Formula. The various steps involved in the calculation of empirical formula of a substance are as follows :

(*i*) Divide the percentage of each element by its atomic mass. This gives the *relative number of atoms*.

(*ii*) Divide the figures obtained in step (*i*) by the lowest one. This gives the *simplest ratio* among the atoms of the various elements present.

(*iii*) If the simplest ratio obtained in step (*ii*) is not a whole number ratio, then multiply the figures with a suitable integer (2, 3 etc.) to make it *simplest whole number ratio.*

(*iv*) Write down the symbols of the various elements present side by side with the above numbers at the lower right corner of each. This gives the *empirical or the simplest formula.*

Molecular Formula. *It is defined as that formula of a substance which gives the actual number of atoms of the various elements present in one molecule of the substance.*

It may be the same as the empirical formula or an integral multiple of the empirical formula. For example, the molecular formula of methane is CH_4, which is the same as the empirical formula, whereas the molecular formula of glucose is $C_6H_{12}O_6$ which is six times the empirical formula (CH_2O). Thus, in general,

$$\text{Molecular Formula} = n \times (\text{Empirical Formula})$$

where n is a simple integer 1, 2, 3, etc. given by the equation

$$n = \frac{\text{Molecular mass of the compound}}{\text{Empirical formula mass of the compound}}$$

Molecular mass of the compound is determined experimentally by one of the methods discussed earlier whereas the empirical formula mass is calculated by adding the atomic masses of all the atoms in the empirical formula.

For example, empirical formula of glucose is CH_2O. So its empirical formula mass is $= 12 + 2 \times 1 + 16 = 30$. The molecular mass of glucose by experiment is found to be 180.

$$\therefore n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{180}{30} = 6$$

$\therefore$ Molecular formula of glucose

$$= 6 \times (CH_2O) = C_6H_{12}O_6$$

Calculation of Molecular Formula

The various steps involved in the calculation of molecular formula of a substance are :

(*i*) *Calculation of the percentage composition.*

(*ii*) *Calculation of the empirical formula.*

(*iii*) *Calculation of the molecular mass.*

(*iv*) *Calculation of the molecular formula by finding the multiplying factor 'n'.*

PROBLEMS ON CALCULATION OF EMPIRICAL AND MOLECULAR FORMULAE

EXAMPLE 16.11. *An organic compound contains $C = 61\cdot00\%$, $H = 11\cdot88\%$ and $O = 27\cdot1290$. Calculate the empirical and molecular formulae of the compound. Molecular mass of the compound is 118.*

Solution. **(a) Calculation of empirical formula**

Element	Percentage	Atomic Mass	Relative No. of atoms	Simplest atomic ratio	Simplest whole No. atomic ratio
Carbon	61·00	12	$\frac{61\cdot00}{12} = 5\cdot08$	$\frac{5\cdot08}{1\cdot70} = 2\cdot99$	3
Hydrogen	11·88	1	$\frac{11\cdot88}{1} = 11\cdot88$	$\frac{11\cdot88}{1\cdot70} = 6\cdot9$	7
Oxygen	27·12	16	$\frac{27\cdot12}{16} = 1\cdot70$	$\frac{1\cdot70}{1\cdot70} = 1$	1

Hence the empirical formula of the compound is C_3H_7O.

(b) Calculation of molecular formula

Empirical formula (C_3H_7O) massof the compound $= 3 \times 12 + 7 \times 1 + 1 \times 16 = 59$

$$\therefore n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{118}{59} = 2$$

Thus, molecular formula of the compound

$$= n \times (\text{Empirical formula})$$

$$= 2 \times C_3H_7O = (C_3H_7O)_2$$

$$= C_6H_{14}O_2$$

EXAMPLE 16.13. *0.45 g of an organic compound gave on combustion $0\cdot792$ g of CO_2 and 0.324 g of water. 0.24 g of the same substance was kjeldahlised and the ammonia liberated was absorbed in 50.0 cm^3 of $N/4\ H_2SO_4$. The excess acid required 77.0 cm^3 of $N/10$ NaOH for complete neutralization. Calculate the empirical formula of the compound.*

Solution. (a) Calculation of percentage composition

(*i*) % of Carbon

$$= \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ produced}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{12}{44} \times \frac{0 \cdot 792}{0 \cdot 45} \times 100 = \mathbf{48 \cdot 0}$$

(*ii*) % of Hydrogen

$$= \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ produced}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{2}{18} \times \frac{0 \cdot 324}{0 \cdot 45} \times 100 = \mathbf{8 \cdot 0}$$

(*iii*) % of Nitrogen :

Volume of H_2SO_4 taken = 50·0 cm^3 N/4 H_2SO_4

= 12.5 cm^3 1N H_2SO_4

Now 77.0 cm^3 of N/10 NaOH

= 77.0 cm^3 of N/10 H_2SO_4

= 7.7 cm^3 of 1 N H_2SO_4

∴ Volume of 1N H_2SO_4 neutralized by NH_3 = 12.5 − 7.7 = 4.8 cm^3

But 4.8 cm^3 1N H_2SO_4 ≡ 4.8 cm^3 1N NH_3

Now, 1000 cm^3 1N NH_3 contain N = 14 g

∴ 4.8 cm^3 1N NH_3 will contain

$$N = \frac{14}{1000} \times 4.8 = 0.0672 \text{ g}$$

Thus, 0.24 of the substance contain 0.0672 g of nitrogen

$$\therefore \ \% \text{ of nitrogen} = \frac{0.0672}{0.24} \times 100 = \mathbf{28.0}$$

(*iv*) % of Oxygen

= 100 − (% of C + % of H + % of N)

= 100 − (48.0 + 8.0 + 28.0) = **16.0**

(b) Calculation of empirical formula

Element	Percentage	Atomic Mass	Relative No. of atoms	Simplest atomic ratio	Simplest whole No. atomic ratio
Carbon	48·0	12	$\frac{48 \cdot 0}{12} = 4$	$\frac{4}{1} = 4$	4
Hydrogen	8·0	1	$\frac{8 \cdot 0}{1} = 8$	$\frac{8}{1} = 8$	8
Nitrogen	28·0	14	$\frac{28 \cdot 0}{14} = 2$	$\frac{2}{1} = 2$	2
Oxygen	16·0	16	$\frac{16 \cdot 0}{16} = 1$	$\frac{1}{1} = 1$	1

Hence, empirical formula of the compound is $C_4H_8N_2O$

EXAMPLE 16.14. *0.246 g of an organic compound containing 58.53% carbon and 4.06% hydrogen gave 22.4 cm^3 of nitrogen at STP. What is the empirical formula of the compound ?*

Solution. (a) Calculation of percentage composition

(*i*) % of Carbon = 58.53 (*Given*)

(*ii*) % of Hydrogen = 4.06 (*Given*)

(*iii*) % of Nitrogen

22400 cm^3 of N_2 at STP weigh = 28 g

∴ 22·4 cm^3 of N_2 at STP will weigh

$$= \frac{28}{22400} \times 22 \cdot 4 = 0 \cdot 028 \text{ g}$$

Thus, 0·246 g of the substance contain 0·028 g of nitrogen

$$\therefore \text{ Percentage of Nitrogen} = \frac{0 \cdot 028}{0 \cdot 246} \times 100$$

$$= 11 \cdot 38$$

(*iv*) Percentage of Oxygen

= 100 − (% of C + % of H + % of N)

= 1 − (58·53 + 4·06 + 11·28) = 26·03

(b) Calculation of empirical formula

Element	Percentage	Atomic Mass	Relative No. of atoms	Simplest atomic ratio	Simplest whole No. atomic ratio
Carbon	58·53	12	$\frac{58\cdot53}{12} = 4\cdot88$	$\frac{4\cdot88}{0\cdot813} = 6$	6
Hydrogen	4·06	1	$\frac{4\cdot06}{1} = 4\cdot06$	$\frac{4\cdot06}{0\cdot813} = 5$	5
Nitrogen	11·38	14	$\frac{11\cdot38}{14} = 0\cdot813$	$\frac{0\cdot813}{0\cdot813} = 1$	1
Oxygen	26·03	16	$\frac{26\cdot03}{16} = 1\cdot63$	$\frac{1\cdot63}{0\cdot813} = 2$	2

Hence, the empirical formula of the compound is $C_6H_5NO_2$.

EXAMPLE 16.15. *0·246 g of an organic compound gave 0·198 g of carbon dioxide and 0·1014 g of water on complete combustion. 0·37 g of the compound gave 0·638 of silver bromide. What is the molecular formula of the compound if its molecular mass is 109 ?* (N.C.E.R.T.)

Solution. (a) Calculation of percentage composition

(*i*) % of Carbon

$$= \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ produced}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{12}{44} \times \frac{0\cdot198}{0\cdot246} \times 100 = \mathbf{21\cdot95}$$

(*ii*) % of Hydrogen

$$= \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ produced}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{2}{18} \times \frac{0\cdot1014}{0\cdot246} \times 100 = \mathbf{4\cdot58}$$

(*iii*) % of Bromine

$$= \frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{80}{188} \times \frac{0\cdot638}{0\cdot37} \times 100$$

$$= 73\cdot37$$

(*iv*) The given compound does not contain oxygen since the sum of the percentage of carbon, hydrogen and bromine is approx. 100 *i.e.* 21·95 + 4·58 + 73·37 = 99·90.

(b) Calculation of empirical formula

Element	Percentage	Atomic Mass	Relative No. of atoms	Simplest atomic ratio	Simplest whole No. atomic ratio
Carbon	21·95	12	$\frac{21\cdot95}{12} = 1\cdot83$	$\frac{1\cdot83}{0\cdot917} = 2$	2
Hydrogen	4·58	1	$\frac{4\cdot58}{1} = 4\cdot58$	$\frac{4\cdot58}{0\cdot917} = 5$	5
Bromine	73·37	80	$\frac{73\cdot37}{80} = 0\cdot917$	$\frac{0\cdot917}{0\cdot917} = 1$	1

Thus, the empirical formula of the compound is C_2H_5Br

(c) Determination of the molecular formula

Empirical formula (C_2H_5Br) mass of the compound = 2 × 12 + 5 × 1 + 1 × 80 = 109

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

$$= \frac{109}{109} = 1$$

Thus, the molecular formula of the compound

$$= n \times (\text{Empirical formula})$$

$$= 1 \times (C_2H_5Br)$$

$$= \mathbf{C_2H_5Br}$$

EXAMPLE 16.16. *On analysis, 0·2 g of a monobasic acid gave 0·505 g of CO_2 and 0·0864 g of H_2O. 0·305 g of this acid required 25 cm^3 of M/10 NaOH for complete neutralization. Find the molecular formula of the acid.* (N.C.E.R.T.)

Solution. **(a) Calculation of percentage composition.**

(*i*) % of Carbon

$$= \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ produced}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{12}{44} \times \frac{0 \cdot 505}{0 \cdot 2} \times 100 = 68 \cdot 86$$

(*ii*) % of Hydrogen

$$= \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{\text{Mass of substance taken}} \times 100$$

$$= \frac{2}{18} \times \frac{0 \cdot 0864}{0 \cdot 2} \times 100 = 4 \cdot 8$$

(*iii*) % of Oxygen = 100 – (% of C + % of H)

$$= 100 - (68 \cdot 86 + 4 \cdot 8)$$

$$= 26 \cdot 34$$

(b) Calculation of empirical formula

Element	Percentage	Atomic Mass	Relative No. of atoms	Simplest atomic ratio	Simplest whole No. atomic ratio
Carbon	68·86	12	$\frac{68 \cdot 86}{12} = 5 \cdot 74$	$\frac{5 \cdot 74}{1 \cdot 65} = 3 \cdot 48$	7
Hydrogen	4·80	1	$\frac{4 \cdot 80}{1} = 4 \cdot 80$	$\frac{4 \cdot 80}{1 \cdot 65} = 2 \cdot 91$	6
Oxygen	26·34	16	$\frac{26 \cdot 34}{16} = 1 \cdot 65$	$\frac{1 \cdot 65}{1 \cdot 65} = 1 \cdot 00$	2

Hence, the empirical formula of the compound is $C_7H_6O_2$

(c) Calculation of molecular mass

0.305 g of acid requires 25 cm^3 of M/10 NaOH for neutralisation

∴ 25 cm^3 of M/10 NaOH neutralize

= 0.305 g of acid

or 25 cm^3 of 1M NaOH neutralize

= 10 × 0.305 g of acid

or 1000 cm^3 of 1M NaOH will neutralize

$$= \frac{10 \times 0 \cdot 305}{25} \times 1000 = 122 \text{ g of acid}$$

But 1000 cm^3 of 1M NaOH contain 1g mole of NaOH.

Thus, mass of acid neutralized by 1 mole of NaOH = 122

Basicity of the acid = 1

∴ Molecular mass of the acid = Mass of acid neutralized by 1 mole of NaOH × basicity of the acid

= 122 × 1 = 122

(d) Calculation of molecular formula

Empirical formula ($C_7H_6O_2$) mass of the compound = (7 × 12 + 6 × 1 + 16 × 2) = 122

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

Thus, molecular formula of the compound

$$= n \times (\text{Empirical formula})$$

$$= 1 \times (C_7H_6O_2) = C_7H_6O_2$$

EXAMPLE 16.17. *An acid of molecular mass 104 contains 34.6% carbon, and 3.85% hydrogen. 3.812 mg of the acid required 7.33 cm^3 of 0.01 M NaOH for neutralisation. Suggest a structure for the acid.*

Solution. **(a) Percentage composition of elements**

(*i*) % of carbon = 34.6 (*Given*)

(*ii*) % of hydrogen = 3.85 (*Given*)

(*iii*) % of oxygen = 100 – (% of C + % of H)

= 100 – (34.6 + 3.85)

= 61.55

(b) Calculation of empirical formula

Element	Percentage	Atomic Mass	Relative No. of atoms	Simplest atomic ratio	Simplest whole No. atomic ratio
Carbon	34·6	12	$\frac{34 \cdot 6}{12} = 2 \cdot 89$	$\frac{2 \cdot 89}{2 \cdot 89} = 1$	3
Hydrogen	3·85	1	$\frac{3 \cdot 85}{1} = 3 \cdot 85$	$\frac{3 \cdot 85}{2 \cdot 95} = 1 \cdot 30$	4
Oxygen	61·55	16	$\frac{61 \cdot 55}{16} = 3 \cdot 85$	$\frac{3 \cdot 85}{2 \cdot 95} = 1 \cdot 30$	4

Thus, the empirical formula of the compound $= C_3H_4O_4$

(c) Calculation of molecular formula of the acid

Empirical formula ($C_3H_4O_4$) mass of the acid

$$= 3 \times 12 + 4 \times 1 + 4 \times 16 = 104$$

But molecular mass of the acid = 104 (*Given*)

$$\therefore\ n = \frac{\text{Molecular formula mass}}{\text{Empirical formula mass}} = \frac{104}{104} = 1$$

∴ Molecular formula of the acid

$$= n \times (\text{Empirical formula})$$

$$= 1 \times (C_3H_4O_4)$$

$$= \mathbf{C_3H_4O_4}$$

(d) Calculation of the basicity of the acid

3·812 mg of the acid requires 7·33 cm^3 0·01 M NaOH for complete neutralization.

Thus, 7·33 cm^3 of 0·01M NaOH neutralize

$$= 3 \cdot 812 \text{ mg of the acid}$$

or 7·33 cm^3 of 1M NaOH neutralize

$$= \frac{3 \cdot 812}{0 \cdot 01} \text{ mg} = 0 \cdot 3812 \text{ g of the acid}$$

or 1000 cm^3 of 1M NaOH will neutralize

$$= \frac{0 \cdot 3812}{7 \cdot 33} \times 100 = 52 \text{ g of the acid}$$

But 1000 cm^3 of 1 M NaOH solution contains one gram mole of NaOH

∴ Mass of the acid neutralized by one mole NaOH = 52 g

If *n* is the basicity of the acid then 1 mole of acid will neutralize *n* moles of NaOH.

∴ Mol mass of acid = *n* × 52

But mol. mass of the acid = 104 (*Given*)

$$\therefore \text{Basicity } (n) = \frac{104}{52} = 2.$$

(e) To suggest a structure of the acid

The acidic character of an organic acid is due to the presence of a carboxylic group (–COOH) as the functional group.

Since the basicity of the acid is 2, therefore, the given acid contains two –COOH groups. Out of the molecular formula ($C_3H_4O_4$), 2 × COOH $= C_2H_2O_4$ is accounted for by the two carboxylic groups.

∴ Rest of the molecule of the acid $= (C_3H_4O_4 - C_2H_2O_4) = CH_2$

Thus, the structure of the acid is *$CH_2(COOH)_2$, i.e. Malonic acid*

EXAMPLE 16.18. *A liquid aromatic organic compound A containing carbon = 92·3% and hydrogen = 7·7% decolourized $KMnO_4$ and on ozonolysis gave methanal and another compound B. The molecular mass of A is 104. On treatment with a suitable catalyst, A gave a high molecular mass solid product C having the same empirical formula as that of compound A. Compound C is used in making toys and household goods. Identify A, B and C and explain the reactions.* **(N.C.E.R.T.)**

Solution. (a) Calculation of empirical formula

Element	Percentage	Atomic Mass	Relative No. of atoms	Simplest atomic ratio	Simplest whole No. atomic ratio
Carbon	92·3	12	$\frac{92 \cdot 3}{12} = 7 \cdot 69$	$\frac{7 \cdot 69}{7 \cdot 69} = 1$	1
Hydrogen	7·7	1	$\frac{7 \cdot 7}{1} = 7 \cdot 70$	$\frac{7 \cdot 70}{7 \cdot 69} = 1$	1

Empirical formula of the compound is CH.

(b) Calculation of molecular formula

Empirical formula (CH) mass

$$= 1 \times 12 + 1 \times 1 = 13$$

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

$$= \frac{104}{13} = 8$$

$\therefore$ Molecular formula $= n \times$ Empirical formula

$$= 8 \times (CH) = (CH)_8 = C_8H_8$$

(c) To determine structures of compounds A and B

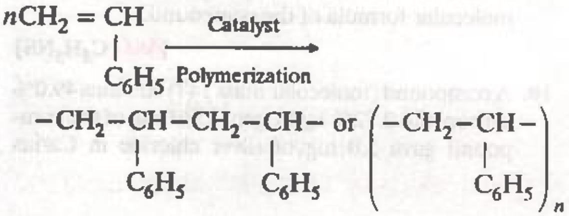
(*i*) Since compound A with M.F. C_8H_8 is aromatic and decolourises $KMnO_4$ solution, it must contain a benzene ring and a side chain containing a site of unsaturation. The only compound which satisfies all these requirements is stryene, $C_6H_5CH = CH_2$.

(*ii*) This structure is supported by ozonolysis which gives methanal and benzaldehyde B

$$\underset{\textbf{Styrene, A}}{C_6H_5CH = CH_2} \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3/CH_2Cl_2} \underset{\textbf{Methanal}}{CH_2 = O} + \underset{\textbf{Benzaldehyde, B}}{C_6H_5CH = O}$$

(d) To determine structure of compound C

Since compound A, *i.e.*, styrene on treatment with a catalyst gives a high molecular mass solid product C having the same empirical formula as that of compound A, therefore, C must be a polymer, *i.e.* polystyrene.



$$n\underset{\substack{|\\ C_6H_5}}{CH_2 = CH} \xrightarrow[\textbf{Polymerization}]{\textbf{Catalyst}} -CH_2-\underset{\substack{|\\ C_6H_5}}{CH}-CH_2-\underset{\substack{|\\ C_6H_5}}{CH}- \text{ or } \left(-CH_2-\underset{\substack{|\\ C_6H_5}}{CH}-\right)_n$$

Polystyrene, C

Polystyrene is used for making toys and household goods.

Thus, A = *styrene,* B = *benzaldehyde and* C = *polystyrene.*

PROBLEMS FOR PRACTICE

1. What is the empirical formula of the compound whose analysis percentage are given below :

(*i*) C = 41.35, H = 6.89, N = 24.12 [Ans. C_2H_4NO]

(*ii*) C = 60, H = 13.3 [Ans. C_3H_8O]

(*iii*) C = 65.73, H = 15.06, N = 19.21 [Ans. C_4H_7N]

(*iv*) C = 50.4, H = 9.25 [Ans. $C_5H_{11}O_3$]

(*v*) C = 10.0, H = 0.84, Cl = 89.2 [Ans. $CHCl_3$]

(*vi*) C = 71.4, H = 3.78, N = 7.57, S = 17.3 [Ans. $C_{11}H_5NS$]

(*vii*) C = 28.2, H = 1.57, S = 12.5, Cl = 13.9, Br = 31.2 [Ans. $C_6H_4SClBr\ O_2$]

(*viii*) C = 39.2, H = 9.79, P = 33.7 [Ans. C_3H_9PO]

2. As organic compound contains carbon 34.6%, and hydrogen 3.84% the rest being oxygen. Its vapour density is 52. Calculate the molecular formula of the compound. [Ans. $C_3H_4O_4$]

3. An organic compound contains 61.0% C and 11.88% H. The molecular mass of the compound is 118. Calculate the molecular formula of the compound. [Ans. $C_6H_{14}O_2$]

4. An organic compound on analysis gave the following results : C : 27.27%, H = 4.55%, O = 36.36%, N=32.32% . The vapour density of the compound was found to be 44. Find out the molecular formula of the compound. [Ans. $C_2H_4N_2O_2$]

5. An organic compound contains carbon, hydrogen and oxygen. 1.80 g of the substance on combustion gave 2.64 g of CO_2 and 1.08 g of H_2O. Calculate the empirical formula of the compound. [Ans. CH_2O]

6. An organic compound (molecular mass 78) has 92.3% carbon and 7.7% hydrogen by weight. Calculate the empirical formula for the compound. [Ans. C_6H_6]

7. A compound contains 40% carbon, 6.67% hydrogen (vapour density = 30). Calculate the empirical and molecular formula. Suggest a possible structure. [Ans. $C_2H_4O_2$, CH_3COOH]

8. 0.45 g of an organic compound containing only carbon, hydrogen and nitrogen on combustion, gave 1.1 g of carbon dioxide and 0.3 g of water. What is the empirical formula of the compound ?

[Ans. C_3H_4N]

9. 1.01 g of an organic compound containing 41.37% carbon and 5·75% of hydrogen on Kjeldahlising, required 11.6 cm^3 of 1N HCl. In Carius determination, 0.2006 g of the substance gave 0.5544 g of barium sulphate. 0.1015 g of the liquid when vaporized displaced 27.96 cm^3 of dry air measured at 288 K and 750 mm pressure. Find out the molecular formula of the compound.

[Ans. C_3H_5NS]

10. A compound (molecular mass 147) contains 49.0% carbon and 2.72% hydrogen. 2.561 mg of the compound gave 5.0 mg of silver chloride in Carius estimation. Find out the molecular formula of the compound.

[Ans. $C_6H_4Cl_2$]

11. 0.1 g of an organic monobasic acid gave 0.2545 g of CO_2 and 0.04428g of H_2O, on combustion. 0.122g of the acid required for complete neutralization 10 cm^3 of a N/10 alkali. Determine the molecular formula of the acid. [Ans. $C_7H_6O_2$]

12. An acid of molecular mass 104 contains 34.6% carbon, 3.85% hydrogen and rest being oxygen. Calculate the molecular formula of the acid.

[Ans. $C_3H_4O_4$]

13. An organic monobasic acid has 68·9% carbon and 4·8% hydrogen, 0·122 g of acid requires 10 ml of N/10 caustic soda solution for neutralization. What is the molecular formula of the acid ?

[Ans. $C_7H_6O_2$]

Conceptual Questions

Q. 1. When do we use fluted filter paper or hot water funnel for filtration ?

Ans. To avoid crystallization during filtration, fluted filter paper is used when the volume of the solution to be filtered is small and hot water funnel when the volume is large.

Q. 2. How will you purify essential oils ?

Ans. Essential oils are volatile and are insoluble in water. Therefore, they are purified by steam distillation.

Q. 3. How will you purify a liquid having non-volatile impurities ?

Ans. Simple distillation will give us the pure liquid while the non-volatile impurities will remain in the flask as residue.

Q. 4. Suggest a method to purify :

(*i*) Camphor containing traces of common salt.

(*ii*) Kerosene containing water.

(*iii*) A liquid which decomposes at its boiling point.

Ans. (*i*) Sublimation. Camphor sublimes while common salt remains as residue in the china dish.

(*ii*) Solvent extraction using a separatory funnel. The lower water layer is run off when kerosene is obtained. It is dried over anhydrous $CaCl_2$ and then distilled to give pure kerosene.

(*iii*) Distillation under reduced pressure.

Q. 5. A reaction is carried out using aniline as a reactant as well as a solvent. How will you remove unreacted aniline ?

Ans. Steam of distillation.

Q. 6. A mixture contains two components A and B. The solubilities of A and B in water near its boiling point are 10 grams per 100 ml and 2 g per 100 ml respectively. How will you separate A and B from this mixture ? *(N.C.E.R.T.)*

Ans. Fractional crystallization. When the saturated hot solution of this mixture is allowed to cool, the less soluble component B crystallizes out first leaving the more soluble component A in the mother liquor.

Q.7. **A mixture contains benzoic acid and nitrobenzene. How can this mixture be separated into its constituents by the technique of extraction using an appropriate chemical reagent ?** ***(N.C.E.R.T.)***

Ans. The mixture is shaken with a dilute solution of $NaHCO_3$ and extracted with ether or chloroform when nitrobenzene goes into the organic layer. Distillation of the solvent gives nitrobenzene. The filtrate is acidified with dil. HCl when benzoic acid gets precipitated. The solution is cooled and benzoic acid is obtained by filtration.

Q.8. **Explain why an organic liquid vaporizes at a temperature below its boiling point in steam distillation ?** ***(N.C.E.R.T.)***

Ans. A liquid boils when its vapour pressure becomes equal to the atmospheric pressure. During steam distillation, the mixture boils when sum of the vapour pressure of water and organic liquid becomes equal to the atmospheric pressure. Since the vapour pressure of water is appreciably higher than that of organic liquid, therefore, the organic liquid will vaporize at a temperature much lower than its normal boiling point.

Q.9. **How will you separate a mixture of o-nitrophenol and p- nitrophenol ?**

Ans. Steam distillation. *o*-Nitrophenol being volatile distils over along with water while *p*-nitrophenol being non-volatile remains in the flask.

Q.10. **Suggest methods for the separation of the following mixtures.**

(i) **A mixture of liquid A (b.p.365 K) and liquid B (b.p. 356 K).**

(ii) **A mixture of liquid C (b.p. 353 K) and liquid D (b.p. 413 K).**

Ans. (*i*) Fractional distillation because the boiling points of the two liquids differ by just 9°.

(*ii*) Simple distillation since the boiling points of the two liquids are widely apart.

Q.11. **A liquid (1·0 *g*) has three components. Which technique will you employ to separate them ?**

Ans. Column chromatography.

Q.12. **The R_f value of A and B in a mixture determined by TLC in a solvent mixture are 0·65 and 0·42 respectively. If the mixture is separated by column chromatography using the same solvent mixture as a mobile phase, which of the two components, A or B, will elute first ? Explain.** ***(N.C.E.R.T.)***

Ans. Since the R_f value of A is 0·65, therefore, it is less strongly adsorbed as compared to compound B with R_f value of 0·42. Therefore, on extraction of the column, A will elute first.

Q. 13. **Name two compounds which do not contain halogen but give positive Beilstein test.**

Ans. Urea and thiourea give positive Beilstein test due to the formation of volatile cupric cyanide.

Q. 14. **Why is an organic compound fused with sodium for testing halogens, nitrogen, sulphur and phosphours ?** ***(N.C.E.R.T.)***

Ans. The organic compound is fused with sodium metal to convert these elements which are present in the covalent form to ionic form.

Q. 15. **Why is nitric acid added to sodium extract before adding silver nitrate solution for testing halogens ?** ***(N.C.E.R.T.)***

Ans. Sodium extract is boiled with nitric acid to decompose NaCN and Na_2S, if present, otherwise these

$$NaCN + HNO_3 \longrightarrow NaNO_3 + HCN\uparrow$$

$$Na_2S + 2HNO_3 \longrightarrow 2\,NaNO_3 + H_2S\uparrow$$

will react with $AgNO_3$ and hence will interfere with the test as shown below :

$$NaCN + AgNO_3 \longrightarrow \underset{\substack{\text{Silver cyanide}\\ (\textit{White ppt.})}}{AgCN} + NaNO_3$$

$$Na_2S + 2\,AgNO_3 \longrightarrow \underset{\substack{\text{Silver sulphide}\\ (\textit{Black ppt.})}}{Ag_2S} + 2\,NaNO_3$$

Q. 16. **Why it is necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test.** ***(N.C.E.R.T.)***

Ans. For testing sulphur, the sodium extract is acidified with acetic acid because lead acetate is soluble and does not interfere with the test. If H_2SO_4 were used, lead acetate itself will react with H_2SO_4 to form white ppt. of lead sulphate which will interfere with the test.

$$Pb(OCOCH_3)_2 + H_2SO_4 \longrightarrow \underset{(White\ ppt.)}{PbSO_4 \downarrow} + 2\,CH_3COOH$$

Q. 17. What precipitate will be formed when $AgNO_3$ solution is added to chloroform or chlorobenzene ?

Ans. The ppt. of AgCl will not be formed since both these are covalent compounds and hence do not ionize to give Cl^- ions which is the essential requirement for the $AgNO_3$ test.

Q. 18. Will CCl_4 give white precipitate of AgCl on heating it with silver nitrate ? Give reason for your answer. *(N.C.E.R.T.)*

Ans. CCl_4 is a covalent compound. It does not ionize in aqueous solution to form Cl^- ion. Therefore, it does not produce white ppt. of AgCl when $AgNO_3$ solution is added to it.

Very Short Answer Questions CARRYING 1 MARK

Q. 1. How will you separate a mixture of two organic compounds which have different solubilities in the same solvent ?

Ans. By fractional crystallization.

Q. 2. What type of compounds are purified by sublimation ?

Ans. Substances whose vapour pressures become equal to the atomospheric pressure much below their melting points.

Q. 3. How will you separate iodine from sodium chloride ?

Ans. Either by sublimation or by extraction with CCl_4 followed by evaporation.

Q. 4. Will you get any precipitate if you add silver nitrate solution to chloromethane ? If not, why ?

Ans. No, because chloromethane is a covalent compound and hence does not contain Cl^- ions.

Q. 5. Explain why sodium extract (Lassaigne's extract) is boiled with dilute HNO_3 before testing for halogens ?

Ans. To decompose NaCN or Na_2S present in the Lassaigne's extract otherwise these will produce white ppt. with $AgNO_3$ and would thus interfere with the test of halogens.

Q. 6. An organic liquid decomposes below its boiling point. How will you purify it ?

Ans. Distillation under reduced pressure *i.e.* vacuum distillation.

Q. 7. Two volatile compounds A and B differ in their boiling points by 15K. Suggest a suitable method for their separation.

Ans. By fractional distillation.

Q. 8. How will you separate a mixture of *o*- and *p*- nitrophenols ?

Ans. *o*-Nitrophenol is steam volatile while *p*-nitrophenol is not and hence these can be separated by steam distillation.

Q. 9. Name two methods which can be safely used to purify aniline.

Ans. Vacuum distillation and steam distillation.

Q. 10. Can we estimate oxygen in an organic compound ?

Ans. Yes. But usually it is indirectly estimated by subtracting the percentage of all the elements present in an organic compound from 100.

Q. 11. Define molecular formula ? How is it related to empirical formula ?

Ans. Refer to the text.

Q. 12. What type of organic compounds cannot be Kjeldahlised ?

Ans. Compounds containing nitrogen atom in the ring and those compounds in which nitrogen is directly linked either to oxygen or to another nitrogen atom such as in nitro (—NO_2) and azo (—N = N) compounds.

Q. 13. Name the method used for determination of molecular mass of volatile liquids.

Ans. Victor-Meyer's method.

Q. 14. Define the term 'elution' as applied to column chromatography.

Ans. It is the process of extraction of different compounds adsorbed on the column by means of a suitable solvent called eluent.

Q. 15. What conclusion would you draw if during Lassaigne's test a blood red colouration is obtained ?

Ans. The formation of blood red colouration during Lassaigne's test indicates the presence of both N and S.

Q. 16. Write the molecular formula of iron (III) hexacyanoferrate (II). *(N.C.E.R.T.)*

Ans. $Fe_4[Fe(CN)_6]_3$.

Q. 17. Why is a solution of KOH used to absorb CO_2 evolved during the estimation of carbon present in an organic compound. *(N.C.E.R.T.)*

Ans. CO_2 is slightly acidic in nature and hence dissolves in KOH forming K_2CO_3

$$2\,KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

Q. 18. A mixture contains 71 per cent calcium sulphate and 29 per cent camphor. Name a suitable technique of separation of the components of this mixture. *(N.C.E.R.T.)*

Ans. Sublimation.

Q. 19. Suggest a suitable technique of separating naphthalene from kerosene oil present in a mixture. *(N.C.E.R.T.)*

Ans. Simple distillation.

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 16.2.

1. List the different methods used for the purification of organic compounds.
2. What is the principle of column chromatography?
3. Explain the principle of steam distillation. *(N.C.E.R.T.)*
4. What is the difference between distillation, distillation under reduced pressure and steam distillation ? *(N.C.E.R.T.)*
5. Explain the principle of paper chromatography.
6. When is the process of fractional distillation employed ?
7. When is the process of fractional crystallisation employed ?
8. How will you separate a mixture of benzoic acid and naphthalene ?
9. How will you purify sugar which has impurities of sodium chloride ?
10. Name and discuss the principle of the method used to separate a mixture of two organic compounds having different solubilities.
11. Describe the method which can be used to separate two components with different solubilities in a solvent X. *(N.C.E.R.T.)*
12. Glycerol decomposes at its boiling point (563 K). Discuss a method which can be used for its purification.
13. How will you separate two components when : (*a*) their boiling points differ by a few degrees
    (*b*) they are soluble in the same solvent
    (*c*) they are almost immiscible in water but are volatile in steam ?
14. What is the difference between fractional distillation, vacuum distillation and steam distillation ? Support your answer with suitable examples.
15. What is a fractionating column ? How does it help in the separation of miscible liquids ? Give one example.
16. What is the basic principle of chromatography ? Explain with one example the use of column chromatography in the purification of organic compounds.

Sec. 16.3. **17.** Describe the chemistry of Lassaigne's test used for the detection of (*i*) Nitrogen, (*ii*) Halogens, and (*iii*) Sulphur. *(N.C.E.R.T.)*

18. Write chemical equations involved in the detection of sulphur and phosphorus in organic compounds.

19. How will you detect the presence of carbon and hydrogen in an organic compound ?

20. Discuss the chemistry of Beilstein test for the detection of halogens. Why is this test not dependable ?

21. How will you detect the presence of halogens in a given compound ? What is the function of nitric acid in this test ? Give chemical equations.

Sec. 16.4. **22.** Outline the principle of estimation of nitrogen in an organic compound by (*i*) Dumas method (*ii*) Kjeldahl's method. *(N.C.E.R.T.)* For what type of compounds, Kjeldahl's method is not applicable ?

23. How can carbon and hydrogen be estimated in the organic compound ? Give outlines of the method alongwith the method of calculation.

Sec. 16.5. **24.** Discuss the principle and the method of calculation of the following :

(*i*) Silver salt method for determing the molecular mass of organic acids.

(*ii*) Chloroplatinate method for determing the molecular mass of organic bases.

(*iii*) Volumetric method for the determination of molecular mass of acids and bases.

25. What is the basic function of mass spectrometry ? What is its principle ? *(N.C.E.R.T.)*

26. How is a mass spectrum obtained ?

27. How can mass spectrometry be used to find accurate molecular mass of an organic compound ?

28. What is the difference between low and high resolution mass spectrometry.

29. Write short notes on : (*i*) Base peak (*ii*) Daughter ions.

30. Define (*i*) empirical formula and (*ii*) molecular formula. What is the relationship between the two formulae ? *(N.C.E.R.T.)*

31. Explain the steps involved to determine the empirical formula of an organic compound. *(N.C.E.R.T.)*

Long Answer Questions CARRYING 5 or more MARKS

Sec.16.2. **1.** Give a briefl description of the principles of the following processes taking an example in each case.

(*i*) Filtration, (*ii*) Simple distillation, (*iii*) Chromatography, (*iv*) Recrystallisation. *(N.C.E.R.T.)*

(*v*) Sublimation, (*vi*) Distillation under reduced pressure , (*vii*) Steam distillation,

(*viii*) Extraction with a solvent.

Sec. 16.3. **2.** Write the principles and chemical equations involved in the detection of nitrogen, halogens, sulphur and phosphorus present in an organic compound. *(N.C.E.R.T.)*

Sec. 16.4. **3.** Discuss the reactions and the principle underlying the estimation of the following:

(*i*) Carbon and hydrogen

(*ii*) Duma's method for estimation of nitrogen

(*iii*) Kjeldahl's method for the estimation of nitrogen

(*iv*) Carius method for the estimation of halogens and sulphur

(*v*) Phosphorus.

Sec.16.5. **4.** Discuss the principle and the method of calculation of the following.

(*i*) Victor Meyer's method for the determination of molecular masses of volatile organic liquids.

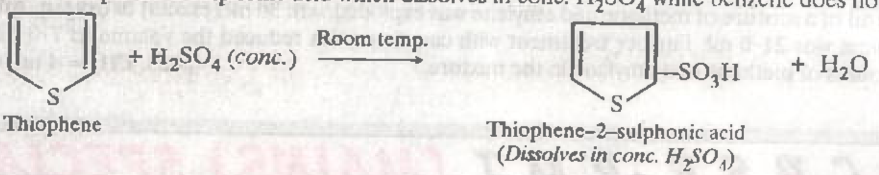
(*ii*) Volumetric method for the determination of molecular masses of acids and bases.

Sec. 16.7. **5.** Discuss the basic principle of mass spectrometry. How is a mass spectrum obtained ? Discuss its use in determining the accurate molecular mass of an organic compound.

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Purification of commercial benzene. Commercial benzene obtained from coal-tar distillation contains 3--5% thiophene as impurity. This thiophene can be removed from commercial benzene by extraction with conc. H_2SO_4. *This purification is based upon the fact that thiophene undergoes sulphonation much more easily than benzene.* Thus, when commerical benzene is shaken with conc. H_2SO_4 in a separating funnel, thiophene undergoes sulphonation to form thiophene-2-sulphonic acid which dissolves in conc. H_2SO_4 while benzene does not



Thiophene

Thiophene–2–sulphonic acid
(*Dissolves in conc.* H_2SO_4)

The H_2SO_4 rayer is removed and the benzene layer is again shaken with fresh conc. H_2SO_4. This process of extraction is repeated 3-4 times till the H_2SO_4 layer does not become black thereby indicating that all the thiophene has been removed. After this treatment, the benzene layer is washed with water to remove the unreacted H_2SO_4, dried over anhydrous $CaCl_2$ and distilled to give pure benzene.

2. Eudiometry *is a direct method for determination of molecular formula of gaseous hydrocarbons without determining the percentage composition of various elements in it and without knowing the molecular mass of the hydrocarbon.*

The actual method used involves the following steps :

(*i*) A known volume of the gaseous hydrocarbon is mixed with an excess (known or unknown volume) of oxygen in the eudiometer tube kept in a trough of mercury.

(*ii*) The mixture is exploded by passing an electric spark between the platinum electrodes. As a result, carbon and hydrogen of the hydrocarbon are oxidised to CO_2 and H_2O vapours respectively.

(*iii*) The tube is allowed to cool to room temperature when water vapours condense to give liquid water which has a negligible volume as compared to the volume of water vapours. Thus, *the gaseous mixture left beind in the eudiometer tube after explosion and cooling consists of only* CO_2 *and unused* O_2.

(*iv*) Caustic potash or caustic soda solution is then introduced into the eudiometer tube which absorbs CO_2 completely and only unused O_2 is left behind.

$$2\,NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Thus, *the decrease in volume on introducing NaOH or KOH solution gives the volume of* CO_2 *formed.*

Sometimes, the volume of O_2 left unused is found by introducing pyrogallol and noting the decrease in volume.

ADDITIONAL USEFUL INFORMATION contd.

Calculations. From the volume of CO_2 formed and the total volume of O_2 used, it is possible to calculate the molecular formula of gaseous hydrocarbon with the help of the following equation.

$$\underset{1\text{ vol}}{C_x H_y} + \underset{(x+y/4)\text{ vol}}{(x + /4)\, O_2} \longrightarrow \underset{x\text{ vol}}{x\, CO_2} + \underset{y/2\text{ vol}}{y/2\, H_2O}$$

(negligible volume on condensation)

From the above equation, it is evident that for one volume of hydrocarbon.

(*i*) $(x + y/4)$ volume of O_2 is used (*ii*) x volume of CO_2 is produced.

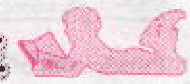
(*iii*) $y/2$ volume of H_2O vapours is produced which condense to give liquid H_2O with negligible volume.

(*iv*) contraction on explosion and cooling $= [(1 + x + y/4) - x] = 1 + y/4$

By equating the experimental values with the theoretical values from the above combustion equation, the values of x and y and hence the molecular formula of the gaseous hydrocarbon can be easily determined.

3. Molarity × Mol. wt. = Normality × Eq. wt.

PROBLEMS FOR PRACTICE



1. 10 ml of a gaseous hydrocarbon were mixed with 100 ml of oxygen and exploded in a eudiometer tube. The volume of the residual gases was 95 ml of which 20 ml was absorbed by caustic soda and the remainder by pyrogallol. Find out the molecular formula of the gas. **[Ans. C_2H_2]**
2. 9·0 ml of a mixture of methane and ethylene was exploded with 30 ml (excess) of oxygen. After cooling, the volume was 21·0 ml. Further treatment with caustic potash reduced the volume to 7·0 ml. Find out the amounts of methane and ethylene in the mixture. **[Ans. CH_4 = 4 ml, C_2H_4 = 5 ml]**

C.B.S.E.-P.M.T. (MAINS) SPECIAL

A. SUBJECTIVE QUESTIONS
(Common with I.I.T.)

Q. 1. Without using column chromatography, how will you separate a mixture of camphor and benzoic acid ?

Ans. Sublimation cannot be used since both camphor and benzoic acid sublime on heating. Therefore, a chemical method using $NaHCO_3$ solution is used when benzoic acid dissolves leaving camphor behind. The filtrate is cooled and then acidified with dil. HCl to get benzoic acid.

Q. 2. Will sodium cyanide give a positive Lassaigne's test for nitrogen ?

Ans. Yes. During fusion with Na metal, the N of the organic compound is actually converted into NaCN which is the primary requirement for Lassaigne's test for nitrogen.

Q. 3. How will you test the presence of nitrogen in hydrazine ?

Ans. If hydrazine (NH_2NH_2) is fused with Na metal, it does not form NaCN since it does not contain carbon and hence will not give +ve test for nitrogen. In order to test the presence of N in such compounds, during fusion with Na, some charcoal or preferably starch (which contains C but not N, S, halogens etc.) is added. Under these conditions, C of starch or charcoal combines with N of the compound to form NaCN which will now give a +ve test for nitrogen.

Q. 4. Lassaigne's test is not shown by diazonium salts. Why ?

Ans. Diazonium salts usually lose N_2 on heating much before they have a chance to react with fused sodium metal. Therefore, diazonium salts do not show positive Lassaigne's test for nitrogen.

Q. 5. **Sometimes a red colour is not produced in the Lassaigne's test even if both nitrogen and sulphur are present in the organic compound. Explain.**

Ans. In principle, if the organic compound contains both N and S, sodium thiocyanate should be formed in Lassaigne's test and this should give blood red colouration with $FeCl_3$

$$\underbrace{Na + C + N + S}_{\text{Organic compound}} \xrightarrow{\text{Fusion}} \underset{\text{Sod. thiocyanate}}{NaCNS}$$

$$3\,NaCNS + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric thiocyanate}\\ \textit{(Blood red colouration)}}}{Fe(SCN)_3} + 3\,NaCl$$

However, if blood red colouration is not obtained, it does not necessarily mean that S is absent. This is because in presence of excess of sodium metal, sodium thiocyanate initially formed, decomposes to form sodium cyanide and sodium sulphide.

$$2\,Na + 2\,NaCNS \xrightarrow{\Delta} NaCN + Na_2S$$

As a result, blood red colouration is not obtained.

Q. 6. **Why is a freshly prepared saturated solution of ferrous sulphate used in the Lassaigne's test for nitrogen ?**

Ans. On keeping aq. $FeSO_4$ solution, it undergoes hydrolysis to form basic ferric sulphate

$$4\,FeSO_4 + 2\,H_2O + O_2 \longrightarrow 4\,Fe(OH)SO_4$$

The pale yellow colour of Fe^{3+} ions interferes with the light green colour usually obtained in Lassaigne's test.

Q. 7. **What is the difference between vapour density and density ? Explain.**

Ans. Vapour density is just a ratio between the mass of a certain volume of a gas or vapours of a volatile substance under certain conditions of temperature and pressure (say STP) to the mass of the same volume of H_2 under same conditions of temperature and pressure. It, therefore, has no units and is just a number. In contrast, density of a substance (solid, liquid or gas) is the mass of one unit volume of the substance. It has, therefore, units of either g/ml or Kg/L.

B. PROBLEMS

Problem 1. **An aromatic compound contains 69·4% carbon and 5·8% hydrogen. A sample of 0·303 g of this compound was analysed for nitrogen by Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0·05 M H_2SO_4. The excess of the acid required 25 ml of 0·1 M NaOH for neutralization. Determine the molecular formula of the compound if its mass is 121. Draw the possible structures for this compound.**

Solution. Step 1. To calculate the % of N

Volume of 0·05 M H_2SO_4 taken = 50·0 ml

Let the volume of 0·05 M H_2SO_4 left unused = v ml

Volume of 0·1 M NaOH required for neutralization of excess acid = 25·0 ml

Applying molarity equation,

$$n_a\,M_a\,V_a\,(H_2SO_4) = n_b\,M_b\,V_b\,(NaOH)$$

i.e., $\quad 2 \times 0{\cdot}05 \times v = 1 \times 0{\cdot}1 \times 25$

or $\quad v = 25$ ml

∴ Volume of 0·05 M H_2SO_4 used

$$= 50 - 25 = 25 \text{ ml}$$

$$\%N = \frac{1{\cdot}4 \times 25 \times 0{\cdot}05 \times 2}{0{\cdot}303} = 11{\cdot}55$$

Step 2. *To determine the molecular formula of the compound*

$$C : H : N : O = \frac{69{\cdot}4}{12} : \frac{5{\cdot}8}{1} : \frac{11{\cdot}55}{14} : \frac{13{\cdot}25}{16}$$

$$= 5{\cdot}78 : 5{\cdot}8 : 0{\cdot}825 : 0{\cdot}828$$

$$= 7 : 7 : 1 : 0$$

∴ E.F. of the compound = C_7H_7NO

E.F. wt. = 7 × 12 + 7 × 1 + 14 + 16

= 121

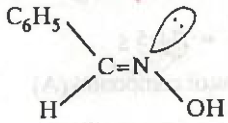
Mol. mass of the compound = 121

∴ M.F. of the compound = $C_7H_7NO \times \frac{121}{121}$

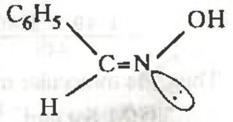
= C_7H_7NO

Step 3. *To draw the possible structures of the compound*

Since the compound is aromatic, it must contain a C_6H_5 group. In other words, the compound may be written as $C_6H_5CH_2NO$ or $C_6H_5CH{=}NOH$. Since oximes show geometrical isomerism therefore, possible structures of the compound are :



syn−Benzaldoxime



Anti−Benzaldoxime

Problem 2. **Two compounds A and B give on analysis, C = 88·82% and H = 11·18%. Both decolourize Br_2 in CCl_4 solution. Compound A gives a precipitate with ammoniacal silver nitrate and on reduc-**

tive ozonolysis gives 2-ketobutanal. Compound B does not give a precipitate with ammoniacal silver nitrate but on reductive ozonolysis gives formaldehyde and glyoxal. Deduce the structure of both the compounds.

Solution. (*i*) $C : H = \frac{88 \cdot 82}{12} : \frac{11 \cdot 18}{1}$

$= 7 \cdot 41 : 11 \cdot 18$

$= 2 : 3$

E.F. of the compounds A and B = C_2H_3 and the lowest M.F. of the compounds = $2 \times C_2H_3 = C_4H_6$.

(*ii*) The M.F. C_4H_6 suggests that A and B may contain a triple bond or two double bonds.

This is supported by the observation that both A and B decolourize Br_2 in CCl_4.

(*iii*) Since compound A gives a white ppt. with ammoniacal $AgNO_3$ solution, therefore, *it must be a terminal alkyne*, *i.e.*, $CH_3CH_2C \equiv CH$,

$$\underset{\text{1-Butyne, A}}{CH_3CH_2C \equiv CH} + [Ag(NH_3)_2]^+ NO_3^-$$

$$\longrightarrow \underset{\substack{\text{Silver 1-butyride} \\ \textit{(White ppt.)}}}{CH_3CH_2C \equiv CAg} + HNO_3$$

(*iv*) The structure of A is further supported by its ozonolysis product.

$$CH_3CH_2C \equiv CH \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3/CH_2Cl_2} \underset{\text{2-Ketobutanal}}{CH_3CH_2COCHO}$$

(*v*) Since compound **B** does not produce a white ppt. with ammoniacal silver nitrate, it may have any one of the following three structures :

$$\underset{\text{2-Butyne}}{CH_3—C \equiv C—CH_3} \qquad \underset{\text{1, 2-Butadiene}}{CH_3—CH_2 = C = CH_2}$$

$$\underset{\text{1, 3-Butadiene}}{CH_2 = CH—CH = CH_2}$$

(*vi*) Since the ozonolysis products of **B** are formaldehyde and glyoxal, therefore, compound **B** is *1, 3-butadiene*

$$\underset{\text{1, 3-Butadiene B}}{CH_2 = CH—CH = CH_2} \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3/CH_2Cl_2}$$

$$\underset{\text{Formaldehyde}}{CH_2 = O} + \underset{\text{Glyoxal}}{O = CH—CH = O} + O = CH_2$$

I.I.T. (MAINS) SPECIAL

Q. 1. A chloro compound (A) showed the following properties :

(i) Decolourized bromine in CCl_4

(ii) Absorbed hydrogen catalytically

(iii) Gave a white precipitate with ammoniacal cuprous chloride

(iv) When vapourized, 1·49 g of (A) gave 448 ml of vapours at STP. Identify (A) and write down the equation for reaction of step (iii).

(Roorkee, 1991)

Ans. Step 1. To determine the molecular mass of compound (A)

448 ml of vapours at STP weigh = 1·49 g

∴ 22400 ml of vapours at STP will weigh

$$= \frac{1 \cdot 49 \times 22400}{448} = 74 \cdot 5 \text{ g}$$

Thus, the molecular mass of compound (A)

$= 74 \cdot 5 \text{ g mol}^{-1}$

Step 2. To identify the functional groups

(*i*) Since (A) decolourizes Br_2 / CCl_4, therefore, (A) must be an unsaturated compound. This is further supported by the fact that (A) also absorbs hydrogen catalytically.

(*ii*) Since (A) gave a precipitate with ammoniacal CuCl, it must be a terminal acetylene, *i.e.* it must contain the grouping-$C \equiv CH$

Step 3. To determine the molecular formula of the compound (A)

Molecular mass of-$C \equiv CH$ group

$= 12 + 12 + 1 = 25$ a.m.u.

Atomic mass of chlorine = 35·5 a.m.u.

Molecular mass of the compound = 74·5 g mol^{-1}

∴ Molecular mass of the remaining portion of compound (A)

$= 74 \cdot 5 - 25 - 35 \cdot 5 = 14$

Since the molecular mass of a CH_2 group is 14, therefore, the compound (A) contains a CH_2 group.

Now compound (A) contains a chlorine atom, one CH_2 group and one terminal acetylenic group, *i.e.*, $-C \equiv CH$, therefore, the structure of the organic compound is

$ClCH_2C \equiv CH$ (3-chloroprop-1-yne).

Step 4. To write the equation for the reaction of step (iii)

$$\underset{\text{3–Chloroprop-1-yne}}{ClCH_2-C\equiv CH} + CuCl + NH_4OH \longrightarrow \underset{\substack{\text{Copper 3–chloroprop–1–ynide}\\ \textit{(Red ppt.)}}}{ClCH_2C\equiv CCu} + NH_4Cl + H_2O$$

Q. 2. A hydrocarbon (A) [C, 9·56%, vapour density 53] was subjected to vigorous oxidation to give a dibasic acid (B). 0·10 g of (B) required 24·1 ml of 0·05 N NaOH for complete neutralization. Nitration of (B) gave a single mono nitro derivative. When (B) was heated strongly with sodalime it gave benzene. Identify (A) and (B) with proper reasoning and also give their structures. ***(Roorkee 1991)***

Ans. **Step 1.** *To determine the molecular formula of the hydrocarbon (A)*

$$C : H = \frac{90\cdot56}{12} : \frac{9\cdot44}{1\cdot0} = 7\cdot55 : 9\cdot44$$
$$= 4 : 5$$

Thus, the E.F. of the hydrocarbon (A) = C_4H_5

E.F. wt. = $4 \times 12 + 5 \times 1 = 53$

But V.D. of A = 53

∴ Mol. mass of A = $2 \times 53 = 106$

Thus, M.F. of hydrocarbon (A)

$$= C_4H_5 \times \frac{106}{53} = C_8H_{10}.$$

Step 2. *To determine the molecular mass of the diabasic acid (B)*

24·1 ml of 0·05 N NaOH neutralize acid = 0·1 g

∴ 1000 ml of 1 N NaOH will neutralize acid

$$= \frac{0\cdot1 \times 1000}{24\cdot1 \times 0\cdot05}$$
$$= 83\ (\textit{approx})$$

Thus, Eq. wt. of dibasic acid (B) = 83

∴ Mol. wt. of dibasic acid (B)

$$= 83 \times 2 = 166\ \text{g mol}^{-1}$$

Step 3. *To determine the molecular formula and structure of the dibasic acid (B)*

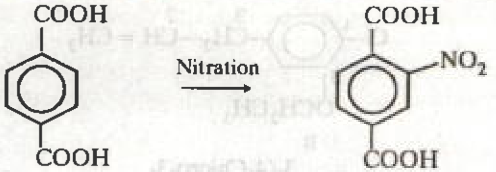
(*i*) Let the M.F. of the dibasic acid (B)

$$= R(COOH)_2$$

∴ $R + 2 \times 45 = 166$ or $R = 76$

Since on strong heating with sodalime, acid (B) gives benzene, *therefore, R must be C_6H_4* and the M.F. of the acid (B) = $C_6H_4(COOH)_2$. In other words, (B) is benzenedicarboxylic acid.

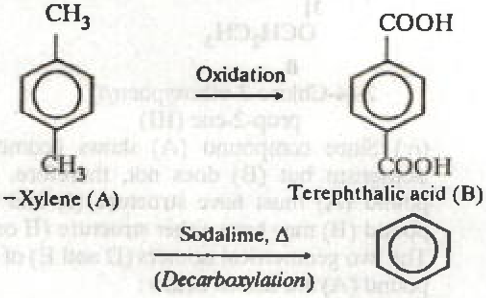
(*ii*) Since the dibasic acid (B) on nitration gave a single mono-nitroderivative, therefore, B is a symmetrical dibasic acid, *i.e., benzene-1, 4-dicarboxylic acid or terephthalic acid.*



Benzene−1, 4−dicarboxylic acid (B) (Terephthalic acid)

2−Nitrobenzene−1, 4−dicarboxylic acid

(*iii*) If (B) is benzene-1, 4-dicarboxylic acid, then the hydrocarbon (A) must be *p*-xylene



p−Xylene (A)

Terephthalic acid (B)

Benzene

Q. 3. Two isomeric compounds (A) and (B) have the same molecular formula $C_{11}H_{13}OCl$. Both are unsaturated and yield the same compound (C) on catalytic hydrogenation and produce 4-chloro-3-ethoxybenzoic acid on vigorous oxidation. (A) exists in geometrical isomers (D) and (E), but not (B). Give structures of (A) to (E) with proper reasoning. ***(Roorkee 1994)***

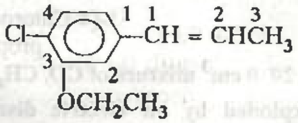
Ans. (*i*) Since (A) and (B) on catalytic hydrogenation give the same compound (C), (A) and (B) are isomers.

(*ii*) Since A and B (M.F. $C_{11}H_{13}OCl$) on vigorous oxidation give the same monobasic acid, *i.e.* 3-chloro-4-ethoxybenzoic acid, having the following structure ;

M.F. $C_9H_9O_3Cl$,

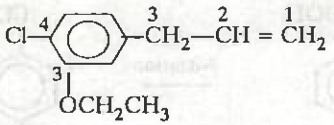
therefore, both (A) and (B) have one side chain in place of COOH group. Further, since the acid has 9 carbon atoms and the compounds (A and B) have 11 carbon atoms, therefore, this side chain consists of three carbon atoms.

(*iii*) The various possible structures for compounds A and B are :



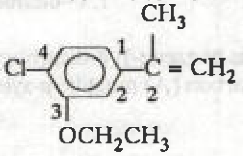
A

1−(4−Chloro−3−ethoxyphenyl) prop−1−ene (I)



B

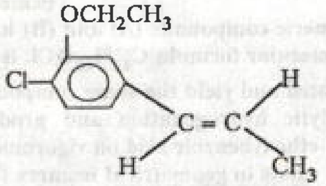
3-(4-Chloro-3-ethoxyphenyl)prop-3-ene (II)



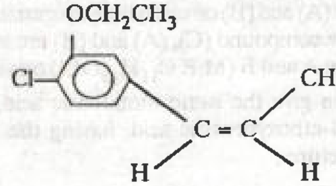
B

2-(4-Chloro-3-ethoxyphenyl) prop-2-ene (III)

(*iv*) Since compound (A) shows geometrical isomerism but (B) does not, therefore, compound (A) must have structure (I) and compound (B) may have either structure (II or III). The two geometrical isomers (D and E) of compound (A) are shown below :

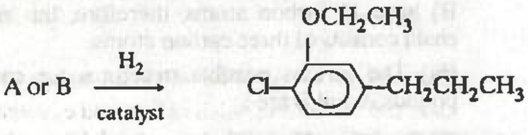


trans-1-(4-Chloro-3-ethoxyphenyl) prop-1-ene (D)



cis-1-(4-Chloro-3-ethoxyphenyl)prop-1-ene (E)

(*v*) Since compounds (A and B) on catalytic hydrogenation give the same compound (C), *therefore, both (A) and (B) have the same structure of the side chain.* In other words, compound (B) has structure (II) and not (III).



1-(4-Chloro-3-ethoxyphenyl) propane (C)

Q. 4. A 20·0 cm^3 mixture of CO, CH$_4$ and He gases is exploded by an electric discharge at room temperature with excess of oxygen. The volume contraction is found to be 13·0 cm^3. A further contraction of 14·0 cm^3 occurs when the residual gas is treated with KOH solution. Find out the composition of the gases mixture.

(I.I.T. 1995)

Ans. Let the vol. of CO in the mixture = x cm^3 and that of CH$_4$ = y cm^3

∴ Vol. of He in the mixture = 20 − ($x + y$) cm^3

Contraction in vol. due to explosion and cooling = 13·0 cm^3 and contraction in volume due to absorption in KOH = 14·0 cm^3 = vol. of CO$_2$ produced.

The chemical equations representing combustion of CO and CH$_4$ respectively are :

$$\underset{x\ \text{cm}^3}{2\,CO} + \underset{x/2\ \text{cm}^3}{O_2} \longrightarrow \underset{x\ \text{cm}^3}{2\,CO_2} \quad ...(i)$$

$$\underset{y\ \text{cm}^3}{CH_4} + \underset{2y\ \text{cm}^3}{2\,O_2} \longrightarrow \underset{y\ \text{cm}^3}{CO_2} + \underset{\text{neg. volume}}{2\,H_2O} \quad ...(ii)$$

Contraction in volume due to reaction (*i*)

$$x + \frac{x}{2} - x = \frac{x}{2}\ \text{cm}^3$$

Contraction in volume due to reaction (*ii*)

$$y + 2y - y = 2y\ \text{cm}^3$$

∴ Total contraction in volume

$$= \left(\frac{x}{2} + 2y\right)\ \text{cm}^3$$

But $\frac{x}{2} + 2y = 13$ (*Given*) ...(*iii*)

Total volume of CO$_2$ produced in reactions (*i*) and (*ii*)

$$= (x + y)\ \text{cm}^3$$

But $x + y = 14$ (*Given*) ...(*iv*)

Solving (*iii*) and (*iv*) for x and y, we have,

$$x = 10 \cdot 0\ \text{cm}^3 \text{ and } y = 4 \cdot 0\ \text{cm}^3$$

Thus, volume of CO = 10 cm^3, of CH$_4$ = 4 cm^3 and of He = 20 − (10 + 4) = 6 cm^3.

Q. 5. A hydrocarbon (A) of molecular weight 54 reacts with an excess of Br$_2$ in CCl$_4$ to give a compound (B) whose molecular weight is 593% more than that of (A). However, on catalytic hydrogenation, with excess of hydrogen, (A) forms (C) whose molecular weight is only 7·4% more than that of (A). (A) reacts with CH$_3$CH$_2$Br in the presence of NaNH$_2$ to give another hydrocarbon (D) which on ozonolysis yields diketone (E). (E) on oxidation gives propionic acid. Give structures of (A) to (E) with reasons.

(Roorkee 1997)

Ans. Step 1. *To determine the molecular weights of compounds (B) and (C).*

(*i*) The mol. wt. of compound (A) is 54 while that of compound (B) which it gives on treatment with an excess of Br_2 in CCl_4 is 593% more than that of A.

$$\therefore \text{ Mol. wt. of (B)} = \frac{(100 + 593)}{100} \times 54$$

$$= \mathbf{374{\cdot}22}$$

Thus, the increase in weight due to addition of Br atoms = 374·22—54·0

$$= \mathbf{320{\cdot}22.}$$

Since the atomic weight of Br is 80, therefore, the number of Br atoms added = 320·22/80

$$= \mathbf{4}$$

Therefore, the hydrocarbon (A) must be *an alkyne.*

(*ii*) Further since the mol. wt. of compound (C) which hydrocarbon (A) gives on catalytic hydrogenation is only 7·4% more than that of (A), therefore, the mol. wt. of (C)

$$= \frac{(100 + 7{\cdot}4) \times 54}{100} = 57{\cdot}994$$

$$= \mathbf{58} \text{ (approx.)}$$

Thus, the increase in weight due to addition of H-atoms = 58—54 = **4**

Since the atomic weight of H is 1, therefore, the number of H-atoms added during catalytic hydrogenation = 4/1 = **4**

Therefore, the hydrocarbon (A) must be *an alkyne.*

Step 2. *To determine the structure of the hydrocarbons (A), (B), (C) and (D).*

(*i*) The two possible structure for the hydrocarbon (A), *i.e.* an alkyne with mol. wt. 54 (M.F. C_4H_6) are :

$$CH_3CH_2—C \equiv CH$$

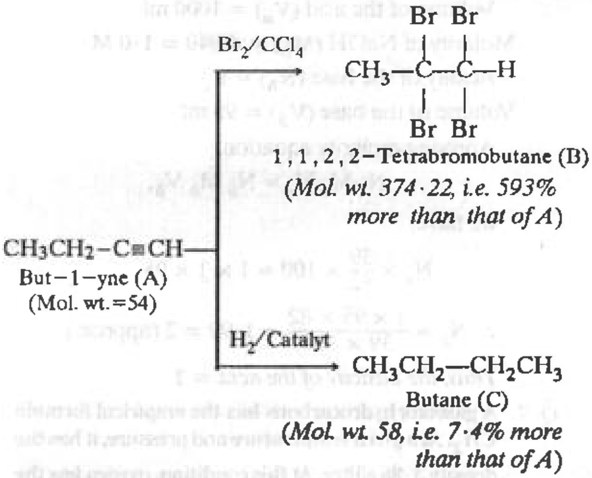
But−1−yne (I)

$$CH_3—C \equiv C—CH_3$$

But−2−yne (II)

(*ii*) Since (A) reacts with CH_3CH_2Br in presence of $NaNH_2$ to give another hydrocarbon (D), therefore, (A) must be a *terminal alkyne, i.e. but-1-yne* and not but-2-yne.

(*iii*) If hydrocarbon (A) is but-1-yne, then the structure of the compounds (B), (C) and (D) may be worked out as follows :



1, 1, 2, 2−Tetrabromobutane (B)

(Mol. wt. 374·22, i.e. 593% more than that of A)

Butane (C)

(Mol. wt. 58, i.e. 7·4% more than that of A)

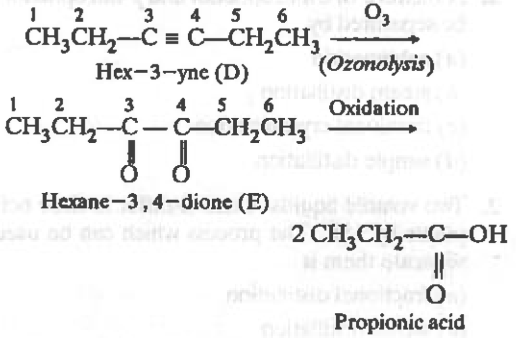
Further,

$$A \xrightarrow[-NH_3]{NaNH_2} CH_3CH_2—C \equiv C^- Na^+ \xrightarrow[-NaBr]{CH_3CH_2-Br}$$

Sod. but−1−ynide

Step 3. *To determine the structure of the diketone (E).*

Since the hydrocarbon (D) *i.e.* hex-3-yne on ozonolysis gives a diketone (E), which on further oxidation gives propionic acid, therefore, *the diketone (E) must be hexane-3, 4-dione* as explained below :



$$\overset{1}{C}H_3\overset{2}{C}H_2—\overset{3}{C} \equiv \overset{4}{C}—\overset{5}{C}H_2\overset{6}{C}H_3 \xrightarrow[\text{(Ozonolysis)}]{O_3}$$

Hex−3−yne (D)

$$\overset{1}{C}H_3\overset{2}{C}H_2—\underset{\|}{\overset{3}{C}}\!\!\underset{O}{}—\underset{\|}{\overset{4}{C}}\!\!\underset{O}{}—\overset{5}{C}H_2\overset{6}{C}H_3 \xrightarrow{\text{Oxidation}} 2\,CH_3CH_2—\underset{\underset{O}{\|}}{C}—OH$$

Hexane−3, 4−dione (E)

Propionic acid

Thus, (A) = but-1-yne, (B) = 1, 1, 2, 2-tetrabromobutane, (C) = butane, (D) = hex-3-yne and (E) = hexane -3, 4-dione.

Q. 6. **The formula weight of an acid is 82·0. In a titration, 100 cm^3 of a solution of this acid containing 39·0 g of the acid per litre were completely neutralized by 95·0 cm^3 of aqueous NaOH containing 40·0 g of NaOH per litre. What is the basicity of the acid ?** *(Roorkee 2000)*

Ans. Molarity of the acid (M_a) = 39/82 M

Let the basicity of the acid = N_a

Volume of the acid (V_a) = 1000 ml

Molarity of NaOH (M_b) = 40/40 = 1·0 M

Acidity of the base (N_b) = 1

Volume of the base (V_b) = 95 ml

Applying molarity equation,

$$N_a M_a V_a = N_b M_b V_b,$$

we have,

$$N_a \times \frac{39}{82} \times 100 = 1 \times 1 \times 95$$

$$\therefore\ N_a = \frac{1 \times 95 \times 82}{39 \times 100} = 1·99 = 2 \text{ (approx.)}$$

Thus, the basicity of the acid = 2

Q. 7. **A gaseous hydrocarbons has the empirical formula CH_2. At a given temperature and pressure, it has the density 3·86 g/litre. At this condition, oxygen has the density 2·21 g/litre. Find out the molecular formula of the compound.** ***(West Bengal J.E.E. 2001)***

Ans. If the density is 2·21 g/litre

then mol. wt. of compound (*i.e.* O_2) = 32

If the density is 3·86 g/litre, then

the mol. wt. of the gaseous hydrocarbon

$$= \frac{32 \times 3·86}{2} = 55·89$$

$$= \text{approx. } 56 \text{ g mol}^{-1}.$$

∴ E.F. wt. of gaseous hydrocarbon (CH_2)

= 14 amu

Now $n = \frac{\text{M.W.}}{\text{E.F. wt.}} = \frac{56}{14} = 4$

∴ M.F. of gaseous hydrocarbon = 4 × CH_2

= C_4H_8

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. Naphthalene can be easily purified by

(*a*) sublimation

(*b*) crystallisation

(*c*) distillation

(*d*) extraction with a solvent.

2. A mixture of *o*-nitrophenol and *p*-nitrophenol can be separated by

(*a*) sublimation

(*b*) steam distillation

(*c*) fractional crystallization

(*d*) simple distillation.

3. Two volatile liquids A and B differ in their boiling points by 15K. The process which can be used to separate them is

(*a*) fractional distillation

(*b*) steam distillation

(*c*) distillation under reduced pressure

(*d*) simple distillation.

4. Separation of two substances by fractional crystallization depends upon their difference in

(*a*) densities (*b*) solubilities

(*c*) melting points (*d*) boiling points.

5. Glycerol which decomposes at its boiling point can be purified by

(*a*) steam distillation

(*b*) simple distillation

(*c*) distillation under reduced pressure

(*d*) fractional distillation.

6. The separation of the constituents of a mixture by column chromatography depends upon their

(*a*) different solubilities

(*b*) different boiling points

(*c*) different refractive indices

(*d*) differential adsorption.

7. In Lassaigne's test, a blood red colouration indicates the presence of

(*a*) nitrogen

(*b*) sulphur

(*c*) both nitrogen and sulphur

(*d*) both nitrogen and halogens.

8. Refining of petroleum involves the process of

(*a*) simple distillation

(*b*) steam distillation

(*c*) distillation under reduced pressure

(*d*) fractional distillation.

ANSWERS

1. ***a*** **2.** ***b*** **3.** ***a*** **4.** ***b*** **5.** ***c*** **6.** ***d*** **7.** ***c*** **8.** ***d***

9. A substance which is insoluble in water and possesses a vapour pressure of 10-15 mm Hg at 373 K can be conveniently purified by
(*a*) sublimation (*b*) crystallization
(*c*) distillation (*d*) steam distillation.

10. An organic substance from its aqueous solution can be separated by
(*a*) distillation (*b*) steam distillation
(*c*) solvent extraction (*d*) fractional distillation.

11. In steam distillation, the vapour pressure of the volatile compound is
(*a*) equal to atmospheric pressure
(*b*) less than atmospheric pressure
(*c*) more than atmospheric pressure
(*d*) exactly half of the atmospheric pressure.

12. 0·2 g of an organic compound on complete combustion produces 0·44 g of CO_2, then the percentage of carbon in it is
(*a*) 50 (*b*) 60
(*c*) 70 (*d*) 80.

13. The formula of the compound which gives violet colour in Lassaigne's test for sulphur with sodium nitroprusside is
(*a*) $Na_4[Fe(CN)_5NOS]$ (*b*) $Na_3[Fe(CN)_5NOS]$
(*c*) $Na_2[Fe(CN)_5S]$ (*d*) $Na_4[Fe(CN)_4S]$.

14. In Kjeldahl's method, the nitrogen present in the organic compound is converted into
(*a*) gaseous ammonia (*b*) ammonium sulphate
(*c*) ammonium phosphate
(*d*) ammonium nitrate.

15. The ratio of molecular mass to empirical formula weight in case of glucose is
(*a*) 2 (*b*) 4
(*c*) 6 (*d*) 8.

16. The empirical formula of a substance is CH_2O, its vapour density is 60, what is the molecular formula?
(*a*) CH_2O (*b*) $C_2H_4O_2$
(*c*) $C_3H_6O_3$ (*d*) $C_4H_8O_4$.

17. An organic compound having carbon, hydrogen and sulphur contains 4% sulphur. The minimum molecular weight of the compound is
(*a*) 200 (*b*) 400
(*c*) 600 (*d*) 800.

18. The molecular mass of a compound containing only one nitrogen atom can be
(*a*) 73 (*b*) 74 (*c*) 146 (*d*) 148.

19. A gaseous hydrocarbon having empirical formula as CH_2 has a density of 1·25 *g*/L at NTP. The molecular formula of the hydrocarbon is
(*a*) C_2H_2 (*b*) C_2H_4
(*c*) C_2H_6 (*d*) C_3H_8.

20. 0·59 *g* of the silver salt of an organic acid (molecular weight 210) on ignition gave 0·36 *g* of pure silver. The basicity of the acid is
(*a*) 1 (*b*) 2
(*c*) 3 (*d*) 4.

21. If two compounds have the same empirical formula but different molecular formulae, they must have
(*a*) different percentage composition
(*b*) different molecular weight
(*c*) same viscosity
(*d*) same vapour density. *(I.I.T. 1987)*

22. The element X (atomic weight = 75) and Y (atomic weight = 16) combine to give a compound containing 75·8% X. The molecular formula of the compound is
(*a*) XY (*b*) X_2Y
(*c*) X_2Y_2 (*d*) X_2Y_3.
(M.L.N.R. Allahabad 1991)

23. A gaseous hydrocarbon has 85% carbon and vapour density of 28. The possible formula of the hydrocarbon will be
(*a*) C_3H_6 (*b*) C_2H_4
(*c*) C_2H_2 (*d*) C_4H_8.
(Haryana C.E.E.T. 1991)

24. Distillation under reduced pressure is employed for
(*a*) C_6H_6 (*b*) Petrol
(*c*) $CH_2OHCHOHCH_2OH$
(*d*) Organic compounds used in medicine.
(C.P.M.T. 1992)

25. Which of the following fertilizers has the highest nitrogen percentage ?

ANSWERS

9. *d* **10.** *c* **11.** *b* **12.** *b* **13.** *a* **14.** *b* **15.** *c* **16.** *d* **17.** *d* **18.** *a*
19. *b* **20.** *c* **21.** *b* **22.** *d* **23.** *d* **24.** *c*

(*a*) Ammonium sulphate
(*b*) Calcium cyanamide
(*c*) Urea
(*d*) Ammonium nitrate. *(C.B.S.E. P.M.T. 1993)*

26. 59 g of an amide obtained from a carboxylic acid, RCOOH, upon heating with alkali liberated 17g of ammonia. The acid is
(*a*) Formic acid (*b*) Acetic acid
(*c*) Propionic acid (*d*) Benzoic acid.
(I.S.M. Dhanbad, 1994)

27. The property which serves as a criterion of purity of an organic compound is
(*a*) Solubility in water (*b*) Melting point
(*c*) Density (*d*) Crystalline nature.

28. Complete combustion of a sample of hydrocarbon gives 0·66 g of CO_2 and 0·36 g of H_2O. The empirical formula of the compound is
(*a*) CH_2 (*b*) C_3H_4
(*c*) C_3H_8 (*d*) C_6H_8.
(D.C.E. 1994)

29. The following is the percentage composition of a compound ; Na = 16·08%, C = 4·19%, O=16·78% and H_2O = 62·95%
Its molecular formula is
(*a*) Na_2CO_3 (*b*) $Na_2CO_3.H_2O$
(*c*) $Na_2CO_3.10H_2O$ (*d*) $Na_2CO_3.5H_2O$.
(B.H.U. 1994)

30. The most satisfactory method to separate sugars is to use
(*a*) Fractional crystallization
(*b*) Sublimation (*c*) Chromatography
(*d*) Benedict's reagent. *(D.P.M.T. 1994)*

31. The Lassaigne's extract is boiled with dil. HNO_3 before testing for halogens because
(*a*) Silver halides are soluble in HNO_3
(*b*) Na_2S and NaCN are decomposed by HNO_3
(*c*) Ag_2S is soluble in HNO_3
(*d*) AgCN is soluble in HNO_3. *(A.F.M.C. 1994)*

32. The compound that does not give a blue colour in Lassaigne's test is
(*a*) Aniline (*b*) Glycine
(*c*) Hydrazine (*d*) Urea.
(A.I.I.M.S. 1994)

33. 0·24 g of a volatile liquid upon vapourization gives 45 ml of vapours at NTP. What will be the vapour density of the substance ? (Density of $H_2 = 0·089\ g\ L^{-1}$).
(*a*) 95·39 (*b*) 5·993
(*c*) 95·93 (*d*) 59·93
(C.B.S.E. P.M.T. 1996)

34. An organic compound containing C, H and N gave the following analysis :
C=40%, H=13·33%, N=46·67%. What would its empirical formula ?
(*a*) C_2H_7N (*b*) $C_2H_7N_2$
(*c*) CH_4N (*d*) CH_3N
(C.B.S.E. P.M.T. 1998, 99)

35. Empirical formula of a compound is CH_2O. If its molecular weight is 180, then the molecular formula of the compound is
(*a*) $C_6H_{12}O_6$ (*b*) $C_5H_{10}O_5$
(*c*) $C_3H_6O_3$ (*d*) $C_4H_8O_4$.
(A.F.M.C. 1999)

36. The Beilstein test for organic compounds is used to detect
(*a*) Nitrogen (*b*) Sulphur
(*c*) Carbon (*d*) Halogens.
(A.F.M.C. 1999)

37. Two organic compounds A and B both containing C and H yield, on analysis, the same percent composition by weight :
C = (12/13) × 100%, H = (1/13) × 100%
A decolourises bromine water, B does not. Identify A and B
(*a*) A = C_2H_2, B = C_6H_6
(*b*) A = C_6H_6, B = C_2H_2
(*c*) A = C_2H_4, B = C_2H_6
(*d*) A = C_2H_2, B = C_3H_8. *(C.P.M.T. 2000)*

38. How should 100 ml of carbon tetrachloride be added to extract maximum amount of iodine ?
(*a*) 100 ml once (*b*) 50 ml twice
(*c*) 25 ml four times (*d*) 10 ml ten times.
(C.P.M.T. 2000)

39. Number of grams of oxygen in 32·2 *g* of $Na_2SO_4.10\ H_2O$ is
(*a*) 20·8 (*b*) 22·4

ANSWERS

25. *c* **26.** *b* **27.** *b* **28.** *c* **29.** *c* **30.** *c* **31.** *b* **32.** *c* **33.** *d* **34.** *a*
35. *a* **36.** *d* **37.** *a* **38.** *d*

(*c*) 2·24 (*d*) 12·08.

(Haryana C.E.E.T. 2000)

40. The haemoglobin contains 0·33% of iron by weight. Its molecular weight is 67200. The number of iron atoms in each molecule is (atomic weight of Fe = 56)

(*a*) 2 (*b*) 3

(*c*) 4 (*d*) 5.

(C.B.S.E. P.M.T. 1998 ; M.P.C.E.E. 2000)

41. 0·1914 *g* of an organic acid is dissolved in about 20 ml of water. 25 ml of 0·12 N NaOH is required for the complete neutralization of the acid solution. The equivalent weight of the acid is

(*a*) 65 (*b*) 64

(*c*) 63·80 (*d*) 62·50.

(M.P.C.E.E. 2000)

42. The density of air is 0·00130 *g*/ml. The vapour density of air will be

(*a*) 0·00065 (*b*) 0·65

(*c*) 14·4816 (*d*) 14·56. *(D.C.E. 2000)*

43. A compound has C, H, N in the following percentage C = 40%, H = 13·33%, N = 46·67%

What is its empirical formula ?

(*a*) CH_2N (*b*) C_2H_5N

(*c*) CH_5N (*d*) CH_4N.

(A.F.M.C. 2000)

44. Percentage of Se in peroxidase anhydrous enzyme is 0·5% by weight (at. wt. = 78·4) then minimum molecular weight of peroxidase anhydrous enzyme is

(*a*) $11·568 \times 10^4$ (*b*) $1·568 \times 10^4$

(*c*) 15·68 (*d*) $2·136 \times 10^4$

(C.B.S.E. P.M.T. 2001)

45. In steam distillation of toluene, the pressure of toluene in vapour is

(*a*) equal to pressure of barometer

(*b*) less than pressure of barometer

(*c*) equal to vapour pressure of toluene in simple distillation

(*d*) more than the vapour pressure of toluene in simple distillation. *(C.B.S.E. P.M.T. 2001)*

46. In a compound, C, H and N atoms are present in 9 : 1 : 3·5 by weight. If molecular weight of the compound is 108, then the molecular formula of the compound is

(*a*) $C_2H_6N_2$ (*b*) C_3H_4N

(*c*) $C_6H_8N_2$ (*d*) $C_9H_{12}N_3$

(A.I.E.E.E. 2002)

47. An organic compound contains 49·3% carbon, 6·84% hydrogen and its vapour density is 73. Molecular formula of the compound is

(*a*) $C_3H_8O_2$ (*b*) $C_3H_{10}O_2$

(*c*) C_6H_9O (*d*) $C_4H_{10}O_2$

(*e*) $C_6H_{10}O_4$ *(Kerala M.E.E. 2004)*

48. 116 mg of a compound on vaporisation in a Victor Meyer's apparatus displaces 44·8 ml of air measured at S.T.P. The molecular mass of the compound is

(*a*) 116 (*b*) 232

(*c*) 58 (*d*) 44·8

(*e*) 46·4 *(Kerala M.E.E. 2004)*

49. In Lassaigne's test, a blue colour is obtained if the organic compound contains nitrogen. Then blue colour is due to

(*a*) $K_4[Fe(CN)_6]$ (*b*) $Fe_4[Fe(CN)_6]_3$

(*c*) $Na_3[Fe(CN)_6]$ (*d*) $Cu_2[Fe(CN)_6]$

(*e*) $Na_2[Fe(CN)_5NO]$ *(Kerala C.E.E. 2004)*

50. The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is

(*a*) $Fe_4[Fe(CN)_6]_3$ (*b*) $Na_3[Fe(CN)_6]$

(*c*) $Fe(CN)_3$ (*d*) $Na_4[Fe(CN)_5COS]$

(A.I.E.E.E. 2004)

51. The ammonia evolved from the treatment of 0·30 g of an organic compound for the estimation of nitrogen was passed in 100 ml of 0·1 M sulphuric acid. The excess of acid required 20 ml of 0·5 M sodium hydroxide solution for complete neutralization. The organic compound is

(*a*) acetamide (*b*) benzamide

(*c*) urea (*d*) thiourea

52. A compound has empirical formula C_2H_4O. An independent analysis gave a value of 132·16 for its molecular mass. What is the correct molecular formula

(*a*) $C_4H_4O_5$ (*b*) $C_{10}H_{12}$

(*c*) C_7O_3 (*d*) $C_6H_{12}O_3$

(*e*) $C_4H_8O_5$ *(Kerala M.E.E. 2004)*

ANSWERS

39. *b* 40. *c* 41. *c* 42. *d* 43. *d* 44. *b* 45. *b* 46. *c* 47. *e* 48. *c*
49. *b* 50. *a* 51. *c* 52. *d*

HINTS/EXPLANATIONS to Multiple Choice Questions

2. *o*-nitrophenol is steam volatile while *p*-nitrophenol is not.

11. The vapour pressure of the volatile compound is less than the atmospheric pressure.

17. Minimum possible mol. wt. must contain one sulphur atom, *i.e.* $\% \text{ S} = \dfrac{1 \text{ S}}{\text{min. mol. wt.}} \times 100$

or $4 = \dfrac{32}{\text{min. mol. wt.}} \times 100$

or $\text{min. mol. wt.} = \dfrac{32 \times 100}{4} = 800.$

18. Compounds containing one N atom always have odd molecular weights, *i.e.*, 73 here.

19. Mol. wt. = wt. of 22·4 litres at N.T.P.

$= 1{\cdot}25 \times 22{\cdot}4 = 28 \text{ g mol}^{-1}.$

$\therefore$ Molecular formula $= CH_2 \times (28/14) = C_2H_4$

20. Eq. wt. of silver salt of acid $= \dfrac{0{\cdot}59}{0{\cdot}36} \times 108 = 177$

$\therefore$ Eq. wt. of the acid $= 177 - 108 + 1 = 70$

Basicity = Mol. wt/Eq. wt. = 210/70 = 3.

22. X : Y = (75·8/75) : (24·2/16) or 2 : 3, *i.e.*, X_2Y_3

23. Since mol. wt. = 2 × V.D. = 2 × 28 = 56

$\therefore$ M.F. = C_4H_8.

25. % N in $(NH_4)_2SO_4$ = 21·8% ; in $CaCN_2$ = 35%, in NH_2CONH_2 = 46·6%

and in NH_4NO_3 = 35%

26. $\underset{(R+44)\,g}{RCONH_2} + NaOH \longrightarrow RCOONa + \underset{17\,g}{NH_3}$

Now 17 *g* of NH_3 are obtained from one mole of $RCONH_2$ = 59 *g*

$\therefore$ R + 44 = 59 or R = 15 *i.e.* R = CH_3

Thus, the acid RCOOH is CH_3COOH (acetic acid)

28. Let the wt. of hydrocarbon taken = *x g*

$\therefore \quad \% \text{ C} = \dfrac{12}{44} \times \dfrac{0{\cdot}66}{x} \times 100 = 18/x$

and $\therefore$ of $\text{H} = \dfrac{2}{18} \times \dfrac{0{\cdot}36}{x} \times 100 = 4/x$

$\therefore \quad \text{C} : \text{H} = (18/12x) : (4/x)$ or 3 : 8.

Thus, M.F. = C_3H_8

32. Lassaigne's test is based upon the formation of NaCN. Since hydrazine (NH_2NH_2) does not contain carbon, it cannot form NaCN during Na fusion and hence does not give blue colour. All the remaining three compounds (aniline, glycine and urea) contain both C and N needed for the formation of NaCN and thus give blue colour.

33. $\text{V.D.} = \dfrac{\text{Wt. of 45 ml of vapours of the volatile liquid at NTP}}{\text{Wt. of 45 ml of } H_2 \text{ at NTP}}$

$= \dfrac{0{\cdot}24}{45 \times (0{\cdot}089/1000)} = 59{\cdot}93$

34. $\text{C} : \text{H} : \text{N} = \dfrac{40}{12} : \dfrac{13{\cdot}33}{1} : \dfrac{46{\cdot}67}{14}$

= 3·33 : 13·33 : 3·33 or 1 : 4 : 1 or **CH_4N.**

37. $\text{C} : \text{H} = \dfrac{12}{13} \times \dfrac{100}{12} : \dfrac{1}{13} \times \dfrac{100}{1}$ or C : H = 1 : 1

Thus, E.F. = CH. If E.F is CH then MF can be either C_2H_2 or C_6H_6. Since A decolourises Br_2 water, therefore, A = C_2H_2. Further since B does not decolourize Br_2-water, it must be C_6H_6 (benzene).

38. With a fixed volume of CCl_4, larger the number of extractions, more is the amount of I_2 extracted. Thus, option (*d*) is correct.

39. Mol. wt. of $Na_2SO_4.10\,H_2O$ = 322. Now 32·2 *g* of $Na_2SO_4.10\,H_2O$ contain oxygen

$= \dfrac{14 \times 16 \times 32{\cdot}2}{322} = 22{\cdot}4\,g.$

40. Wt. of Fe present in 67200 *g* of haemoglobin

$= \dfrac{0{\cdot}33}{100} \times 67200 = 221{\cdot}76\,g.$

But at. wt. of iron = 56 $\therefore$ No. of atoms of Fe present in one molecule of haemoglobin =221·76/56=3·96=4·0.

41. 25 ml of 0·12 N NaOH = 0·1914 *g* of acid

$\therefore$ 1000 ml of 1 N NaOH

$= \dfrac{0{\cdot}1914}{0{\cdot}12} \times \dfrac{1000}{25} = 63{\cdot}80.$

42. V.D. = Density of air/wt. of 1 ml of H_2 or

$\text{V.D.} = \dfrac{0{\cdot}00130}{0{\cdot}00089} = 14{\cdot}56.$

43. C : H : N = (40/12) : (13·33/1) : (46·67/14)

= 1 : 4 : 1

$\therefore$ E.F. = CH_4N.

44. $\text{Min. mol. wt.} = \dfrac{78{\cdot}4 \times 100}{0{\cdot}5} = 1{\cdot}568 \times 10^4$

46. Ratio of wts. $\text{C} : \text{H} : \text{N} = \dfrac{9}{12} : \dfrac{1}{1} : \dfrac{3{\cdot}5}{14} = 3 : 4 : 1$

$\therefore$ E.F. of the compound = C_3H_4N

and E.F. wt. = 3 × 12 + 4 × 1 + 14 = 54

But mol. wt. = 108 g mol^{-1}

$\therefore \quad \text{M.F.} = \text{E.F.} \times \dfrac{\text{Mol. wt.}}{\text{E.F. wt.}}$

$= C_3H_4N \times \dfrac{108}{54} = \mathbf{C_6H_8N_2}$

47. $C : H : O = \frac{49 \cdot 3}{12} : \frac{6 \cdot 84}{1} : \frac{43 \cdot 86}{16}$
$= 1 \cdot 5 : 2 \cdot 5 : 1 = 6 : 10 : 4$

48. Mol. mass $= \frac{116}{44 \cdot 8} \times \frac{22400}{1000} = 58 \text{ g mol}^{-1}$

51. Let the vol. of acid left unused
$= v$ ml of 0·1 M H_2SO_4
$\therefore \quad v \times 0 \cdot 1 \times 2 = 20 \cdot 05 \times 1$ or $v = 50$ ml

$\%N = \frac{1 \cdot 4 \times 2 \times 50 \times 0 \cdot 1}{0 \cdot 3} = 46 \cdot 6$

%N in urea (NH_2CONH_2) = (28/60) × 100 = 46·6% in acetamide (CH_3CONH_2) (14/59) × 100 = 23·72%, in benzamide ($C_6H_5CONH_2$) = (14/21) × 100 = 11·57% and in thiourea (NH_2CSNH_2) = (28/76) × 100 = 36·84%

Thus, option (*c*) is correct.

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The following questions consist of an 'Assertion' in column 1 and the 'Reason' in column 2. Use the following key to choose the appropriate answer.

(*a*) If both assertion and reason are CORRECT, but reason is not the CORRECT explanation of the assertion.

(*b*) If both assertion and reason are CORRECT, but reason is not the CORRECT explanation of the assertion.

(*c*) If assertion is CORRECT, but reason is INCORRECT.

(*d*) If assertion is INCORRECT, but reason is CORRECT.

	Assertion (Column 1)	**Reason (Column 2)**
1.	Acetone (b.p. 329 K) and methyl alcohol (b.p. 338 K) are separated by fractional distillation.	Fractional distillation helps in separating two liquids from their mixture when their boiling points differ by 10° or so.
2.	A mixture of *o*-nitrophenol and *p*-nitrophenol can be separated by steam distillation.	*o*-Nitrophenol is steam volatile but water soluble while *p*-nitrophenol is not steam volatile.
3.	Essential oils are purified by steam distillation.	Essential oils are volatile and are insoluble in water.
4.	Hydrazine contains nitrogen but does not give Lassaigne's test for nitrogen.	Hydrazine reacts with fused sodium to give H_2 gas.
5.	Lassaigne's test is not shown by diazonium salts.	Diazonium salts lose N_2 on heating much before they have a chance to react with fused sodium.
6.	Vapour density is the same thing as density	Molecular weight is twice vapour density.
7.	Dumas method is more applicable to nitrogen containing organic compounds than Kjeldahl's method.	Kjeldahl's method does not give satisfactory results for compounds in which nitrogen is linked to oxygen. (*A.I.I.M.S. 1995*)

True/False Statements

Which of the following statements are true and which are false ? Rewrite the false statement correctly.

1. Melting point, boiling point, refractive index are generally used as criteria of purity of an organic compound.
2. Benzoic acid can be extracted from water using ethanol.
3. Beilstein test for halogens is not always dependable.
4. The rapid cooking in pressure cookers is based upon the principle that boiling point of water increases with increase in pressure.
5. Kjeldahl's method for estimation of nitrogen is applicable to all types of nitrogen containing organic compounds.
6. If the organic compound contains nitrogen and sulphur, sodium thiocyanate is always formed in the Lassaigne's test.
7. Anhydrous $CuSO_4$ is blue.

Fill In The Blanks

1. Benzoic acid containing an impurity of naphthalene can be purified by crystallisation using................ as the solvent.
2. In column chromatography.............. constitutes the stationary phase and the .... as the mobile phase.

3. The boiling point of a liquid is the temperature at which its..........becomes equal to the atmospheric pressure.
4. Liquids which decompose at or below their boiling points are purified by..............
5. Liquids whose boiling points differ by about 10 K can be separated by..............
6. In column chromatography, the .... adsorbed component will elute with the more........... solvent.
7. Steam distillation is used to separate compounds which are .... with water but volatile in .... .
8. In Lassaigne's test for halogens, conc. HNO_3 is used to destroy.............. and ....
9. In Beilstein test, the bluish green flame is due to the formation of volatile.............. .
10. In sublimation, a solid changes directly from the.............. state to the.............. state.
11. In the detection of phosphorus, the organic compound is fused with..............
12. In the estimation of carbon and hydrogen, the CO_2 formed is absorbed in .... and the water formed is absorbed in.............. .
13. In Duma's method, the function of reduced copper gauze is to convert oxides of.............. to ....
14. In Carius method for the estimation of halogens, the organic compound is heated with.............. and a few crystals of.............. in a sealed tube.
15. In Carius method for sulphur and phosphorus, sulphur is estimated as.............. and phosphorus is estimated as.............. .
16. The molecular mass of an organic acid = Eq. mass × ....
17. In Kjeldahl's method during digestion, nitrogen of the organic compound is converted into............ .
18. Gram molecular mass of a substance = weight of .... cm^3 of the vapours of the substance at ....
19. The volumetric method for the determination of equivalent mass of acids and bases is based upon the principle that acids and bases always react in......
20. When an ammonium salt is heated with aqueous alkali solution .... is evolved.

Matching Type Questions

Match the appropriate entries in columns X and Y

	X		Y
1.	Victor-Meyer's method	1.	Detection of phosphorus
2.	Kjeldahl's method	2.	N_2 gas is collected over conc. KOH solution
3.	Duma's method	3.	Displaced air is collected over water
4.	Beilstein test	4.	Ammonium sulphate is heated with strong aqueous alkali
5.	Ammonium molybdate	5.	Volatile cupric halides.

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. (*a*) **2.** (*c*) **3.** (*a*) **4.** (*b*) **5.** (*a*) **6.** (*d*) **7.** (*b*)

TRUE/FALSE STATEMENTS

1. True **2.** False, using benzene, chloroform etc. **3.** True **4.** True **5.** False, not applicable to compounds containing —NO_2, —N = N—groups or nitrogen in the ring **6.** False, sodium thiocyanate is formed only when the amount of sodium is insufficient as compared to C, N and S content of the organic compound. **7.** False, hydrated copper sulphate ($CuSO_4.5H_2O$) is blue.

FILL IN THE BLANKS

1. Water **2.** Silica gel or alumina, organic solvent **3.** vapour pressure **4.** distillation under reduced pressure **5.** fractional distillation **6.** strongly, polar **7.** immiscible, steam **8.** NaCN, Na_2S **9.** cupric halides **10.** solid, gaseous **11.** sodium peroxide **12.** KOH, anhydrous $CaCl_2$ **13.** nitrogen to N_2 gas **14.** fuming HNO_3, $AgNO_3$ **15.** $BaSO_4$. $Mg_2P_2O_7$ **16.** basicity **17.** $(NH_4)_2SO_4$ **18.** 22400, STP **19.** equivalent amounts **20.** NH_3.

MATCHING TYPE QUESTIONS

1—3, 2—4, 3—2, 4—5, 5—1