Chapter 1

Introduction

The division of chemistry into organic and inorganic domains has its origin in earliest antiquity. Many organic compounds like alcohol, sugar, fats, soap, vinegar, indigo and starch were known to prehistoric peoples. In the 18th century many organic compounds were isolated from natural sources. Thus Scheele (1742—86) obtained tartaric acid, citric acid and malic acid from grapes, lemons and apples respectively. He also prepared lactic acid from sour milk, oxalic acid by oxidation of sugar with nitric acid and glycerol from animal fats. Rouelle (1773) isolated urea from human urine and Serturner (1805) obtained the alkaloid morphine from opium.

It was Berzelius (1807) who first named the substances derived from living organisms (plants or animals) as 'organic compounds' and the branch of chemistry dealing with them came to be known as **Organic Chemistry**. On the other hand, substances such as salt, lime, sulphur and iron which were obtained from the mineral world were classed as 'inorganic' and their study was called **Inorganic Chemistry**.

VITAL FORCE THEORY AND ITS DECLINE

It was long believed that organic compounds were produced in plants and animals through the operation of a vital force—inherent in living cells. So the synthesis of an organic compound from inanimate matter in the laboratory was considered impossible. However, in 1828 the German chemist Wohler accidentally discovered that urea, a well-known organic compound derived from urine, could be produced by boiling the aqueous solution of ammonium cyanate which is a typical inorganic compound.

$$\underset{\text{amm. cyanate}}{NH_4CNO} \xrightarrow[\textit{heat}]{H_2O} \underset{\text{urea}}{NH_2-\overset{\overset{O}{\|}}{C}-NH_2}$$

Urea contains the same number and kind of atoms as ammonium cyanate, but these atoms are arranged differently.

The above chance discovery of Wohler did much to dispel the idea of vital force theory in the formation of organic compounds. A few years later, Kolbe was able to synthesise acetic acid starting from the constituent elements. This further confirmed the belief that no special force was needed for the preparation of organic compounds. Thereafter numerous organic compounds were synthesised in chemical laboratories and by 1860 the vital force theory stood completely discredited.

MODERN DEFINITION OF ORGANIC CHEMISTRY

With the fall of the vital force theory (or vitalism), the term 'organic' lost its original significance. It was, however, established that all the so-called organic compounds contained the element carbon as an essential constituent. Hence the term organic is now used in a broad sense to describe all compounds of carbon whether they are found in nature or prepared in the laboratory. Thus in modern practice **Organic Chemistry is defined as the study of the compounds of carbon**, the study of the rest of the elements and their compounds falling under the scope of inorganic chemistry. This definition of organic chemistry is not strictly adhered to. Some compounds which

according to this definition would be called organic have been studied under Inorganic Chemistry. Thus carbonates ($CaCO_3$), cyanides (KCN), carbides (CaC_2) as also carbon monoxide (CO) and carbon dioxide (CO_2) are treated as inorganic compounds, while they all contain carbon.

Since the various organic compounds known contained carbon and were also invariably associated with hydrogen, these could well be considered as divided from hydrocarbons. Thus a more precise definition of organic chemistry would be — "*the study of hydrocarbons and the compounds which could be thought of as their derivatives.*"

WHY STUDY ORGANIC CHEMISTRY AS A SEPARATE BRANCH ?

Having established that organic compounds could be obtained by ordinary laboratory processes and that they obeyed the same fundamental laws which hold for inorganic compounds, there was hardly any justification for their separate study. However, there are marked differences between the composition, structure and behaviour of organic and inorganic compounds which make their study as a separate branch of chemistry more practical and fruitful. The main reasons advanced for it are :

(1) **Large number of compounds.** No one today knows exactly how many organic compounds are present in nature. The number of compounds which have been actually prepared or isolated in the laboratory is about four million. This far exceeds the total number of inorganic compounds which is nearly 50,000 only. If the study of four million carbon compounds were included with that of carbon under Inorganic Chemistry, it would throw the subject out of balance.

(2) **Built of relatively few elements.** Organic compounds are built from relatively few elements. The elements most frequently encountered in organic chemistry are hydrogen, oxygen, nitrogen, sulphur, phosphorus, and halogens. In contrast, inorganic compounds are formed from any of 105 elements known.

(3) **Functional groups as basis of classification.** Organic molecules contain active atoms or groups of atoms which determine their chemical behaviour. These are called *functional groups*. Thus organic compounds with similar functional groups display similar properties and form a 'class'. There are many such classes of compounds *e.g.*, alcohols (—OH), aldehydes (—CHO), carboxylic acids (—COOH), amines ($—NH_2$), *etc.* This classification based on functional groups makes the study of organic chemistry simple and easier. Most of the inorganic substances which have been studied are either acids, bases or salts.

(4) **Molecules formed by covalent bondings.** Organic molecules are characterised by the presence of covalent bondings. The inorganic salts contain ionic or electrovalent bondings. Thus,



(methane has covalent bondings)

$Na^+ \overline{Cl}$

(sodium chloride has ionic bonding)

Many differences in the properties of organic and inorganic compounds are due to different types of bondings present in their molecules.

(5) **Unique characteristic of Carbon to undergo 'Catenation'.** In fact, carbon is unique among the elements. Its atoms possess the wonderful capacity to unite with each other by means of stable covalent bonds. Carbon atoms joined each to each in straight chains, branched chains or rings of all sizes, form a large number of simple as well as complex molecules. This self-linking property of carbon known as **Catenation** is responsible for the variety and large number of organic compounds. Inorganic molecules having atoms joined by ionised bondings are incapable of exhibiting a phenomenon akin to catenation.

(6) **They exhibit Isomerism.** Carbon atom is almost always quadrivalent in its compounds. Also, we know that carbon-to-carbon covalent bonds are rigid and directional. Hence

they give rise to a variety of spatial arrangements of atoms in organic molecules. Thus organic compounds display the phenomenon of *isomerism* where a single molecular formula can represent a number of compounds with different properties. Inorganic compounds contain ionic bonds (non-rigid and non-directional) which cannot give rise to isomerism.

(7) **Physical State.** Organic compounds exist as gases, liquids or solids. They frequently possess characteristic colour and odour. Inorganic substances predominantly exist as colourless and odourless solids while certain metallic salts possess distinct colours.

(8) **Pattern of Solubility.** The majority of organic compounds are insoluble in water but they readily dissolve in non-polar solvents like benzene, chloroform and ether. However, the organic compounds containing polar groups *e.g.* —OH, —COOH, $-SO_3H$ are soluble in water. The inorganic compounds on the contrary are readily soluble in water and insoluble in organic solvents.

(9) **Electrical Conductions.** Organic compounds in aqueous solutions and melts are non-conductors of electricity. On the contrary inorganic compounds which furnish ions in solutions and melts, are conductors of electricity.

(10) **Low Melting and Boiling Points.** Organic compounds are volatile and possess low melting and boiling points. The inorganic compounds are non-volatile and their melting and boiling points are high. There is hardly an organic compound which melts above 300° while no inorganic salt melts below 700°.

(11) **Combustibility.** Organic compounds are combustible. They readily burn in a stream of oxygen, leaving no residue. In contrast, inorganic compounds are generally incombustible.

(12) **Nature of Chemical reactions.** Organic reactions being molecular are slow and reversible. They often require heat and a catalyst for good yield. The relatively poor yield in many cases is due to simultaneous side reactions. The inorganic reactions being ionic in nature are fast and go in quantitative yield without a catalyst.

Table. General features of Organic and Inorganic compounds.

Organic	*Inorganic*
1. Covalent molecules.	1. Ionic molecules.
2. Have classes: alcohols, aldehydes, carboxylic acids, etc., with characteristic properties.	2. Exist as acids, bases and salts.
3. Melting and boiling points low.	3. Melting and boiling points high.
4. Solubility in water low; in organic solvents high.	4. Solubility in organic solvents low; in water high.
5. High volatility; flammable.	5. Low volatility; inflammable.
6. Many have characteristic colour and odour.	6. Colourless and odourless generally.
7. Reactions molecular.	7. Reactions ionic.
8. Exhibit isomerism.	8. No isomerism possible.

Note. The differences between the two types of compounds listed above arise from the nature of the bonds in their molecule. One with covalent bond would resemble 'organic' and another with 'ionic' inorganic. The properties of a polar covalent compound will be midway. In fact, there are no fundamental differences between the two types of compounds, the difference being only of degree.

SCOPE OF ORGANIC CHEMISTRY

The scope of organic chemistry is vast indeed. The organic chemist has to isolate the numerous compounds from natural sources and study their properties. Then he proceeds to determine their structure by correlating these properties with those of known compounds. From a knowledge of structure, the chemist synthesises a compound in the laboratory.

The synthesis of a compound verifies its structure and makes it available more widely at a lower cost. Vitamins, ethyl alcohol, indigo and camphor are but a few examples of natural compounds that are now prepared synthetically for commercial purposes. By synthesis the organic chemist further endeavours to create new substances which may improve upon the properties of those found in nature. Thus we have synthetic fabrics like nylon and orlon, organic dyes, plastics, drugs (barbiturates, Novocaine) and synthetic rubber which have now replaced the corresponding products made from natural sources.

IMPORTANCE OF ORGANIC CHEMISTRY IN MODERN LIFE

There is no art, science or industry where a knowledge of organic chemistry is not applied. The tremendous importrance of organic chemistry in modern everyday life and industry as also to life phenomenon is briefly outlined below.

(1) **Applications in Daily life.** In our day-to day life we find ourselves in a strange panorama of things that in one way or the other are connected with organic chemistry. The organic substances of common use are listed below.

Food : Starch, fats, proteins, vegetables

Clothes : Cotton, wool, nylon, dacaron, terylene

Fuels : Coal, kerosene, diesel oil, petrol

Leather and Wood products

Rubber and *plastics* : Polyethylene, polystyrene

Paints and Varnishes

Dyes of all kinds

Medicines : Penicillin, streptomycin, cartison, antibiotics, sulphonamides

Drugs : Morphine, cocaine, *LSD*

Cosmetics

Insecticides : DDT, gammexane

Refrigerants

Stationery : Pencil, paper, writing ink

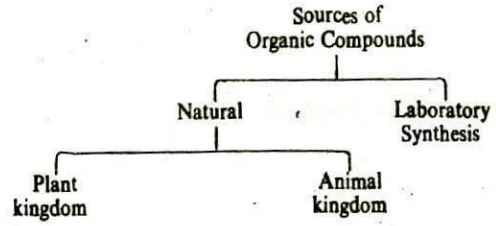
(2) **Applications in Industry.** A knowledge of organic chemistry is necessary in many important chemical industries e.g., preparation of foods, pharmacy, manufacture of dyes and explosives, paper industry, sugar industry, alcohol industry, synthetic rubber and plastics, soil fertilisers, petroleum industry and its recent development to produce a veritable galaxy of organic chemicals (petrochemical industry), etc.

(3) **Study of Life processes.** Organic chemistry is the chemistry of life. The study of the nature of material and of the processes of living organisms is the privilege of organic chemist. The investigation of the tissues, the secretions and other constituents of animals and plants is based upon organic chemistry. The vitamins and hormones are important organic compounds produced in our body which ensure its proper development.

Organic chemists are now busy round the clock to study and control the vital functions of plants and animals. The first success towards this has recently been achieved by Dr. Hargobind Khorana an Indian born American scientist. He has synthesised RNA and DNA, and interpreted the genetic code, whereby it may be possible to correct genetic defects and control heredity. There is no wonder that with further advances in the field, scientists may soon be able to produce test-tube babies.

SOURCES OF ORGANIC COMPOUNDS

Organic compounds, as already mentioned, are obtained from natural sources and are also prepared by synthesis in the laboratory. The natural sources of these substances may be traced to either the plant or animal kingdom.



Source	*Compounds obtained*
(1) Plants	Sugars, starches, cellulose, citric acid, oxalic acid, tartaric acid, indigo, oils, vitamins, etc.
(2) Animals	Fats, proteins, urea, uric acid vitamins, harmones, etc.
(3) Wood distillation	Acetic acid, methyl alcohol, and acetone.
(4) Coal-tar distillation	Benzene, toluene, naphthalene, carbolic acid, cresols, pyridine, dyes, perfumes, drugs, etc.
(5) Natural gas and petroleum distillation	Alkanes and their derivatives such as methyl chloride, chloroform, methyl alcohol, ethyl alcohol, allyl chloride, benzene, toluene.
(6) Fermentation processes	Ethyl alcohol, amyl alcohol, acetic acid, etc.

About 40 years back, the main sources of organic compounds were the processes of fermentation and wood distillation, while fewer compounds were derived from coal and petroleum. With the recent development of petrochemical industry and low temperature coking techniques of coal, the number of organic compounds derived from petroleum and coal is far greater than from any other natural source. Although the fermentation processes are still in use, wood distillation is almost obsolete. At the present day the vast majority of organic compounds are obtained by synthetic methods and even the fermentation processes are employed in relatively few cases out of necessity and convenience.

QUESTIONS

1. What was the Vital force theory ? How was it discarded ?
2. What is Organic chemistry ? Describe in detail the similarities and differences between organic and inorganic compounds.
3. Give a brief survey of the scope and applications of organic chemistry.
4. What are the chief sources of organic compounds ? Which is the most dominating source at present ?
5. What is Catenation ? *(Indore BSc. 1994)*

Chapter **2**

Purification of Organic Compounds

Organic compounds derived from natural sources are seldom pure. They are often mixed with other substances which occur with them. Similarly, the compounds prepared in the laboratory are generally contaminated with other compounds which are also formed during the course of a reaction. Thus it becomes essential to obtain an organic compound in a state of purity before determining its properties and molecular formula. The various methods employed for effecting purification depend upon the nature of the organic compound and the impurities present in it. The processes commonly used for the separation and purification of organic compounds are :

(1) *Crystallisation* ;
(2) *Sublimation* ;
(3) *Distillation* ;
(4) *Fractional distillation* ;
(5) *Distillation under reduced pressure* ;
(6) *Steam distillation* ;
(7) *Extraction with solvents* ; *and*
(8) *Chromatography.*

CRYSTALLISATION

This is the process most commonly employed for the purification of solid organic compounds. The impure solid is dissolved in the minimum volume of a suitable organic solvent. The soluble impurities pass into solution while the insoluble ones are left behind. The hot solution is then filtered and allowed to cool undisturbed till crystallisation is complete The crystals are then separated from the mother liquor by filtration and dried. It is possible that purification may not be completed after one crystallisation and the process may have to be repeated.

The efficiency of the process of crystallisation depends on the skill with which the following steps are carried out.

(1) **Choice of the solvent.** For a judicious choice of the solvent, about 50 mg of the solid is taken in a test-tube and shaken with a few drops of the solvent. The solvent is unsuitable if the whole of the solvent goes into solution at room temperature. If the solid substance dissolves upon heating and throws out maximum crystals on cooling, the solvent is suitable. This process is repeated with solvents such as benzene, petroleum ether, methyl alcohol, ethyl alcohol, acetone etc. till the most satisfying one is sorted out.

(2) **Preparation of solution.** A suitable quantity of the solid substance is taken in a conical flask fitted with a reflux condenser. A small volume of the solvent selected in step (1) is also placed in the flask. The quantity of the solvent should be just enough to dissolve the whole solid on boiling. In case of less volatile solvents, it is advisable to fit the vessel with a long glass tube instead of water-condenser. This tube acts as air-condenser and also prevents the inflammable solvent vapours to reach the flame of the burner. The heating may be done on a water-bath or wire gauze according as the solvent is 'low boiling' or 'high boiling'.

(3) Filtration of the solution. The hot saturated solution obtained above is then filtered through a fluted filter paper placed in an ordinary glass funnel. If the quantity of the solution is large, it takes longer and the crystals may form in the funnel during filtration. To prevent this, a 'hot-water funnel' may be used with advantage.

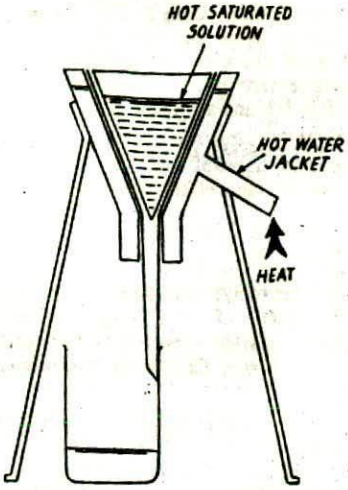


Fig. 2·1. Filtration with the help of a hot-water funnel.

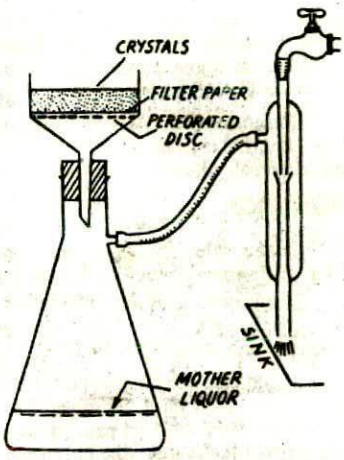


Fig. 2·2. Filtration under suction, using Buchner funnel.

(4) Crystallisation. The hot filtrate is then allowed to cool undisturbed in a beaker or a 'crystallising dish'. The pure solid substance separates as crystals. When a rich crop of crystals has

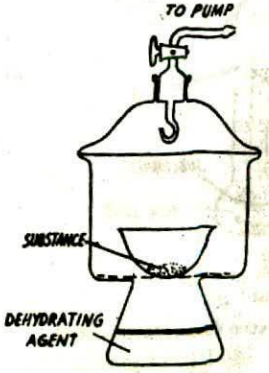


Fig. 2·3. Drying crystals in a vacuum desiccator.

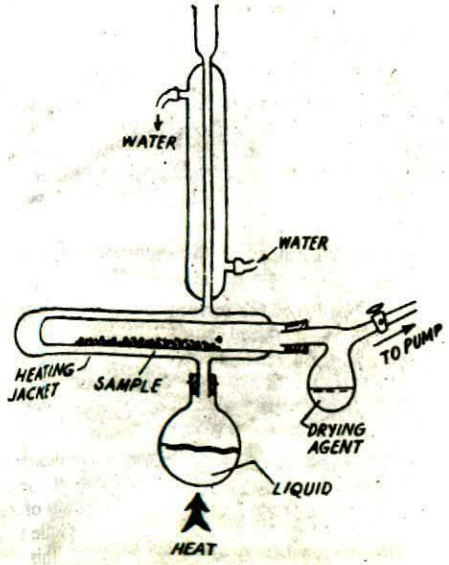


Fig. 2·4. Drying crystals in a 'Drying piston'.

been obtained, crystallisation is complete. Sometimes crystallisation does not occur even after cooling the filtrate for a sufficiently long time due to supersaturation of the solution. In such a

case the crystallisation is induced either by scratching the walls of the vessel with a glass rod or by adding a few crystals of the pure compound to the solution (seeding). The added crystals serve as nuclei for the growth of the new crystals from the solution.

(5) **Separation and drying of Crystals.** The crystals are separated from the mother liquor by filtration. The filtration is generally effected under reduced pressure using Buchner (or Hirsch) funnel as shown in Fig. 2·2. When the whole of the mother liquor has been drained into the filtration flask, the crystals are washed with small quantities of the pure cold solvent to remove adhering impurities. The crystals are then dried by pressing between pads of filter papers or in an oven. Often the drying is done in a vacuum desiccator (Fig. 2·3) and a 'drying piston' (Fig. 2·4) is used for analytical samples.

Sometimes the crystals obtained are coloured owing to traces of impurities present. In such a case, the crystals are redissolved in a small quantity of the solvent, boiled with a little animal charcoal, filtered and crystallised once again.

SUBLIMATION

Certain substances when heated, pass directly from the solid to the vapour state without melting. The vapours when cooled give back the solid substance.

This process known as **sublimation** is very helpful in separating volatile from non-volatile solid. It is, however, of limited application as only a few substances like naphthalene, camphor and benzoic acid can be purified by this process.

The impure substance is placed in a china dish which is gently heated on a sand-bath. The dish is covered with a perforated filter-paper over which is placed an inverted funnel. The vapours rising from the solid pass through the holes in the filter-paper and are deposited as solid on the walls of the funnel. The filter paper has two functions : (*i*) it does not permit the sublimed substance to drop back into the dish and (*ii*) it keeps the funnel cool by cutting off the direct heat from the dish (Fig. 2·5).

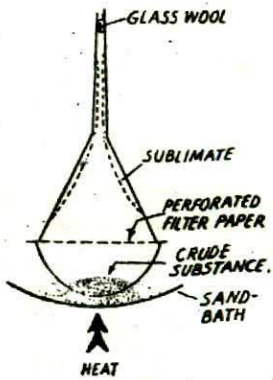


Fig. 2·5 Sublimation.

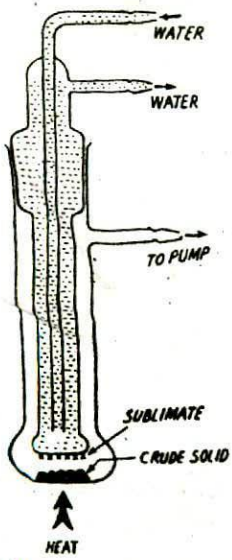


Fig 2·6 Sublimation under reduced pressure.

Organic substances such as benzoic acid, naphthalene etc. which have high vapour pressure at temperatures below their melting points, can be sublimed relatively quickly. These can be conveniently purified by the laboratory operations described above. Such substances which have very small vapour pressure or tend to decompose upon heating, are purified by sublimation under reduced pressure.

A simple glass apparatus now used for sublimation under reduced pressure is shown in Fig. 2·6. The chief features of this apparatus are a large heating and a large cooling surface with a small distance in between. This is necessary because the amount of the substance in the vapour phase is much too small in case of a substance with low vapour pressure.

DISTILLATION

The operation of distillation is employed for the purification of liquids from non-volatile impurities. The impure liquid is boiled in a flask and the vapours so formed are collected and condensed to give back the pure liquid in another vessel. The non-volatile impurities are left behind in the flask.

The apparatus used for distillation is shown in Fig. 2·7. It consists of a distillation flask fitted with a thermometer in its neck and a condenser at the side-tube. The liquid to be purified is placed in the distillation flask and the thermometer so adjusted that its bulb stands just below the opening of the side-tube. This ensures the correct recording of the temperature of the vapour passing over to the condenser. A suitable vessel is attached to the lower end of the condenser to receive the condensed liquid. On heating the distillation flask, the thermometer first records a rise in temperature which soon becomes constant. At this point, which is the boiling temperature of the pure liquid, most of the liquid passes over. Towards the end of the operation the temperature rises once again on account of the superheating of the vapour. The distillation is stopped at this stage and the receiver disconnected.

In case of liquids having boiling points higher than 110°, the water-condenser is replaced by air-condenser. To prevent bumping, it is customary to put a few pieces of unglazed porcelain in the distillation flask.

While distilling a very volatile and inflammable liquid such as ether, the distillation flask is heated on a water-bath and not on a wire gauze. In case of very high-boiling liquids, the flask is heated directly with a naked flame.

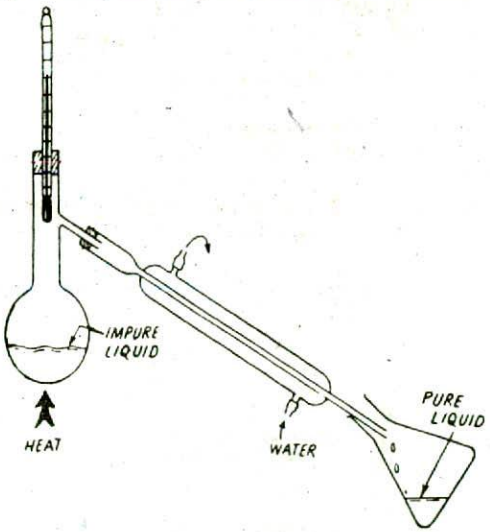


Fig. 2·7. Distillation.

FRACTIONAL DISTILLATION

A mixture of two or more volatile liquids can be separated by fractional distillation. When their boiling points differ by more than 40°, the operation can be carried with the help of ordinary distillation apparatus described in Fig. 2·7. The more volatile liquid passes over first and is collected in a receiver. When the temperature begins to rise for the second time, the first receiver is disconnected. A new receiver is attached as soon as the temperature becomes constant once again. Thus the distillate is collected in fraction and the process is termed *Fractional Distillation*.

When the liquids present in the mixture have their boiling points close to each other, the separation is best effected by fitting the distillation flask with a *fractionating column*. For laboratory use a simple and effective fractionating column consists of a long glass tube blown in bulbs (as shown in Fig. 2·9). The glass tube packed with beads is another type of fractionating column. There are various other patent designs of fractionating columns that are in vogue. Some of these are shown in Fig. 2·8. All these are designed to provide a large sur-

face area for the upgoing vapours. On heating, the vapours of the more volatile liquid A, along with a little of the vapours of less volatile liquid B, rise up and come in contact with the large cooling surface of the fractionating column. The vapours of B condense first and that of A pass on. The condensed liquid flowing down the column meets the fresh hot ascending vapour. It snatches more of B from the vapour mixture and gives up any dissolved vapour of A. This process is repeated at every bulb of the fractionating column, so that the vapour escaping at its top consists almost exclusively of A and the condensed liquid flowing back into the distillation flask is rich in B. If necessary, the process can be repeated with the distillate and the liquid left in the distillation flask.

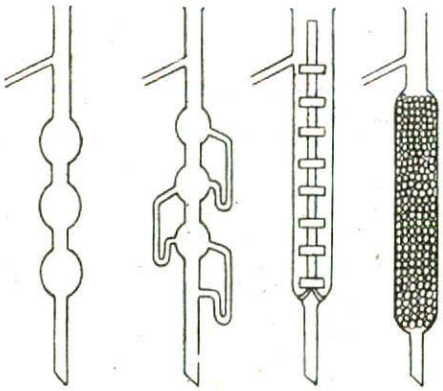


Fig. 2·8. Different types of fractionating columns.

Instead of the ordinary fractionating column used in laboratory, a fractionating tower is used with great advantage in modern chemical industry, especially for distillation of crude alcohol, refining of petroleum and distillation of coal-tar. The crude substance is fed into a still fitted with steam coils for heating. The vapours of the substance raised in the still pass up the fractionating column.

A fractionating tower is divided into several compartments by means of the trays set one above the other (Fig. 2·10). Each of these trays has a hole in the centre which is covered

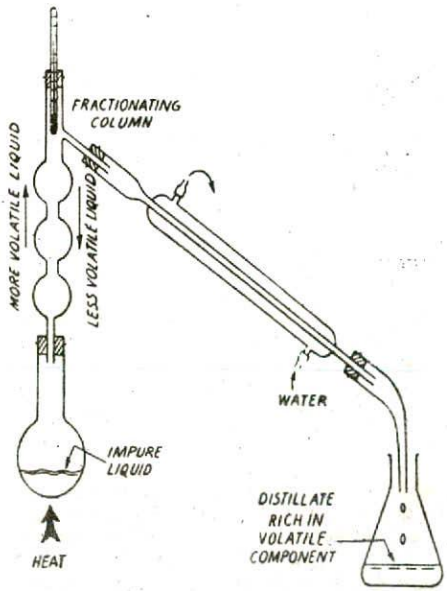


Fig. 2·9. Fractional distillation.

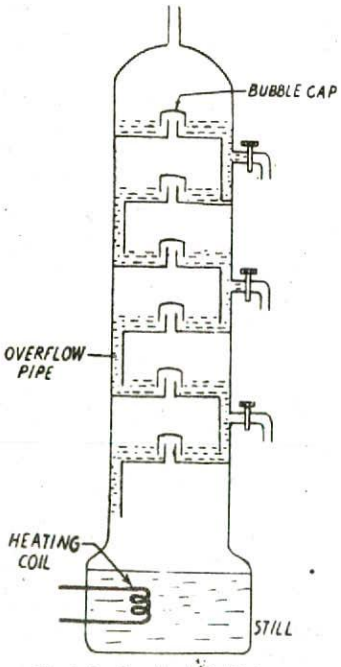


Fig. 2·10. Fractional distillation on industrial scale.

by a bubble cap or 'baffle plate'. The upgoing vapours are condensed at these trays while the uncondensed vapours pass up. The condensed liquid stays in the trays and the excess liquid drops down through the overflow pipes. In passing from bottom to top of the tower, the temperature falls. At various levels of the tower a fixed temperature is automatically maintained if the crude liquid in the still is heated steadily by steam coils. The liquid fractions collecting at appropriate trays having the required 'boiling ranges' are drained out through the outlet taps.

DISTILLATION UNDER REDUCED PRESSURE

The 'straight' distillation is suitable only for liquids which boil without decomposition at atmospheric pressure. In case of organic liquids which decompose before their boiling point is reached, the distillation is carried under reduced pressure when the liquid boils at a lower temperature*.

The apparatus used for distillation under reduced pressure is shown in Fig. 2·11.

(*i*) *Claisen Flask*, having two necks. It is fitted with a long drawn jet, dipping in the liquid to be distilled. During the distillation, a stream of bubbles rises through the capillary of this jet and prevents bumping, which is so pronounced here than in ordinary distillation.

(*ii*) *Condenser*, connected with the Claisen flask on the one hand and a filtration flask, serving as a receiver, on the other.

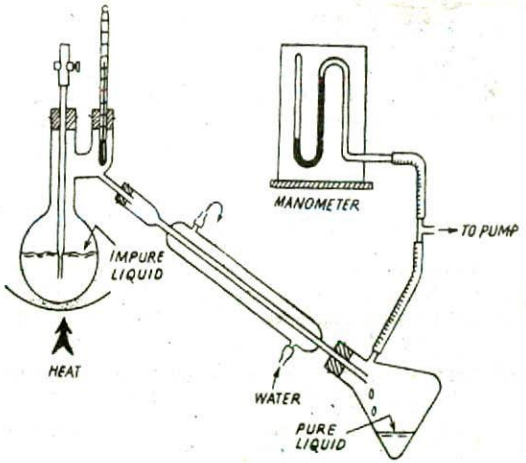


Fig. 2·11. Distillation under reduced pressure.

(*iii*) *Manometer*. The receiver flask is connected to an exhaust pump through (*a*) a mercury manometer which tells the pressure under which the distillation is being carried, and (*b*) a trap, to eliminate any condensed liquid.

The pressure in the apparatus is reduced with the help of a water pump. Whenever a lower pressure is desired, the water pump is replaced by a mercury pump.

An important application of this process is the recovery of glycerol from spent-lye in soap industry. Glycerol is decomposed at its boiling point (298°) but can be distilled unchanged at 12 mm pressure when it boils at 180°. Another application of 'vacuum distillation' is the concentration of sugar juice under reduced pressure.

*A liquid boils when its vapour pressure is equal to the atmospheric pressure. When the pressure is reduced by suction, the liquid boils at a lower temperature.

STEAM DISTILLATION

Many substances that are insoluble in water and are volatile in steam, can be purified by distillation in a current of steam (*Steam Distillation*). The non-volatile impurities are left behind in the distillation flask.

The impure mixture together with some water is placed in a round-bottom flask which is then connected to a steam-generator on one side and a water condenser on the other (Fig. 2·12) The flask is adjusted in a slanting position so that no droplets of the mixture splash into the condenser on brisk boiling and bubbling of steam. The mixture in the flask is heated and then a current of steam passed into it. Heating of the flask is controlled so as to avoid unnecessary condensation of steam in it. Steam picks up the volatile substance from the mixture and passes into the condenser. The distillate collected in the receiver consists of a mixture of water and the organic substance. The distillation is stopped when the droplets or the solid particles of the organic substance cease to appear in the condenser.

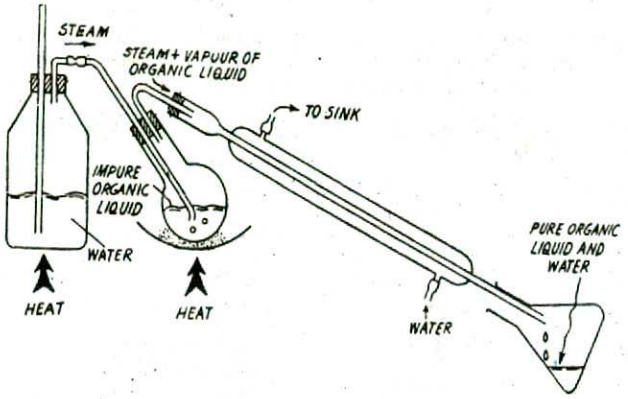


Fig. 2·12. Steam distillation.

The distillate is then treated to recover the organic substance by a suitable method. In case it is a solid, the substance may be separated by simple filtration, and if it is a liquid, it can be removed by means of a separating funnel. The aqueous layer in both cases may be extracted with a solvent.

Steam distillation is employed in industry for the recovery of various essential oils from plants and flowers. It is also used in the manufacture of aniline and turpentine oil.

Principle of Steam Distillation. A liquid boils when its vapour pressure is equal to the atmospheric pressure. In steam distillation, a mixture of water and an organic liquid is heated. The mixture boils when the combined vapour pressure of water (p_1) and that of the organic liquid (p_2) is equal to the atmospheric pressure (P) *i.e.*, $P = p_1 + p_2$.

Naturally, the boiling temperature of the mixture would be lower than the boiling temperature of the pure organic liquid when the vapour pressure of this liquid alone would be equal to the atmospheric pressure. Thus in steam distillation the liquid is distilled at a lower temperature than its boiling point when it might decompose. It serves the same purpose as distillation under reduced pressure.

EXTRACTION WITH A SOLVENT

When an organic substance is present as solution in water, it can be recovered from the solution by the following steps :

(*i*) *The aqueous solution is shaken with an immiscible organic solvent in which the solute is more soluble*

(*ii*) *The solvent layer is separated by means of a separating funnel.*

(*iii*) *The organic substance is then recovered from it by distilling off the solvent.*

The process of removing a substance from its aqueous solution by shaking with a suitable organic solvent is termed **extraction**.

Procedure. The aqueous solution is placed in a separating funnel. A small quantity of the organic solvent, say ether or chloroform, is then added to it. The organic solvent being

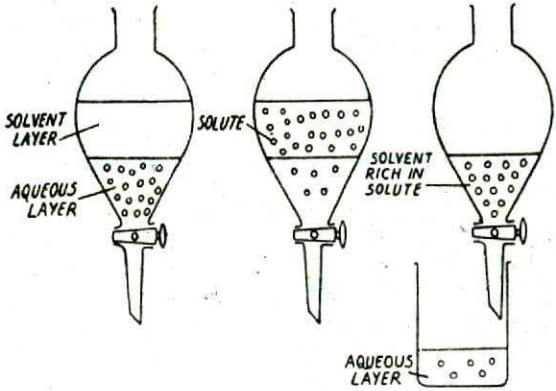


Fig. 2·13. Extraction with a solvent — the three stages

immiscible with water, will form a separate layer. The mouth of the funnel is closed with a stopper or the palm of the hand and the contents shaken gently. The solute being more soluble in the organic solvent is transferred to it. The solvent layer is then separated by opening the tap and running out the lower layer. The organic substance dissolved in it is finally recovered by distilling off the solvent.

Note. It is always better to extract two or three times with smaller quantities of the solvent than once with the whole bulk of the solvent provided.

Soxhlet Extraction. When an organic substance is to be recovered from a solid, it is extracted by means of an organic solvent in which the impurities are insolubie. In actual practice the extraction from solids is often tedious and requires thorough contact and heating with the solvent. This is done in a special apparatus, the *Soxhlet Extractor* (Fig. 2·14). It consists of a glass cylinder C having a side-tube T and syphon S. The cylinder carries a water condenser at the top and is fitted below into the neck of a boiling flask.

The powdered material is placed into the thimble made of stout filter paper and the apparatus is fitted up as shown in Fig. 2·14. The flask containing a suitable solvent is heated on a water-bath. As the solvent boils, its vapours rise through the side tube T up into the water condenser. The condensed liquid drops on the solid in the thimble, dissolves the organic substance and filters out into the space between the thimble and the glass cylinder. As the level of liquid here rises, the solution flows through the syphon back into the boiling flask. The solvent is once again vaporised, leaving behind the extracted substance in the flask. In this way, a continuous stream of pure solvent drops on the solid material, extracts the soluble substance and returns to the flask. At the end of the operation the solvent in the boiling flask is distilled off, leaving the organic substance behind.

Soxhlet Extractor is used with advantage for the extraction of oils and fats from flowers and seeds, and alkaloids from plants. The apparatus ensures maximum extraction with a limited quantity of the solvent.

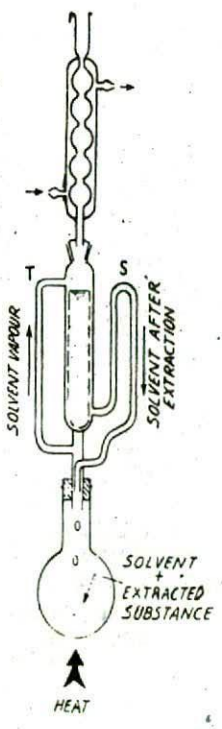


Fig. 2·14. Soxhlet extractor.

CHROMATOGRAPHY

This new technique is now extensively used for the purification and separation of organic compounds on a laboratory scale. The name *chromatography* owes its origin to the fact that Iswett (1906) first used it for the separation of coloured substances from plants (Greek *chromos*, meaning

colour). Since the scope of this technique has been widely extended to include colourless mixtures, the idea of colour is no longer connected with the concept.

Chromatography is based on the general principle of distributing the components of a mixture of organic compounds between two phases—a stationary phase and a moving phase. The stationary phase can be a solid or liquid supported on a solid, while the moving phase is a liquid or a gas. When the stationary phase is a solid, the basis of separation is adsorption ; and when it is a liquid, the basis is partition.

Liquid-Solid Chromotography. When the moving phase involved in a chromotographic system is a liquid and the stationary phase a solid, the method of separation is called *Liquid-Solid Chromotography.* The solid phase may be packed in a column (**column chromotography**) or take the form of a sheet of paper (**paper chromatography**) or a thin coating of material deposited on a glass sheet (**thin layer chromatography**). Here we will describe only the column chromatography in some detail.

Column Chromatography. The technique is a type of a liquid-solid chromatography. The stationary phase is a finely divided solid (alumina, silica gel) which is packed in a column, and the moving phase is a solvent (pentane, carbon disulphide, benzene, ether) containing the mixture to be separated.

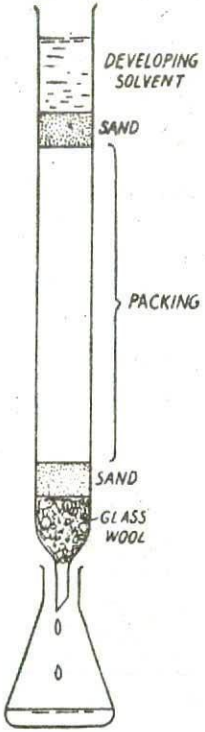
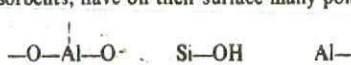


Fig. 2·15. Apparatus for column chromatography.

The sample of the mixture is first applied to the column at the top. Some components of the mixture are adsorbed strongly, while others less strongly. The more strongly a substance is adsorbed, the more slowly it moves down the column. Thus the components moving down with different rates undergo a process of partial separation. Now a suitable solvent is passed through the column gradually and the compounds of the mixture are removed from the adsorbent surface. *The process forcing various compounds to be dissolved away from the adsorbent is termed* **elution** *and the solvent used is called* **eluent**. The elution and re-adsorption of the various components is repeated several times as they travel down. This eventually results in the separation of the components as 'bands'. This operation is often referred to as the development of the **chromatogram** and is illustrated in Fig. 2·16. Each band as it comes out of the lower end of the column is received in a separate container. Alternatively, after the development of the chromatogram the flow of the solvent into the column is arrested. The solvent column is taken out and the bands separated by cutting out. Each band so removed is then extracted with a solvent to recover the individual compounds. This method is particularly used for separation of coloured mixture when the bands in the chromatogram are distinctly visible.

Since the phenomenon of adsorption is involved in column chromatography, it is also referred to as **adsorption chromatography**. The alumina and silica gel (aluminium and silicon oxides) which are used as adsorbents, have on their surface many polar groups such as



Also, the compounds in the sample to be separated have different polarity due to the presence of certain polar functional groups. Thus the adsorption of the components of a mixture to the adsorbent surface in varying degree is due to electrostatic attractions between them. The strength of adsorption of compounds containing the following functional groups increases in the order noted below on any given adsorbent.

$$-Cl\ ,\ -Br\ ,\ -I\ <\ >C=C<\ <\ >C=O$$

$$<\ -CHO\ <\ -NH_2\ <\ -OH\ <\ -CO_2H$$

For the same reason, solvents with different polarity are used for development of chromatograms when a single solvent fails to achieve the same.

Gas-Liquid Chromatography or GLC. This is a much more recent method of separation of components of a liquid sample which is available only in a very small quantity (0·1 to 10 ml).

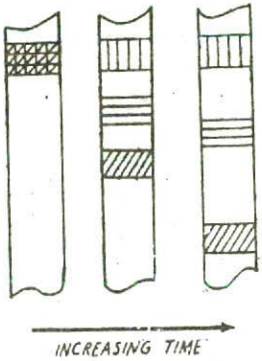


Fig. 2·16. Development of the chromatogram.

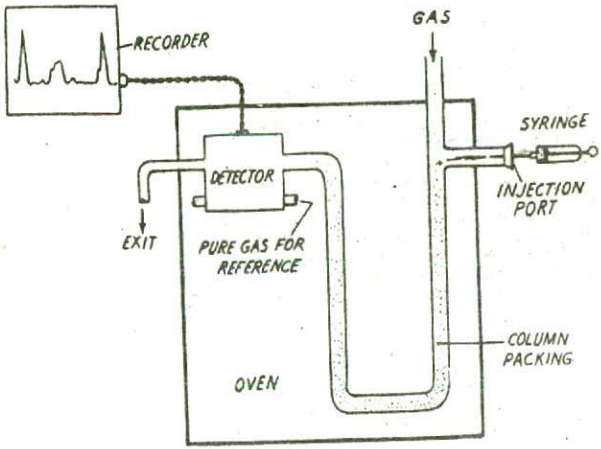


Fig. 2·17. Gas-liquid chromatography apparatus.

It is often incorrectly called **Vapour-phase Chromatography** (VPC). Here the *stationary phase* is a film of relatively less volatile liquid (say ether) on a solid support and the *moving phase* is a mixture of vaporized sample and an inert *carrier gas* (helium or nitrogen). The sample is distributed between the liquid film and the carrier gas. The process of glc is illustrated in Fig. 2·17.

With the help of a syringe is injected the liquid sample into a hot chamber where it is vaporized all at once. The vapour is pushed through a several feet long tightly packed column by means of *carrier gas*. The packing consists of a finely divided solid substance (crushed firebrick) on the surface of which is adsorbed an appropriate liquid of low volatility. As the vapour travels through the column, the various components are continually dissolving in and vaporizing from the packing liquid. Thus interaction with the liquid is not uniform and depends on factors such as boiling point of the compound, its polarity and possibility of hydrogen bonding. The net result is that different compounds move at different rates through the column. Thus the components of the sample separate into individual 'bands' in the carrier gas which then pass through the detector. As the vapour of each component emerges from the column, the detector produces an electronic signal which causes a peak to be traced by the recorder. The vapour of the component are then collected at the 'exit port' and condensed.

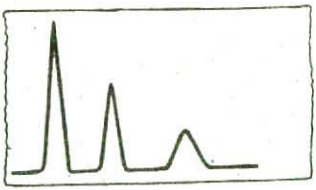


Fig. 2·18. A typical gas chromatogram of a mixture of three components.

The gas-liquid chromatography is far superior to a good distilling column. If the efficiency of a gas chromatic column is expressed in 'theoretical plates' for comparison with distillation, it is found that the gas chromatographic column provides 50 times as many theoretical plates as an efficient distillation column of the same length.

TESTS OF PURITY

A pure organic substance has characteristic physical properties, crystalline form, refractive index, specific gravity, melting point and boiling point. If a given sample of a substance shows

the properties that the pure compound is known to possess, it may be considered pure. The numerical value of these properties changes with the nature of the amount of impurities present. In most laboratory work, the melting point of a solid substance and the boiling point of a liquid substance is considered a sufficient indication of its purity.

Melting Point. A pure solid substance melts sharply at a definite temperature, while an impure substance will have a lower and indefinite point.

Determination. The apparatus employed for the determination of the melting point of a given solid substance is shown in Fig. 2·19. The crystals are powdered finely and charged into a capillary tube sealed at one end. The capillary tube should be 5 to 6 cms long and 1 mm in diameter. The substance should stand in the capillary 3·4 mm from the bottom when thoroughly packed. The capillary tube is wetted with the liquid in the bath and placed along side a thermometer fixed in an iron stand. The capillary remains sticking to the thermometer by itself. Alternatively, the capillary tube is fastened to the thermometer using a rubber band so that the substance under examination stands just opposite to the middle of the mercury bulb. The thermometer carrying the capillary is then lowered in the beaker containing a suitable liquid (higher boiling point), keeping the rubber band above the liquid level. The thermometer is clamped with an iron stand (not shown in the Fig.). The beaker is now heated slowly and the temperature of the bath is kept uniform by gentle but constant stirring with the help of a 'ring stirrer'. To ensure uniform heating of the liquid, Thiele replaced the beaker by a specially designed tube, known after him as Thiele tube (Fig. 2·19 (*b*)). Here the liquid is heated by convection currents, eliminating the use of the stirrer.

When the substance in the capillary just shows signs of melting, the burner is removed and the stirring continued. The temperature at which the substance just melts and becomes transparent is recorded. The experiment is repeated with a new capillary charged with fresh substance and the average of the two melting points thus determined is the correct melting point of the substance under examination.

The sulphuric acid bath can be replaced by a water-bath for melting points below 100°C.

Another convenient and quick method for determination of melting point now frequently used in industrial laboratories, is known as **Metal block method**. It eliminates the use of liquid

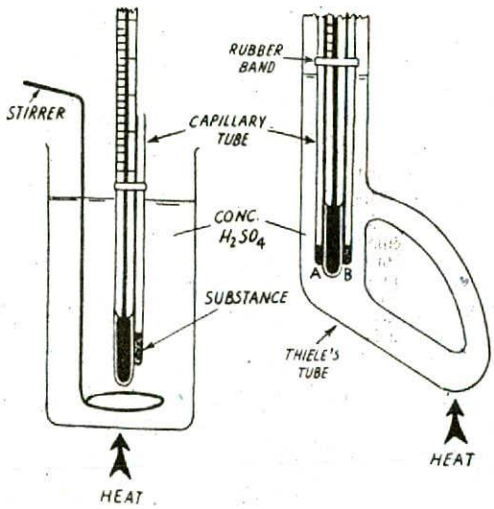


Fig. 2·19. Determination of melting point.

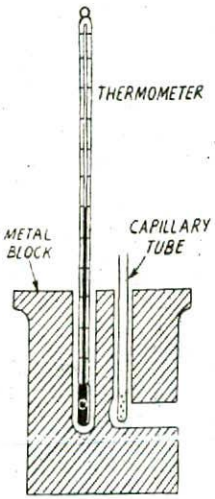


Fig. 2·20. Metal block method of determining melting points.

baths for the purpose of heating. The sample in the capillary tube and the thermometer are placed in the groove in the metal block. The block is electrically heated. The temperature recorded by the thermometer at which the solid just becomes transparent (seen through the window in the side of the block) is accurately noted.

Mixed Melting Point. The method of mixed melting point as a means of establishing the purity of a substance depends upon the fact that *a pure organic compound possesses a sharp melting point while the presence of impurities usually lowers the melting point.* A substance mixed with impurities does not melt sharply at a fixed temperature but does so over a range of temperature. It will start melting at a certain temperature but will not become entirely liquid until a higher temperature is reached.

The substance whose purity is to be ascertained is mixed with a sample of the authentically pure substance. The melting point of the mixture is determined as usual. If this mixture melts sharply and the melting point comes out to be the same as that of the sample under experiment taken alone, it is proved that the two are indeed the samples of the same substance. In other words, the substance under trial is proved to be pure beyond doubt.

Boiling Point. A pure organic liquid boils at a fixed temperature which is characteristic of that substance. The presence of impurities raises its boiling point.

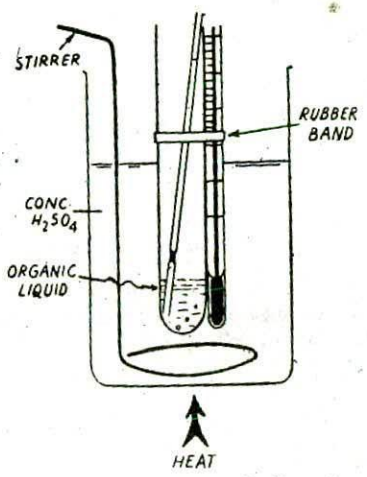


Fig. 2·21. Determination of boiling point.

(1) *Distillation Method.* If enough liquid is available, its boiling point is determined in an ordinary distillation apparatus (Fig. 2-21.) A pure liquid will distil at a constant temperature which is its boiling point. In case the liquid is impure, the boiling point will rise during distillation.

(2) *Capillary-tube Method.* When only a small quantity of the liquid is available, its boiling point is determined by the 'Capillary-tube method'. A few drops of the liquid are placed in a thin-walled small test-tube. A capillary tube sealed at about one centimeter from one end, is dropped into it. The glass tube containing the liquid and the capillary, is then tied alongside a thermometer so that the liquid stands just near the bulb. The thermometer is then lowered in a beaker containing water or sulphuric acid (any liquid whose boiling point is higher than that of the substance under investigation).

The beaker is heated and the bath liquid stirred continuously with a ring stirrer. When the boiling point is reached, bubbles issue in a rapid stream from the lower end of the capillary. The thermometer is read when the evolution of bubbles just stops. The experiment is repeated with a fresh liquid in a new capillary and the boiling point recorded as before. The mean of the two readings is taken to be the correct boiling point of the liquid under examination.

In the above determination of the boiling point the tube containing the liquid and capillary may be heated in a *Thiele Tube* instead of the beaker. It is handy and eliminates the use of a stirrer.

QUESTIONS

1. Write an account of the various methods by which organic compounds are purified.
2. The isolation of organic compounds is sometimes effected by distillation in steam, sometimes by extraction with a suitable solvent. Describe how each of these processes is employed, giving an example of each. Write a short account of the physical principles on which they depend for their success.
3. What are the methods generally employed for the purification of organic compounds ? How can you obtain a sample of pure ether from a mixture of alcohol, acetic acid and ether ?
4. Write an essay on methods of purification and criteria of purity of organic compounds.
5. Describe how you would separate in a pure condition each component of a mixture of ethyl alcohol, benzoic acid and acetanilide.
6. You are given an organic liquid ; how would you proceed to test its purity ? If it contains dissolved liquid impurity, describe a simple method for purifying it.
7. Write a note on : Chromatography and its applications. *(Delhi BSc, 1993)*
8. What are the criteria by which purity of an organic compound can be established ? *(Jiwaji BSc, 1994)*
9. Write a note on : Solvent extraction. *(Sambalpur BSc Hons, 1993)*
10. Write a note on : Column chromatography. *(Aligarh BSc Hons, 1994)*

Composition of Organic Compounds

1. Detection of Elements

The first step in the analysis of an organic compound is the detection of elements present in it. Most of these compounds contain 2 to 5 different elements. The principal elements present are :—carbon, hydrogen and oxygen. Often, in addition to these, they may contain nitrogen, sulphur and halogens. Phosphorus and metals are also present but only rarely. The order of abundance in which these elements are found in organic compounds is indicated below :

Elements		*Order of Abundance*
Carbon	—	Always present
Hydrogen	—	Nearly always present
Oxygen	—	Generally present
Nitrogen, Halogens and Sulphur	—	Less commonly present
Phosphorus and Metals	—	Rarely present

DETECTION OF CARBON AND HYDROGEN

If the compound under investigation is known to be organic, there is no need to test for carbon. This test is performed only to establish whether a given compound is organic or not. With the exception of few compounds *e.g.*, carbon tetrachloride, all organic compounds also contain hydrogen. The presence of both these elements is confirmed by the following common test.

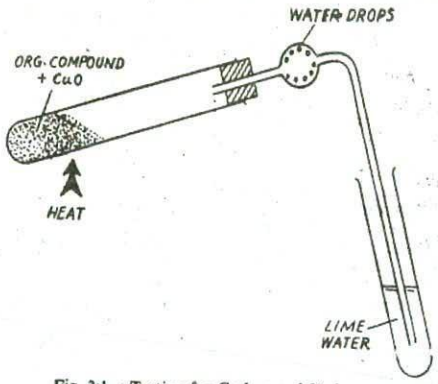


Fig. 3·1. Testing for Carbon and Hydrogen.

The organic substance is mixed intimately with about three times its weight of *dry* copper oxide. The mixture is then placed in a hard glass test-tube fitted with a bent delivery tube (Fig. 3·1), the other end of which is dipping into lime water in another test-tube. The mixture is heated strongly when the following reactions take place :—

$$C + 2CuO \longrightarrow CO_2 + 2Cu$$

$$2H + CuO \longrightarrow H_2O + Cu$$

Thus if carbon is present, it is oxidised to carbon dioxide which turns lime water milky. If hydrogen is also present, it will be oxidised to water which condenses in small droplets on the cooler wall of the test-tube and inside the bulb. The formation of water is further confirmed by testing the condensed liquid with anhydrous copper sulphate (*white*) that is turned blue.

If the substance under investigation is a gas or a volatile liquid, the above test is modified. The vapours of the substance are passed over heated copper oxide contained in a hard-glass combustion tube. The issuing gases are tested for carbon dioxide and water vapour as described before.

NOTE. While testing for hydrogen, it is essential that the apparatus and copper oxide used are absolutely dry. Copper oxide being hygroscopic in nature it is heated strongly just before use.

DETECTION OF OXYGEN

There is no conclusive test for oxygen, though its presence in organic compounds is often inferred by indirect methods.

(1) The substance is heated alone in a dry test-tube, preferably in an atmosphere of nitrogen. Formation of droplets of water on cooler parts of the tube obviously shows the presence of oxygen. A negative result, however, does not necessarily show the absence of oxygen.

(2) The second method is to test for the presence of various oxygen-containing groups such as *hydroxyl* (OH), *carboxyl* (COOH), *aldehyde* (CHO), *nitro* (NO_2), etc. If any of these is detected, the presence of oxygen is confirmed.

(3) The sure test for oxygen depends on the determination of the percentage of all other elements present in the given compound. If the sum of these percentages falls short of hundred, the remainder gives the percentage of oxygen and thus confirms its presence.

DETECTION OF NITROGEN

The presence of nitrogen in an organic compound is shown by the following tests :

(1) A little of the substance is heated strongly in a test-tube or by directly placing it in the Bunsen flame. A smell of burnt feathers may indicate nitrogen.

(2) **Sodalime Test.** The given substance is mixed with double the amount of sodalime ($NaOH + CaO$) and heated in a test-tube. The vapours of ammonia evolved show the presence of nitrogen. A negative result, however, is not a proof of the absence of nitrogen. Many classes of nitrogenous compounds including *nitro* and *diazo* derivatives, do not respond to this test.

(3) **Sodium Test** (*Lassaigne's Test*). This is a golden test for the detection of nitrogen in all classes of nitrogenous compounds. It involves the following steps :

(*i*) *The substance is heated strongly with sodium metal.*

$$\underset{\text{from Org. Compd.}}{Na + C + N} \longrightarrow NaCN$$

(*ii*) *The water extract of the fused mass is boiled with ferrous sulphate solution.*

$$FeSO_4 + \underset{\substack{\text{from excess}\\ \text{of sodium}}}{2NaOH} \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$6NaCN + Fe(OH)_2 \longrightarrow \underset{\text{sod. ferrocyanide}}{Na_4[Fe(CN)_6]} + 2NaOH$$

(*iii*) *To the cooled solution is then added a little ferric chloride solution and excess of concentrated hydrochloric acid.*

$$\underset{\text{sod. ferrocyanide}}{3Na_4[Fe(CN)_6]} + 4FeCl_3 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

The formation of Prussian blue or green coloration confirms the presence of nitrogen.

Hydrochloric acid is added in this step to dissolve the greenish precipitate of ferrous hydroxide produced by the excess of sodium hydroxide on ferrous sulphate in step (*ii*), which would otherwise mark the Prussian blue precipitate.

NOTE. In case sulphur is also present along with nitrogen in the given organic compound, a blood red coloration may appear while performing the above test. This is due to the formation of sodium sulphocyanide which again reacts with ferric chloride to produce blood red coloration :

$$Na + C + N + S \longrightarrow \underset{\text{sodium sulphocyanide}}{NaCNS}$$

$$3NaCNS + FeCl_3 \longrightarrow \underset{\substack{\text{ferric sulpho-}\\\text{cyanide}\\(\textit{blood red})}}{Fe(CNS)_3} + 3NaCl$$

Procedure of Sodium Test. Fix a fusion tube in an iron stand, clamping it just near the upper end (Fig. 3·2). Take a freshly cut piece of sodium of the size of a pea and dry it by pressing between the folds of a filter paper. Place the metal in a fusion tube and heat it from below. When it melts to a shining globule, put a pinch of the organic compound on it. Heat the tube with the tip of the flame till all reaction ceases and it becomes red hot. Now plunge it in about 50 ml of distilled water taken in a china dish and break the bottom of the tube by striking against the dish. Boil the contents of the dish for about ten minutes and filter. Label the filtrate as 'sodium extract' and proceed with it as follows.

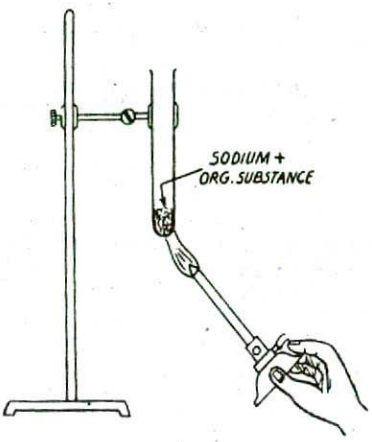


Fig. 3·2. Sodium test for Nitrogen.

Take a portion of the sodium extract in a test-tube and note if it is alkaline. If it is not, make it so by adding sodium hydroxide. Then add to it freshly prepared ferrous sulphate solution and heat it to boiling. Put 2-3 drops of ferric chloride solution, cool and acidify with conc. hydrochloric acid. A Prussian blue or green precipitate, or even coloration, confirms the presence of nitrogen.

DETECTION OF SULPHUR

The presence of sulphur in organic substances is shown as described below.

(1) **Sodium Test.** Sulphur if present in the given organic compound, upon fusion with sodium reacts to form sodium sulphide.

$$2Na + S \longrightarrow \underset{\text{sodium sulphide}}{Na_2S}$$

Thus, the 'sodium extract' obtained from the fused mass may be tested as :

(*i*) To a portion, add freshly prepared sodium nitroprusside solution. A deep violet coloration indicates sulphur.

(*ii*) Acidify a second portion of the extract with acetic acid and then add lead acetate solution. A black precipitate of lead sulphide confirms the presence of sulphur.

$$\underset{\text{lead acetate}}{Pb(CH_3COO)_2} + Na_2S \longrightarrow \underset{\substack{\text{lead sulphide}\\(\textit{black ppt})}}{PbS} + 2CH_3COONa$$

(2) **Oxidation Test.** The organic substance is fused with a mixture of potassium nitrate and sodium carbonate. The sulphur if present, is oxidised to sulphate.

$$Na_2CO_3 + S + 3O \longrightarrow Na_2SO_4 + CO_2$$

The fused mass is extracted with water, acidified with hydrochloric acid and then barium chloider solution is added to it. A white precipitate indicates the presence of sulphur.

$$BaCl_2 + Na_2SO_4 \longrightarrow \underset{\substack{\text{barium sulphate}\\(\textit{white ppt.})}}{BaSO_4} + 2NaCl$$

DETECTION OF HALOGENS

(1) **Sodium Test.** Upon fusion with sodium, the halogens in the organic compound are converted to the corresponding sodium halides. Thus,

$$Cl + Na \longrightarrow NaCl$$
$$Br + Na \longrightarrow NaBr$$
$$I + Na \longrightarrow NaI$$

Acidify a portion of 'sodium extract' with dilute nitric acid and add to it silver nitrate solution.

White precipitate soluble in ammonia indicates CHLORINE,

Yellowish precipitate sparingly soluble in ammonia indicates BROMINE,

and *Yellow precipitate insoluble in ammonia indicates* IODINE.

NOTE. When nitrogen or sulphur is also present in the compound, the 'sodium extract' before testing for halogens is boiled with strong nitric acid to decompose the cyanide and the sulphide formed during the sodium fusion. If not removed, these radicals will form a white and black precipitate respectively on the addition of silver nitrate.

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

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

(2) **Copper Wire Test** (*Beilstein's Test*). The copper wire flattened at one end is heated in an oxidising Bunsen flame till it ceases to impart any green colour to the flame. A small quantity of the substance under investigation is now taken on the flattened end of the wire which is re-inserted in the Bunsen flame. Upon heating for a while, the halogen present in the substance is converted to a volatile copper halide which imparts a blue or green colour to the flame. This test though very sensitive, is not always reliable. A substance like urea which contains no halogen, also colours the flame green.

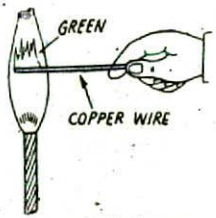


Fig. 3·3. Beilstein's test.

DETECTION OF PHOSPHORUS

The solid substance is heated strongly with an oxidising agent such as conc. nitric acid or a mixture of sodium carbonate and potassium nitrate. The phosphorus present in the substance is thus oxidised to phosphate. The residue is extracted with water, boiled with some nitric acid, and then a hot solution of ammonium molybdate is added to it in excess. A yellow coloration or precipitate indicates the presence of phosphorus.

DETECTION OF METALS

The substance is strongly heated in a crucible, preferably of platinum, till all reaction ceases. An incombustible residue indicates the presence of a metal in the substance. The residue is extracted with dilute acid and the solution tested for the presence of metallic radical by the usual scheme employed for inorganic salts.

2. Estimation of Elements

Having known the elements present in a given organic compound, we proceed to determine their composition by weight. The estimation of carbon, hydrogen, nitrogen and other elements can be done accurately by methods described below.

ESTIMATION OF C AND H

Both carbon and hydrogen are estimated together in one operation. A known weight of the organic substance is burnt in excess of oxygen when the carbon and hydrogen present in it are oxidised to carbon dioxide and water respectively.

$$C_xH_y + \underset{\text{(excess)}}{O_2} \longrightarrow xCO_2 + y/2\ H_2O$$

The weights of carbon dioxide and water thus formed are determined and the amounts of *carbon* and *hydrogen* in the original substance calculated.

Apparatus. The apparatus employed for the purpose consists of three units :

(*i*) *Oxygen supply,*

(*ii*) *Combustion tube, and*

(*iii*) *Absorption apparatus.*

Oxygen Supply. Oxygen from the aspirator is allowed to bubble through sulphuric acid contained in a Drechsel bottle and then passed through U-tubes charged with sodalime. The

oxygen gas thus freed from moisture and carbon dioxide enters the combustion tube.

Combustion tube. A hard-glass tube about 33 inches in length and ½ inch in diameter, and open at both ends is used for the combustion of the organic substance. It is filled as shown

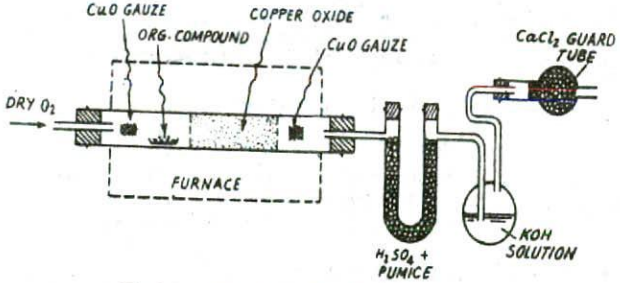


Fig. 3·4. Apparatus for the estimation of C and H.

in Fig. 3·4, with (*i*) a roll of oxidised copper gauze to prevent the backward diffusion of the products of combustion ; (*ii*) a porcelain boat containing a known weight (about 0·2 g) of the organic substance ; (*iii*) coarse copper oxide packed in about two-thirds of the entire length of the tube, and kept in position by loose asbestos plugs on either side ; and (*iv*) a roll of oxidised copper gauze placed towards the end of the combustion tube to prevent any vapours of the organic substance leaving the tube unoxidised. The combustion tube is enclosed in a furnace, heated by gas burners.

Absorption Apparatus. The products of combustion containing moisture and carbon dioxide are then passed on to the absorption apparatus which consists of : (*i*) a weighed U-tube packed with pumice soaked in concentrated sulphuric acid, to absorb water ; (*ii*) a set of bulbs containing strong solution of potassium hydroxide, to absorb carbon dioxide ; and finally (*iii*) a guard-tube filled with anhydrous calcium chloride to prevent the entry of moisture from atmosphere.

Procedure. To start with, before loading it with the boat, the combustion tube is detached from the absorption unit. The tube is heated strongly to dry its contents and carbon dioxide present in it is removed by passing a current of pure, dry oxygen through it. It is then cooled slightly and connected to the absorption apparatus. The other end of the combustion tube is opened for a while and the boat containing weighed organic substance introduced. The tube is again heated strongly till the whole of the substance in the boat has burnt away. This takes about two hours. Finally, a strong current of oxygen is passed through the combustion tube to sweep away any traces of carbon dioxide or moisture which may have been left in it. The U-tube and the potash bulbs are then detached and the increase in weight of each of them determined.

Let the weight of the substance taken $= x$ g
Increase in weight of U-tube (H_2O) $= y$ g
Increase in weight of potash bulbs (CO_2) $= z$ g
Since 18 g of water contain hydrogen $= 2$ g

y g of water contain hydrogen $= \frac{2}{18} \times y$ g

Also, 44 g of CO_2 contain carbon $= 12$ g

z " " " " $= \frac{12}{44} \times z$ g

Hence the given organic substance contains :—

$$H = \frac{2y}{18} \times \frac{100}{x}\ \%$$

and $$C = \frac{12z}{44} \times \frac{100}{x}\ \%.$$

NOTE. (1) If the organic substance under investigation also contains nitrogen, upon combustion it will produce oxides of nitrogen which will also be absorbed in the potash bulbs. Hence a spiral of copper is introduced at the right extreme of the combustion tube, so that the oxides of nitrogen are reduced to free nitrogen which escapes unabsorbed.

(2) If the compound contains halogens as well, a spiral of silver is also introduced in the combustion tube. The free halogens, which would have been otherwise absorbed in the potash bulbs, are converted to silver halides and thus eliminated from the products of combustion.

(3) In case the substance also contains sulphur, the copper oxide in the combustion tube is replaced by lead chromate. The sulphur dioxide formed during combustion is thus converted to lead sulphate and is thus prevented from passing into the absorption unit.

Example 1. *0·2475 g of an organic substance gave on combustion 0·4950 g of carbon dioxide and 0·2025 g of water. Calculate the percentage of carbon and hydrogen in it.*

Weight of the substance taken = 0·2475 g

Weight of CO_2 formed = 0·4950 g

Weight of H_2O formed = 0·2025 g

Now, we know $\underset{44}{CO_2} \equiv \underset{12}{C}$ and $\underset{18}{H_2O} \equiv \underset{2}{2H}$

Weight of C in 0·4950 g of CO_2 $= \frac{0{\cdot}4950 \times 12}{44}$ g

Weight of H in 0·2025 g of H_2O $= \frac{0{\cdot}2025 \times 2}{18}$ g

Hence, percentage of C $= \frac{0{\cdot}4950 \times 12}{44} \times \frac{100}{0{\cdot}2475}$

$= 54{\cdot}54$

and percentage of H $= \frac{0{\cdot}2025 \times 2}{18} \times \frac{100}{0{\cdot}2475}$

$= 9{\cdot}09$

Example 2. *0·2346 g of an organic compound containing carbon, hydrogen and oxygen only was analysed by the combustion method. The increase in weight of the U-tube and the potash bulbs at the end of the operation was found to be 0·2754 g and 0·4488 g respectively. Determine the percentage composition of the compound.*

Wt of CO_2 (increase in wt. of potash bulbs) = 0·4488 g

Wt of H_2O (increase in wt. of U-tube) = 0·2754 g

Since we know that $\underset{44}{CO_2} \equiv \underset{12}{C}$ and $\underset{18}{H_2O} \equiv \underset{2}{2H}$

Wt of C in 0·4488 g of CO_2 $= \frac{0{\cdot}4488 \times 12}{44}$ g

Wt of H in 0·2754 g of H_2O $= \frac{0{\cdot}2754 \times 2}{18}$ g

But the wt of the compound taken for analysis = 0·2346 g

∴ Percentage of C in it $= \frac{0{\cdot}4488 \times 12}{44} \times \frac{100}{0{\cdot}2346} = 52{\cdot}18$

Percentage of H $= \frac{0{\cdot}2754 \times 2}{18} \times \frac{100}{0{\cdot}2346} = 13{\cdot}04$

Percentage of O (*difference*) = 34·78.

ESTIMATION OF NITROGEN

The two chief methods for the estimation of nitrogen in an organic substance are :

(*i*) *The Dumas Method,* and (*ii*) *The Kjeldahl Method.*

Dumas Method. This method is based upon the fact that nitrogenous compounds when heated with copper oxide in an atmosphere of carbon dioxide yield free nitrogen. Thus,

$$C_xH_yN_z + (CuO) \longrightarrow xCO_2 + y/2\ H_2O + z/2\ N_2 + (Cu)$$

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

Apparatus. The apparatus used in the Duma's method consists of :

(*i*) CO_2 *generator,* (*ii*) *Combustion tube,* and (*iii*) *Schiff's Nitrometer.*

CO_2 *GENERATOR.* The carbon dioxide needed in this process is prepared by heating magnesite or sodium bicarbonate contained in a hard-glass test-tube, or by the action of dilute hydrochloric acid on marble in a Kipp's apparatus. The gas is passed into the combustion tube after being dried by bubbling through concentrated sulphuric acid contained in a Drechsel bottle.

COMBUSTION TUBE. The combustion tube of about 90 cm length, which is heated in a combustion furnace, is charged with :

(*i*) *a roll of oxidised copper gauze* to prevent the back diffusion of the products of combustion and to heat the organic substance mixed with copper oxide by radiation ;

(*ii*) a weighed amount (about 0·2 g) of the *organic substance* mixed with excess of copper oxide :

(*iii*) *a layer of coarse copper oxide* packed in about two-thirds of the entire length of the tube, and kept in position by loose asbestos plugs on either side ; this oxidises the organic vapours passing through it ; and

(*iv*) *a reduced copper spiral* which reduces any oxides of nitrogen formed during combustion, to nitrogen.

SCHIFF'S NITROMETER. The nitrogen gas obtained by the decomposition of the substance in the combustion tube is mixed with considerable excess of carbon dioxide. It is estimated by passing into Schiff's nitrometer where carbon dioxide is absorbed by caustic potash solution and the nitrogen collects in the upper part of the graduated tube.

Procedure. The apparatus is fitted up as shown in Fig. 3·5, and to start with the tap of the nitrometer is left open. Carbon dioxide is passed through the combustion tube to replace

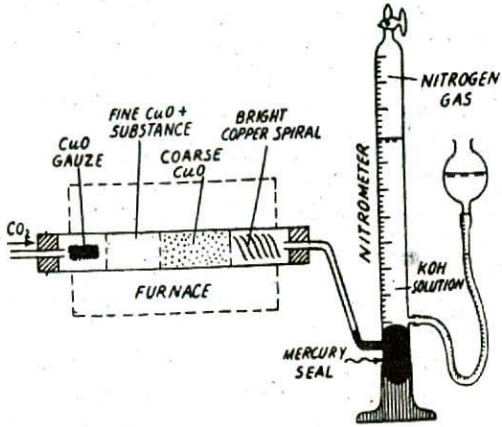


Fig. 3·5. Duma's method for Nitrogen estimation.

the air in it. When the gas bubbles rising through the potash solution fail to reach the top of it and are completely absorbed, it shows that only carbon dioxide is coming and that all the air has been displaced from the combustion tube. The nitrometer is then filled with potassium hydroxide solution by lowering the reservoir and the tap closed. The combustion tube is now heated in the furnace, raising the temperature gradually. The nitrogen set free from the compound collects in the nitrometer. When the combustion is complete, a strong current of carbon dioxide is sent through the apparatus in order to sweep the last traces of nitrogen from it. The volume of the gas collected is noted after adjusting the reservoir so that the level of solution in it and the graduated tube is the same. The atmospheric pressure and the temperature are also recorded.

Calculations :

Let w = weight of the substance in grams

v = volume of moist N_2 in ml

t = room temperature in °C

B = barometric pressure in mm of mercury

b = aq. tension at room temperature (t°C)

$$\text{Volume of } N_2 \text{ at NTP} = \frac{v(B - b)}{t + 273} \times \frac{273}{760} = V \text{ ml } (say)$$

Now, 22,400 ml of N_2 at NTP weigh = 28 g

V ml " " " $= \frac{28}{22400} \times V$ g

$\therefore$ Percentage of N $= \frac{28V}{22400} \times \frac{100}{w}$

Example 3. *0·1877 g of an organic substance when analysed by the Dumas method yield 31·7 ml of moist nitrogen measured at 14°C and 758 mm mercury pressure. Determine the percentage of nitrogen in the substance. (Aqueous tension at 14°C = 12 mm)*

Volume of N_2 at NTP $= \frac{v(B-b)}{t+273} \times \frac{273}{760} = V$ ml

Substituting the various values in the above equation,

$$V = \frac{31{\cdot}7\,(758-12)}{14+273} \times \frac{273}{760} = 29{\cdot}6 \text{ ml}$$

Weight of 29·6 ml of nitrogen $= \frac{28}{22400} \times 29{\cdot}6$ g

$\therefore$ Percentage of nitrogen $= \frac{28 \times 29{\cdot}6}{22400} \times \frac{100}{0{\cdot}1877} = 19{\cdot}72$

Example 4. *In the estimation of nitrogen present in an organic compound by Dumas method, 0·200 g. yielded 20·7 ml of nitrogen at 15°C and 760 mm pressure. Calculate the percentage of nitrogen in the compound.*

Volume of N_2 at NTP $= \frac{v \times B}{t+273} \times \frac{273}{760} = V$ ml

Substituting the values in the above equation,

$$V = \frac{20{\cdot}7 \times 760}{288} \times \frac{273}{760} = 19{\cdot}63 \text{ ml}$$

Weight of 19·63 ml of Nitrogen $= \frac{28}{22400} \times 19{\cdot}63$ g

$\therefore$ Percentage of Nitrogen $= \frac{28}{22400} \times 19{\cdot}63 \times \frac{100}{0{\cdot}2} = 12.27.$

Kjeldahl Method. This method is carried much more easily than the Dumas method. It is used largely in the analysis of foods and fertilisers.

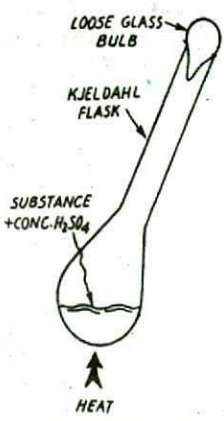


Fig. 3·6. Kjeldahl flask.

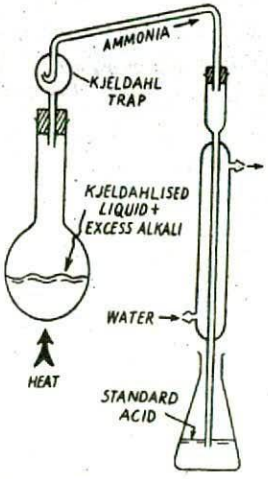


Fig. 3·7. Distillation of ammonia.

Kjeldahl method is based on the fact that when an organic compound containing nitrogen is heated with concentrated sulphuric acid, the nitrogen in it is quantitatively converted into

ammonium sulphate. The resultant liquid is then treated with excess of alkali and the liberated ammonia gas absorbed in excess of standard acid. The amount of ammonia (and hence of nitrogen) is determined by finding the amount of acid neutralised by back titration with some standard alkali.

Procedure. A weighed quantity of the substance (0·3 to 0·5 g) is placed in a special long-necked *'Kjeldahl flask'* made of resistant glass. About 25 ml of concentrated sulphuric acid together with a little potassium sulphate and copper sulphate is added to it. Potassium sulphate raises the boiling point and thus ensures complete reaction, while copper sulphate acts as a catalyst. The flask is loosely stoppered by a glass bulb and heated gently in an inclined position. The heating is continued till the brown colour of the liquid first produced, disappears leaving the contents clear as before. At this point all the nitrogen in the substance is converted to ammonium sulphate. The Kjeldahl flask is then cooled and its contents diluted with some distilled water, and then carefully transferred into a one-litre round-bottom flask. An excess of sodium hydroxide solution is poured down the side of the flask and it is fitted with a Kjeldahl trap and a water condenser, as shown in Fig. 3·7. The lower end of the condenser dips in a measured volume of excess of the N/10 H_2SO_4 solution. The liquid in the round-bottom flask is then heated and the liberated ammonia distilled into sulphuric acid. The Kjeldahl trap serves to retain any alkali splashed up on vigorous boiling. When no more ammonia passes over (test the distillate with red litmus), the receiver is removed. The excess of acid is then determined by titration with N/10 alkali, using phenolphthalein as the indicator.

Calculations. Let the weight of the organic substance be x g and V ml of N HCl is required for complete neutralisation of ammonia evolved.

$$\text{V ml N HCl} \equiv \text{V ml of N } NH_3$$

1000 ml of N NH_3 contain 17 g of ammonia or 14 g of nitrogen.

$$\text{Amount of nitrogen present in V ml of N } NH_3 = \frac{14}{1000} \times V \times N \text{ g}$$

$$\text{Percentage of Nitrogen} = \text{wt. of nitrogen} \times \frac{100}{\text{Wt of substance}}$$

$$= \frac{14}{1000} \times V \times N \times \frac{100}{x} = \frac{1{\cdot}4VN}{x}$$

where N stands for normality of the acid used

V stands for volume of the acid used up

and x stands for the wt. of the substance kjeldahlised.

Example 5. *0·257 g of an organic substance was heated with conc. sulphuric acid and then distilled with excess of strong alkali. The ammonia gas evolved was absorbed in 50 ml of N/10 hydrochloric acid which required 23·2 ml of N/10 NaOH for neutralisation at the end of the operation. Determine the percentage of nitrogen in the substance.*

Volume of N/10 HCl neutralised by ammoina = 50 − 23·2 = 26·8 ml

Now, 26·8 ml of N/10 HCl ≡ 26·8 ml of N/10 NH_3

≡ 26·8 ml of N/10 N (*combined*)

26·8 ml of N/10 N solution contains $\frac{14}{10} \times \frac{26{\cdot}8}{1000}$ g of nitrogen

This weight of Nitrogen was originally present in 0·257 g of the organic substance.

$\therefore$ Percentage of Nitrogen = $\frac{14 \times 26{\cdot}8}{10 \times 1000} \times \frac{100}{0{\cdot}257} = 14{\cdot}6$.

Example 6. *0·4 g of an organic compound was kjeldahlised and ammonia evolved was absorbed into 50 ml of semi-normal solution of sulphuric acid. The residual acid solution was diluted with distilled water and the volume was made up to 150 ml. 20 ml of this diluted solution required 31 ml of N/20 NaOH solution for complete neutralisation. Calculate the percentage of nitrogen in the compound.*

(*i*) Calculation of Acid used by Ammonia

Volume of $\frac{N}{2}$ H_2SO_4 taken = 50 ml

Let the volume of N/2 H_2SO_4 left unused by ammonia = V ml
V ml of this acid solution was diluted to 150 ml and titrated against N/20 NaOH
20 ml of diluted solution ≡ 31 ml of N/20 NaOH

$\therefore$ Normality of diluted solution $= 31 \times \frac{N}{20} \times \frac{1}{20} = \frac{31}{400}$ N

Normality of 150 ml of acid solution $= \frac{31}{400}$ N

i.e., V ml of $\frac{N}{2}$ H_2SO_4 ≡ 150 ml of $\frac{31}{400}$ N diluted acid

$$\therefore \quad V = 150 \times \frac{31}{400} \times \frac{2}{1} = 23{\cdot}25 \text{ ml}$$

i.e., Volume of $\frac{N}{2}$ H_2SO_4 left = 23·25 ml

$\therefore$ Volume of acid used up by ammonia = 50 − 23·25 = 26·75 ml

(*ii*) Calculation of Percentage of N

26·75 ml of N/2 H_2SO_4 ≡ 26·75 ml of N/2 NH_3 solution
≡ 26·75 ml of N/2 N (*combined in solution*)

$\therefore$ Wt of nitrogen in 26·75 ml of N/2 solution

$$= \frac{14}{2} \times \frac{1}{1000} \times 26{\cdot}75 \text{ g}$$

This wt of Nitrogen was originally present in 0·4 g of the substance

$\therefore$ Percentage of Nitrogen $= \frac{14}{2} \times \frac{1}{1000} \times 26{\cdot}75 \times \frac{100}{0{\cdot}4} = 46{\cdot}81$

ESTIMATION OF HALOGENS

Carius Method. It consists in oxidising the organic substance with fuming nitric acid in the presence of silver nitrate. The halogen of the substance is thus converted to silver halide which is separated and weighed.

The Carius method of estimating halogens involves the use of a stout hard-glass tube (*bomb tube*) of about 50 cm length and closed at one end. About 5 ml of fuming nitric acid together with 2 to 2·5 g of pure silver nitrate is placed in it. A narrow 'weighing tube', containing an accurately weighed quantity of the substance is then slipped into the bomb tube, taking care to avoid the mixing of the substance with nitric acid. The open end of the tube is then sealed off. It is now heated in an iron jacket of the furnace heated by burners from below. The temperature of the furnace is gradually raised to 300°C. After heating for about six hours, the tube is allowed to cool. The high pressure developed inside the tube is released by softening the sealed end with a small flame, when a hole is blown open through which the gases escape. The end of the tube is now cut off and the contents transferred into a beaker. The halide formed is collected in a Gooch crucible, washed, dried and weighed.

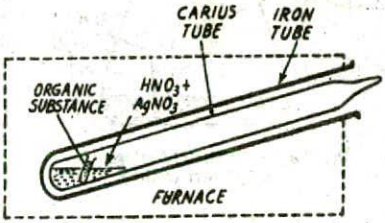


Fig. 3·8. Heating the bomb tube in a furnace (*Carius Method*).

Let *w* g of the organic substance give *x* g of the silver halide.

$$\therefore \text{ Percentage of Halogen} = \frac{\text{At Wt of Halogen}}{\text{M Wt of silver halide}} \times \frac{100\,x}{w}$$

Example 7. *0·197 g of an organic substance when heated with excess of strong nitric acid and silver nitrate gave 0·3525 g of silver iodide. Find the percentage of iodine in the compound.*

Since $\frac{AgI}{(108+127)} = \frac{I}{127}$

In this case 0·197 g of the compound gave 0·3525 g of AgI ≡ $\frac{0{\cdot}3525 \times 127}{235}$ g iodine

$$\therefore \text{ Percentage of Iodine } = \frac{0{\cdot}3525 \times 127}{235} \times \frac{100}{0{\cdot}197} = 96{\cdot}68$$

Example 8. *0·2562 g of an organic substance when heated with excess of strong nitric acid and silver nitrate gave 0·3066 g of silver bromide. Find the percentage of bromine in the compound.*

Since $\underset{(108+80)}{AgBr} \equiv \underset{80}{Br}$

Here, 0·2562 g of the substance gave 0·3066 g of AgBr = $\frac{0{\cdot}3066 \times 80}{188}$ g bromine

$$\therefore \text{ the percentage of bromine } = \frac{0{\cdot}3066 \times 80}{188} \times \frac{100}{0{\cdot}2562} = 50{\cdot}93$$

Oxygen Flask Method. This method of estimating halogens has been introduced only recently. It is simple in operation and general in application. The organic sample is ignited in an atmosphere of oxygen and the products of combustion are absorbed in aqueous alkaline hydrogen peroxide. The chlorine and bromine of the organic substance are converted into chloride and bromide respectively, whereas iodine if present is changed into molecular iodine with some iodate. These products are then determined by titration method.

Procedure. A known weight of the organic sample is wrapped in a filter paper so that a small tail of paper is left out as a fuse. The wrapped sample is clasped between the folds of a platinum gauze attached to the glass stopper by platinum wire. Dilute sodium hydroxide and a few drops of hydrogen peroxide (H_2O_2) are placed in a conical flask (*see* Fig. 3·9). The flask is briskly flushed with a stream of oxygen from an 'oxygen cylinder'. The paper fuse is ignited and the ground glass stopper carrying the sample replaced rapidly into the flask. The stopper is pressed with hand to make the joint air-tight for the few seconds of combustion. The 'oxygen flask' (from which the method takes its name) is now shaken vigorously to ensure complete absorption of the gaseous products. The stopper and the platinum mounting (gauze and holding wire) are carefully washed into the flask and the contents analysed as follows.

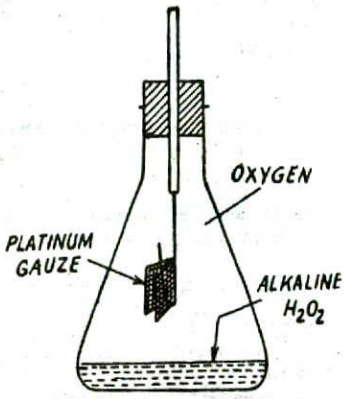


Fig. 3·9. Estimation of halogens by oxygen flask method.

Chlorine and Bromine are estimated by making the contents of the flask slightly acidic with sulphuric acid and then titrating with standard solution of silver nitrate. If the weight of the organic sample taken be x g and V ml of N silver nitrate is required to reach the end point, the percentage of chlorine can be calculated.

Since $Cl \equiv AgNO_3$

V ml of N $AgNO_3 \equiv$ V ml of N chlorine (Cl)

But 1000 ml of N chlorine (Cl) solution contains Cl = 35·5 g

$\therefore$ V ml of N chlorine (Cl) solution contains Cl

$$= \frac{35{\cdot}5}{1000} \times N \times V \text{ g}$$

$$\text{Hence percetage of Cl in the sample } = \frac{35{\cdot}5}{1000} \times N \times V \times \frac{100}{x}$$

Similarly, the percentage of bromine (Br) in the organic sample would be

$$= \frac{80}{1000} \times N \times V \times \frac{100}{x}$$

Iodine is determined by first converting it into iodate by adding excess of bromine. Then potassium iodide and sulphuric acid is added to liberate iodine which is titrated with standard thiosulphate.

$$I_2 + 5Br_2 + 6H_2O \longrightarrow 2HIO_3 + 10HBr$$

$$HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O$$

If x g of the sample require V ml of N sodium thiosulphate,

$$\text{Percentage of I} = \frac{127}{1000} \times \frac{N}{6} \times V \times \frac{100}{x}$$

ESTIMATION OF S AND P

Sulphur is estimated by a slight modification of the *Carius Method.* The organic substance is heated with fuming nitric acid but no silver nitrate is added. The sulphur of the substance is oxidised to sulphuric acid which is then precipitated as barium sulphate by adding excess of barium chloride solution. The precipitate is filtered, washed, dried and weighed. From the weight of the barium sulphate so obtained, the percentage of sulphur can be calculated.

Phosphorus is also estimated like sulphur. The organic substance is heated with fuming nitric acid whereupon its phosphorus is oxidised to phosphoric acid. The phosphoric acid is precipitated as ammonium phosphomolybdate, $(NH_4)_3PO_4.12MoO_3$, by the addition of ammonia and ammonium molybdate solution. This is then separated, dried and weighed.

Example 9. *In an estimation of sulphur by the Carius method 0·2175 g of the substance gave 0·5825 g of barium sulphate. Calculate the percentage of sulphur in the substance.*

We know, $\underset{(137+32+64)}{BaSO_4} \equiv \underset{32}{S}$

Or, 233 g of $BaSO_4$ contain 32 g of Sulphur

0·5825 „ „ „ $\frac{32}{233} \times 0{\cdot}5825$ g of Sulphur

This is the weight of Sulphur is present in 0·2175 g of the substance

Hence, percentage of S $= \frac{32 \times 0{\cdot}5825}{233} \times \frac{100}{0{\cdot}2175} = 36{\cdot}77.$

Example 10. *0·395 g of an organic compound by Carius method for the estimation of sulphur gave 0·582 g of $BaSO_4$. Find the percentage of sulphur in the compound.*

We know, $\underset{233}{BaSO_4} \equiv \underset{32}{S}$

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

$\therefore$ 0·582 g „ „ $\frac{32}{233} \times 0{\cdot}582$ g of sulphur

This is the weight of sulphur present in 0·395 g of the substance

Hence, the percentage of sulphur $= \frac{32}{233} \times 0{\cdot}582 \times \frac{100}{0{\cdot}395} = 20{\cdot}23.$

ESTIMATION OF OXYGEN

Until recently, the percentage of oxygen in a given organic compound was found by difference. Any percentage of the total composition not accounted for by the foregoing determination was taken to be oxygen. This rather faulty procedure of estimating oxygen has now been replaced by a direct experimental method described below.

Principle. The given organic sample is pyrolysed (decomposed by heating) in a stream of nitrogen gas. The elemental oxygen along with other gaseous products is passed through hot carbon (1100°). All the oxygen is thereby converted to carbon monoxide. This when passed through warm (175°) iodine pentoxide (I_2O_5) is oxidised to carbon dioxide producing iodine.

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

$$O_2 + 2C \xrightarrow{1100^\circ} 2CO$$

$$5CO + I_2O_5 \xrightarrow{175^\circ} 5CO_2 + I_2$$

By determining the amount of CO_2 (or I_2) produced, the percentage of carbon in the original organic compound can be calculated.

Procedure. The pyrolysis of the given organic compound is carried in a combustion apparatus similar to the one used for the estimation of carbon and hydrogen.

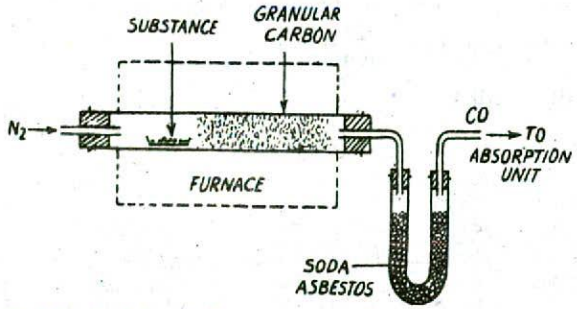


Fig. 3·10. Pyrolysis unit of the apparatus used for the estimation of Oxygen.

A weighed quantity of the sample is charged in a porcelain boat which is loaded into the combustion tube. The latter part of the combustion tube is packed with granular carbon. The temperature of the heating furnace jacket is kept at 1100°C. Pure nitrogen from a cylinder enters the tube from the left end and sweeps through it.

The gases emerging from the combustion tube containing carbon monoxide are first passed through a U-tube containing soda-asbestos (asbestos impregnated with dry NaOH). This retains any acidic materials obtained from halogens, nitrogen or sulphur present in the organic sample. The gaseous mixture free from the acidic materials is then passed through a wide glass tube packed with iodine pentoxide kept at 175°C. It converts carbon monoxide to carbon dioxide and generating iodine.

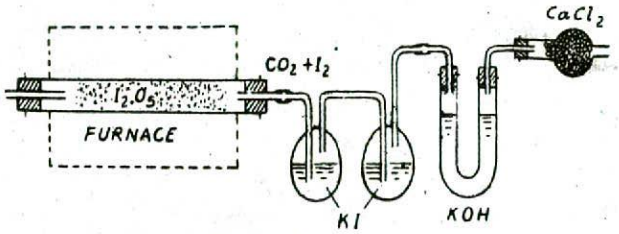


Fig. 3·11. Absorption unit.

The resulting gaseous mixture is now allowed to pass over a bed of potassium iodide (KI) laid in a wide glass tube. This removes iodine. The residual gases containing carbon dioxide are finally passed through a soda-asbestos U-tube where CO_2 is retained. The soda-asbestos tube is weighed before and after pyrolysis. The difference in weight gives the amount of CO_2 obtained from the given sample of the organic compound.

Calculations :

Let the weight of organic substance taken $= x$ g

Increase in the weight of KOH tube $= y$ g

Since $C \equiv CO \equiv CO_2$

16 g of oxygen present in the substance can form 44 g of CO_2

$\therefore$ 44 g of CO_2 are obtained from oxygen $= 16$ g

y g of CO_2 are obtained from oxygen $= \frac{16}{44} \times y$ g

Hence the weight of oxygen in the weight of sample taken $= \frac{16}{44} \times y$ g

$\therefore$ **Percentage of oxygen** $= \frac{16}{44} \times \frac{y}{x} \times 100$

QUESTIONS

1. How are carbon and hydrogen detected in an organic compound ?
2. How is nitrogen detected in an organic compound ?
   (Agra BSc, 1993 ; Madurai BSc, 1993 ; Baroda BSc, 1994 ; Bundelkhand BSc, 1994 ; Nagpur BSc, 1994)
3. How is sulphur detected in an organic compound ?
   (Kerala BSc II, 1993 ; Shivaji BSc, 1993 ; Dibrugarh BSc Hons, 1994 ; Vikram BSc, 1994)
4. How are halogens detected in an organic compound ?
   (Delhi BSc, 1993 ; Madras BSc, 1993 ; North Eastern Hill BSc Hons, 1994 ; Vikram BSc, 1994)
5. How are carbon and hydrogen estimated in an organic compound ?
6. 0.2 g of an organic compound gave on combustion 0.55 g of CO_2 and 0.0892 g of H_2O. Calculate the percentage composition of the compound. *(Vikram BSc, 1994)*

   Answer. C = 75% ; H = 4.95% ; and O = 20.05%
7. How is nitrogen estimated in an organic compound ? *(Madurai BSc, 1993 ; Saugar BSc, 1994)*
8. 0.788 of an organic compound was Kjeldahlised and ammonia absorbed in 100 ml of 1N sulphuric acid. The excess acid required 73.7 ml sodium hydroxide solution for neutralisation. Calculate the percentage of nitrogen in compound.

   Answer. 46.72 *(Nagpur BSc, 1992)*
9. The ammonia evolved from 0.21 g of an organic compound by Kjeldahl's method neutralised 15 ml of N/20 H_2SO_4 solution. Calculate the percentage of nitrogen. *(Baroda BSc, 1994)*

   Answer. 5
10. 0.4 g of an organic compound, on Kjeldahl's analysis, gave enough ammonia to neutralise 40 ml of 0.1N H_2SO_4. Calculate the percentage of nitrogen in the compound. *(Punjabi BSc, 1994)*

    Answer. 14
11. 0.38 g of an organic compound gives 1.17 g of barium sulphate. Calculate the percentage of sulphur in the compound.

    Answer. 42.28 *(Karnataka BSc, 1993)*
12. 0.2340 g of an organic compound, containing nitrogen, was Kjeldahlised and the ammonia evolved was absorbed in 90.35 ml of 0.1N HCL. The excess of the acid required 20 ml of N/5 NaOH for neutralisation. Calculate the percentage of nitrogen.

    Answer. 30.12 *(Vikram BSc, 1993)*
13. An organic compound, on analysis, gave the following results : (*i*) 0.73 g of the compound gave 1.32 g of carbon dioxide and 0.6 g of water, (*ii*) 0.365 g of the compound gave 56 cc of nitrogen at NTP. Calculate the percentage composition of the compound. *(Mysore BSc, 1993)*

    Answer. C = 49.31% ; N = 19.17% ; H = 9.13% ; and O = 22.39%
14. How is sulphur estimated in an organic compound ? *(Madurai BSc, 1993 ; Osmania BSc, Hons, 1994)*
15. 0.2595 g of an organic compound, when treated by Carius method gave 0.35 g of $BaSO_4$. Calculate the percentage of sulphur in the compound. *(Jammu BSc, 1993)*

    Answer. 18.52
16. How are halogens estimated in an organic compound ? *(Gulbarga BSc, 1993 ; Delhi BSc Hons, 1994)*

    Answer. 18.52
17. 0.147 g of an organic compound containing chlorine was heated with nitric acid and silver nitrate and gave 0.287 g of silver chloride. Calculate the percentage of chlorine in the compound. *(Nagpur BSc, 1994)*

    Answer. 48.29

Chapter **4**

Empirical and Molecular Formulæ. Determination of Molecular Weights

1. Empirical Formula

The **Empirical formula** of a compound is *the simplest formula which expresses its percentage composition.* Such a formula, while it tells us the ratio of the atoms of different elements present in the molecule, does not indicate the actual number of atoms of each element present in it.

CALCULATION OF EMPIRICAL FORMULA

Having determined the percentage of each element present in a compound as described in Chapter 3, its empirical formula is calculated by the following steps.

(1) *The percentage of each element is divided by its atomic weight.* This gives the relative number of different kinds of atoms in the molecule.

(2) *The numbers obtained in step* (1) *are then divided by the smallest of these numbers* (HCF) so as to give a simple atomic ratio.

(3) The figures expressing the simple atomic ratio as obtained from step (2), give the number of atoms of each element in the molecule, minor fractions being neglected as due to experimental error. *However, if necessary, they are further reduced to whole numbers by multiplying with a suitable factor.*

Example 1. *An organic substance on analysis was found to contain 10·06 per cent carbon, 0·84 per cent hydrogen, and 89·10 per cent chlorine. Calculate its empirical formula.*

Step 1. Divide the percentage composition of each element by its respective atomic weight.

Carbon	*Hydrogen*	*Chlorine*
$\frac{10{\cdot}06}{12} = 0{\cdot}84$	$\frac{0{\cdot}84}{1} = 0{\cdot}84$	$\frac{89{\cdot}10}{35{\cdot}5} = 2{\cdot}51$

Step 2. Divide these numbers by the smallest number (in this case 0·84).

$\frac{0{\cdot}84}{0{\cdot}84} = 1$	$\frac{0{\cdot}84}{0{\cdot}84} = 1$	$\frac{2{\cdot}51}{0{\cdot}84} = 3$

Hence, the empirical formula is $C_1H_1Cl_3$ or $CHCl_3$.

Example 2. *Percentage composition of an organic substance as determined by analysis was Carbon 14·5, Hydrogen 1·8, Chlorine 64·46, Oxygen 19·24. Calculate its empirical formula.*

Element	%age		At Wt		Atomic Ratio		HCF	Atoms present
C	14·5	÷	12	=	1·21 ÷ 1·20	=	1·0	1 × 2 = 2
H	1·8	÷	1	=	1·8 ÷ 1·20	=	1·5	1·5 × 2 = 3
Cl	64·46	÷	35·5	=	1·81 ÷ 1·20	=	1·5	1·5 × 2 = 3
O	19·24	÷	16	=	1·20 ÷ 1·20	=	1·0	1 × 2 = 2

In this case, the final figures representing the number of atoms of each element are multiplied by 2 so as so get whole numbers. Hence the empirical formula of the compound is $C_2H_3Cl_3O_2$.

Example 3. *When analysed by the combustion method, 0·20 g of an organic substance yielded : (i) 0·147 g of carbon dioxide and 0·12 g water and (ii) 74·6 ml of nitrogen gas at STP. Find the simplest formula of the substance.*

CALCULATION OF PERCENTAGE OF ELEMENTS :

Since $CO_2 \equiv C$; $H_2O \equiv 2H$; 22,400 ml $N_2 = 28$ g

Percentage of Carbon $= \frac{0{\cdot}147 \times 12}{44} \times \frac{100}{0{\cdot}2} = 20{\cdot}04$

,, ,, Hydrogen $= \frac{0{\cdot}12 \times 2}{18} \times \frac{100}{0{\cdot}2} = 6{\cdot}66$

,, ,, Nitrogen $= \frac{74{\cdot}6 \times 28}{22400} \times \frac{100}{0{\cdot}2} = 46{\cdot}63$

,, ,, Oxygen (by difference) $= 26{\cdot}77$

CALCULATION OF EMPIRICAL FORMULA :

	% age		At Wt		Atomic Ratio		HCF		Atoms present
C	20·04	÷	12	=	1·67	÷	1·66	=	1
H	6·66	÷	1	=	6·66	÷	1·66	=	4
N	46·63	÷	14	=	3·33	÷	1·66	=	2
O	26·77	÷	16	=	1·66	÷	1·66	=	1

Hence the empirical formula of the substance is CH_4N_2O.

Example 4. *0·21 g of an organic substance containing C, H, O and N only, gave on combustion 0·462 g carbon dioxide and 0·1215 g water. 0·104 g of it when distilled with caustic soda evolved ammonia which was neutralised by 15 ml of N/20 H_2SO_4. Calculate the empirical formula.*

CALCULATION OF PERCENTAGE COMPOSITION :

Percentage of Nitrogen :

15 ml of $\frac{N}{20}$ $H_2SO_4 \equiv$ 15 ml of $\frac{N}{20}$ $NH_3 \equiv$ 15 ml of $\frac{N}{20}$ N (combined)

$\therefore$ wt of Nitrogen in 0·104 g substance $= 15 \times \frac{14}{20} \times \frac{1}{1000} = 0{\cdot}0105$ g

% age of the Nitrogen $= \frac{0{\cdot}0105}{0{\cdot}104} \times 100 = 10{\cdot}09$

Percentage of C and H :—

Since $CO_2 \equiv C$; $H_2O \equiv 2H$

% age of C $= \frac{0{\cdot}462 \times 12}{44} \times \frac{100}{0{\cdot}21} = 60{\cdot}0$

,, H $= \frac{0{\cdot}1215 \times 2}{18} \times \frac{100}{0{\cdot}21} = 6{\cdot}43$

Percentage of Oxygen (by difference) = 23·48

CALCULATION OF EMPIRICAL FORMULA :

	% age		At Wt		Atomic Ratio		HCF		Atoms present
C	60·00	÷	12	=	5·00	÷	0·72	=	7
H	6·43	÷	1	=	6·43	÷	0·72	=	9
N	10·09	÷	14	=	0·72	÷	0·72	=	1
O	23·48	÷	16	=	1·46	÷	0·72	=	2

Hence Empirical formula is $C_7H_9NO_2$

II. Molecular Formula

The **Molecular formula** of a substance expresses *the actual number of atoms of each element present in its molecule.* It may be the same as the empirical formula of the substance or an exact multiple of it

Substance	*Empirical Formula*	*Molecular Formula*		
Methane	CH_4	CH_4	or	$(CH_4)_1$
Ethylene	CH_2	C_2H_4	or	$(CH_2)_2$
Acetic acid	CH_2O	$C_2H_4O_2$	or	$(CH_2O)_2$
Glucose	CH_2O	$C_6H_{12}O_6$	or	$(CH_2O)_6$

Thus we can write :

$$Molecular\ Formula = (Empirical\ Formula)_n$$

when $n = 1, 2, 3$ etc. When $n=1$, the molecular formula coincides with the empirical formula. It follows from the above relation that

$$M\ Wt = Emp\ Formula\ Wt \times n$$

whence

$$n = \frac{M\ Wt}{Emp\ Formula\ Wt}$$

If the molecular weight is known, the value of n can be found with the help of this relation.

Example 5. *An organic compound has been found to possess the empirical formula CH_2O and the molecular weight = 90. Give its molecular formula ($C=12$; $H=1$; $O=16$)*

Molecular formula = (Empirical formula)$_n$

But $$n = \frac{\text{M Wt}}{\text{Emp F Wt}}$$

In this case, M Wt = 90

Emp F Wt = 12+2+16 = 30

$$n = \frac{90}{30} = 3$$

Hence, the molecular formula = $(CH_2O)_3$ or $C_3H_6O_3$

Example 6. *An organic liquid contains 12·8 per cent carbon, 2·1 per cent hydrogen and 85·1 per cent bromine. 0·188 g of it in a Victor Meyer experiment, displaced 24·2 ml of moist air measured at 14°C and 752 mm pressure. Find the molecular formula of the substance. (Aq. tension at 14°C = 12 mm).*

Calculation of Molecular Weight :

Volume of dry air replaced at NTP $= \frac{24{\cdot}2\ (752-12)}{287} \times \frac{273}{760} = 22{\cdot}42$ ml

Now, the wt of 22·42 ml of vapour of substance = 0·188 g

" " 22400 " " " $= \frac{0{\cdot}188}{22{\cdot}42} \times 22400 = 187{\cdot}9$ g

Molecular weight of the substance = 187·9

Calculation of Empirical Formula :

	%age		*At Wt*		*Atomic ratio*		*HCF*		*Atoms present*
C	12·8	÷	12	=	1·066	÷	1·064	=	1
H	2·1	÷	1	=	2·10	÷	1·064	=	2
Br	85·1	÷	80	=	1·064	÷	1·064	=	1

∴ Empirical formula is CH_2Br

Calculation of Molecular Formula :

Let the molecular formula be $(CH_2Br)_n$

But $$n = \frac{\text{M Wt}}{\text{Emp F Wt}} = \frac{187{\cdot}9}{12+2+80} = 2$$

∴ Molecular formula = $C_2H_4Br_2$

Example 7. *An organic dibasic acid contains $C=17{\cdot}39$; $H = 1{\cdot}4$. $Br = 57{\cdot}97$ per cent. The vapour density of its ethyl ester is 166. Determine the molecular formula of the acid.*

Calculation of Molecular Weight of Acid :

Let the dibasic acid be RH_2 and its ethyl ester $R(C_2H_5)_2$.

Molecular weight of ethyl ester = 2 × VD = 2 × 166 = 332

Thus $R(C_2H_5)_2 = R + 2(24+5) = 332$

Whence $R = 274$

$\therefore$ Molecular weight of the acid $RH_2 = 274 + 2 = 276$

CALCULATION OF EMPIRICAL FORMULA :

Percentage of Oxygen $= 100 - (17{\cdot}39 + 1{\cdot}45 + 57{\cdot}97) = 23{\cdot}19$

	%age		*At Wt*		*Atomic Ratio*		*HCF*		*Atoms present*
C	17·39	÷	12	=	1·45	÷	0·72	=	2
H	1·45	÷	1	=	1·45	÷	0·72	=	2
Br	57·97	÷	80	=	0·72	÷	0·72	=	1
O	23·19	÷	16	=	1·45	÷	0·72	=	2

Hence, the empirical formula is $C_2H_2BrO_2$

Let the molecular formula of the acid be $(C_2H_2BrO_2)_n$

But $$n = \frac{\text{M Wt}}{\text{Emp. F Wt}} = \frac{276}{24+2+80+32} = \frac{276}{138} = 2$$

$\therefore$ Molecular formula is $C_4H_4Br_2O_4$

Example 8. *0·20 g of anhydrous organic acid gave on combustion 0·040 g water and 0·195 g carbon dioxide. The acid is found to be dibasic and 0·5 g of its silver salt leaves on ignition 0·355 g silver. What is the molecular formula of the acid ?*

CALCULATION OF MOLECULAR WEIGHT :

$$\frac{\text{M Wt of silver salt}}{2 \times 108} = \frac{0{\cdot}5}{0{\cdot}355}$$

$$\text{M Wt of silver salt} = \frac{0{\cdot}5}{0{\cdot}355} \times 2 \times 108 = 304{\cdot}2$$

If RH_2 be the dibasic acid, its silver salt is RAg_2.

But $RH_2 = RAg_2 - 2Ag + 2H$

$= 304{\cdot}2 - 216 + 2 = 90{\cdot}2$

CALCULATION OF EMPIRICAL FORMULA :

$$\text{Percentage of C} = \frac{0{\cdot}195 \times 12}{44} \times \frac{100}{0{\cdot}2} = 26{\cdot}59$$

$$\text{,, H} = \frac{0{\cdot}040 \times 12}{18} \times \frac{100}{0{\cdot}2} = 2{\cdot}22$$

,, ,, O (by difference) $= 71{\cdot}19$

	% age		*At Wt*		*Atomic Ratio*		*HCF*		*Atoms present*
C	26·59	÷	12	=	2·22	÷	2·22	=	1
H	2·22	÷	1	=	2·22	÷	2·22	=	1
O	71·19	÷	16	=	4·45	÷	2·22	=	2

$\therefore$ Empirical formula is CHO_2

CALCULATION OF MOLECULAR FORMULA :

Let it be $(CHO_2)_n$; when $n = \frac{\text{M Wt}}{\text{Emp F Wt}} = \frac{90{\cdot}2}{12+1+32} = 2$

Hence, Molecular formula of the acid is $C_2H_2O_4$

Example 9. *An organic monobasic acid gave the following percentage composition : C = 70·59 ; H = 5·88 ; O = 23·53.*

0·272 g of the acid required 20 ml of N/10 NaOH for complete neutralisation.

Deduce the empirical and the molecular formulae of the acid.

CALCULATION OF MOLECULAR WEIGHT :

$$20 \text{ ml } \frac{N}{10} \text{ NaOH} \equiv 20 \text{ ml } \frac{N}{10} \text{ acid} \equiv \frac{20}{1000} \times \frac{N}{10} \text{ g acid}$$

Thus, $$\frac{20}{1000} \times \frac{N}{10} = 0{\cdot}272$$

Whence $N = 500 \times 0{\cdot}272 = 136$

Molecular weight of acid $= N \times \text{Basicity} = 136 \times 1 = 136$

CALCULATION OF EMPIRICAL FORMULA :

	% age		At Wt		Atomic Ratio		HCF		Atoms present
C	7·059	÷	12	=	5·88	÷	1·47	=	4
H	5·88	÷	1	=	5·88	÷	1·47	=	4
O	23·53	÷	16	=	1·47	÷	1·47	=	1

Hence, empirical formula is C_4H_4O

CALCULATION OF MOLECULAR FORMULA :

Let molecular formula be $(C_4H_4O)_n$

But $$n = \frac{\text{M Wt}}{\text{Emp F Wt}} = \frac{136}{48 + 4 + 16} = \frac{136}{68} = 2$$

Hence, molecular formula is $C_8H_8O_2$

Example 10. *A monoacid organic base gave the following results on analysis :—*

(i) 0·100 g gave 0·2882 g CO_2 and 0·0756 g H_2O.

(ii) 0·200 g gave 21·8 ml nitrogen at 15°C and 750 mm.

(iii) 0·400 g of the platinichloride left on ignition, 0·125 g of Pt.

What is the molecular formula of the base ?

CALCULATION OF MOLECULAR WEIGHT :

$$\text{M Wt of platinichloride} = 195 \times \frac{\text{Wt of salt taken}}{\text{Wt of Pt left}} = 195 \times \frac{0{\cdot}4}{0{\cdot}125} = 624$$

$$B = \frac{B_2H_2PtCl_6 - H_2PtCl_6}{2} = \frac{624 - 410}{2} = 107$$

∴ Molecular weight of the base is 107

CALCULATION OF EMPIRICAL FORMULA :

$$\text{Volume of nitrogen at NTP} = 21{\cdot}8 \times \frac{273}{288} = 20{\cdot}66 \text{ ml}$$

$$\text{Percentage of C} = \frac{0{\cdot}2882 \times 12}{44} \times \frac{100}{0{\cdot}1} = 78{\cdot}6$$

$$\text{,, H} = \frac{0{\cdot}0756 \times 2}{18} \times \frac{100}{0{\cdot}1} = 8{\cdot}4$$

$$\text{,, N} = \frac{20{\cdot}66 \times 28}{22400} \times \frac{100}{0{\cdot}2} = 12{\cdot}91$$

Element	%age		At weight		At Ratio		HCF		Atoms present
C	78·6	÷	12	=	6·25	÷	0·92	=	7
H	8·4	÷	1	=	8·40	÷	0·92	=	9
N	12·95	÷	14	=	0·92	÷	0·92	=	1

∴ Empirical formula is C_7H_9N

CALCULATION OF MOLECULAR FORMULA :

Let the molecular formula be $(C_7H_9N)_n$

But $$n = \frac{\text{M Wt}}{\text{Emp F Wt}} = \frac{107}{84+9+14} = \frac{107}{107} = 1$$

∴ Molecular formula is $(C_7H_9N)_1$ or C_7H_9N.

MOLECULAR FORMULA OF GASEOUS HYDROCARBONS

The molecular formula of a gaseous hydrocarbon may be determined directly without a previous knowledge of the percentage composition. A known volume of the hydrocarbon is mixed with a measured excess of oxygen and the mixture exploded in a eudiometer tube. The carbon and hydrogen of the substance is oxidised to form carbon dioxide and water respectively. The equation of explosion reaction can be written as

$$C_xH_y + (x + y/4)O_2 = x\,CO_2 = y/2\,H_2O$$

The following observations are recorded :—

(1) *The volume of the gaseous products after explosion and cooling (V_1).* This corresponds to the volume of carbon dioxide and unreacted oxygen, the water vapour being condensed to liquid which occupies negligible volume.

(2) *The volume of the residual oxygen after introducing alkali* (V_2). When a little alkali is introduced in the eudiometer tube, it absorbs carbon dioxide, leaving behind unreacted oxygen. The volume of carbon dioxide alone would thus be equal to $(V_1 - V_2)$.

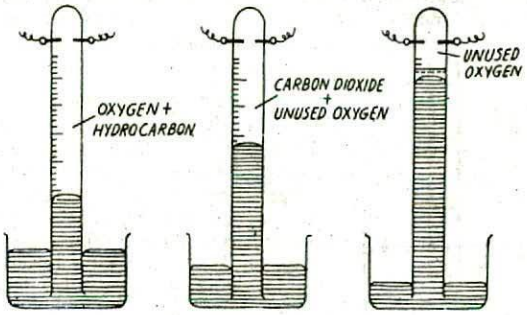


Fig. 4·1. Explosion of gaseous hydrocarbons in eudiometer tube.

The molecular formula of the hydrocarbon is then found by the application of Avogadro law.

Example 11. *10 ml of a gaseous hydrocarbon was mixed with 100 ml of oxygen and the mixture exploded in a eudiometer tube. The volume of the mixture after cooling was reduced to 90 ml which upon treatment with potash solution was further reduced to 70 ml. Determine the molecular formula of the hydrocarbon.*

Volume of oxygen used = 100 − 70 = 30 ml

" " carbon dioxide formed = 90 − 70 = 20 ml

If C_xH_y be the formula of the hydrocarbon, $C_xH_y + (x + y/4)O_2 = xCO_2 + y/2\ H_2O$

Applying the converse of Avogadro Law

1 ml $C_xH_y + (x + y/4)$ ml $O_2 = x$ ml $CO_2 + y/2$ ml H_2O

or 10 ml $C_xH_y + 10(x + y/4)$ ml $O_2 = 10x$ ml $CO_2 + 10y/2$ ml H_2O

Thus $10(x + y/4) = 30$ and $10x = 20$ whence $x = 2$ and $y = 4$

Therefore, the molecular formula of the hydrocarbon is C_2H_4

Alternative Solution :

Total oxygen used (for CO_2 and H_2O) = 30 ml $C + O_2 = CO_2$ ∴ 1 vol CO_2 = 1 vol O_2

Hence for 20 ml CO_2 formed, volume of oxygen used = 20 ml

∴ Volume of oxygen used for water alone = 30 − 20 = 10 ml

$2H_2 + O_2 = 2H_2O$; 1 vol $O_2 \equiv 2$ vol H_2O

Hence for 10 ml oxygen used, volume of water formed = 20 ml

Now, 10 ml hydrocarbon + 30 ml $O_2 = 20$ ml $CO_2 + 20$ ml H_2O

or 1 ml " + 3 ml $O_2 = 2$ ml $CO_2 + 2$ ml H_2O

Applying Avogadro Law, 1 molecule of hydrocarbon yields two molecules of CO_2 (containing two C atoms) and two molecules of H_2O (containing four H atoms). Hence the molecular formula of the hydrocarbon is C_2H_4.

III. Determination of Molecular Weight

The **Molecular weight** of a compound is *the weight of one molecule of it as compared to the weight of an atom of hydrogen as 1.*

The methods commonly employed for the determination of molecular weights of organic substances are :

Physical Methods	*Chemical Methods*
1. Victor Meyer method	1. Silver salt method for acids
2. Dumas method	2. Platinichloride method for bases
3. Hofmann method	3. Volumetric method for Acids and Bases
4. Freezing point and Boiling point method	

I. Physical Methods

VICTOR MEYER METHOD FOR VOLATILE SUBSTANCES

In this method, a known weight of the substance is converted into vapour by dropping in a hot tube. The vapour displaces its own volume of air which is collected over water and its volume measured at the observed temperature and pressure.

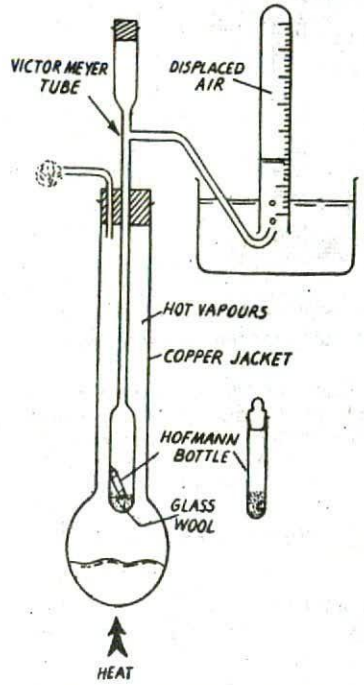


Fig. 4·2. Victor Meyer method for Mol Wt determination.

The apparatus used in this method consists of : (*i*) a '*Victor Meyer Tube*' of hard glass, having a side-tube leading to the arrangement for collection of displaced air over water ; (*ii*) an *Outer Jacket* of copper, containing a liquid boiling about 30° higher than the substance whose molecular weight is to be determined ; and (*iii*) a '*Tiny Stoppered Bottle*' (Hofmann bottle), in which the substance is weighed and introduced into the heated Victor Meyer tube.

Procedure. The apparatus is fitted up as shown in Fig. 4·2. The liquid in the copper jacket is boiled by heating it with a Bunsen burner, when the hot vapours of the liquid in turn heat the Victor Meyer tube. When no more air bubbles escape from the side-tube, a graduated tube filled with water is inverted over its end dipping in water. The Hofmann bottle containing a weighed quantity (0·1—0·2 g) of the substance and loosely stoppered, is then dropped into Victor Meyer tube opening its cork for a while. The substance at once converts into vapours which blow out the stopper and displace an equal volume of air from the upper part of the Victor Meyer tube. The volume of air collected in the graduated tube is read off after carefully levelling in a cylinder of water and the atmospheric pressure and temperature recorded. The volume is reduced to STP and the weight of 22·4 litres of vapour calculated. This is numerically equal to the molecular weight of the substance.

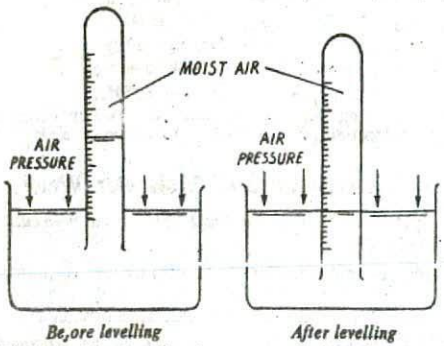


Fig. 4·3. After levelling the pressure of moist air collected is equal to the atmospheric pressure.

Example 1. *In a Victor Meyer determination of molecular weight 0·1 g of the substance displaced 27 ml of moist air measured at 15°C and 745 mm pressure. What is the molecular weight of the substance ? (Vapour tension of water at 15°C = 12·7 mm)*

Volume of displaced air, $V_{15} = 27$ ml

Atmospheric temperature = 15°C or on absolute scale $T_{15} = 273 + 15 = 288°$

Pressure of dry air, $P_{15} = 745 - 12{\cdot}7 = 732{\cdot}3$ mm

$$\frac{P_N \times V_N}{T_N} = \frac{P_{15} \times V_{15}}{T_{15}} \quad \text{or} \quad V_N = \frac{P_{15} \times V_{15} \times T_N}{T_{15} \times P_N}$$

Hence, volume of displaced air at NTP $= \frac{732{\cdot}3 \times 27 \times 273}{288 \times 760} = 24{\cdot}67$ ml

Thus the weight of 24·67 ml of vapour of the substance = 0·1 g

" " 22400 " " " $= \frac{0{\cdot}1 \times 22400}{24{\cdot}67} = 90{\cdot}80$ (mol wt)

Example 2. *0·22 g of a substance when vaporised by Victor Meyer method displaced 45·0 ml of air measured over water at 20°C and 755 mm pressure. Calculate the molecular weight of the substance. (Vapour pressure of water at 20°C is 17·4 mm)*

(*i*) Calculation of Volume at NTP :

Initial Conditions		*Final Conditions*	
Volume	$(V_1) = 45$ ml	Volume	$= V_2$
Pressure	$(P_1) = 755 - 17{\cdot}4$	Pressure	$= 760$ mm
	$= 737{\cdot}6$ mm	Temperature	$= 273°A$

Temperature $(T_1) = 20 + 273 = 293°A$

Applying the General Gas Equation

$$\frac{760 \times V_2}{273} = \frac{45 \times 737{\cdot}6}{293}$$

$$\therefore \quad V_2 = \frac{45 \times 737{\cdot}6}{293} \times \frac{273}{760} = 40{\cdot}70 \text{ ml}$$

(*ii*) Calculation of M Wt :

Wt of 40·7 ml of vapours at NTP = 0·22 g

$\therefore$ Wt of 22400 ml of vapours at NTP $= \frac{0{\cdot}22}{40{\cdot}7} \times 22400 = 121{\cdot}1$

Thus the molecular weight of the substance = 121·1

Dumas Method. This is based on the principle of weighing a known volume of the vapour of the substance in a glass bulb at an elevated temperature. The calculation of the molecular weight is done as in Victor Meyer method.

Hofmann Method. This method is suitable for determining molecular weight of substances at their boiling point under atmospheric pressure.

A known weight of the substance is vaporised above a mercury column in a barometric tube and the volume of the vapour formed noted. The molecular weight of the substance is then calculated as described under Victor Meyer method.

CRYOSCOPIC METHOD OR FREEZING POINT METHOD

The molecular weight of a nonvolatile organic compound can be easily determined by noting the depression of freezing point of a solvent produced by dissolving a definite weight of the substance in a known weight of solvent.

$$m = \frac{1000 \text{ K } w}{\Delta T \text{ W}}$$

m = molecular weight of the dissolved compound,
K = molecular depression constant,
w = weight of dissolved compound, and,
ΔT = depression of freezing point.

The **Molecular depression constant** or the **Freezing point constant** is defined as the depression of freezing point which would be produced by dissolving one gram-molecule of the solute in 1000 grams of the solvent. Its value is usually given in ready-reference tables.

Values of K for some Solvents

Water	1·86°C	Acetic acid	3·82°C
Benzene	5·12°C	Phenol	7·3°C

Determination of Depression of Freezing point. The apparatus which is almost exclusively employed for the determination of the lowering of freezing point was designed by Beckmann (Fig. 4·4). It consists of : (*i*) the *inner freezing point tube* provided with a side-tube for introducing the solute and fitted with Beckmann thermometer reading up to ·01°C and a platinum stirrer ; (*ii*) the *outer air-jacket* surrounding the inner tube which ensures a slower and more uniform rate of cooling of the liquid ; (*iii*) a stout *glass cylinder* which contains freezing mixture and is also provided with a stirrer.

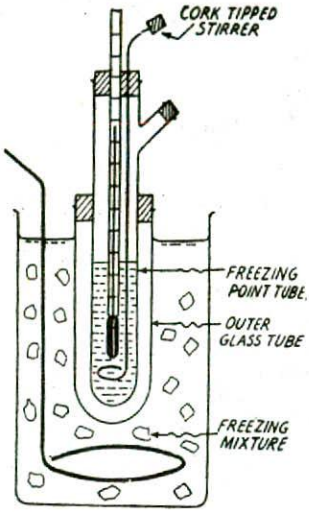


Fig. 4·4. Determination of depression of freezing point.

In an actual determination 15·20 g of the solvent is taken in the inner freezing point tube and the apparatus set up as shown in the diagram. The solvent is gently stirred and the mercury thread of the thermometer watched carefully. The temperature first falls below the freezing point of the solvent but later as it begins to solidify, it rises rapidly owing to the latent heat set free, and finally remains steady at the true freezing point.

The freezing point of the solvent having been accurately determined, the solvent is remelted by removing the tube from the bath, and a weighed amount (0·1—0·2 g) of the solute is introduced through the side-tube. Now the freezing point of the solution is determined in the same way as that of the solvent alone. A further quantity of the solute may then be added and another reading taken. Knowing the depression of the freezing point produced, the molecular weight of the solute can be calculated.

Example 1. *0·512 g of an organic substance when dissolved in 25 g of water lowered its freezing point by 0·19°C. Calculate the molecular weight of the substance. (Molecular depression constant for water is 1·85).*

Substituting the values in the expression

$$m = \frac{100\ K\ w}{\Delta T\ W} = \frac{100 \times 1{\cdot}85 \times 0{\cdot}512}{0{\cdot}19 \times 25} = 199{\cdot}5$$

Example 2. *1·355 g of a substance dissolved in 55 g of acetic acid and produced depression of 0·618°C in the freezing point. Calculate the molecular weight of the dissolved substance. The molecular depression of the freezing point of acetic acid (100 g) is 38·5°C.*

Depression of freezing point = 0·618°

Weight of solute = 1·355 g

Weight of solvent = 55 g

Substituting the values in the expression

$$m = \frac{1000\ K\ w}{\Delta T \times W} = \frac{1000 \times 38{\cdot}5 \times 1{\cdot}355}{0{\cdot}618 \times 55} = 153{\cdot}5$$

EBULLIOSCOPIC METHOD OR BOILING POINT METHOD

The molecular weight of a nonvolatile organic compound can also be determined by noting the elevation of boiling point produced by dissolving a definite weight of it in a known weight of the solvent.

$$m = \frac{100\ K\ w}{\Delta T\ W}$$

m = molecular weight of the dissolved compound

K = molecular elevation constant

w = weight of dissolved substance

W = weight of solvent

ΔT = elevation of boiling point.

The **Molecular elevation constant** or the **Boiling point constant** is defined as the elevation of the boiling point which would be produced by dissolving one gram-mole of the solute in 1000 grams of the solvent. Its value is generally given in ready-reference tables.

VALUES OF K FOR SOME SOLVENTS

Water	0·52°C	Benzene	2·67°C
Ethyl alcohol	1·15°C	Ether	2·10°C
Acetone	1·67°C	Acetic acid	2·53°C

Determination of Elevation of boiling point. The apparatus now commonly used for the determination of the elevation of boiling point was designed by Landsberger. It consists of : (*i*) *a boiling flask* which sends vapours of the solvent into the inner tube ; (*ii*) an *inner boiling tube* which has a bulb with a hole in the side, and is graduated in ml. It is fitted with a thermometer reading up to ·01°C and a glass tube having a rose-head at the lower end. The rose-head ensures uniform distribution of the vapours through the solvent. The bulb reflects back any particles of the solvent which happen to fly about when the boiling becomes brisk ; (*iii*) *an outer covering tube* which receives hot vapours from the inner tube through the side hole. This forms a protecting jacket round the boiling tube and prevents the loss of heat due to radiation.

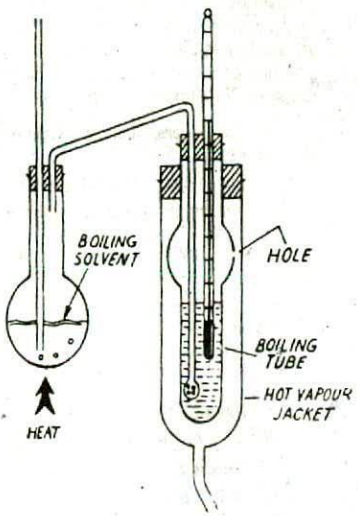


Fig. 4·5. Determination of elevation of boiling point by Landsberger method.

In an actual determination 5·7 ml of solvent are placed in the inner tube and the vapours of the solvent passed through it. At the start the solvent vapours condense and as more vapours are passed the liquid begins to boil. As soon as the temperature has become steady, the temperature is read on the thermometer. This is the boiling point of the pure solvent. Now the supply of solvent vapours is cut off for a while and a weighed quantity (0·2-0·5 g) of the substance whose molecular weight is to be determined is dropped into the solvent in the boiling tube. The boiling point of the solution is then determined as before. Immediately after reading the temperature, the thermometer and the rose-head are carefully raised out of the solution and the volume of the solution noted. The weight of the solvent can be found by multiplying its volume with density.

Example 1. *The boiling point of pure acetone is 56·38°C at normal pressure. A solution of 0·717 g of a compound in 10 grams of acetone boiled at 56·88°C. What is the molecular weight of the compound ? The molecular elevation constant for acetone is 1·67°.*

Elevation in boiling point = 56·88 − 56·38 = 0·50°

Substituting the given values in the expression

$$m = \frac{1000\ K_w}{\Delta T W}$$ we have $$m = \frac{1000 \times 1{\cdot}67 \times 0{\cdot}717}{0{\cdot}50 \times 10} = 239{\cdot}4$$

Example 2. *A solution made by dissolving 1·5126 g of a substance is 21·01 g of benzene has a boiling point 1·05°C higher than the boiling point of pure benzene. Find the molecular weight of the substance.*

Molecular elevation of boiling point of 100 g benzene is 25·70.

Elevation of boiling point = 1·05°C

Substituting the given values in the expression

$$m = \frac{100\ K_w}{\Delta T W} = \frac{100 \cdot 25{\cdot}7 \cdot 1{\cdot}5126}{1{\cdot}05 \quad 21{\cdot}01} = 176{\cdot}2$$

II. Chemical Methods

SILVER SALT METHOD FOR ACIDS

This method of determining molecular weights of organic acids is based on the fact that they form insoluble silver salts which upon heating decompose to leave a residue of metallic silver.

Procedure. A small quantity of the unknown acid is dissolved in water and treated with a slight excess of ammonium hydroxide. The excess of ammonia is then boiled off. To this is added sufficient quantity of silver nitrate when a white precipitate of silver salt is obtained. The precipitate is separated by filtration, washed successively with water, alcohol and ether and dried in the steam oven. About 0·2 g of the dry silver salt is weighed into a crucible and ignited until all decomposition is complete. Ignition is repeated till the crucible with the residue of silver has attained constant weight. The molecular weight of the acid is then calculated from the weight of the silver salt taken and the weight of the residue of metallic silver obtained from it.

Calculations. Let the weight of the silver salt taken be x g and the weight of the residue of metallic silver be a g.

The weight of silver salt that would leave 108 g (equivalent weight of the silver) of residue $= \frac{x}{a} \times 108$ and this is the equivalent weight of the silver salt of the acid.

But Eq Wt of acid = Eq Wt of the silver salt — Eq Wt of silver + Eq Wt of Hydrogen

$$= \frac{x}{a} \times 108 - 108 + 1 = \frac{x}{a} \times 108 - 107$$

Molecular weight of the acid

$$= \text{Eq Wt} \times \text{Basicity} = \left(\frac{x}{a} \times 108 - 107 \right) \times n$$

Example 3. *0·759 g of the silver salt of a dibasic organic acid was ignited, when a residue of 0·463 g of metallic silver was left. Calculate the molecular weight of the acid.*

Weight of silver salt taken = 0·759 g

Weight of silver left as residue = 0·463 g

∴ The weight of silver salt that would leave 108 g of silver

$$= \frac{0{\cdot}759}{0{\cdot}463} \times 108 = 177{\cdot}05 \text{ g}$$

and this is the equivalent weight of silver salt.

Now, the equivalent weight of the acid = 177·05 − 108 + 1 = 70·05

∴ Molecular weight of the acid = 70·05 × 2 (basicity) = 140·1

Example 4. *When heated cautiously in a crucible, 0·3652 g of silver benzoate gave 0·1720 g silver. Find the molecular weight of benzoic acid.*

The weight of silver benzoate that would leave 108 g of silver

$$= \frac{0{\cdot}3652}{0{\cdot}1720} \times 108 = 229{\cdot}2 \text{ g}$$

∴ Equivalent weight of benzoic acid = 229·2 − 108 + 1 = 122·2

Since benzoic acid is a monobasic acid, its molecular weight = 122·2 × 1 = 122·2

PLATINICHLORIDE METHOD FOR BASES

Most organic bases (amines) combine with hydrochloroplatinic acid, H_2PtCl_6, to form insoluble salts known as *platinichlorides*. These double salts may be represented by the general formula $B_2H_2PtCl_6$, where B stands for one equivalent of the base. Platinichlorides on ignition decomposes to leave a residue of platinum.

$$B_2H_2PtCl_6 \longrightarrow Pt$$

Knowing the weights of the platinichloride taken and the platinum left behind, the molecular weight of the base can be calculated.

Let x g be the weight of the platinichloride taken and a of the platinum residue after ignition.

(1) Since one molecule of the platinichloride of the base, $B_2H_2PtCl_6$, contains one atom of platinum (atomic weight = 195), 195 g of platinum will be left by 1 g molecular weight of the platinichloride.

But a g of platinum is left by x g platinichloride

$\therefore$ 195 g " " " $\frac{x}{a} \times 195$ g "

Hence Mol Wt of platinichloride $= \frac{x}{a} \times 195$

(2) The equivalent weight of the base, B

$$= \frac{B_2H_2PtCl_6 - H_2PtCl_6}{2} = \frac{\text{M Wt of platinichloride} - 410}{2}$$

$$= \frac{\frac{x}{a} \times 195 - 410}{2}$$

(3) If the acidity of the base is n, the Mol Wt of the base,

$$= \left(\frac{x}{a} \times 195 - 410\right)\frac{n}{2}$$

Example 5. *0·6387 g of the platinichloride of a monoacid base on ignition gave 0·209 g of platinum. Find the molecular weight of the base (Pt = 195).*

(*i*) 0·209 g platinum is left by 0·6387 g of platinichloride

$\therefore$ 195 g " " " $\frac{0{\cdot}6387}{0{\cdot}209} \times 195$ g

Hence Mol Wt of the platinichloride $= \frac{0{\cdot}6387}{0{\cdot}209} \times 195 = 596{\cdot}0$

(*i*) Eq Wt of base $= \frac{\text{Mt Wt of platinichloride} - 410}{2} = \frac{596 - 410}{2} = 93{\cdot}0$

(*ii*) Mol Wt of base = Eq Wt × Acidity = 93·0 × 1 = 93·0

Example 6. *0·98 g of the platinichloride of a diacid base left on ignition 0·3585 g of platinum. Find the molecular weight of the base.*

(*i*) 0·3585 g Pt is left by 0·98 g platinichloride

195 g " " $\frac{0{\cdot}98}{0{\cdot}3585} \times 195$ g "

$\therefore$ M Wt of platinichloride $= \frac{0{\cdot}98}{0{\cdot}3585} \times 195 = 533$

(*ii*) Eq Wt of base $= \frac{\text{M Wt of platinichloride} - 410}{2} = \frac{533 - 410}{2} = \frac{123}{2}$

(*iii*) M Wt of base = Eq Wt × Acidity = 123/2 × 2 = 123

VOLUMETRIC METHOD FOR ACIDS AND BASES

The molecular weight of an acid can be determined by dissolving a known weight of it (x g) in water and titrating the solution against standard alkali solution (say N/10) using phenolphthalein as indicator.

Suppose V ml of N/10 alkali neutralise x g acid

$\therefore$ 1000 ml " 1N " " $\frac{x}{V} \times 1000 \times 10$ g acid

Since acids and bases neutralise each other in equivalent proportions, and 1000 ml of 1 N alkali contain one gram equivalent of it,

the Eq Wt of acid $= \frac{x}{V} \times 1000 \times 10$ and Mol Wt of acid = Eq Wt × Basicity

The molecular weight of a base may also be determined exactly as above by titrating a known weight of it against a standard acid and applying the relationship :

Mol Wt = Eq Wt × Acidity

Example 7. *0·183 g of an aromatic monobasic acid required 15 ml of N/10 sodium hydroxide solution for exact neutralisation. Calculate the molecular weight of the acid.*

15 ml N/10 NaOH solution ≡ 0·183 g acid

1000 ml 1 N NaOH solution ≡ $0{\cdot}183 \times \frac{1000}{15} \times 10$ g acid

But 1000 ml of 1 N sodium hydroxide contain 1 g equivalent of it and will neutralise 1 g equivalent weight of acid.

$\therefore$ Eq Wt of acid = $0{\cdot}183 \times \frac{1000}{15} \times 10 = 122$

Mol Wt of solid = Eq Wt × Basicity = 122 × 1 = 122

Example 8. *0·25 g of a dibasic organic acid were dissolved in water and the volume made to 100 ml. 10 ml of this solution required 12·3 ml of N/30 sodium hydroxide solution for complete neutralisation. Find the molecular weight of the acid.*

12·3 ml N/30 NaOH solution ≡ 10 ml of acid

123 ml N/30 NaOH solution ≡ 100 ml of acid ≡ 0·25 g acid

1000 ml 1 N NaOH solution ≡ $\frac{0{\cdot}25}{123} \times 1000 \times 30$ g

$\therefore$ Eq Wt of acid = $\frac{0{\cdot}25}{123} \times 1000 \times 30 = 61{\cdot}0$

Mol Wt of acid = Eq Wt × Basicity = 60·96 × 2 = 121·92

Example 9. *0·20 g of a diacid base required 25 ml of N/8 HCl for exact neutralisation. What is the molecular weight of the base?*

25 ml of N/8 HCl = 0·20 g of the base

1000 ml of N HCl = $\frac{0{\cdot}20}{25} \times 1000 \times 8$ g of base

But 1000 ml of N HCl contain 1 g equivalent of acid and will neutralise 1 g equivalent of the base.

$\therefore$ Eq Wt of base = $\frac{0{\cdot}20}{25} \times 1000 \times 8 = 64$

Mol Wt of base = Eq Wt × Acidity = 64 × 2 = 128

QUESTIONS

1. List any three methods of determining the molecular weight of organic compounds. *(Agra BSc, 1992)*
2. How is molecular weight of an organic acid determined by silver salt method? *(Indore BSc, 1993)*
3. 0.1982 g of Platinichloride of an organic base gave 0.0563 g of metallic platinum on ignition. Calculate its molecular weight, if it is a monoacid base. (At wts : Pt = 195, Cl = 35.5) *(Maharshi Dayanand BSc, 1993)*

   Answer. 138.24
4. In a determination by Victor Meyer method, 0.6 g of volatile compound expelled 123 cc of air measured over water at 20°C and 757.4 mm pressure. Find the molecular weight of the compound. (Aq. tension at 20°C = 17.4 mm)

   Answer. 120.5
5. 0.177 g of a monobasic acid requires 30 ml of N/10 NaOH solution for complete neutralisation. Calculate the molecular weight of the acid.

   Answer. 59.
6. 0.607 g of silver salt of a tribasic acid, on combustion, deposited 0.37 g of pure silver. Calculate the molecular weight of the acid.

   Answer. 210.51
7. 0.135 g of an organic diacid base required 20 ml of N/10 acid for complete neutralisation. Calculate the molecular weight of the base.

   Answer. 135
8. An organic compound contains 41.37% carbon ; 5.75% hydrogen ; 16.08% nitrogen ; and 36.79% sulphur. Find the empirical formula of the compound.

   Answer. C_3H_5NS
9. A dibasic acid, containing 26.66% carbon and 2.22% hydrogen, gave a silver salt containing 71.05% of silver. What is the molecular formula of the acid ?

   Answer. $C_2H_2O_4$

10. An organic compound gave, on analysis, C = 78.6% , H = 8.4% ; and N = 12.92%. Derive the empirical formula of the compound. If the molecular weight is 107, what is the molecular formula ?

Answer. C_7H_9N

11. The vapour density of an organic compound is 30. The compound contains, C = 40%, H = 6.7% and O = 53.3%. Find out the molecular formula of the compound. *(Meerut BSc, 1994)*

Answer. $C_2H_4O_2$

12. 3 ml of a gaseous hydrocarbon was sparked with 34 ml of oxygen and on cooling the residual gases occupied 28 ml. After shaking with KOH solution, a contraction of 9 ml took place. All volumes are measured under the same conditions of temperature and pressure. What is the molecular formula of the hydrocarbon ? *(Vikram BSc, 1994)*

Answer. C_3H_8

Each of the following questions can be divided into two parts : (1) Calculation of empirical or molecular formulas on the basis of given data ; and (2) Derivation of the structural formulas on the basis of given reactions or chemical test. Attempt the following questions after studying the rest of the book, so that you are well versed with the chemical properties of various organic compounds/families. Questions 13 to 22 involve reactions of Aliphatic compounds. Questions 23 to 30 involve reactions of Aromatic compounds.

13. The isomeric organic compounds, with vapour density 28, gave the following results on analysis C = 85.71% and H = 14.29%. Each one of them decolourises bromine water and alkaline KMnO4. Give their structural formulas.

Answer. The structural formulas of the three isomers are :

$CH_3CH_2CH{=}CH_2$ 2-Butene $CH_3CH{=}CHCH_3$ 2-Butene $CH_3-\underset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2$ 2-Methylpropene

14. An organic compound (A) containing C = 40.00% ; H = 6.67% reduced Fehling's solution. On treatment with NaOH, it gave an alcohol (B) and the sodium salt of an acid (C). Compound (B) can be obtained by reduction of (A). The vapour density of (A) is 15. Give structures of (A), (B) and (C) and explain all reactions with the help of equations.

Answer. (A) = $H-\overset{\displaystyle O}{\overset{\|}{C}}-H$ (Formaldehyde

(B) = CH_3OH (Methyl alcohol)

(C) = HCOOH (Formic acid)

15. A compound containing C = 39.13% and H = 8.62% gave on treatment with HNO_3, a dibasic acid, with sulphuric acid an unsaturated aldehyde, with hydrochloric acid gas in acetic acid secondary alcohol and with PCl_5 a chlorinated hydrocarbon. What was the compound ? Give all reaction equations. *(Jiwaji BSc, 1993)*

Answer. Glycerol

16. A organic compound (A) gave the following results : C = 61.01%, H = 15.25%, and N = 23.74. (A) on treatment with HNO_2, gave another product (B) which contains C = 60.0%, H = 13.33% and no nitrogen. (B) on careful oxidation gave a compound (C) which gave iodoform on treatment with iodine and alkali and had a MW = 58. Assign structural formulas to (A), (B) and (C). Explain all the reactions.

Answer. (A) is Isopropylamine ; (B) is Isopropyl alcohol; and (C) is Acetone.

17. Two compounds (A) and (B) have the same percentage composition, C = 40% and H = 6.67%. The vapour density of (A) is 15 while that of (B) is 30. (B) reduces Fehling's solution but does not give any effervescence with $NaHCO_3$ while (B) gives effervescence with $NaHCO_3$ but does not reduce Fehling's solution. Assign structural formulas to (A) and (B).

(Osmania BSc Hons, 1993)

Answer. (A) is HCHO; and (B) is CH_3COOH.

18. Compound (A) with the percentage composition C = 69.77%, H = 11.63% H = 11.63% and O = 18.60% has a molecular weight of 86. It does not reduce Fehling's solution but forms a sodium bisulphite compound and gives the iodoform test. Write a possible structure of the compound. *(Kurukshetra BSc, 1994)*

Answer. (A) is 2-Pentanone.

19. A dibasic acid contains carbon 40.68% and hydrogen 5.08%. 0.332 g of silver salt of the acid gives 0.216 g of silver on ignition. the acid gives following reactions :

(*a*) On distillation forms an anhydride.

(*b*) The potassium salt of the acid forms ethane on electrolysis.

Explain the reactions and determine the structural formula of the acid. (At Wt of Ag = 108) *(South Gujarat BSc, 1994)*

Answer. Succinic acid (1,4-Butanedioic acid).

20. An organic compound (A) containing carbon 65.45%, hydrogen 9.09% and the rest nitrogen, evolves ammonia when boiled with caustic potash solution. It has a vapour density of 27.5 and on reduction with sodium and alcohol it forms a base which reacts with nitrous acid giving off nitrogen and yielding an alcohol. The alcohol can be oxidised to propionic acid. What is the original compound (A) and explain the reactions involved. *(Anna BSc, 1994)*

Answer. (A) is Ethyl cyanide.

21. An organic compound (A) contains carbon 40% and hydrogen 6.7%. Its vapour density is 15. On reaction with a concentrated solution of potassium hydroxide, it gives two compounds (B) and (C). When (B) is oxidised, the original compound (A) is obtained. When (C) is treated with conc. HCl, it gives a compound (D) which reduces Fehling's solution and ammoniacal silver nitrate solution. Write the structures of (A), (B), (C), and (D) and explain the reactions.

Answer. (A) is Formaldehyde (HCHO) ; (B) is Methyl alcohol (CH_3OH) ; and (C) is Formic acid (HCOOH).

22. A neutral organic compound (A), on analysis, gave C = 60% and H = 13.33%. On mild oxidation, (A) gave another neutral compound (B). (B) on treatment with dilute alkali gave a compound (C) with double the molecular weight. (C) readily loses water on heating to form (D) which on oxidation gave an α, β-unsaturated acid. Identify (A), (B), (C), and (D) and explain the reactions. *(Jiwaji BSc, 1993)*

Answer. (A) is 1-Propanol ; (B) is Propanal ; (C) is 3-Hydroxy-2-methylpentanal ; and (D) is 2-Methyl-2-pentanoic acid.

23. A compound (A) contains C = 66.4%, H = 5.53%, and Cl = 28.06%. When oxidised with $KMnO_4$ it yields an acid (B) containing C = 68.8% and H = 4.9%. When (A) is treated with aq. NaOH, compound (C) is produced which contains C = 77.8%, and H = 7.4%. Give the structural formulas of (A), (B) and (C). Explain the reactions involved.

Answer. (A) is Benzyl chloride ; (B) is Benzoic acid ; and (C) is Benzyl alcohol.

24. An organic compound (A) contains C = 91.3% and H = 8.7%. On nitration it gives compound (B). The reduction product of (B) on treatment with $NaNO_2$ and HCl at 0°C and subsequent treatment by Sandmeyer's reaction using Cu_2Cl_2 and HCl gives compound (C). On oxidation compound (C) gives *o*-chlorobenzoic acid. Assign structural formulas to (A), (B) and (C) and explain the reactions. *(Bangalore BSc, 1994)*

Answer. (A) is Toluene ; (B) is *o*-Nitrotoluene ; and (C) is *o*-Chlorotoluene.

25. An organic compound having 79.25% of carbon and 5.66% of hydrogen had to vapour density 53. It had a characterstic smell and on oxidation with $KMnO_4$, it gave an acid. The sodium salt of the above acid on distillation with sodalime gave benzene. What is the orginal compound ? *(Baroda BSc, 1993)*

Answer. Benzaldehyde (C_6H_5CHO).

26. An aromatic hydrocarbon (A) containing C = 91.3% and H = 8.7% on treatment with chlorine, under suitable conditions, gave three isomeric monochloro compounds (X), (Y) and (Z) each having 28% chlorine. On oxidation with $KMnO_4$ all the three gave monobasic acids. The acid from (X) on distillation with sodalime gave benzene while those from (Y) and (Z) gave monochlorobenzene. Assign structural formulas to (A), (Y) and (Z) and explain all the reactions involved by giving equations. *(Nehu BSc Hons, 1994)*

Answer. (A) is Toluene; (X) is Benzyl chloride ; (Y) *o*-Chlorotoluene ; and (Z) is *p*-Chlorotoluene.

27. When an organic liquid (A) was mixed with cold NaOH solution, two compounds (B) and (C) are obtained. (B) is an acid and (C) is a primary alcohol. (A) $C_7H_6O_2$ forms a crystalline derivative with $NaHSO_3$. (B) contains C = 60.9% ; H = 4.35% and may also be obtained by oxidation of (A). (B) when distilled with sodalime gives phenol (C) which contains C = 67.75%, H = 6.45% and may also be obtained by reducing (A). Explain all the reactions and give structural formulas for (A), (B) and (C).

Answer. (A) is Salicylaldehyde ; (B) is Salicylic acid; and (C) is 2-Hydroxybenzyl alcohol.

28. An organic compound (A) containing carbon, hydrogen, and oxygen gave on anlysis C = 76.6% and H = 6.38%. This compound dissolves in NaOH solution and imparts violet colour with $FeCl_3$ solution. Its solution in aqueous NaOH on being heated with CCl_4 gave an acid (B) of equivalent weight 138. What are (A) and (B). *(Manglore BSc, 1994)*

Answer. (A) is Phenol and (B) is Salicylic acid.

29. An organic compound (L) contains C = 79.4% and H = 5.6%. Its vapour density is 53. It forms a sodium bisulphite derivative. On treatment with alcoholic KCN, it gives a compound (M) having the formula $C_{14}H_{12}O_2$ which no longer forms a bisulphite derivative. (L) on refluxing with sodium acetate and acetic anhydride gives an aromatic acid (N) having the molecular formula $C_9H_8O_2$ which decolourises bromine water without liberating HBr. Assign structures to (L), (M) and (N) and explain the reactions involved. *(Madurai BSc, 1993)*

Answer. (L) is Benzaldehyde ; (M) is Benzoin ; and (N) is Cinnamic acid.

30. An organic compound (A), the vapour density of which is 53, contains C = 79.20%, H = 5.5%. On treatment with concentrated KOH solution it gave two compounds (B) and (C). (B) on oxidation gave (A) while (C) on distillation with sodalime gave benzene. Determine the structural formulas of (A), (B) and (C) and explain the reactions. *(Saugar BSc, 1994)*

Answer. (A) is Benzaldehyde ; (B) is Benzyl alcohol and (C) is Benzoic acid.

Chapter **5**

Structure of Organic Molecules

Molecules result by the union of atoms. Before a comprehensive study of the structure of organic molecules could be made, it is necessary to know what an atom is ; why and how it combines with other atoms to form molecules.

EARLY CONCEPTS

According to Bohr's atomic model (1913) an atom consists of a central positively charged *nucleus* containing positively charged particles called *protons* and neutral particles called *neutrons*, both having unit mass. The nucleus is surrounded by negatively charged particles called electrons which carry unit negative charge and negligible weight. Since an atom is electrically neutral, the number of protons in the nucleus equals the number of electrons around the nucleus.

The surrounding electrons, often called the *extranuclear electrons*, are said to be moving about the nucleus in closed concentric *orbits* or *energy levels*. While an electron moves in such a level it possesses a definite amount of energy and it neither emits nor absorbs energy as long as it remains in that level or orbit. The electrons are arranged in these orbits so that the maximum number of electrons in the various orbits starting from the first one is 2, 8, 18, 32, 18, 8. The outermost orbit cannot have more than eight electrons and the penultimate orbit cannot have more than eighteen electrons. The outermost orbit of electrons in different atoms (except those of inert gases) is incomplete and the electrons in it are known as *valency electrons*.

Electronic Theory of Bonding. Kossel and Lewis (1916) gave their *Electronic theory of bonding* to explain the formation of bonds or unions between atoms. They visualised that the atoms of inert gases have either two (helium) or eight electrons in the outermost orbit. These gases do not enter into chemical combination and, therefore, they are assumed to have complete or stable orbits. The atoms of all other elements have incomplete last orbits and tend to complete them by chemical combination with other atoms. This inert gas electronic grouping of two or eight electrons can be achieved by the combining atoms by *losing*, *gaining* or *sharing* electrons among themselves. Hence it must be emphasized here that *it is this tendency of atoms to acquire inert gas electronic configuration which causes the atoms to unite to form the chemical bonds.*

The different modes of bond formation arise as a result of different manners in which the electron distribution occurs between the combining atoms to attain the stable inert gas electronic configuration. The chemical bonds thus established are of three types.

(1) **Ionic Bonding** or **Ionic Linkage**. This type of chemical bonding is formed as a result of complete transference of one or more electrons from one atom to the other so that both the atoms acquire inert gas electronic configuration. The atom that loses the electron/s becomes positively charged and the atom that gains the electron/s becomes negatively charged. The charged species (called ions) thus produced are held together by electrostatic force of attraction. It is for this reason that the bond thus formed is called 'ionic' or 'electrovalent' bond. An example of this type of bonding is found in sodium chloride molecule. In its formation, sodium atom loses its lone electron of the third orbit (valency orbit) to acquire a stable *octet*, and chlorine accepts this electron to complete the third orbit of eight electrons.. Thus,

$$\underset{2,8,1}{Na} - le^- \longrightarrow \underset{2,8 \text{ (neon configuration)}}{Na^+}$$

$$\underset{2,8,7}{Cl} + le^- \longrightarrow \underset{2,8,8 \text{ (argon configuration)}}{Cl^-}$$

The oppositely charged ions Na^+ and Cl^- so produced are held together as Na^+Cl^- molecule by electrostatic lines of force. These ionic compounds, in general, are nonvolatile solids, soluble in water, have high melting points and conduct electricity in the fused state or in aqueous solutions.

Ionic bondings are formed between those reacting atoms which differ widely in their electronegativities *i.e.*, one is electropositive and the other is electronegative. Electron transfer would then occur from electropositive atom to electronegative atom and the ionic bonding would be established. Such bondings are commonly met within inorganic compounds.

(2) **Covalent Bonding** or **Covalent Linkage**. This type of bonding is formed between atoms which have similar or identical electronegativities. Here the sharing of electrons takes place between the combining atoms to attain the inert gas configuration. An example of covalent bonding is provided by hydrogen molecule. Both the atoms of hydrogen are short of one electron each and tend to have the inert gas configuration (helium). Each atom contributes its lone electron and the shared pair counts towards both of the hydrogen atoms. Thus the two hydrogen atoms acquire the helium gas configuration.

$$H\cdot + \cdot H \longrightarrow \underset{\text{shared pair}}{H:H} \text{ or } H-H$$

Since this type of bonding comes into existence by mutual sharing of electrons, it is called a **Covalent bonding**. A covalent bonding or bond is usually signified by a horizontal line (—).

It is not always necessary that the combining atoms share only one pair of electrons. Weare aware that atoms are also known to share two or three pairs of electrons to attain the inert gas configuration. The covalent bonds thus established are referred to as **single**, **double** or **triple bonds** according as the combining atoms share one, two or three pairs of electrons respectively. Since single bonds are represented by a single horizontal line between the combining atoms, so double and triple bonds are represented by two and three horizontal lines respectively. The formation of oxygen and nitrogen molecules illustrate the formation of double and triple bonds.

$$:\ddot{O}: + :\ddot{O}: \longrightarrow :\ddot{O}: :\ddot{O}: \text{ or } \underset{\text{(double bond)}}{O=O}$$

$$\ddot{N}: + :\ddot{N} \longrightarrow \ddot{N}: :\ddot{N} \text{ or } \underset{\text{(triple bond)}}{N\equiv N}$$

such multiple bonds occurring between carbon atoms are very common in organic compounds.

Covalent compounds are generally volatile, insoluble in water and possess low melting and boiling points. Their solutions do not conduct electricity.

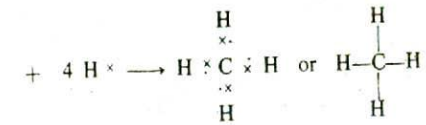
(3) **Coordinate-covalent bonding** or **Coordinate bond**. It is a special type of covalent bond in which both the shared electrons are contributed by one atom only, and not one by each atom as in a simple covalent bond. The atom that donates the electron pair (donor atom) has a spare unshared pair of electrons in the outer orbit and the one that accepts (acceptor atom) is short by an electron pair. However, after the formation of the bond, the electron pair involved is held in common and counts towards both the atoms. A coordinate bond is represented by an arrow pointing away from the donor atom and towards the acceptor atom. An example of this type of bonding is provided by sulphur trioxide (SO_3) molecule.

(*i*)
$$:\ddot{O}: + :\ddot{S}: \longrightarrow :\ddot{O}::\ddot{S}: \text{ or } \underset{\text{lone pair}}{O=S:}$$

(*ii*)
$$\underset{\text{donor atom}}{O=S} + \underset{\text{acceptor atom}}{:\ddot{O}:} \longrightarrow O=S:\ddot{O}: \text{ or } \underset{\text{sulphur dioxide}}{O=S\rightarrow O}$$

since a coordinate bond requires the transference of an electron pair from one atom to the other, the resulting molecule acquires polarity. Thus a coordinate bond is also referred to as a **'semipolar double bond'**.

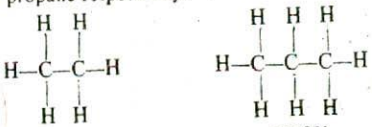
Tetracovalency of Carbon. The atomic number of carbon is six. Therefore, it has two electrons in the first orbit and four electrons in the second or the last orbit *i.e.* 2, 4. It can complete its octet by sharing one electron each with four monovalent atoms such as hydrogen. Thus a carbon atom joins with four hydrogen atoms to form four covalent bonds and a molecule of methane (CH_4) results.



methane

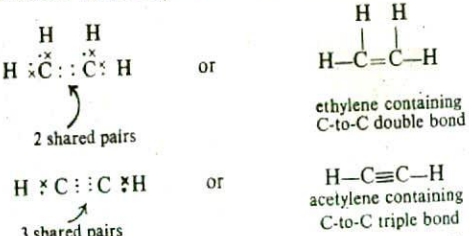
This characteristic of carbon by virtue of which it forms four covalent bonds is generally referred to as **Tetracovalency of carbon.**

A carbon atom has the remarkable property of catenation as a result of which it unites with other carbon atoms through covalent bonds. This helps to construct the carbon structure of organic molecules. Thus two or three carbon atoms may be linked by covalent bonds to give the molecules of ethane and propane respectively.



ethane propane

The carbon atoms may also be joined together by showing two or three electron pairs between them, producing double (=) and triple (≡) bond respectively. Thus ethylene molecule has a double bond while acetylene molecule has a triple bond.



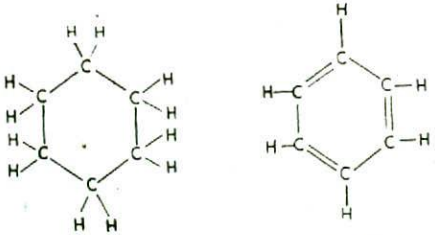
2 shared pairs

ethylene containing C-to-C double bond

3 shared pairs

acetylene containing C-to-C triple bond

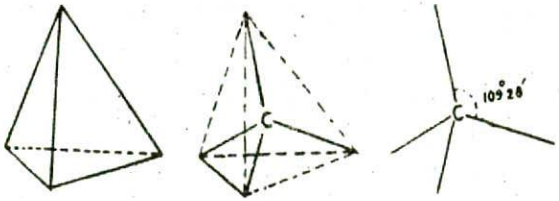
Carbon atoms not only form carbon-to-carbon chains that are free at both ends, but they also form closed rings. Thus cyclohexane and benzene contain closed rings of six carbon atoms each.



CYCLOHEXANE BENZENE

The compounds which contain closed chains of carbon atoms are called **Cyclic** or **Ring compounds.**

Tetrahedral Model of Carbon atom. According to Le Bel and van't Hoff (1874) the four covalent bonds of carbon are not situated in one plane but instead are symmetrically distributed in space. According to the hypothesis named after these workers (**Le Bel Van't Hoff hypothesis**), the four bonds of a carbon atom are directed towards the four corners of a regular tetrahedron constructed around the carbon atom as the centre. On mathematical calculations, the angle contained by any two bonds of carbons as described above comes out to be 109° 28'.



a regular tetrahedron | space model of carbon atom | normal direction of carbon bonds

Fig. 5·1

The tetrahedral structure of the carbon atom went a long way in explaining the relative instability of compounds containing the double and triple bonds as also the space isomerism in certain organic compounds.

WAVE MECHANICAL MODEL OF ATOM AND CHEMICAL BONDING

With the emergence of *Wave Mechanics*, the Bohr model of the atom suffered a serious set back and so did the principles of bonding that were based on it. The present-day model of the atom considers the electron to be free to move about in the entire volume surrounding the nucleus. The electron executes back and forth motion about the nucleus rather than moving in closed orbits as was originally believed. By moving rapidly towards the nucleus and away from it in all possible directions, the electron virtually occupies all space around it. So that if the moving electron were visible to the eye, it would not appear as a particle but would offer the appearance of a diffused spherical 'cloud' formed by its motion. Since the formation of this cloud is due to the motion of the electron, it is commonly referred to as **Electron cloud**. The concept of electron cloud can be easily understood by considering the case of a revolving ceiling fan. When at rest or moving slowly, the four-blade fan occupies only a section of the circle but as the fan turns rapidly it appears to occupy the entire circular space. Similarly, the rapidly moving electron would occupy effectively the entire space around the nucleus but at any given instant the electron would be found somewhere in a three dimensional space best described by points of highest probability. *The shape and size of this region in space around the nucleus, where the probability of finding an electron with certain energy is maximum, is called an* **Orbital**. An electron can be anywhere within an orbital at any given time, although it tends to occupy certain portions of its orbital to a greater extent than other portions.

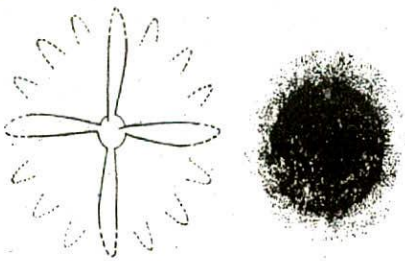


Fig. 5·2. The fan occupies only a portion of the circle, but it occupies effectively the whole circular space, when it revolves rapidly. The same reasoning applies to the formation of a cloud when electron moves briskly in a shell.

The electrons in an atom may be identified by four **Quantum Numbers** *i.e., principal quantum number, azimuthal quantum number, magnetic quantum number* and *spin quantum number*. The principal quantum number refers to the size of the orbital and also the energy of the electron in it, the azimuthal quantum number, to the shape of the orbital, the magnetic quantum number to the orientation of the orbital in space ; and the spin quantum number, to the direction of the spin of the electron about its own axis. According to **Pauli's Exclusion**

Principle, the two electrons in an atom may have the same principal, azimuthal and magnetic spin quantum numbers but they must have different spin quantum numbers. Such pairs of electrons with opposite spin are referred to as 'spin-paired electrons'.

Electrons having the same principal quantum number are said to occupy a **Shell** which is further subdivided into **subshells**. Starting from the shell nearest to the nucleus, the shells enveloping each other are designated by numerals 1, 2, 3, 4, 5, 6 and 7 or by letters K, L, M, N, O, P and Q. The number of subshells in a shell is equal to the number of the principal shell. For example, the third shell contains three subshells and the fourth shell contains four subshells. So far only four subshells designated as *s*, *p*, *d* and *f* are known and their relative energies increase in the order mentioned above. The subshells of different shells are identified by giving the number of the principal shell before the type of the subshell *i.e.*, *s*, *p*, *d* or *f*. The first shell has only one subshell designated as 1*s* ; the second shell has two subshells designated as 2*s* and 2*p* ; the third shell has three subshells designated as 3*s*, 3*p*, 3*d* ; and the fourth shell has four subshells namely 4*s*, 4*p*, 4*d* and 4*f*. The subshells are further divided into smaller units called the **Orbitals** which are the actual seat of electrons. An *s* subshell is made up of *one* orbital ; a *p* subshell of *three* orbitals ; a *d* subshell of *five* orbitals and *f* subshell of *seven* orbitals.

It may, however, be emphasised that shells, subshells and orbitals correspond to principal, azimuthal and magnetic quantum numbers respectively.

Electron population in Shells, Subshells and Orbitals. Before an attempt at writing down the electronic configuration of certain elements is made, it becomes necessary to consider the following rules which govern the distribution of electrons in shells, subshells and orbitals.

(1) *A shell can have at the most* $2n^2$ *electrons, where n refers to the principal quantum number of the shell.* Thus the first shell can accommodate two, the second eight, the third eighteen and the fourth thirty-two.

(2) *The maximum number of electrons in a subshell is equal to twice the number of orbitals it contains.* Thus a *s* subshell can have two electrons because it has only one orbital, *p* subshell can have 6 electrons due to three orbitals, *d* can have 10 electrons due to five orbitals and *f* can have 14 electrons due to seven orbitals.

The following figure depicts beautifully the concept of shells, subshells and the maximum quota of electrons.

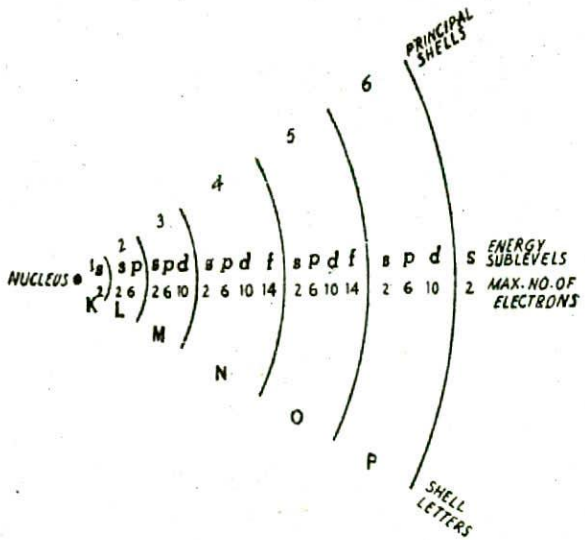


Fig. 5·3. Electron shells of an atom indicating the number of electrons that can be accommodated in various energy levels.

(3) *An orbital at the maximum can have two electrons that too of opposite spins* (Pauli Exclusion Principle).

(4) *Electrons have a tendency to fill the orbital of the lowest energy first and then the filling of the orbitals of higher energy starts.*

The energy of the orbitals of the various subshells follows the sequence :

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d$$

Evidently, the order of filling of various orbitals follows the same sequence given above. This tendency of electrons to populate the orbitals of lower energy is often referred to as **Aufbau Principle** (German *Aufbau*=building up).

(5) *In a subshell, all the available degenerate (of the same energy) orbitals are occupied singly first and then the pairing of electrons in each orbital occurs.* Thus of the three degenerate orbitals of p subshell namely p_x, p_y and p_z, no one will have two electrons as long as any other is vacant This principle is called **Hund's Rule of Maximum Multiplicity**. Hence in accordance with this rule, the electron configuration

 is more stable than provided the orbitals are degenerate *i.e.*, are of equal energy.

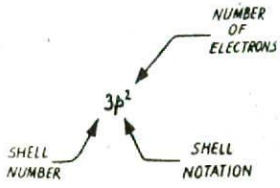


Fig. 5·4.

The distribution of electrons in an atom, by convention, is always written in terms of electrons which each of the subshells occupies. In common practice, the number of electrons in the subshell of a shell are indicated as superscripts, Fig. 5·4.

A complete electronic configuration of any element is written by listing the subshells in the order of increasing energy and the number of electrons occupying each subshell are denoted by superscripts.

By the application of the above principles, the electronic configuration of some elements most commonly encountered in organic chemistry are given in the Table below.

Element	*At No*	*Electronic Configuration*				
H	1	$1s^1$				
He	2	$1s^2$				
Li	3	$1s^2$	$2s^1$			
Be	4	$1s^2$	$2s^2$			
B	5	$1s^2$	$2s^2$	$2p_x^1$		
C	6	$1s^2$	$2s^2$	$2p_x^1$	$2p_y^1$	
N	7	$1s^2$	$2s^2$	$2p_x^1$	$2p_y^1$	$2p_z^1$
O	8	$1s^2$	$2s^2$	$2p_x^2$	$2p_y^1$	$2p_z^1$
F	9	$1s^2$	$2s^2$	$2p_x^2$	$2p_y^2$	$2p_z^1$
Ne	10	$1s^2$	$2s^2$	$2p_x^2$	$2p_y^2$	$2p_z^2$

Geometry of Atomic Orbitals. Since an atomic orbital, by definition, represents a particular region in space, so all the four types of orbitals *i.e.*, *s*, *p*, *d* and *f* must possess a characteristic shape of their own. For the purpose of chemical bonding in organic chemistry, we shall be concerned mainly with only *s* and *p* orbitals.

Shape of *s* orbitals. According to mathematical derivations from Schrodinger's wave equation, an *s orbital* has a spherical shape with the nucleus lying at its centre. The atomic nucleus is indicated either by a dot (.) or by a plus (+) sign. As discussed in the previous section, each shell has one *s* orbital. The 2*s* orbital is very much like 1*s* orbital except that it is larger and, therefore, more diffused and also has higher energy. Thus 1*s* orbital lies completely within the 2*s* orbital which in turn is surrounded by 3*s* orbital and so on (Fig. 5·5).

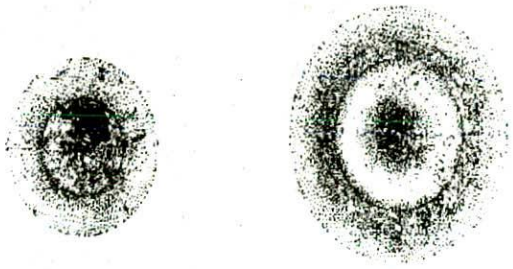


Fig. 5·5. Spherical *s* orbitals symmetrically disposed about the nucleus.

Shape of *p* orbitals. A *p* orbital has a dumb-bell shape with two lobes disposed symmetrically about the nucleus along a line. This line is referred to as the *orbital axis*. The two lobes of the orbital have a position concentric with the atomic nucleus where the probability of finding an electron is zero. This point is termed a *node* and the plane passing through it and perpendicular to the orbital axis is called a *nodal plane*.

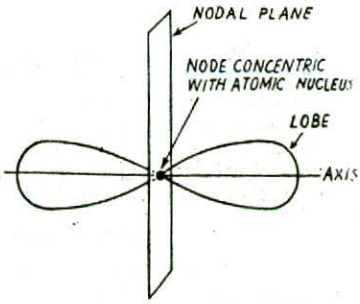


Fig. 5·6. Geometry of a *p* orbital.

Thus *p* orbital has a shape and a direction about the atomic nucleus. Since there are three *p* orbitals for a shell, these are directed in space along the three axes (namely *x*, *y*, *z*) and are designated as p_x, p_y and p_z.

Atomic Orbital Theory applied to Chemical bonding. A chemical bond between atoms is believed to be formed if there is a resultant decrease in the total energy of the system when the bonding atoms approach closer. Thus the new arrangement of electrons and nuclei formed as a result of bond formation is much less energetic than the arrangement in isolated atoms. The orbital structure of chemically stable inert gases, reveals that all the available orbitals in their atoms are completely filled (containing spin-paired electrons). While on the other hand, atoms of all other elements are known to be reactive and have partially filled (half-filled) orbitals. During bond formation, the half-filled orbitals of such atoms tend to acquire another electron in order to become stable by having completely filled orbitals as in He, Ne, etc. Thus it is evident that only those atoms which have half-filled orbitals would combine with each other to form molecules which have fully completed orbitals. The half-filled orbitals involved in bond formation to give molecules are often referred to as **Bonding Orbitals.**

Ionic or Electrovalent Bonding is explained in the same way as proposed by the classical theory based on Bohr atomic model. There occurs a transfer of an electron from a partially filled orbital of an electropositive atom to the partially filled orbital of an electronegative atom which will now have a pair of electrons in the formerly partially filled orbital. Thus Li transfers its single electron from the 2*s* orbital to the $2p_z$ orbital of F atom. to form Li^+ and F^- ions

$$Li\ (1s^2\ 2s^1) \longrightarrow Li^+\ (1s^2\ 2s^0)$$

$$F\ (1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1) \longrightarrow F^-\ (1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^2)$$

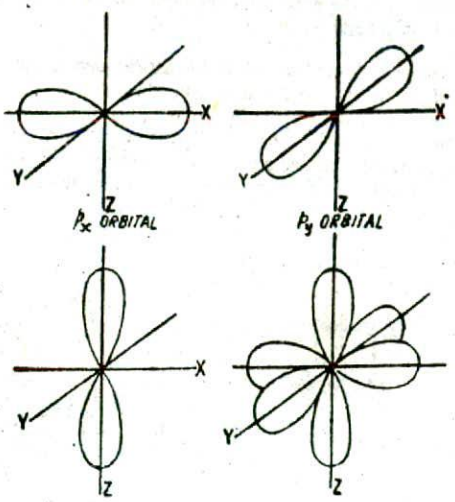


Fig. 5·7. The three *p* orbitals are dumb-bell shaped and arranged at right angles to each other, the nucleus of the atom lying at the intersection of the axes.

It is clear that all the orbitals in Li^+ and F ions have two electrons each and hence acquire stability. The two ions thus produced are held together by electrostatic force of attraction as Li^+F^- molecule.

The Nature of Covalent Bond. In the perspective of the orbital theory of atoms, a covalent bond between two atoms is formed when the half-filled orbital on one atom is filled by the electrons of the other atom without detracting it from its original orbital. This happens when the two atoms draw close enough so that their bonding orbitals start interacting. Thus a covalent bond is formed as a result of the progressive overlapping of the bonding or combining orbitals. The original orbitals ultimately merge to form a bigger new **Molecular Orbital (MO).** The essential condition for an effective overlap are :

(*i*) The two combining orbitals must be half-filled ;

(*ii*) The bonding orbitals must approach each other in proper alignment needed for an effective overlap ;

(*iii*) The electrons in the bonding orbitals must have opposite direction of spin.

In actual practice, the two combining orbitals of two atoms generate two Molecular Orbitals. One of these is of lower energy than that of the atomic orbitals of the combining atoms and hence is called the '*bonding molecular orbital*'. The other is of higher energy than that of the atomic orbitals of the combining atoms and hence is called the '*antibonding molecular orbital*' or simply '*antibonding orbital*'. Since the bond formation is due to the bonding molecular orbital, here we shall discuss in detail the bonding molecular orbitals only. Thus in the following treatment a molecular orbital will imply a bonding orbital.

The molecular orbital encompasses both the nuclei of combining atoms and has two electrons with opposite spins. These electrons are now under the influence of two nuclei rather than one as in their isolated atoms. This arrangement leads to greater attractive forces because each electron is being attracted by both the nuclei. This new molecular orbital (MO) provides greater space and hence greater degree of freedom of movement to the 'paired electrons' in it. Consequently, this greater degree of freedom of movement to the electrons makes the system more stable by lowering its energy.

Since the bonding molecular orbital has lower energy than that of the isolated (combining) atoms, the bond formation is accompanied by a decrease in energy of the system. *The energy which is given off or released at the time of overlapping of orbitals to form one mole of bonds* termed **Bond energy** or **Stabilization energy**. It also implies that *this much amount of energy must be supplied to separate the bonded atoms in a mole* ($6{\cdot}625 \times 10^{23}$) *molecule.* Thus the bond energies provide a very useful clue to the relative strengths of various bonds.

It may, however, be pointed out that there is a limit to the extent of overlap between orbitals. In fact, the overlapping of orbitals of two approaching atoms halts at a stage when their nuclei start repelling each other. The atoms, therefore, cannot approach beyond a specific distance. At this distance between the nuclei of two atoms, there is established an equilibrium between the repulsive action of the two nuclei and the force of attraction on account of overlapping. The equilibrium distance at which the two atomic nuclei are now held is called the **Bond length**.

In the bond formation, the greater the extent of overlap greater is the energy set free and hence higher will be the bond strength. This is referred to as the **Principle of Maximum Overlap**.

It can be inferred that for a bond to be stronger, greater should be the overlap which in turn would shorten the distance between the nuclei *i.e.*, bond length. A stronger bond has, therefore, a shorter bond length. The following table gives some of the bond energies and bond lengths.

Table. *Bond energies and Bond lengths.*

Type of Bond	*Covalent Bond*	
	Energy (Kcal/mole)	*Length (Å)*
H—H	103·2	0·74
C—H	98·7	1·10
C—C	83·0	1·54
C—N	148·1	1·29
C—O	84·0	1·43

Two atoms having only one bonding orbital each, after the overlap get arranged such that their nuclei be in a straight line *i.e.*, the molecule is a linear one. But when an atom has two bonding orbitals, these are localized in a specific direction (*e.g.*, *p* orbitals inclined at an angle 90°) subtending a certain angle between them. These bonding orbitals will overlap with two other bonding orbitals of other atoms to form bonds. *The angle subtended by the two axes of overlaps or the new bonds is referred to as* **Bond angle**. This definition will be amply illustrated in the discussion to follow.

Types of Covalent Bonding

We have learnt so far that a covalent bond is formed as a result of overlapping of atomic orbitals of the combining atoms, giving a molecular orbital. Thus a covalent bond formation may involve the following types of overlaps.

(*i*) *s* and *s* overlap ; (*ii*) *s* and *p* overlap ;

(*iii*) *p* and *p* overlap in (*a*) linear manner ; or (*b*) side-wise fashion.

Each one of these overlaps results in the formation of a different molecular orbital having a different shape and energy. Depending upon the directional disposition of the atomic orbitals involved in the process of overlap, two main types of MO are formed. Thus we have two types of covalent bonds : (1) *Sigma* (σ) *bond* ; and (2) *Pi* (π) *bond.*

Sigma Bond. When two bonding orbitals overlap to form a MO which is symmetrically distributed about the nuclear axis (the line joining the nuclei of the two atoms), the molecular orbital is referred to as SIGMA (Greek $\sigma = s$). The bond thus established is called *Sigma bond* or *single bond.* This is often written as 'σ bond'.

It will be seen from the following treatment that σ bonds are formed as a result of the overlaps of —

(*a*) *s* orbital of one atom and *s* orbital of the other ;

(*b*) *s* orbital of one atom and *p* orbital of the other ;

(*c*) *p* orbital of one atom and *p* orbital of the other (in a linear fashion).

Let us now illustrate the formation of some molecules having a σ bond in them.

Formation of H_2 molecule. It offers an example of *s-s* orbital overlap resulting in the formation of a σ bond. A molecule of hydrogen is formed from two hydrogen atoms each having one electron in *s* orbital. As the two atoms approach each other, their *s* orbitals overlap as shown in Fig. 5·8 to form a σ bond.

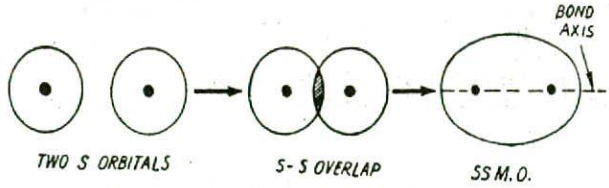


Fig. 5·8. Formation of *s-s* Molecular Orbital of Hydrogen molecule.

The atomic orbitals of hydrogen atoms, having one electron each, tend to fill themselves by giving one more electron. Thus *s* orbitals of the two H-atoms overlap to form a molecular orbital which would have two electrons of opposite spins. The new molecular orbital is called a σ MO or *ss* MO because of its symmetrical shape as is clear from Fig. 5·8. The boundary of the MO takes up an ovoid shape which is symmetrically disposed about the nuclear axis (or bond axis). Although the electrons may be present anywhere in this orbital, the probability of finding the electrons is maximum between the two nuclei, for they are attracted equally by both the nuclei.

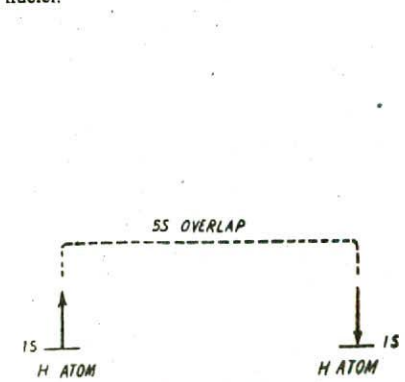


Fig. 5·9. Schematic overlap of *s-s* orbitals each having one electron of opposite spin.

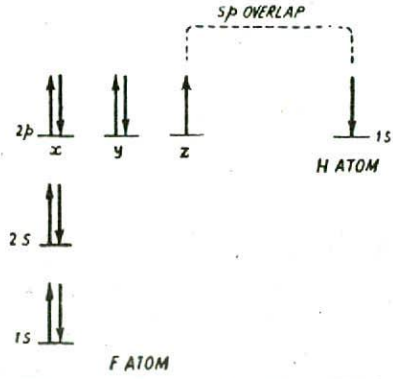


Fig. 5-10. Schematic overlap of an *s* and *p* orbitals involved in the formation of HF molecule.

Formation of HF molecule. The formation of hydrogen fluoride (HF) molecule involves the overlap of *s* and *p* orbitals to give a symmetrical molecular orbital. Here the singly filled 1*s* orbital on hydrogen atom overlaps with a similar half-filled orbital on fluorine atom ($1s^2$, $2s^2$, $2p_x^2$, $2p_y^2$, $2p_z^1$) to form a molecular orbital, while the rest of the orbitals on fluorine are completely filled and hence not available for overlap or bond formation. The situation is represented above in Fig. 5·10, where arrows indicate the direction of spins of electrons in the different orbitals.

The overlap of a spherical *s* orbital and a dumb-bell shaped *p* orbital may be pictorially represented as in Fig. 5·11.

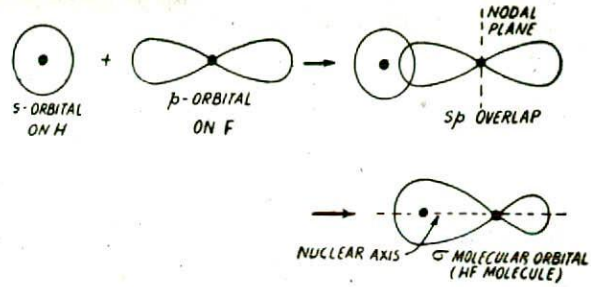


Fig. 5·11. Pictorial representation of *s-p* overlap resulting in the formation of HF molecule

The resulting molecular orbital (σ MO) is also symmetrical about the nuclear axis and the bond thus created between H and F will be a *sigma bond.* It is also noteworthy that the new MO has a nodal plane that stands at right angles to the nuclear axis.

Formation of F_2 molecule. It furnishes an example of *p* and *p* orbital overlap in the 'head-on' or linear fashion. Here one half-filled 2*p* orbital on a fluorine atom ($1s^2$, $2s^2$, $2p^2_z$, $2p^2_y$, $2p_x^1$) overlaps with a similar 2*p* orbital on the other F atom in a head-on fashion, while the remaining orbitals of F atoms being completely filled are inert.

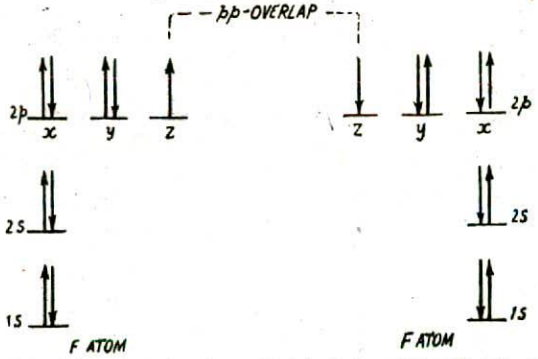


Fig. 5·12. Schematic overlap of *p-p* orbitals in the formation of F_2 molecule.

The orbitals concerned in the overlap have the same orbital axis and in the process of overlap they meet each other in the head-on fashion as is pictorially represented below.

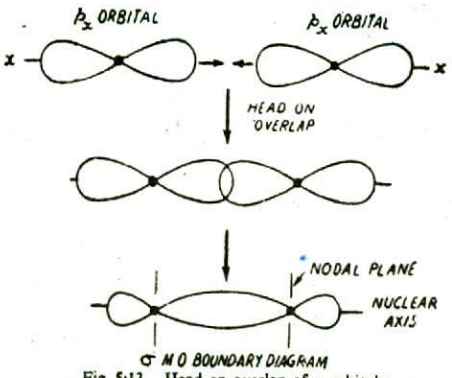


Fig. 5·13. Head-on overlap of *p* orbitals.

It may be pointed out here that the MO formed is cylindrically symmetrical about the internuclear axis and gives rise to a *sigma bond* between the two F atoms. Unlike the σ MO of HF molecule which has one nodal plane, the σ MO of F_2 molecule has two nodal planes which are prependicular to the internuclear axis.

In general, it may be noted that MO formed in the molecules of H_2, HF and F_2 are symmetrically distributed about the internuclear axis and involve a σ bond in each case. For reasons of space and convenience, a pictorial representation of σ MO is not always possible. Therefore, in actual practice, a single horizontal line (—) between the two atoms thus linked is used to depict a sigma bond. For example,

H—H	H—F	F—F
hydrogen	hydrogen fluoride	fluorine

Pi Bond. This type of covalent bond is formed as a result of the lateral or sidewise overlap of the *p* orbitals of two atoms. For such an overlap, the two *p* orbitals must be held parallel and should approach each other as shown in Fig. 5·14.

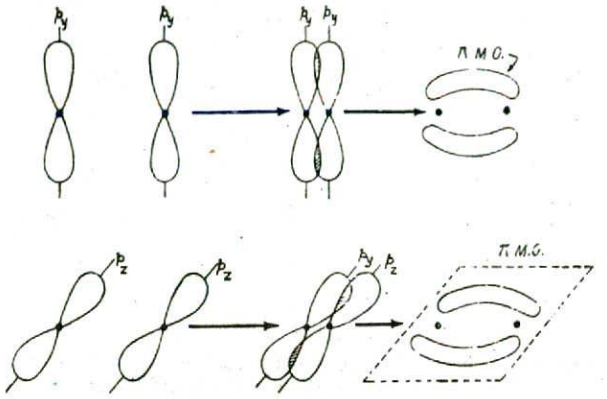


Fig. 5·14. *p* orbitals belonging to two atoms approach such that their orbital axes are parallel. They overlap in a sidewise manner to form a π MO.

As is clear from the above diagram, the overlap here takes place at both the lobes of the *p* orbitals simultaneously. The MO thus formed lies above and below the nuclear axis and has a 'sausage like' shape. This is called a *pi* MO and the bond thus established is referred to as a *pi* bond or π bond.

The nodal planes of a π MO contain the internuclear axis, unlike a σ MO. The π MO has an increased electron density in the inter nuclear region though not on the bond axis. Thus, here π MO differs from a σ MO.

There are two distinguishing features of a π bond from a σ bond.

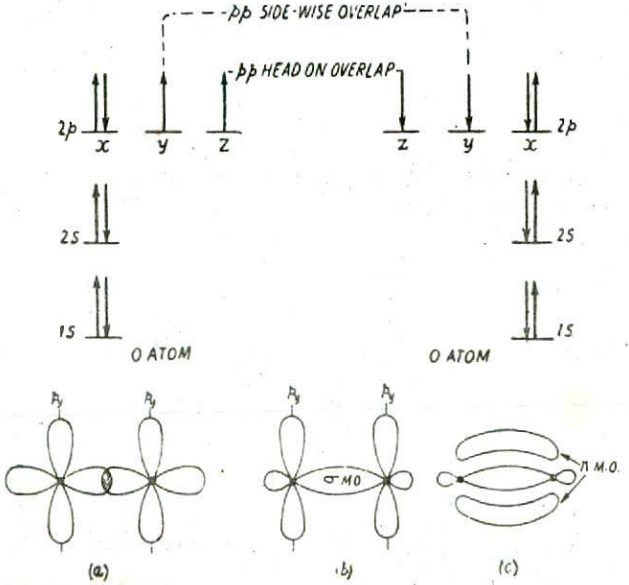


Fig. 5·15. Schematic overlaps of atomic orbitals of the two oxygen atoms in the formation of O_2 molecule.

(*a*) represents a head-on overlap of p_z orbitals ;
(*b*) the formation of σ bond ; and
(*c*) formation of π MO around σ MO.

(*i*) It is weaker than a σ bond since the extent of overlap is relatively smaller and hence there is a lesser decrease in the energy of the new system.

(*ii*) The possibility of free rotation of atoms about the nuclear axis is absent in a π bond. If an attempt is made to do so, the lobes of the *p* orbitals of the two atoms will no longer be coplanar. Consequently the extent of overlap would be decreased and the energy of the system would increase. In other words, the rotation about the bond axis of a π bond will be restricted because work will have to be done for the same. This property of a π bond is very useful in explaining the phenomenon of *cis-trans* isomerism.

Let us now consider the formation o a few molecules involving one or more π bonds.

Formation of O_2 molecule. Each of the two oxygen atoms possesses two bonding *p* orbitals *i.e.*, $2p_y$ and $2p_z$ which are perpendicular to each other. Thus, if $2p_x$ orbitals on oxygen atoms overlap in a head-on manner to form a σ bond (shown in Fig. 5·15 *a*), the remaining $2p_y$ orbitals on the two atoms are parallel and hence experience a sidewise or lateral overlap to give a π bond.

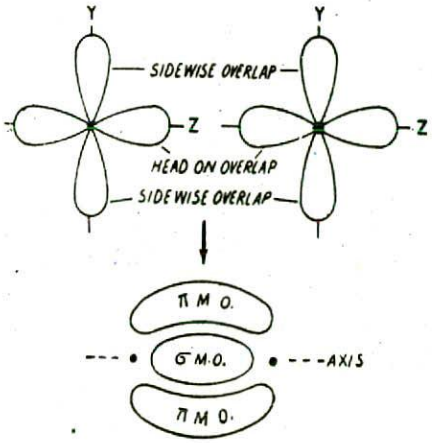


Fig. 5·16. Overlap of bonding orbitals in Oxygen molecule.

Thus in oxygen molecule there are two bonds, one of which is a σ bond and the other a π bond. Both of them together are referred to as a **double bond**. In order to show both sigma and pi bonds in a molecule the latter is represented by an arc over the horizontal line signifying the π bond *e.g.*, oxygen molecule is represented as shown in Fig. 5·17 below.

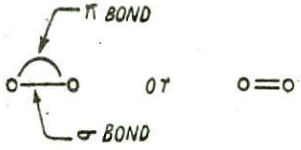


Fig. 5·17. Schematic representation of σ and π bond in O_2 molecule. For convenience the two bonds (σ and π) although different, are indicated by two parallel lines.

Formation of N_2 molecule. The nitrogen molecule offers an example of two π bonds and a σ bond between two atoms. Nitrogen atoms have three bonding *p* orbitals which are directed along the three axes *i.e.*, are at right angles to each other. If $2p_x$ orbitals of the two nitrogen atoms overlap in a head-on fashion to form a σ bond, there are left two sets of parallel *p* orbitals *i.e.*, $2p_y$ and $2p_z$ which overlap in a sidewise manner to produce two π bonds as shown in Fig. 5·18.

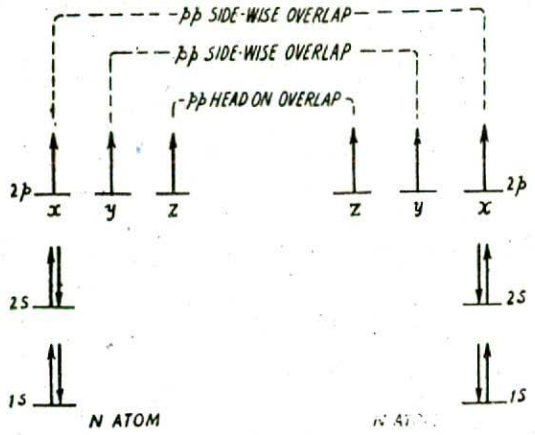


Fig. 5·18. Schematic overlaps in N_2 MO.

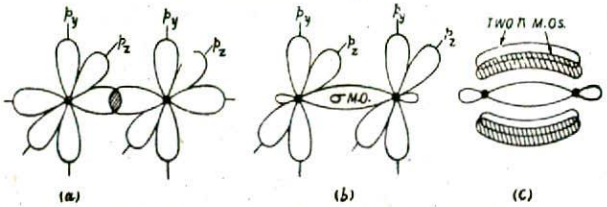


Fig. 5·19. Orbital representation of N_2 molecule formation.
(*a*) indicates the approach of p_z orbitals for headon overlap ;
(*b*) the formation of σ bond ; and
(*c*) the formation of two π MOs by sidewise overlap.

Thus there is one σ bond and 2π bonds in a molecule of N_2. These are collectively referred to as a **Triple bond**. The two π bonds may be differentiated from a σ bond by depicting the former by arcs and the latter by a horizontal line as shown below.

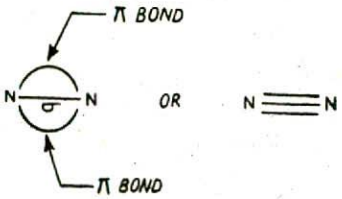


Fig. 5·20. Schematic representation of a σ bond and two π bonds in N_2 molecule. A triple bond is made of two π bonds and one σ bond but for convenience it is usually indicated by three equal parallel lines.

HYBRIDIZATION AND TETRACOVALENCY OF CARBON

The electronic configuration of carbon ($1s^2$, $2s^2$, $2p^1_x$, $2p^1_y$) reveals that it has two half-filled atomic orbitals. Consequently the carbon atom should be divalent. But it is an established fact that carbon exhibits a valency of four in methane (CH_4) and all other compounds.

To provide an explanation for the tetracovalency of carbon, it has been suggested that one of the 2*s* electrons gets uncoupled and is promoted to the vacant $2p_z$ orbital which will now have higher energy and hence less stability. The electron configuration of carbon in the 'excited' state could then be written as below.

$1s^2\ 2s^2\ 2p^1_x\ 2p^1_y$ (ground state) $\qquad$ $1s^2\ 2s^1\ 2p^1_x\ 2p^1_y\ 2p^1_z$ (excited state)

Thus in the excited state, carbon atom has four half-filled atomic orbitals which could possibly overlap with the four $1s^1$ orbitals of hydrogen atoms (in case of methane) to form four σ bonds which in turn would lower the energy of the system. It stands to reason that the lowering of energy thus caused by the formation of two additional σ bonds of carbon overweighs the energy necessary (96 Kcal/mole) for the promotion of a $2s^2$ electron to $2p_z$ orbitals.

We have already seen that the excited carbon atom has four half-filled orbitals in the second principal shell — one *s* and three *p* orbitals. On overlapping with four 1*s* orbitals of hydrogen atoms to form methane molecule, there would result four σ bonds — three by overlap of *s-p* orbitals and one by overlap *s-s* orbitals.

$1s^2\ 2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^1$ (excited carbon)

$1s^1\ 1s^1\ 1s^1\ 1s^1$ ($1s^1$ orbitals of four hydrogen atoms)

overlapping

s-s s-p s-p s-p

Naturally, one of the σ bonds of carbon (*s-s*) should be different from the other three (*s-p*). But this is contrary to experimental facts which show that the four covalent bonds of carbon in methane are equivalent.

To account for the above situation, the concept of hybrid orbitals has been introduced. According to that concept, the atomic orbitals of an atom which lie close to one another in energy tend to merge or mix and then redistribute their energy and shape to produce an equivalent number of new orbitals which are identical in all respects. This phenomenon is called **Hybridization.**

Thus hybridization may precisely be defined as *the concept of mixing or merger of orbitals on an atom having nearly equal energy, to produce entirely new orbitals (equal in number to the mixing orbitals) which have same energy contents, identical shapes and are symmetrically disposed in space.*

Therefore, the following conditions must be satisfied if the atomic orbitals of an atom are to undergo hybridization.

(1) Only the orbitals of an isolated single atom can undergo hybridization.

(2) The hybridizing orbitals must differ only slightly in their energy content.

The **characteristics of hybridized orbitals** produced as above are :

(1) The hybrid orbitals generated are equal in number to that of the pure atomic orbitals which mix up.

(2) A hybrid orbital, like the atomic orbitals, cannot have more than two electrons in it, that too of opposite spins.

(3) The electron waves in hybrid orbital repel each other and hence tend to be farthest apart.

(4) While distributing themselves in space, the hybrid orbitals assume the direction of the dominating orbitals. Since *s* orbital has no directional character of its own, the mixing *p* orbitals largely determine the shape and direction of the resulting hybrid orbitals.

The hybrid orbitals are designated according to the type and the number of mixing orbitals.

Mixing orbitals	*Hybrid orbital produced*	*Type of Hybridrization*
one *s* and one *p*	Two *sp* (ess-pee)	*sp* hybridization
one *s* and two *p*	Three sp^2 (ess-pee-two)	sp^2 hybridization
one *s* and three *p*	Four sp^3 (ess-pee-three)	sp^3 hybridization

As indicated above the *s* and *p* orbitals mix to give *two sp* orbitals and the process is termed *sp* (*ess*-pee) *hybridization*. The mixing of the *s* and two *p* orbitals to form three sp^2

orbitals is called sp^2 (ess-pee-two) *hybridization*. The mixing of the *s* and three *p* orbitals to produce four sp^3 orbitals is referred to as sp^3 (ess-pee-three) hybridization.

The concept of hybridization has been advantageously employed to explain the **Tetracovalency of Carbon**. Thus in an excited carbon atom it is assumed that one 2*s* orbital and three 2*p* orbitals combine (or mix) and redistribute their energy to produce four equivalent hybrid orbitals called sp^3 orbitals. Each of these four hybrid orbitals possesses three-fourths characteristics of *p* orbitals and one-fourth of *s* orbital and a shape similar to *p*-orbital. The hybrid orbitals (like *p* orbitals) possess two lobes, one of which is quite big while the other shrinks down

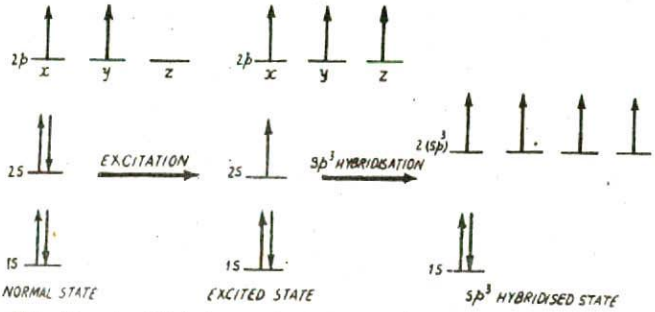


Fig. 5·21. Normal and Excited states of a C-atom, the orbitals undergoing sp^3 hybridization to produce four sp^3 hybrid orbitals of equivalent energy.

to a negligible size. It is the bigger lobe of hybrid orbitals that is involved in the overlaps for the formation of bonds. Their smaller lobes are, therefore, omitted in the pictorial representations for the sake of simplicity. Thus sp^3 hybridization may be depicted as in Fig. 5·22.

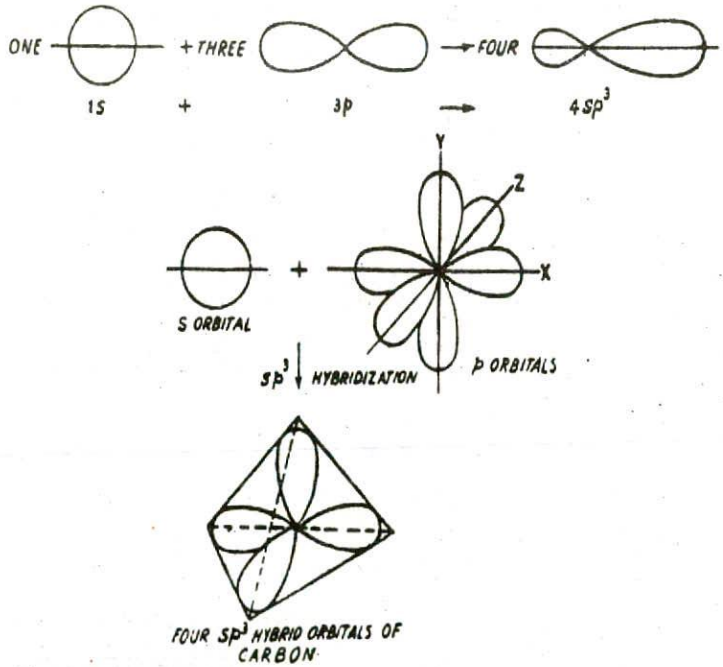


Fig. 5·22. Mixing of orbitals of a carbon atom in space results in four hybrid orbitals so that each one is directed towards the four corners of a tetrahedron. The angle between each of them is 109° 28′.

As the four new orbitals have been obtained by mixing of orbitals which were distributed in space, they would also lie in space. These would tend to be as far apart as possible because of the mutual repulsions of electron waves of each one of them. An arrangement which keeps them farthest apart is that of a *tetrahedron*. Thus each of the hybrid orbitals is directed towards the four corners of a regular tetrahedron (Fig. 5·23). Because of their tetrahedral disposition, this type of

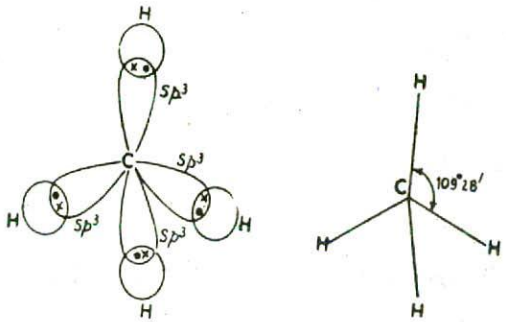


Fig. 5·23. Orbital structure of methane molecule formed by the overlaps of four sp^3 orbitals of carbon and s orbitals of four hydrogen atoms, resulting in four σ bonds.

hybridization is also called **Tetrahedral hybridization**. The four sp^3 hybrid orbitals have the same shape and are inclined at an angle of 109° 28′. Each of these four orbitals possesses one electron and overlaps with 1s orbital of a H atom, thus forming four equivalent bonds in methane molecule (see Fig. 5·23).

In **Ethane molecule** the two carbon atoms (each having a set of four sp^3 hybrid orbitals) combine such that one sp^3 orbital of each carbon overlaps in a head-on fashion forming a σ bond. The remaining three orbitals on each carbon get bonded to three hydrogen atoms forming (sp^3-s) σ bonds as in methane molecule (Fig. 5·24).

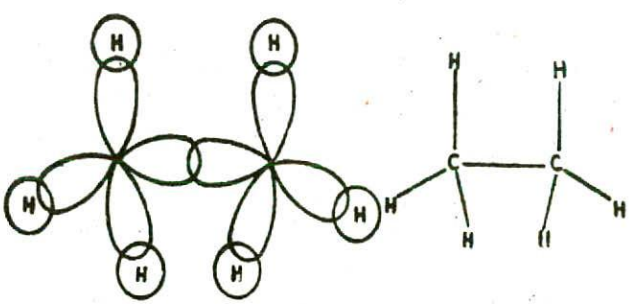


Fig. 5·24. Orbital structure of ethane molecule.

It may be noted how beautifully the sp^3 hybridization of orbitals of carbon as illustrated above has theoretically substantiated the Le Bel and van't Hoff's hypothesis of tetrahedral arrangement of carbon valency bonds in saturated hydrocarbons.

Unsaturated hydrocarbons involve a σ bond and π bond (s) between two carbon atoms which are beautifully explained by **Huckel model of hybridization**. According to him *all the bonding atomic orbitals of the carbon atom do not necessarily undergo hybridization*. In ethylene (having one σ and one π bond), the 2s orbital and two 2p orbitals (*i.e.*, $2p_x$ and $2p_y$) of the excited carbon atom are hybridized to give these equivalent hybrid orbitals. These orbitals formed by the hybridization of one s and two p orbitals are called **sp^2 hybrid orbitals**.

These three sp^2 hybrid orbitals are very much similar in shape to sp^3 hybrid orbitals except that the bigger lobe is slightly fatter here. Since $2s$, $2p_x$ and $2p_y$ orbitals of the excited

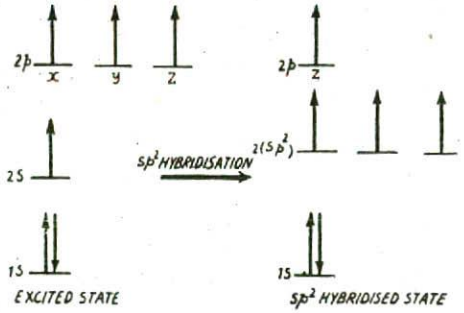


Fig. 5·25. Orbitals of the excited carbon atom undergoing sp^2 hybridization, leaving behind a pure $2p_z$ orbital

carbon atom are hybridized, the new orbitals lie in xy plane. These have to be farthest apart in the plane and so are inclined at an angle of 120°. Therefore, this type of hybridization is also called **Trigonal hybridization**. This sp^2 hybridized carbon atom has a fourth pure $2p_z$ orbital which is not involved in hybridization and lies at right angles to the plane of the hybridized orbitals with its two lobes disposed above and below the plane.

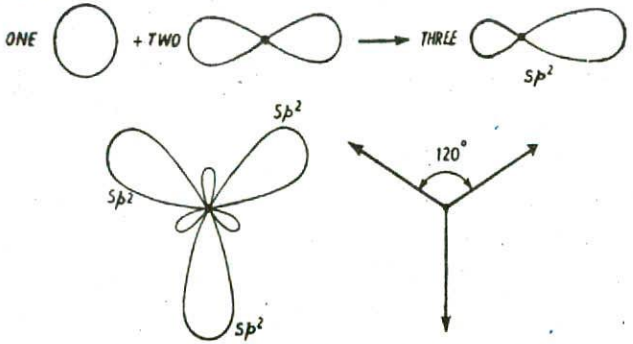


Fig. 5·26. Pictorial representation of sp^2 hybridization of the atomic robitals, These are inclined at an angle of 120° to one another.

In the formation of **Ethylene molecule** sp^2 hybridized carbon atoms are used. Two such carbon atoms form one sigma bond by head-on overlap of two sp^2 orbitals contributed one

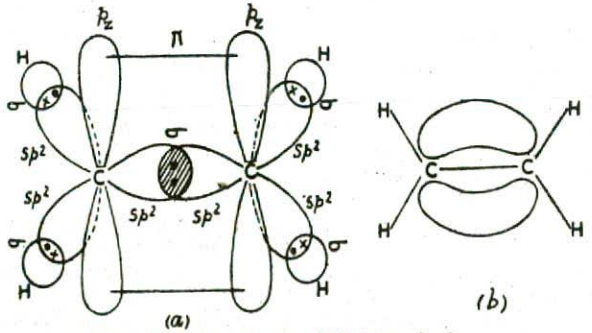
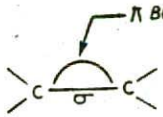


Fig. 5·27. Orbital structure of Ethylene molecule,
(*a*) depicts the scheme of overlaps ;
(*b*) shows a π bond and a σ bond (*straight line*).

each by the two atoms. The remaining two sp^2 orbitals of each carbon form σ bonds with H-atoms. The unhybridised $2p_z$ orbitals of the two carbon atoms undergo a sidewise overlap forming a π bond. Thus, the carbon-to-carbon double bond in ethyiene is made up of one σ bond and one π bond. Since the energy of a π bond is less than that of a σ bond, the two bonds constituting the ethylene molecule are not identical in strength. The π bond being weaker and exposed is readily ruptured in addition reactions of ethylene. The molecule is a planar one. To distinguish the π bond from a sigma bond, the ethylenic linkage may be represented as



The formation of **acetylene molecule** containing a triple bond between two carbons, is interpreted by another kind of hybridization. Here one *s* orbital and only one *p* orbital is believed to hybridize to form two collinear orbitals, while the other two *p* orbitals on the excited carbon remain unhybridized and these lie perpendicular to the axis of the hybrid orbitals.

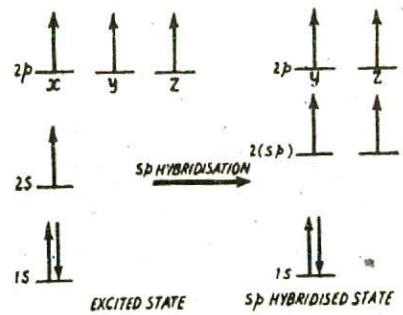


Fig. 5·27. Excited carbon atom with its orbitals undergoing *sp* hybridization.

Since one *s* and one *p* orbital is involved in hybridization, this is known as **sp hybridization** and the new orbitals are named as *sp* hybrid orbitals. Due to their disposition along a line, this type of hybridization is often referred to as **linear hybridization**. Their mutual repulsion causes them to be oriented in a manner to be farthest apart and thus the two *sp* bonds lie in a straight line. In other words, the angle formed between them is 180°.

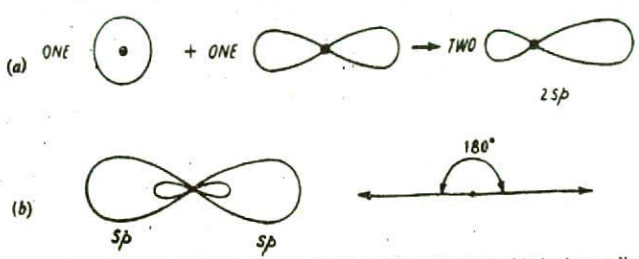


Fig. 5·28. (*a*) *sp* hybridization; (*b*) Disposition of hybrid orbitals along a line.

As is clear from the pictorial representation of *sp* orbitals, their shape essentially remains the same as of the previous hybrid orbitals. However, the bigger lobe becomes still smaller here.

In the **Acetylene molecule** (C_2H_2), one of the two *sp* hybrid orbitals on each of the two carbons may be used in forming a σ bond between them. This leaves two pure 2*p* orbitals (*i.e.*, $2p_y$ and $2p_z$) along with one available *sp* orbital on each carbon. The two carbon atoms form one C—H σ bond by overlap of their *sp* hybrid orbital and *s* orbital of hydrogen atom. The pure

two *p* orbitals are mutually prendicular as also to H–C–C–H axis. These are capable of forming two π bonds by sidewise overlaps (*see* Fig. 5·29).

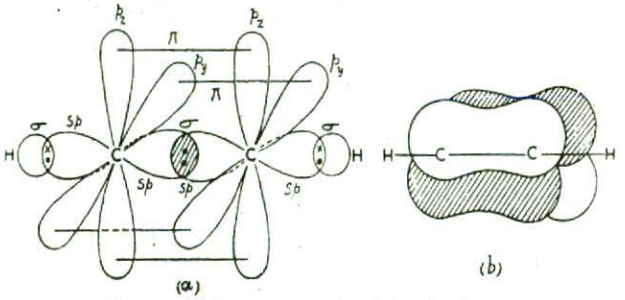


Fig. 5·29. Orbital structure of Acetylene molecule:
(a) **shows scheme of overlaps.**
(b) **shows the bonds, σ bonds being indicated by straight lines.**

Thus acetylene molecule contains one σ and two π bonds between the two carbons and each carbon is again linked to one H-atom through σ bond.

Other atoms generally present in organic compounds are N and O. Both of them may use either pure atomic orbitals or hybridized orbitals (*i.e.*, sp^3, sp^2, *sp*) for bond formation with carbon atoms.

ELECTRONEGATIVITY

An element that tends to acquire rather than lose electrons in its chemical interactions is said to be *electronegative*. Atoms of different electronegative elements differ in their tendency to attract electrons. *A measure of the tendency of an atom of an electronegative element in a molecule to attract electrons to itself (and away from its bond partner) is called its* **Electronegativity.**

Thus in a molecule AB joined by a pair of electrons we may have

A : B or A : B
I II

In formula I, the two electrons are half-way between the nuclei of atoms A and B which naturally exert equal attraction on electrons and hence electronegativities of A and B are equal. In formula II, the two electrons are nearer A which implies that they are attracted more by A than by B, and the electronegativity of A is somewhat greater than that of B.

Based on the methods proposed by Pauling, Mullikan, and others, numerical values of electronegativities have been assigned to almost all elements of the Periodic table.

Table. *Electronegativities of some Elements.*

H						
2·1						
Li	Be	B	C	N	O	F
0·97	1·5	2·0	2·5	3·1	3·5	4·1
Na	Mg	Al	Si	P	S	Cl
1·0	1·2	1·5	1·7	2·1	2·4	2·8
K	Ca	Ga	Ge	As	Sc	Br
0·90	1·0	1·5	2·0	2·2	2·5	2·7
Rb	Sr	In	Sn	Sb	Te	I
0·89	1·0	1·5	1·72	1·82	2·0	2·2
Cs	Ba	Tl	Pb	Bi	Po	At
0·86	0·97	1·1	1·5	1·7	1·8	1·9

The tendency of an atom to acquire electrons depends on two factors : (*i*) its nuclear charge (at. no.) ; and (*ii*) the distance of the valency shell (atomic radius). Atoms possessing more nuclear charge *i.e.*, higher atomic number, and less atomic radii, will have higher electronegativities. This leads to the prediction that electronegativities of the elements will be higher in the upper right of the Periodic table than in the lower left. It may also be noted that, in general, electronegativities of elements increase from left to right in 'periods' and from bottom to top in 'groups' of the Periodic table. Exceptions to this statement occur when the factor of 'atomic size' overweighs that of 'nuclear charge'.

The concept of electronegativity has proved very useful in predicting the nature of chemical bonds as also the properties of compounds.

POLARITY IN COVALENT BONDS

We have seen that a covalent bond between two atoms is formed as a result of overlap of two atomic orbitals. The overlapping orbitals, each having one electron, then merge to form a new molecular orbital containing a pair of electrons. When the atoms joined by a covalent bond are similar, say as in H – H molecule the two hydrogen atoms possessing same electronegativity, exert equal attractive force on the two electrons which are, therefore, symmetrically disposed in the molecular orbital. Thus,



Fig. 5·30. Uniform electron cloud in H_2 molecule.

The covalent bond in hydrogen molecule is, therefore, nonpolar.

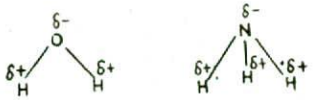
In a molecule having two different atoms joined by a covalent bond, the atom having higher electronegativity will exert a greater attractive pull on the shared pair of electrons. Thus the two electrons will spend more time near this than the other atom, making it slightly negative Thus in hydrogen fluoride molecule, H – F, the electronegativity of H atom and F atom is 2·1 and 4·1 respectively. Hence the fluorine atom will exert greater attraction on the shared electrons in comparison to hydrogen atom. The electron population in the molecular orbital would be more around the F-atom as indicated by the density of the cloud in the following diagram



Fig. 5·31. Electron cloud displacement in HF molecule.

Thus the covalent bond joining H and F atoms develops polarity and is called a **Polar bond**. By and large the covalent bonds between different atoms are polar (ionic). The per cent of polar character in a covalent bond depends upon the relative electronegativity of the atoms joined by the bond ; the greater the difference in electronegativity, the greater the polar character of the bond.

Water and ammonia offer important examples of the polar molecules.



The polar molecules behave like small magnets and have a greater attraction for each other as also for ions, and thus acquire characteristic physical and chemical properties.

RESONANCE

The concept of resonance was forwarded on purely chemical grounds when Kekule structure of benzene was found unsatisfactory to explain its properties in full. Later was discovered

that there are, in fact, numerous substances which like benzene could be assigned two or more structural formulas differing only in the placement of bonds or electrons, and the actual behaviour of the substance was not represented by any of these structures but by a new structure which is a 'blend' or 'hybrid' of the various possible structures.

The concept of hybridization of two or more conventional valence bond structures to yield a new stable hybrid form with less energy is termed **Resonance**.

It may be clearly understood that the old concept that two or more structural formulas oscillate between themselves and each of them contribute to the properties of the substance, is incorrect. Resonance really involves the delocalization of electrons in the molecule so as to give a new stable form which explains adequately its behaviour.

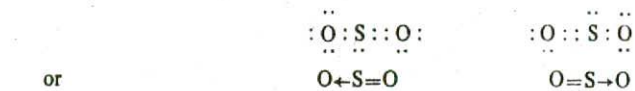
Thus carbon-to-carbon double bond in benzene and several other organic compounds behaves as stronger than a normal ethylene linkage This is explained by the fact that one of the electronpairs between the two carbons is delocalized or displaced to give a stable resonance hybrid form as follows.

$$>C=C< \quad \leftrightarrow \quad >\overset{+}{C}-\overset{-}{C}< \quad \leftrightarrow \quad >\overset{-}{C}-\overset{+}{C}<$$

(Resonance structures)

It may be noted that as one electron pair shifts to one or the other carbon atom, the double bond becomes a single bond with polarity developed on it. Therefore, the resonance hybrid form of the double bond in such a case becomes stable as in benzene and possesses a character intermediate between that of a double and a single bond.

Sulphur dioxide could be represented by the following two possible structures which differ only in the disposition of a pair of electrons.



or $O \leftarrow S = O$ (*A*) $\qquad O = S \rightarrow O$ (*B*)

None of these formulas can properly account for the properties of sulphur dioxide. These postulate two different types of linkages (one double and one coordinate) in the molecule, while it has been established by experiment that both S-to-O linkages in sulphur dioxide are equivalent in all respects. Thus none of the structures (A or B) represents the structure of SO_2 molecule but a new 'hybrid' structure having 'equivalent' S—O bonds, explains its behaviour. This new hybrid is stable and has independent existence.

$$O \leftarrow S = O \quad \leftrightarrow \quad \overset{-}{O}-\overset{+}{S}=O$$

(*A*)

$$O = S \rightarrow O \quad \leftrightarrow \quad O=\overset{+}{S}-\overset{-}{O}$$

(*B*)

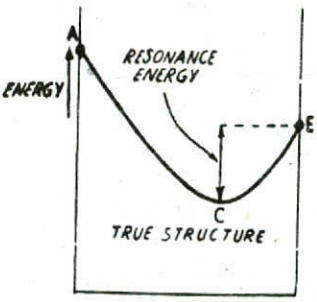


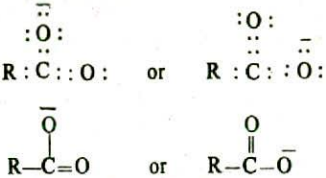
Fig. 5·32

Quantum mechanics reveals that the resonance hybrid possesses less energy than that calculated for any one of the canonical structures. If A and B correspond to the calculated energies of the structures (*a*) and (*b*), and (*c*) stands for the energy of the actual structure, the energy diagram assumes the shape as shown in Fig. 5·32.

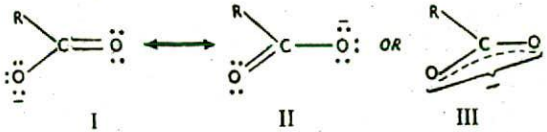
The amount by which the energy of the resonance structure is less than that of the canonical structure with lowest energy, is termed the **Resonance energy** and this difference of energy is a measure of the added stability conferred by resonance.

Another typical example of resonance is offered by the carboxylate ion. It is capable of being represented by the structures.

Thus,



These forms, while they have the same arrangement of atoms, differ only in that the double bond is possessed by alternate oxygen atoms. None of these actually represents the behaviour of carboxylic acids. Each of these forms resonates to give a new stable 'hybrid' form (III) which explains fully the behaviour of this class of compounds.



I II III

The above 'hybrid' form warrants 'equivalence' of the two C–O bonds which is confirmed by the measurement of 'bond lengths'. It has been found that the two carbon-oxygen bonds in carboxylate group are equal in length (1·27Å). On the other hand, the carbon-oxygen bond length for a double bond is 1·24Å and for a single bond 1·43Å. Hence, it stands to reason that the hybrid carboxylate ion is symmetrical and possibly half the negative charge on the oxygen atom of the original structure now resides on each oxygen of the hybrid as indicated in the above diagram.

Similarly, the benzene molecule which is a resonance hybrid of the structures



has carbon-carbon bond lengths midway between those of C–C and C=C bonds. The C–C distance in ethane molecule, has been determined to be 1·54Å, while C=C bond length in ethylene is 1·33Å. For all carbon-carbon bonds in benzene molecule the value is 1·39Å, indicating clearly their hybrid nature.

The concept of resonance has proved very useful in explaining the unexpected stability and chemical behaviour of many organic molecules. We have seen how the stability of benzene molecule could be explained by resonance, while ordinarily it could have been expected to behave like ethylene, since it contains three double bonds. Also, while aldehydes and ketones can be reduced easily to yield alcohols, the carboxyl group in fatty acids is stable and difficult to reduce.

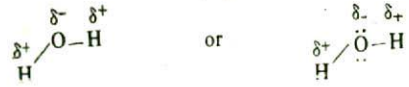
Resonance and tautomerism must be carefully distinguished from each other.

(*a*) Resonance involves only a shift of electrons while tautomerism requires the transference of a hydrogen atom or a proton.

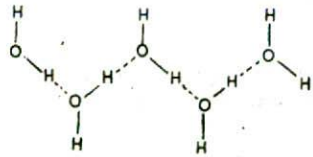
(*b*) Tautomerism implies the simultaneous existence of two molecular forms in equilibrium. In case of resonance, only one molecular form exists which is an intermediate arrangement between the two possible forms.

Hydrogen Bonding

When a hydrogen atom is linked with a very strongly electronegative atom (as with O in water), it forms positive end of the dipole.

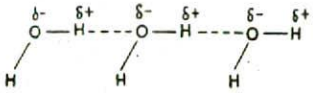


Here the hydrogen atom has an extraordinary urge to become linked with atoms of other molecules possessing a highly electronegative atom (O in water). There is a strong evidence in support of the fact that hydrogen, though univalent, behaves as a bivalent element under certain conditions. It is noticed that molecules which contain O–H or N–H bonds (*e.g.*, in water, alcohols, carboxylic acids, phenols, amines and amides) have a great tendency to 'associate' or link up to form larger molecules. Investigation of the crystal structure of ice reveals that the molecules in it are linked in the following fashion.



As indicated above, the hydrogen atom seems to form a linkage between two oxygen atoms *i.e.*, hydrogen bridges them. This mode of linking is called **Hydrogen bonding** or 'hydrogen bridging'. As it is impossible for the H atom to participate in a second covalent bond, the additional bond is shown with the help of dotted line.

In general, hydrogen bonds may be represented as —A—H ··· A′ where A and A′ may be atoms possessing very high electronegativity (O, N, F, Cl and rarely C also). The A—H bond will be polar with H atom as the positive end. Similarly —A′ being highly electronegative, will bear a negative charge. So, the hydrogen bonding between H and A′ is more or less due to electrostatic attractive force. Thus in water molecule, association by hydrogen bonding may be represented as

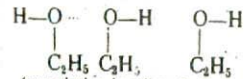


It is the attractive force between every positive H atom and negative O atom which holds them together. Greater the electronegativity of A and A′ atoms (which may be the same as O in water), stronger will be the H bond (H O). Hydrogen bond energies lie in the range 2 to 8 Kcal/mole, as compared with O–H bond energy 110 Kcal/mole. The H bonds are rather weak but are wide spread and have a very significant effect on the physical properties (boiling point, solubility, ionisation) of organic compounds.

(*a*) **Boiling Points.** It is understandable that substances having nearly the same molecular weights, have the same boiling points. The boiling points of ethers and alkanes of comparable molecular weights are not far apart, but the boiling points of alcohols having almost equal molecular weights are considerably higher.

$CH_3-CH_2-CH_3$	CH_3-O-CH_3	CH_3-CH_2-OH
bp −45°C	bp −25°C	bp 78°C
(m wt = 44)	(m wt = 46)	(m wt = 46)

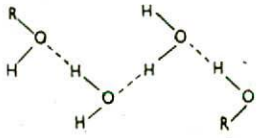
This could be explained in light of hydrogen bonding. Alcohol molecules are held together by hydrogen bonds and, therefore, more energy is required to separate the molecules for vaporisation.



(association in ethyl alcohol)

Such an association is entirely absent in propane and ethane and hence their low boiling oints.

(*b*) **Water Solubility.** Organic substances owe their solubility in water to a hydrogen bonding effect between the solute and solvent molecules which are polar in nature. This may be illustrated in the case of alcohols as follows.



As the molecular weight (or the molecular size) of the alcohol increases, the degree of hydrogen bonding with water decreases and there will be a corresponding decrease in the solubility of alcohol in water. However, the high solubility of sugars in water is attributed to a large number of —OH groups, making more hydrogen bonding possible.

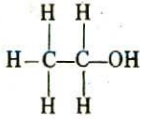
The organic compounds containing (*i*) C and H ; (*ii*) C, H, S ; (*iii*) C, H, X, do not dissolve in water appreciably since they are not capable of forming hydrogen bridges with water molecules. Alcohols and acids have a marked tendency to form hydrogen bridges with water and hence are very soluble.

STRUCTURAL FORMULA

We have seen that a molecular formula states the number and kind of atoms in the molecule. Thus ethyl alcohol has molecular formula C_2H_6O which implies that a molecule of this compound is made up of two carbon atoms, six hydrogen atoms and one oxygen atom. The molecular formula, however, remains silent as to how these atoms of various elements are joined in a molecule.

A formula showing a completed picture as to how the various atoms are joined to each other in the molecule is known as a **Structural formula.**

For example, ethyl alcohol having molecular formula C_2H_6O has the structural formula



It may be noted that structural formula of an organic compound does not necessarily specify the exact shape of the molecule. Firstly because the four valency bonds of carbon are distributed in space in tetrahedral perspective and thus a representation written in the plane of the paper does not convey the exact picture of the molecular structure. Secondly, there are organic compounds known which have the same molecular structure but exist in two or more different space arrangements. Also, the carbon-to-carbon single bonds are capable of rotation and thereby a single structural formula may actually represent a number of 'conformations' with different arrangements of the atoms in space.

A model of a molecule is often useful to facilitate our thinking about the structure of the molecule. One simple kind of model to represent the structure of a molecule consists of coloured balls and sticks or pegs of metal wire. This is called a **ball-and-stick model** or **ball-and-peg model.** The model of methane shown in Fig. 5·32 gives a three-dimensional structure of its molecule. Such models show the exact angles between the bonds and are particularly helpful in telling us as to how the various atoms of the molecule are arranged in space.

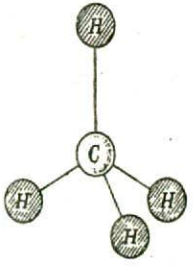


Fig. 5·32. Ball-and-Stick model of methane.

It is true that the beginning student finds it useful to construct models of organic molecules. In this way he can visualise their shape better. But it is difficult to draw a three-dimensional sketch each time. Since we must write on flat surface for convenience, we should always keep in mind that the actual molecule is really three-dimensional and that the formula we have written is simply a projection of the former. This is illustrated by the models of a molecule of methylene chloride (CH_2Cl_2). We should not forget

despite the appearance of the projection formulae that carbon bond angles are not 90° and the molecules are not flat. In other words, the formulae written in one plane do not represent the structure of a molecule faithfully in all aspects.

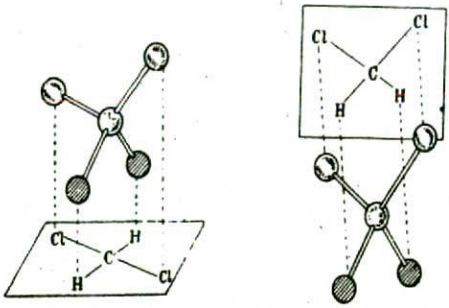


Fig. 5·33. Projections of CH_2Cl_2 molecular models give the flat formulae on the paper.

We have discussed above the ball-and-stick models of organic substances. These models consist of coloured wooden or plastic balls of the same size connected by sticks or pegs. While they give an adequate method of indicating which atoms are bonded to which atoms and also give an idea of the bond angles, the size of the individual atoms is ignored. This defect has been overcome in the **Stuart models**. In these models, the balls representing the various atoms are made of a size proportional to the effective atomic radii. The model is undoubtedly more compact but there is a certain loss of visual clarity with the bond angles.

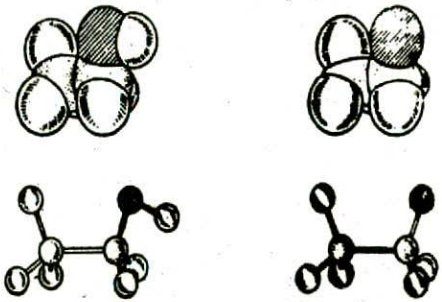


Fig. 5·34. Stuart and ball-and-stick models of ethyl alcohol and chloroethane. In space-filling or Stuart models, the spheres representing atoms in the molecule, are designated so as to indicate sharing of electron clouds.

There are yet another type of models called **Dreiding models** which are very useful in studying conveniently the stereochemistry or the spatial arrangement of carbon atoms of relatively complex organic molecules. These precision models have the standard bond angles and the scaled bond distances. The bonds are represented by stainless steel rods which fit perfectly into stainless steel sleeves. The advantage of these models lies in the fact that the rotation about the bonds is smooth and there is sufficient flexibility to accommodate some bond strain. The Dreiding models of the boat and chair conformations of cyclohexane are given in Fig 5·35.

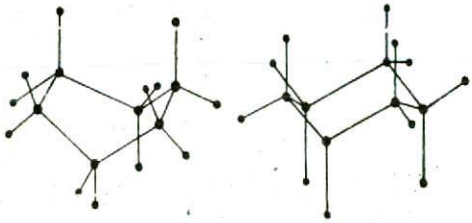


Fig. 5·35. Dreiding models of the 'boat' and 'chair' cyclohexanes.

How Structural Formulae are written

We have seen that the real molecules are three-dimensional as illustrated by models. Usually the chemists write formulae in the plane of the paper and indicate the angles between the valency bonds of carbon atoms as right angles. This is only for convenience. In tetrahedral perspective the carbon bonds contain an angle of 109° 28′ and, therefore, the bonds joining carbon atoms in long open-chain compounds lie in a zig-zag fashion.

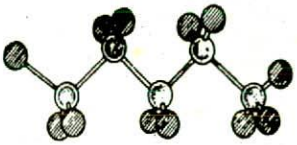


Fig. 5·36. Valency bonds of carbon in n-pentane lie in a zig-zag fashion.

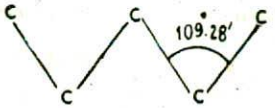
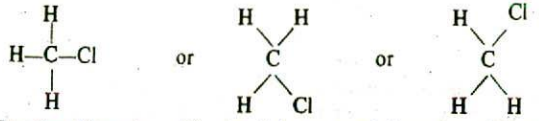


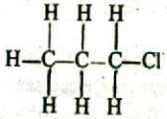
Fig. 5·37. Zig-zag carbon chain in n-pentane.

In fact, the structural formulae written on paper simply indicate the manner in which the various atoms are joined to each other and do not give any idea of their disposition in space. In other words, they only depict the structural representation of a molecule regardless of the angles between various bonds. Thus while writing structural formulae the valency bonds may be put in any direction for convenience. Methyl chloride may be written as



Condensed Structural formulae. The detailed structural formulae of the type given above use a great deal of space and are often not necessary. Therefore, the organic chemist has to often write what we call the 'condensed structural formulae'. These are written more rapidly and in less space.

In a condensed formula, all atoms linked to a given carbon atom are mentioned after 'C' and in the same line but their bonds are not shown. Even the practice of putting dots between carbon atoms in a structural formula has now been given up. Thus,



Structural formula of n-propyl chloride

or $CH_3—CH_2—CH_2—Cl$

or $CH_3CH_2CH_2Cl$

Condensed Structural formula

It may be noted that while writing the condensed formulae the atoms other than hydrogen are written, customarily, after the hydrogen atoms.

Skeletal formulae. Sometimes for brevity or to make the differences in the carbon chains more apparent, only the carbon skeleton of the structural formula is written. This is called the 'skeletal formula' of a compound. The skeletal formulae of the two butanes may be written as



It is understood that all the remaining valencies of carbon atoms are filled by hydrogen atoms.

SPECTROSCOPY OF ORGANIC COMPOUNDS

The structural formulae of organic compounds were for long derived from a study of the chemical reactions of these compounds and then confirmed by their synthesis by proven steps from known starting materials. The last two decades have witnessed a virtual revolution in this field and now sufficient information regarding the chemical structure of an unknown compound can be obtained directly by purely physical methods. One such modern method is the exami-

nation of 'spectra' of organic compounds or **Spectroscopy**. This is based on the fact that when light is made to pass through a sample of a given organic substance, certain portions of it are absorbed while others are transmitted. The wavelength or frequency of the portion absorbed depends on the chemical structure of the substance. Thus a study of its absorption spectrum can provide us valuable clues to its structure.

How is Absorption Spectrum caused by Radiant energy? We know that light consists of electromagnetic waves which travel in a straight line (velocity = 3×10^{10} cm in vacuum) away from the source, the direction of vibrations being perpendicular to the direction of propagation. While ordinary light is made of components having wavelength range $7{\cdot}5 \times 10^{-5}$ cm to 4×10^{-5} cm, a monochromatic source gives a single wavelength component.

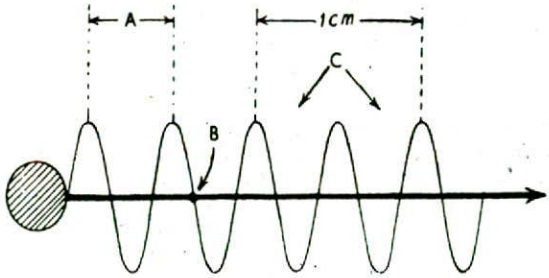


Fig. 5·38

A = Wavelength, λ (cm).
B = Number of waves passing per second = frequency, ν (sec^{-1})
C = Number of waves per cm = Wave Number, $1/\lambda$ (cm^{-1}).

Quantum theory tells us that in addition to its wave nature, light also consists of discrete quanta ('packets' of energy) and that a particular wavelength is associated with a quantum of energy (ergs). This is given by the following simple relation

$$E = h\nu = \frac{hc}{\lambda}$$

where E = energy of light; λ its wavelength or ν its frequency; c = velocity of light; and h, the Planck's constant. From the above relation it is evident that shorter the wavelength, greater the energy.

For the study of absorption spectra we generally consider three kinds of light:

(*i*) *Visible*, those wavelengths (4 to $7{\cdot}5 \times 10^{-5}$ cm) which human eye can see unaided,

(*ii*) *Ultraviolet*, having shorter wavelength (1 to 4×10^{-5} cm) than the visible light; and

(*iii*) *Infrared*, having longer wavelength (3×10^{-2} to 7×10^{-5}) than the visible light

Radiation	*Wavelength (cm)*	*Wave Number (cm^{-1})*	*Energy (ergs)*
1. Infrared	3×10^{-2} to 7×10^{-5}	33 to $1{\cdot}4 \times 10^{4}$	66 to $2{\cdot}8 \times 10^{-13}$
2. Visible	$7{\cdot}5 \times 10^{-5}$ to 4×10^{-5}	$1{\cdot}0 \times 10^{4}$ to $2{\cdot}5 \times 10^{4}$	$2{\cdot}7 \times 10^{-13}$ to 5×10^{-13}
3. Ultraviolet	4×10^{-5} to 10^{-5}	$2{\cdot}5 \times 10^{4}$ to 10^{5}	5×10^{-13} to $2{\cdot}8 \times 10^{-11}$

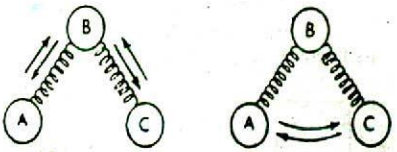
In addition to energy of electrons, a molecule has kinetic energy due to the rotational and vibrational motions of the atoms in each chemical bond. For example, a non-linear molecule made of three atoms A, B and C with bonds represented by springs could be visualised to be executing vibrations as shown in Fig. 5·3

The total energy E of the molecule (leaving aside the nuclear energy) may be taken as the sum of the three energy terms :

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$$

When light radiations are made to pass through an organic substance (or its solution), not only the electrons of the component atoms are excited but the vibrational and rotational energies are also increased.

According to Quantum theory, both vibrations and rotations are quantised and the kinetic energy due to these is also increased by certain definite levels. Hence any wavelengths (or frequencies) of light that a particular molecule will absorb, will be determined by the changes in the electronic, vibrational or rotational energy levels permissible for its atoms. The wavelengths or radiations absorbed are measured with the help of a *spectrometer* and are said to constitute a *spectrum*. The spectrum of a compound is generally presented in the form of a continuous graph indicating the absorption of light at all wavelengths (or frequencies) over a particular range. The shape of such a plot is highly characteristic of the compound's structure and provides an excellent diagnostic technique to ascertain the molecular structure of unknown substances.



Stretching vibrations Bending vibrations

Fig. 5·39. Vibratory motion in a molecule.

Ultraviolet and Visible absorption spectra. It is one of the earliest physical methods of elucidating the structure of organic molecules. Absorption of visible and ultraviolet light produces changes in the energy of electrons, in atoms of the molecule from a stable to an unstable orbital. The significant feature of these spectra are the positions of maximum absorption, λ_{max} and the intensity of absorption at these maxima.

In general, carbon compounds having an alternate single and multiple bonds are apt to absorption in this region of wavelength. A system having only a few *conjugated multiple bonds absorbs the radiation in this region less strongly than those possessing an extended series of conjugated multiple bonds. For example, butadiene (having two conjugated double bonds) gives λ_{max} as $2{\cdot}17 \times 10^{-6}$ cm, while β carotene (having 11 conjugated double bonds) absorbs strongly at $4{\cdot}5 \times 10^{-5}$ cm. The following table bears out the statement that value of λ_{max} increases with increased conjugation.

Compound	$\lambda_{max} \times 10^{-6}$ cm
Ethylene ($H_2C=CH_2$)	1·65
1,3-Butadiene ($H_2C=CH\ \ CH=CH_2$)	2·17
1,3,5-Hexatriene ($H_2C-CH\ \ CH=CH-CH=CH_2$)	2·58
Acetone ($CH_3—CO—CH_3$)	1·88 and 2·79

Since structural environments also influence the value of λ_{max} in ultraviolet and visible spectra, the technique in general reveals fewer structural features than infrared spectra. However in many cases ultraviolet spectra are useful to confirm structural features derived by other means.

Infrared spectra. Unlike the situation obtaining in visible and ultraviolet absorption spectra, all organic molecules absorb light in the infrared region. In this region, the absorbed radiation brings about predominant changes in vibrational energy which depends upon (or is a function of) the masses of the atoms, as also the strengths of bonds between atoms and their spatial arrangements in the molecule. Thus it stands to reason that no two compounds except optical enantiomers, can have similar Infrared (IR) absorption spectra. Just as fingerprints are taken as a characteristic of identity of every individual, the bands in IR spectra are also chara-

*A **conjugated system** of double bonds may be as (C−C=C−C C−, the one which contains a double bond and single bond alternately on the carbon chain.

teristic of a compound. In other words, the bands in the spectrum of a molecule can be regarded as its 'molecular fingerprints' leading to its recognition.

The IR spectrum of an organic compound helps in—

(*a*) *proving its identity by comparison* ; *and*

(*b*) *showing the presence of certain groups or atoms in its molecule.*

In order to clinch the proof of identity of an organic molecule, its IR spectrum is compared with IR spectrum of a previously reported compound of known structure. If the two are found resembling, we can conclude without least hesitation that the two compounds are identical.

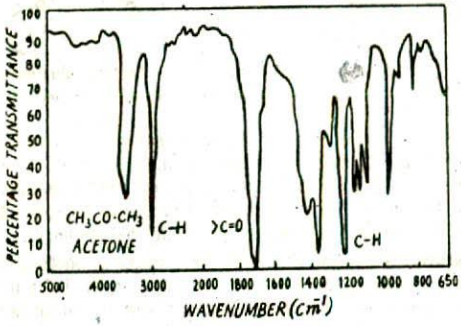


Fig. 5-40. Infrared spectrum of acetone.

A particular functional group gives rise to characteristic absorption bands in the infrared spectrum. In other words, a particular group strongly absorbs light of certain wavelength no matter to which compound it belongs to. For example, a carbonyl group ($>C=O$) strongly absorbs the radiation in the region 1720—1740 cm^{-1} The maximum absorption bands in the accompanying plot of IR spectrum of acetone show absorptions at 1710 cm^{-1} and 2863 cm^{-1}, indicating the presence of a carbonyl group and carbon hydrogen bonds of the methyl group.

Sufficient information can be derived from IR spectra of molecules and their determination is now a routine operation in establishing the structure of an unknown compound. This ingenious technique of establishing the identity or analysis of organic compounds has the distinctive advantage that it can be carried out with a very small amount of the sample (1—2 mg) which too can be recovered unchanged after the required measurements have been made.

Table : *Some Characteristic Infrared Absorption Frequencies*

Bond	*Type of Compound*	*Frequency* cm^{-1}
$-\overset{|}{\underset{|}{C}}-H$	Alkanes	2850—2960
$=\overset{|}{C}-H$	Alkenes	3010—3100
$\equiv C-H$	Alkynes	3300
$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-$	Alkanes	600—1500
$>C=C<$	Alkenes	1620—1680
$-C\equiv C-$	Alkynes	2100—2260
$>C=O$	Aldehydes	1720—1740
$>C=O$	Ketones	1705—1725
$>C=O$	Acids	1700—1750
$-OH$	Alcohols	3590—3650
$-NH_2$	Amines	3300—3500

Nuclear Magnetic Resonance (NMR) Spectroseopy. The nucleus of an atom can spin about its own axis, since the nucleus is charged, its rotation generates an electric current which in turn produces a magnetic field. Thus certain nuclei behave like tiny bar magnets and because of this they try to align themselves when placed in any imposed magnetic field. Such a nucleus can be lined up with the magnetic field (low energy position *a*) or opposed to it (high energy position *b*). The nucleus in position (*a*) absorbs energy to go in position (*b*). This energy is quantised and associated with radiation of a specific frequency for a given magnetic field.

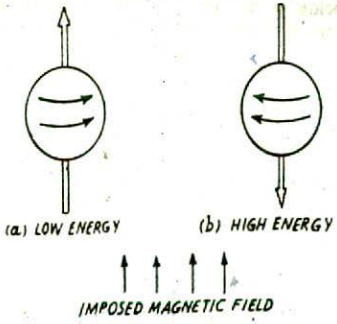


Fig. 5·41. The nucleus aligned in a uniform imposed magnetic field (*a*) with the field ; and (*b*) opposed to the field.

In NMR Spectroscopy, the strength of the magnetic field is varied, while electromagnetic radiation of a fixed frequency is passed through the sample of a compound under examination (Fig. 5·42).

A graph of the absorption radiation plotted against the magnetic field strength gives an absorption spectrum just as for infrared and ultraviolet radiation.

Here we will concern overselves only with the hydrogen atom nucleus (a proton) because it has yielded the greatest amount of chemical information and is the simplest system to deal

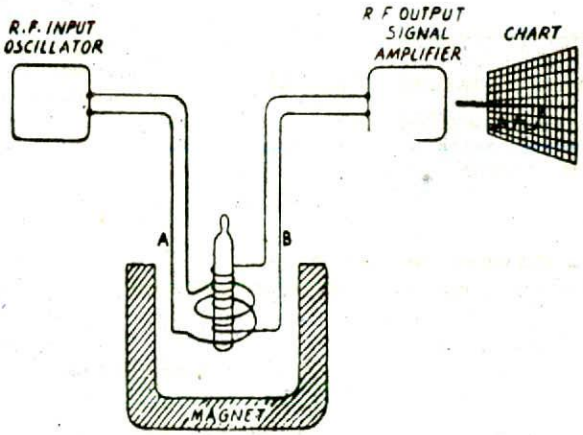


Fig. 5·42. Nuclear Magnetic Resonance Spectroscope.

with. In a magnetic field a spinning proton along the field, when subjected to long wavelength radiation absorbs energy and changes its spin to the opposite orientation. All the protons in an organic compound do not absorb radiation at the same value of field strength.

This is so because different protons are shielded to different extents by the surrounded electrons. The magnitude of this shielding depends upon the environments of the proton under consideration. Thus H-atoms present in different groups would absorb a specific radiation at different values of field strength. Three effects are then observed in an NMR spectrum.

(1) *Each group containing a different type of hydrogen atom records a distinct peak in the various energy regions of the spectrum.*

(2) *The area under the absorption peak is proportional to the number of H-atoms in that particular situation or group in the molecule.*

Thus the spectrum of ethyl alcohol, CH_3CH_2OH, (Fig. 5·43) has three peaks having area below in the ratio 3 : 2 : 1. These peaks correspond to the group —OH (one H atom), $>CH_2$ (two H atoms); and $—CH_3$ (three H atoms).

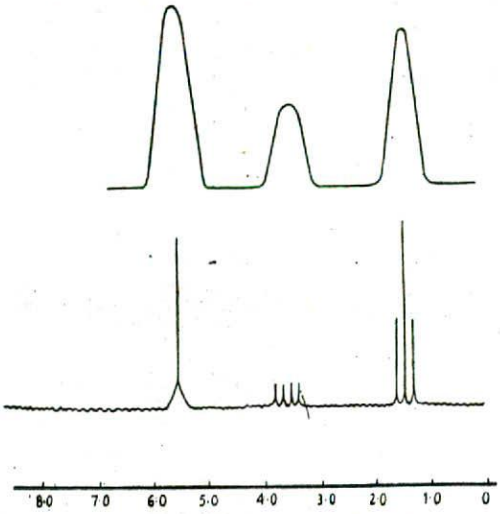


Fig. 5·43. NMR Spectrum of Ethyl alcohol : *A High Resolution.*

(3) *Under more carefully controlled conditions (high resolution), due to the presence of H atoms on adjacent carbon atoms, the splitting of a single peak into several peaks appears. The number of components into which a peak is split up, is equal to the number of H atoms on the adjacent carbon atoms plus one.*

Thus in the high-resolution spectrum of CH_3CH_2OH, methylene (CH_2) peak is resolved into four components by the methyl (CH_3) hydrogen (3 + 1). The methyl peak has three components caused by two H atoms of CH_2 group (2 + 1).

In the past decade, NMR spectroscopy has developed as a powerful tool in the elucidation of structure of organic compounds. It not only reveals the number and type of hydrogen atoms in a molecule but it also tells us the environments in which they are situated. Thus the technique of NMR spectroscopy has solved some of the most difficult stereochemical problems. UV and IR, on the other hand, are less informative because they reveal only the nature of the functional groups present in a compound.

QUESTIONS

1. Explain giving suitable examples, sp and sp^2 hybridisations. (*Madras BSc, 1993*)
2. How would you account for the fact that while CH_4 and CCl_4 have no dipole moment, $CHCl_3$ has a dipole moment ? (*Delhi BSc, 1994*)
3. Write a note on : Resonance. (*Bangalore BSc, 1993*)
4. What is hydrogen bonding ? How does it modify the properties of organic compounds ? (*Kerala BSc II, 1993 ; Goa BSc, 1994*)
5. What are the distinguishing features of sp^2 and sp hybrid orbitals ? Explain with suitable examples. (*Madurai BSc, 1994*)
6. Write notes on : (*a*) sp^3 Hybridisation : (*b*) sp Hybridisation ; and (*c*) Hydrogen bonding . (*Andhra BSc, 1993*)
7. What type of hybridisations are found in alkanes, alkenes, and alkynes ? Explain the involved differences including stereochemical features. (*North Bengal Hons, 1994*)
8. Discuss the molecular orbital structure of acetylene. (*Kerala BSc, 1994*)
9. Write a note on : Resonance. (*Agra BSc, 1993 ; Saugar BSc, 1993 ; Delhi BSc Hons, 1994 ; Kakatiya BSc III, 1994 ; Udaipur BSc, 1994*)
10. What is resonance energy ? (*Aligarh BSc Hons, 1993*)
11. What is hydrogen bonding ? Illustrate with an example the effect of hydrogen bonding on a physical property of organic compounds. (*Osmania BSc Hons, 1994*)