

**TEXT-BOOK OF
ORGANIC CHEMISTRY**
(FOR B.Sc. STUDENTS)

by

B.S. BAHL, M.Sc.,

*Principal, D.A.V. College, Jullundur City
Fellow and Syndic; Member, Board of Studies in Chemistry,
G.N. University, Amritsar*

AND

**ARUN BAHL, M.S. (Boston), Ph.D. (Edinburgh);
A.R. C. (London).**

*Department of Chemical Engineering and Technology,
Panjab University, Chandigarh.*

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ELEVENTH REVISED EDITION

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PREFACE TO ELEVENTH EDITION

Some modern concepts of Organic Chemistry such as the Orbital concept of bonding and the mechanistic principles of Organic reactions were introduced in the previous edition of the book. The authors are happy that these new innovations were appreciated and the 10th edition of the text-book of Organic Chemistry had to be reprinted in 1969 and again in 1970. That was the first phase of modernising the subject matter which has been followed up in the eleventh edition of the book. The new edition has been considerably enlarged and improved in all respects. The chief features of the new edition are :

(1) A separate chapter covering the principles of mechanism of organic reactions has been given and these principles have been applied to interpret the mechanism of almost all important reactions in the remaining portions of the text.

(2) A new chapter on 'Classification and Nomenclature' giving details of the latest IUPAC system of naming all classes of organic compounds has been included. The naming of higher organic compounds on the basis of 'seniority of functional groups' is the latest innovation that has also been described.

(3) Some modern topics such as sublimation under vacuum, chromatography, oxygen flask method for estimation of halogens, direct estimation of oxygen have been given.

(4) Spectroscopy of organic compounds especially the ultra-violet and Infrared spectra, their explanation and application to some important substances is a new feature of this edition.

(5) The description of Optical Isomerism has been given modern touches and *R* and *S* conventions have been discussed in detail.

(6) Under the chapter on alkanes the new topic 'Conformations of ethane and propane' has been included.

(7) The chapter on 'Carbohydrates' has been re-written and enlarged so as to give the latest conventions of writing structural formulae of aldoses.

(8) Numerous new illustrations of industrial processes, mechanism of reactions, molecular models, the geometry of certain organic molecules form a novel feature of this edition.

(9) The latest numerical problems and questions asked in the various universities of India have been included at the end of each chapter.

The authors hope that the eleventh revised edition of the book which has been rewritten and modernised in many respects will be well received by our colleagues and the student community. Any suggestions for further improvement of the book will be acknowledged with thanks.

Jullundur
July, 1970

B. S. BAHL
ARUN BAHL

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1

Introduction



Friedrich Wohler
(1800—1822)

German chemist. Well-known for the historical synthesis of urea, which gave a death blow to the Vital Force theory.

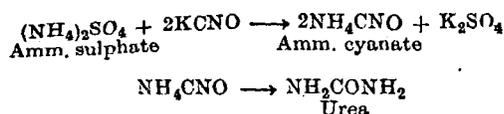
WHAT IS ORGANIC CHEMISTRY ?

Organic Chemistry owes its name and origin to the study of those substances which had been produced in living organisms, whether vegetable or animal. Such substances were classed as **Organic** in distinction to those which were derived from the mineral world and were known as **Inorganic**. Thus common salt, marble, soda and carbon dioxide were inorganic substances whereas acetic acid (*from vinegar*), alcohol (*from wine*), tartaric acid (*from grapes*), and sugar (*from sugarcane*) were organic.

The Vital Force Theory. It was long believed that organic compounds were produced in plants and animals under the influence of 'Vital force', *i.e.*, the same force which was responsible for the growth of the plant or the animal. Thus it was considered impossible to synthesise organic substances in the laboratory.

However, in 1828, Wohler accidentally discovered that urea, a typical organic compound, could be obtained by heating together ammonium sulphate and potassium cyanate, both of which are

inorganic compounds.



This simple reaction did much to dispel the absurd idea of vital force in the formation of organic compounds. A few years later Kolbe was able to synthesise acetic acid starting from the elements carbon, hydrogen and oxygen, thus showing clearly that no special life process was needed for the preparation of organic compounds. Thereafter numerous organic compounds were synthesised in the laboratory and by 1850 *The Theory of Vital Force* had been gradually overthrown.

Modern Definition of Organic Chemistry. With the fall of the *Vital force theory*, the term 'organic' lost its original significance. It was, however, established that all the so-called organic compounds contained carbon as an essential constituent. Therefore, the name 'organic' has been retained to describe all carbon compounds irrespective of their origin or the method of preparation. Thus in modern practice the term **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. However, a few common compounds of carbon like carbon monoxide, carbon dioxide and carbonates are still classed as inorganic substances for obvious reasons.

Thus the modern definition of Organic Chemistry could be given as the study of compounds of carbon other than the oxides, carbonates and bicarbonates, and hydrogen cyanide and its salts.

Since all the organic compounds could be considered as derived from hydrocarbons (containing C and H only), a more precise definition of Organic Chemistry could be given as

"A study of hydrocarbons and their derivatives."

REASONS FOR SEPARATE STUDY

The organic compounds obey the same fundamental laws of Chemistry that hold for Inorganic compounds. However, they are studied as a separate branch of Chemistry as a matter of convenience mainly for two reasons :

(1) The total number of organic compounds known is about 20,00,000, which exceeds several times the total number of inorganic compounds which is hardly 50,000. If the study of twenty lakhs of carbon compounds be included with that of carbon in Inorganic Chemistry, it would throw the subject out of balance.

(2) There are marked differences between the composition, structure and behaviour of the organic and inorganic compounds which make their separate study more fruitful.

The chief differences between organic and inorganic compounds are stated below :—

ORGANIC	INORGANIC
<p>(1) Organic compounds are built mostly from 10 elements viz., C, H, O, N, S, P, Cl, Br, F and I.</p>	<p>(1) Inorganic substances are formed from any of 101 elements known.</p>
<p>(2) Carbon has the wonderful capacity to unite with itself and also with other elements <i>with the help of covalent bonds</i>. Carbon atoms joined each to each in straight chains or rings give rise to the formation of a large number of simple as well as complex compounds with huge molecules.</p>	<p>(2) The atoms in the molecules of inorganic substances are joined by electrovalent bonds, forming relatively simple and smaller number of compounds.</p>
<p>(3) Organic compounds with similar 'groups of atoms' display similar chemical behaviour. Thus they form many such classes of compounds e.g., alcohols, ethers, ketones, acids, amines, etc.</p>	<p>(3) Most of the inorganic compounds which have been studied are either <i>acids, bases, or salts</i>.</p>
<p>(4) They frequently possess pronounced colour and odour which are characteristic of certain classes of compounds.</p>	<p>(4) They are, in general, colourless and odourless. Certain metallic salts possess distinct colours.</p>
<p>(5) They are, in general, insoluble in water but soluble in organic solvents such as ether, alcohol, benzene etc.</p>	<p>(5) They are generally soluble in water but insoluble in organic solvents.</p>
<p>(6) They are volatile compounds having relatively lower melting points and boiling points.</p>	<p>(6) They are generally non-volatile and possess high melting points and boiling points.</p>
<p>(7) Burn readily. Solutions and melts do not conduct electric current.</p>	<p>(7) Hard to burn. Conduct electric current in solutions and melt.</p>
<p>(8) Their reactions being 'molecular' in nature are slow and usually complex.</p>	<p>(8) Their reactions for the most part being ionic in nature are rapid and simple.</p>
<p>(9) Covalent bonds being rigid and directional, give rise to 'Chain isomerism' and different types of 'Space isomerism' in organic compounds.</p>	<p>(9) Electrovalent bonds being non-rigid and non-directional, cannot give rise to isomerism in inorganic substances.</p>
<p>(10) Law of multiple proportions in its rigid form, is not applicable to many organic compounds. In such compounds the weights of an element combining with a fixed weight of the other, bear only an integral ratio and not a simple one.</p>	<p>(10) Law of multiple proportions is universally applicable to inorganic compounds.</p>

SCOPE OF ORGANIC CHEMISTRY

The scope of organic chemistry is vast indeed. There is no art, science or industry in which this branch of chemistry is not applied. It will be of interest to outline here very briefly some of the applications of organic chemistry in everyday life and industry.

(1) **Applications in Everyday life.** No other branch of science has so many contacts with human life as organic chemistry has. In our day-to-day life we find ourselves in a strange panorama of things that are in one way or the other connected with this branch of chemistry. From the basic requirements of life like food, fuel, clothing and health aids, to the obviously luxurious things like perfumes and cosmetics—and in-between these two extremes come

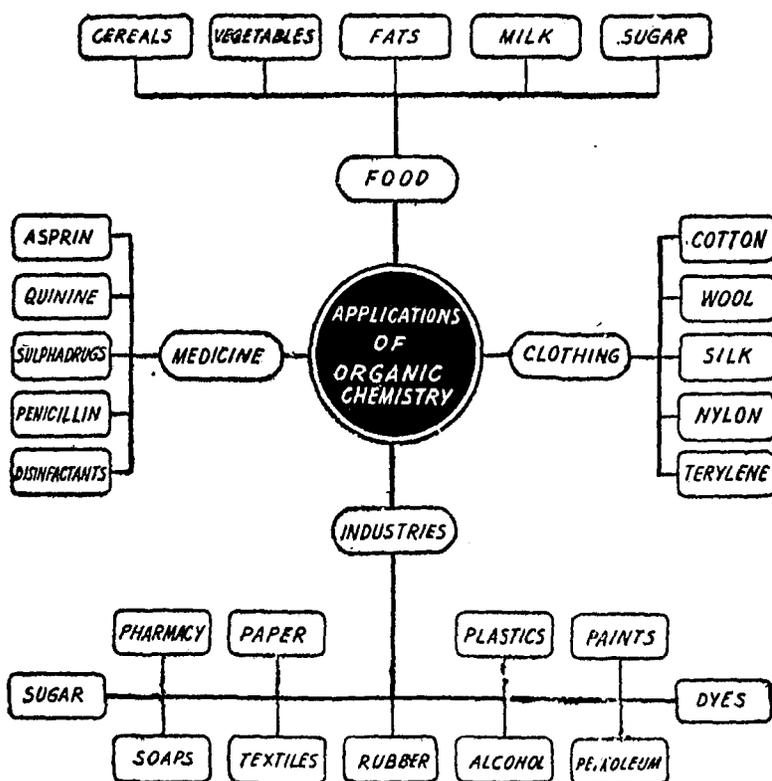


Fig. 1-1.

the following with varying degrees of importance : leather and wooden products ; pencil, paper and writing inks ; fuels like coal, oil and wood ; dyes of all kinds whether natural or synthetic ; rubber, plastics ; oils, fats, paints and varnishes ; photographic films and developers ; medicines, anaesthetics and antiseptics—all things seem to have organic origin and touch. It is no wonder, therefore, organic chemistry is a part and parcel of our daily life. In fact, we are ourselves nothing but complex structures built of thousand

organic compounds which are derived from the plant and animal foods.

(2) **Applications in Industry.** A knowledge of organic chemistry is necessary in many important chemical industries, e.g., preparation of foods, pharmacy, manufacture of soap and other cosmetics, textile industry, manufacture of dyes and explosives, paper industry, fertilizers, leather industry, sugar industry, fermentation industries, wood-distillation industry, synthetic rubber and transparent wrappings for foods and other commodities, petroleum industry, etc.

(3) **Study of Life processes.** The most important application of organic chemistry is the study of the nature of the material and of the processes of living organisms. The investigation of the tissues, the secretions and other constituents or products of plants and animals is based upon organic chemistry. The understanding of the process of digestion and assimilation of food involves the fundamental principles of organic chemistry. The vitamins and the hormones are organic compounds that are produced in our body and play an important role in its development. The injection of a hormone can turn a male into female and *vice versa*. All such miracles of nature concerned with the life process can be interpreted only by the aid of organic chemistry.

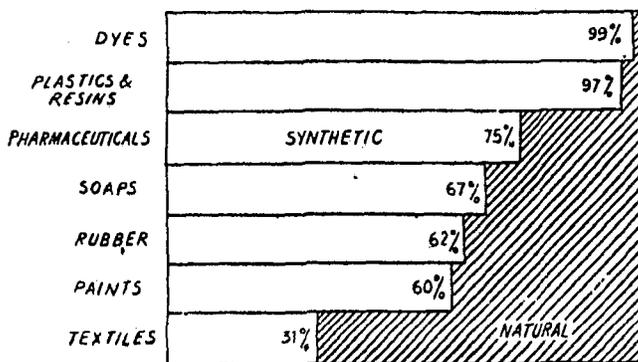


Fig. 2-2. Proportions of synthetic and natural products capturing industry.

There are other fields of organic chemistry at present less developed. Further researches may bring these in the front rank. This naturally means a more thorough study of what we already know. The subject itself is worthy of study from the purely scientific and cultural standpoint. The intellectual beauties of the closely inter-woven relations of organic chemistry will be revealed to the student only when he studies the subject logically, keeping before him the molecular structure of the compounds involved.

SOURCES OF ORGANIC COMPOUNDS

Organic compounds are obtained from natural sources and are prepared by synthesis in the laboratory. The natural sources

of these substances may be traced to either the plant or animal kingdom. Thus :

Sources of
Organic Compounds

```

graph TD
    A[Sources of Organic Compounds] --> B[Natural]
    A --> C[Laboratory Synthesis]
    B --> D[Plant kingdom]
    B --> E[Animal kingdom]
  
```

SOURCE	COMPOUNDS OBTAINED
(1) Plants (direct)	Sugars, starches, cellulose, citric acid, oxalic acid, tartaric acid, indigo, oils, vitamins, etc.
(2) Animals	Fats, proteins, urea, uric acid, vitamins, hormones, etc.
(3) Wood distillation	Acetic acid, methanol 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, etc.
(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 carbon compounds now derived from petroleum and coal is far greater than from any other source. While the fermentation processes are still in use for the preparation of a large number of organic compounds, wood distillation is almost obsolete and replaced by synthetic methods.

How long the World's Coal and Petroleum Reserves would last ?

Coal and petroleum are undoubtedly the biggest natural sources of organic compounds. For the past 100 years coal dominated the scene but during the last 20 to 30 years, petroleum has assumed comparable importance. To meet the great demand of organic compounds, the world's production of coal increased enormously during the last decade or so. In 1966 the total production was 2,800,000,000 long tons. Although coal is far more **SOU** and widely distributed in nature, petroleum resources

also

equally vast. The total crude oil production of the world in the year 1966 recorded 1,601,000,000 long tons

A chemist is naturally interested to know the extent of world's coal and petroleum reserves as also the probable time of their consumption. Ultimately it is he who has to face the problem of replenishing their consumption by other synthetic means. The world's total coal reserves are estimated to be 5,562,656 million long tons, while oil reserves as estimated on Dec. 31, 1966 amount to 2,886,915 million long tons.

There are many speculations regarding the coal and oil supply of the world. According to some specialists, the reserves are enough to last for a few generations even at the present rate of production. Prof. N.N. Chatterji puts India's total reserves of coal at 20,000 million tons which are sufficient to last for another four centuries. India's oil reserves are estimated to be 6580 tons only.

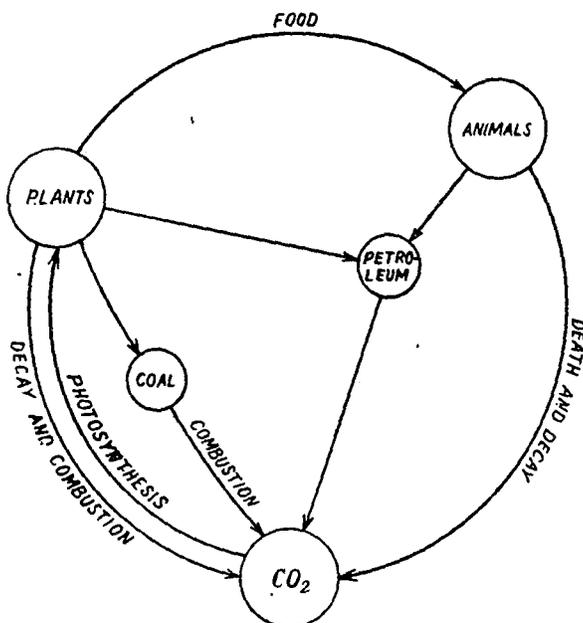
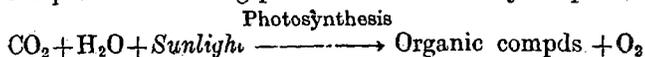
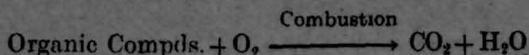


Fig. 1-3. Decay and Formation Cycle of Coal and Petroleum.

At the present rapid rate of depleting the natural resources of coal and petroleum, some economists are raising alarm for their conservation by other sources of energy. In this context, it may be pointed out that due to the external reaction between carbon dioxide and water in presence of sunlight (Photosynthesis), the organic compounds are being produced continuously in plants.



The organic compounds whether in the form of coal or petroleum on combustion give back CO_2 .



The cycle of formation of plants and animal products and their ultimate decay and combustion to give carbon dioxide is a perpetual one. This indicates that the deposits of carbon compounds will continue to be used up and reformed in the ages to come. However, the location of the deposits may be shifted from place to place.

QUESTIONS

1. State clearly what you understand by an Organic and inorganic substance. Give examples.
2. What was the *Vital Force Theory*? How was it overthrown?
3. What was the original meaning of the term organic? Give the modern definition of this term.
4. What are the reasons usually advanced for a separate study of organic chemistry?
5. Give a brief survey of the scope and applications of the organic chemistry.
6. Trace briefly the development of organic chemistry in the nineteenth century.
7. How would you justify the treatment of organic compounds as a distinct branch of chemistry?
8. Mention the chief sources of organic compounds. Indicate the development of new sources during the last ten years.
9. How long the world's petroleum and coal reserves are likely to last?

2

Purification of Organic Compounds



Justus F. Von Liebig
(1803—1873)

German. He was the founder of Agricultural Chemistry. Liebig invented many pieces of laboratory apparatus which are still in daily use.

The organic compounds derived from natural sources are seldom pure. They are often mixed with other substances which also occur with them. Similarly, the compounds prepared in the laboratory are generally mixed with the products which may also have been formed during the course of reaction. In order to study its properties and to determine its formula, a given substance must be first of all obtained in a state of purity. The methods employed for purification depend on the nature of the organic compound and the impurities present in it. The processes commonly used for the separation and purification of organic substances are :

- (1) *Crystallisation.*
- (2) *Sublimation,*
- (3) *Distillation,*
- (4) *Fractional Distillation,*
- (5) *Distillation under Reduced Pressure,*
- (6) *Steam Distillation, and*
- (7) *Extraction with Solvents.*

CRYSTALLISATION

The most general method for the purification of solid organic substances is crystallisation. In principle it is the same as employed for inorganic salts. The only difference is that here, in addition to water, several other solvents are used. The more common solvents are acetone, alcohol, ether, chloroform, benzene, etc.

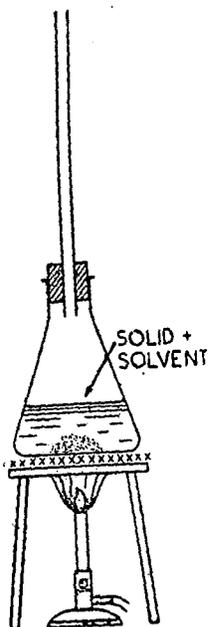


Fig. 2-1. Preparation of solution.

Procedure. A solvent in which the given substance is more soluble at higher temperature than the room temperature is selected. The solvent is heated with excess of the solid substance. The saturated solution thus prepared is filtered while still hot. As the filtrate cools, the pure solid crystals separate which may be removed by filtration.

Preparation of the solution. A suitable quantity of the powdered substance is taken, say, in a conical flask and treated with a small quantity of the solvent. The quantity of the solvent should be just enough to dissolve the whole of the solid on boiling. In case of volatile solvents, it is advisable to fit the vessel with a long glass tube which serves as a 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'.

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

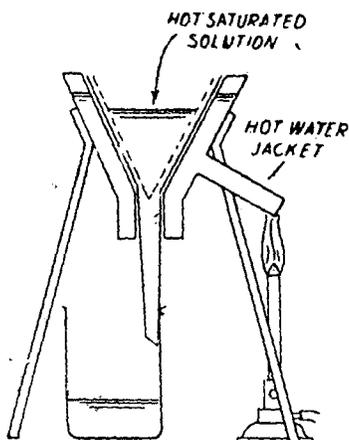


Fig. 2-2. Filtration through fluted filter paper.

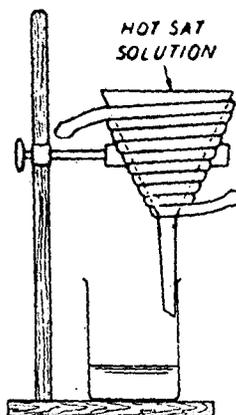


Fig. 2-3. Hot-water funnel.

PURIFICATION OF ORGANIC COMPOUNDS

longer time to filter and the crystals may form in the funnel during filtration. To prevent this, a "Hot-water funnel" may be used with advantage.

Crystallisation. The filtrate is allowed to cool undisturbed in a beaker or a "crystallising dish". After some time the solid substance separates in beautiful geometrical forms called crystals. Sometimes the crystals do not appear due to supercooling of the solution. In such a case the crystallisation is induced either by scratching the sides of the vessel with a glass rod or by sowing a few crystals of the same substance in solution.

Separation and Drying of Crystals. The crystals are separated from the mother liquor by filtration. This may be done more rapidly with the help of a Buchner funnel and a suction pump as shown in Fig. 2.4. When the whole of the mother liquor has been drained into the filtration-flask, the crystals are washed two or three times with small quantities of the pure solvent. The filter paper carrying the crystals is then placed over a porous plate and dried in a steam or air-oven.

Sometimes, the crystals obtained are coloured owing to the traces of impurities present. In such cases, the crystals are redissolved in a small quantity of the solvent, boiled with a little animal charcoal, filtered and crystallised once again as described above. The process is repeated till the substance is obtained in absolute pure form as indicated by its sharp melting point.

SUBLIMATION

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

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 rise from the solid pass through the holes in the filter-paper and

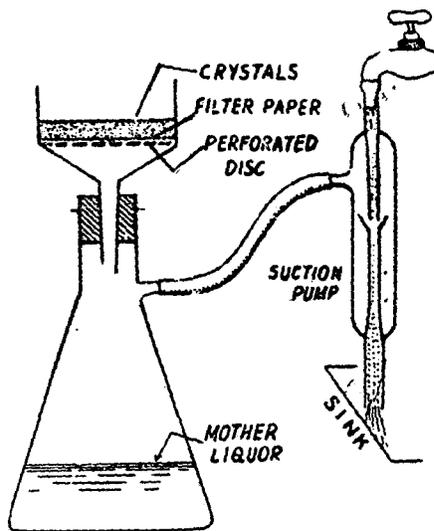


Fig. 2.4. Filtration under suction.

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).

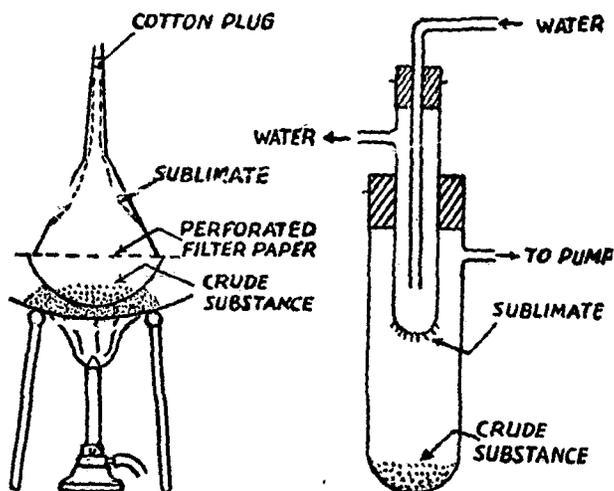


Fig. 2.5. Sublimation.

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 point can be sublimed relatively quickly. These can be conveniently purified by the laboratory operations described above. Such

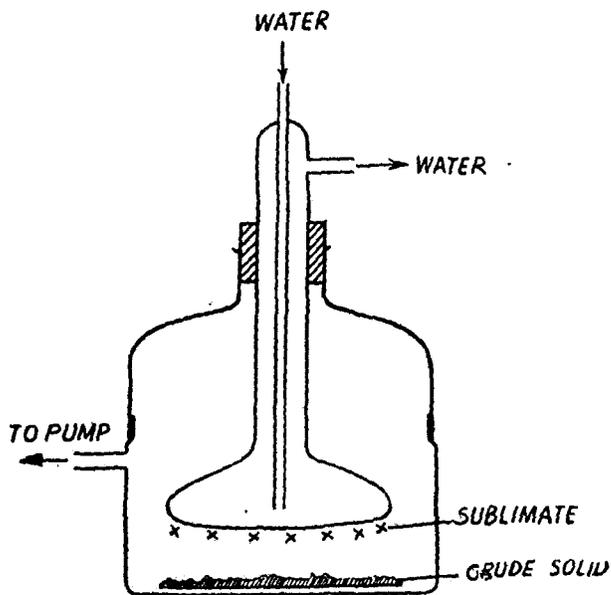


Fig. 2.7. Sublimation under vacuum.

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. 2-7. 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 pressures.

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°C , 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.

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. 2-8. 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 fractions 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* which in turn is

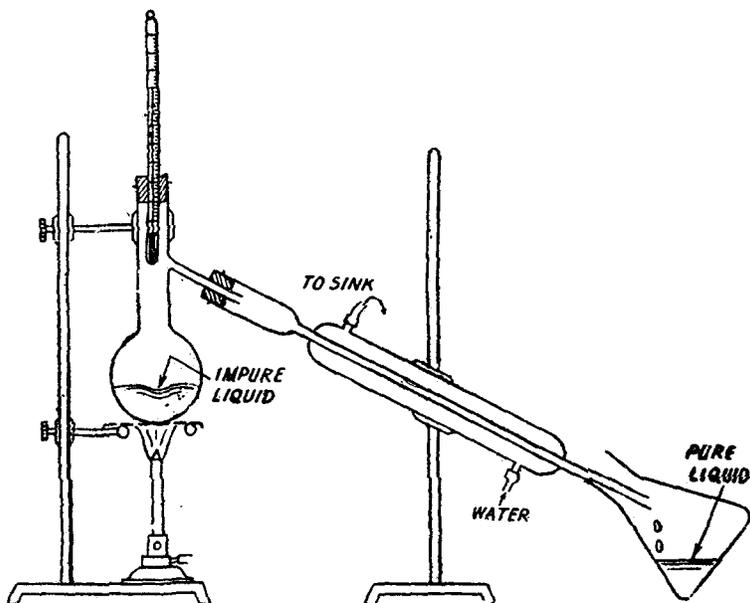


Fig. 2-8. Distillation.

connected to the condenser (Fig. 2-9). On heating, the vapours of

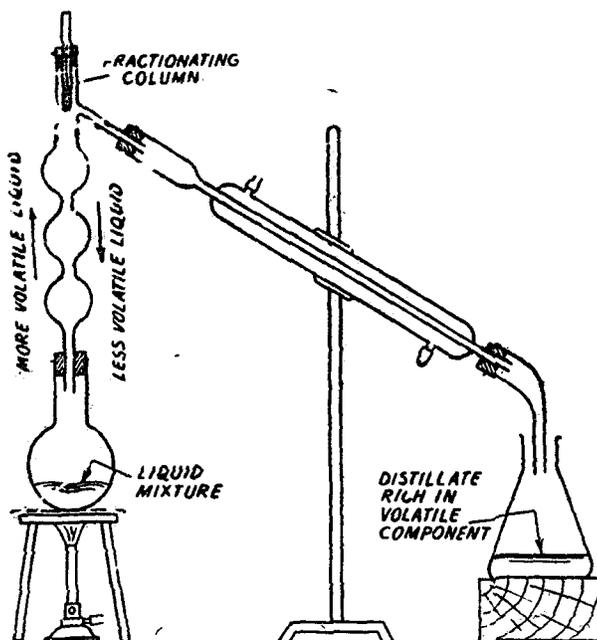


Fig. 2-9. Fractional distillation.

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

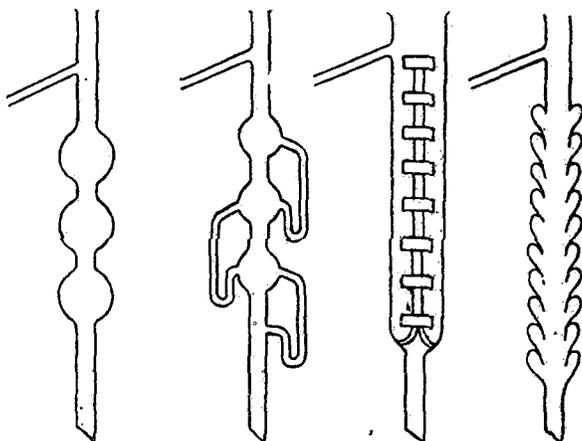


Fig. 2-10. Different types of fractionating columns.

rich in B. If necessary, the process can be repeated with the distillate and the liquid left in the distillation flask.

The use of a fractionating column has found a remarkable application in modern industry, especially in the distillation of petroleum, coal-tar and crude alcohol.

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

*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.

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

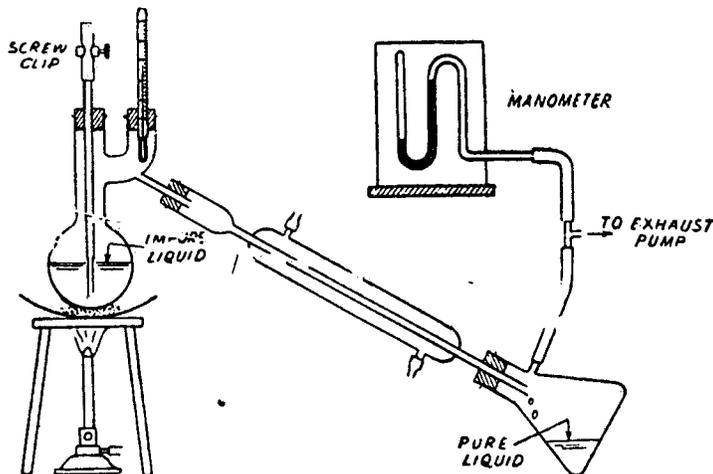


Fig 2-11. Distillation under reduced pressure.

(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°C) 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.

STEAM DISTILLATION

Many substances that are insoluble in water 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 passes 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

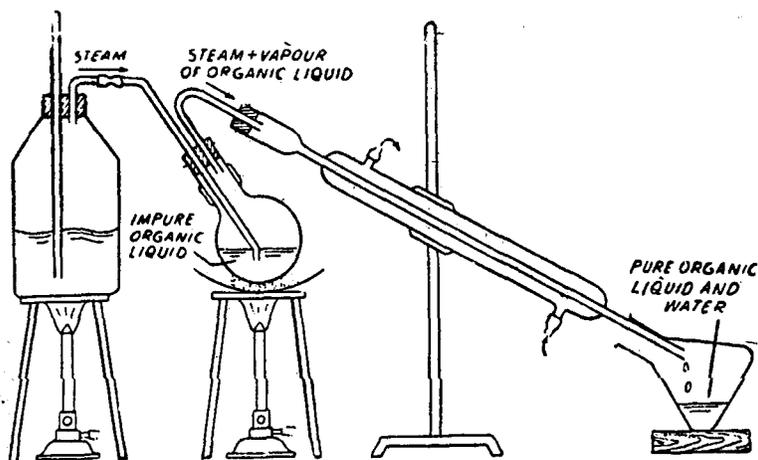


Fig. 2-12. Steam distillation.

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

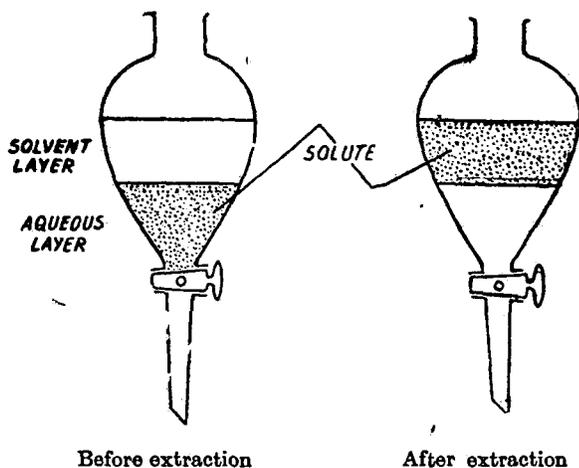


Fig. 2-13. Extraction with a solvent.

chloroform, is then added to it. The organic solvent being 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 insoluble. 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. 2-13). It consists of a glass of cylinder C having a side tube T and siphon 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 or sand 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 C. 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.

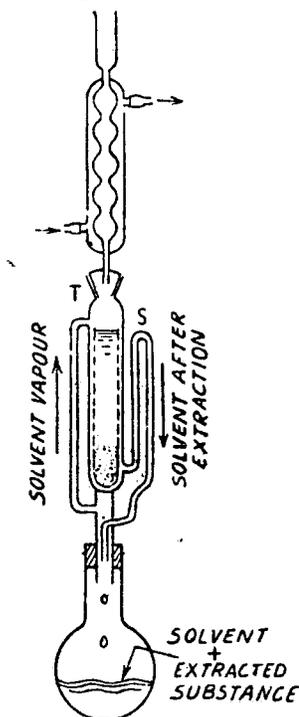


Fig. 2-14. Soxhlet extractor.

This new technique of purification and separation of organic substances was discovered by a Russian scientist Tswett in 1903. It is now extensively used for separation of small samples of organic mixtures when the routine methods like crystallisation and distillation fail.

The chromatographic separation of organic mixtures depends on the selective adsorption of the components from solutions. When solution of the mixture is passed through a column of the adsorbent (say alumina), the different solutes present in the solution will be adsorbed to different extents. The most highly adsorbed solute will be retained at the top of the column while the weakly adsorbed solutes will penetrate various distances down the column depending on their degree of adsorbability. The solutes thus separated in the column can be washed down, one at a time by passing fresh solvent through it and this process is known as *elution*.

This new technique of separation of organic mixtures was first applied to a mixture of leaf pigments (dyes) which separated as coloured bands on the column of white alumina. Hence its name **chromatography**, meaning 'colour writing'. This process is now widely used for separating organic substances whether coloured or

colourless, though the term chromatography still remains.

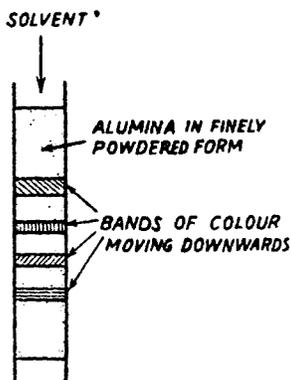


Fig. 2-15. Column Chromatography (Illustrated).

of the column are water, alcohol, acetone, petroleum ether etc.

In case of coloured substances, the separation can be observed visually. If colourless mixtures are being separated, ultraviolet light may be used to illuminate the column to show up the separation. Sometime it may be necessary to use some chemical on the adsorbent to change the colourless into coloured substances.

The above procedure which makes use of a column of solid adsorbent such as alumina, magnesium oxide or silica gel is termed **column chromatography**. The solvents commonly used for elution

Porous paper or filter paper may also be used as the adsorption medium instead of the column of adsorbent, when the technique is known as **Paper Chromatography**.

In another technique the vaporised mixture dissolved in a gas such as nitrogen or helium is separated by passing through a tube packed with, say, fire brick granules and this is termed **Vapour Phase Chromatography (VPC)**.

The following experiments will illustrate the techniques of Chromatography.

Experiment 1. Separation of screened methyl orange into its component dyes by Column Chromatography.

Set up the apparatus as shown in Fig. 2-16. Fill three-quarters of the tube with alumina suspended in ethyl alcohol. Remove the air bubbles by tapping it and keep the alumina covered with ethyl alcohol throughout the experiment. Add a few drops of screened methyl orange to the top of the column. Go on adding ethyl alcohol until the yellow and

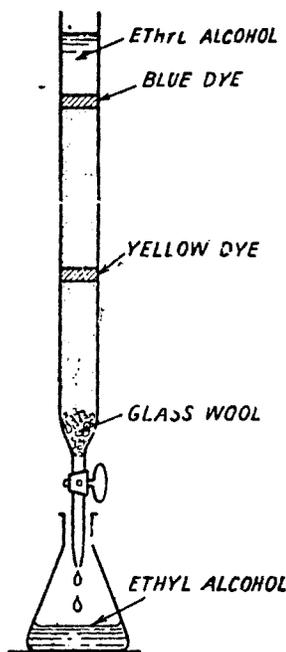


Fig. 2-16. Separation of dye mixture by column chromatography.

PURIFICATION OF ORGANIC COMPOUNDS

the blue dye have separated. The yellow dye moves down leaving behind the blue dye near the top of the column.

Experiment 2. Separation of a mixture of food dyes by Paper Chromatography.

Cut a filter paper eight inches square. Roll it up into the shape of a cylinder and fix the two ends with plastic clips. Place a

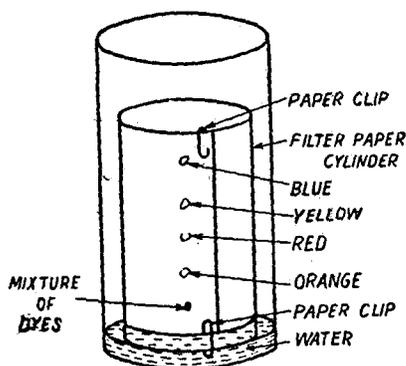


Fig. 2-17. Paper chromatography.

spot of mixed food dyes (green, red and yellow) at one-quarter of an inch from one end of the paper.

Place the paper cylinder in a large beaker containing water to about one-eighth of an inch. Cover the beaker with a glass plate and leave it undisturbed for about half an hour. Now take out the filter paper and you will see that the mixture is completely separated into blue, yellow, red and orange components.

DRYING OF SUBSTANCES

Organic substances, otherwise pure, often contain a small amount of water. Before it is fit for analysis, a substance must be absolutely dry. Even traces of moisture present may alter the results of analysis and interfere with the study of its reactions.

How to dry a Solid. The preliminary drying of freshly prepared crystals is done by pressing between pads of filter papers or by spreading them over a porous plate. The final removal of moisture is then carried by heating the crystals in an oven below their melting point. In case the substance decomposes on heating it may be dried by placing in a desiccator or better still in a *Vacuum Desiccator* (Fig. 2-18).

How to dry a Liquid. Liquids are dried by allowing them to stand with a dehydrating substance with which they do not react. One of the following substances may be used: calcium chloride, sodium hydroxide, sodium sulphate, lime, sodium metal, or phosphorus pentoxide. In actual practice, the liquid is placed in

contact with appropriate dehydrating agent in a stoppered bottle or flask and kept over-night. Next day, the upper clear layer of the liquid is decanted off and distilled in a dry flask.

TESTS OF PURITY

A pure organic substance has characteristic physical properties, crystalline form, refractive index, specific gravity, melting

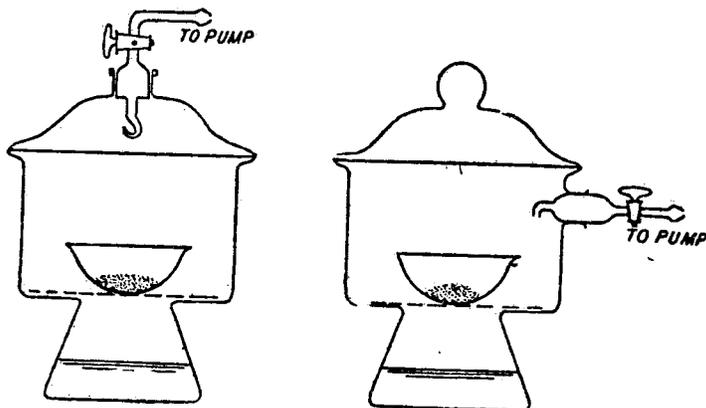


Fig. 2-18. Drying of organic solids.

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 melting 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 and is so adjusted that the solid in it stands just opposite to the middle of the mercury bulb. The thermometer is now lowered in a beaker containing sulphuric acid and the apparatus set up as shown in Fig. 2-19. The beaker is heated slowly and the temperature of the bath kept uniform by gentle but constant stirring with a ring 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.

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

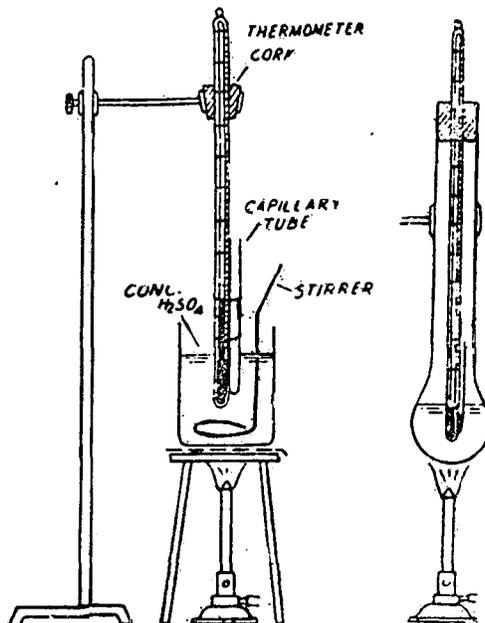


Fig. 2-19. Determination of melting point.

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 temperatures. 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.

(1) *Distillation Method.* If enough liquid is available, its boiling point is determined in an ordinary distillation apparatus (Fig. 2-20). 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 centimetre 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),

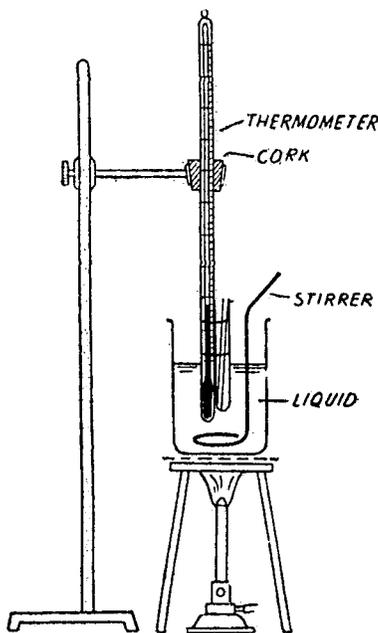


Fig. 2-20. Determination of boiling point.

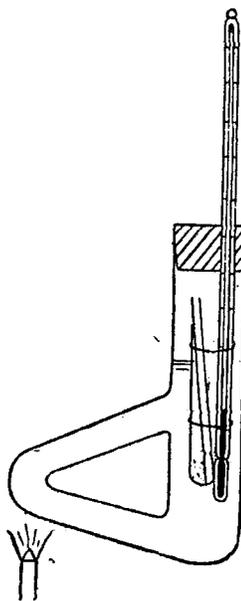


Fig. 2-21. The use of Thiele tube.

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. Give a brief description of the process of "extraction with solvents" and its use in the purification of organic compounds. Describe the construction and use of Soxhlet apparatus.

8. What is the significance of melting point and boiling point in Organic Chemistry? How would you proceed to find the boiling point of a liquid, only 0.5 ml. of which is available.

9. Give an organic compound for identification, how would you proceed to determine whether it is a single pure compound or an impure substance or a mixture.
(Banaras B.Sc., 1958)

10. With the help of a sketch describe the extraction of oil seeds using Soxhlet's apparatus.
(Bangalore B.Sc., 1969)

3

Composition of Organic Compounds



Friedrich K. Beilstein
(1836–1906)
Russian organic chemist. He discovered
isomerism of benzyl chloride and
chlorotoluene. Students know him
through his test of halogens

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 :

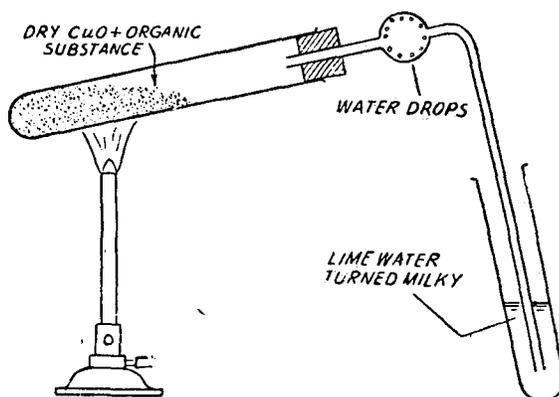
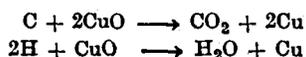


Fig. 3-1. Testing for carbon and hydrogen.

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 :—



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. Cupric oxide being hygroscopic in nature it is heated strongly just before use.

DETECTION OF OXYGEN

There is no conclusive test for oxygen, through 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* (NO₂), 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

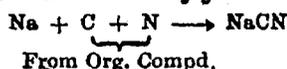
(1) The presence of nitrogen in an organic compound is shown by the following tests :

(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 indicates nitrogen.

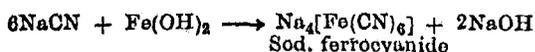
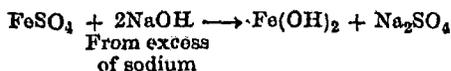
(2) **Soda-lime Test.** The given substance is mixed with double the amount of soda-lime (NaOH + CaO) and heated in a test tube. The vapours of ammonia evolved show the presence of nitrogen. A negative result, however, is not a proof of the absence of nitrogen. Many classes of nitrogenous compounds including *nitro* and *dialzo* 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 :

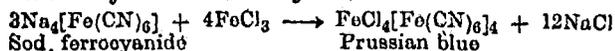
(i) *The substance is heated strongly with sodium metal.*



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



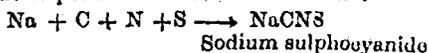
(iii) *To the cooled solution is then added a little ferric chloride solution and excess of concentrated hydrochloric acid.*

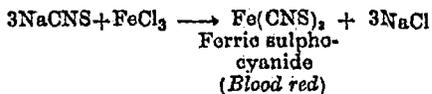


The formation of Prussian blue or green coloration confirms the presence of nitrogen.

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 :





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 mls. 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.

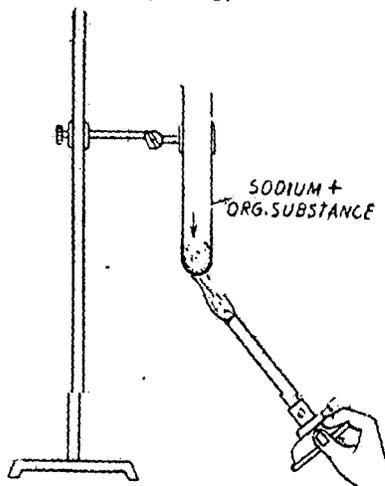


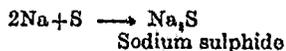
Fig. 3.2. Sodium test for nitrogen.

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 :

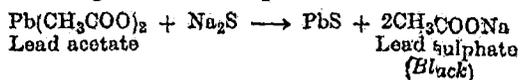
(1) **Sodium Test.** Sulphur, if present, in the given organic compound, upon fusion with sodium reacts to form sodium sulphide.



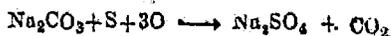
Thus, the 'sodium extract' obtained from the fused mass may be tested as :

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

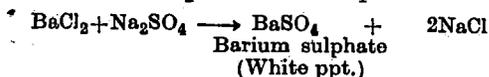
(ii) Acidify a second portion of the extract with acetic acid and then add lead acetate solution. A black precipitate of lead sulphide confirms the presence of sulphur.



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

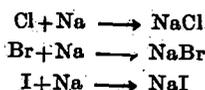


The fused mass is extracted with water, acidified with hydrochloric acid and then barium chloride solution is added to it. A white precipitate indicates the presence of sulphur.



DETECTION OF HALOGENS

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



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

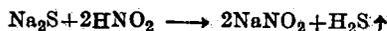
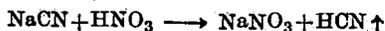
White precipitate soluble in ammonia indicates CHLORINE,

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.



(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 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.

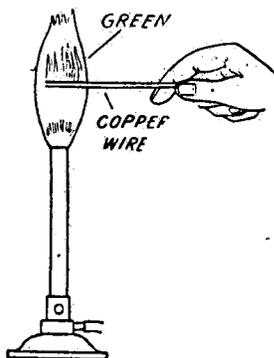


Fig. 3-3. Beilstein's test.

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

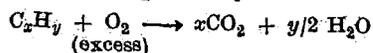
The substance is strongly heated in a crucible, preferably of platinum, till all reaction ceases. An incombustible residue indicates the presence of a metal in the substance. The residue is extracted with dilute acid and the solution tested for the presence of metallic radical by the usual scheme employed 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. No dependable method is, however, available for the determination of oxygen and hence its amount is always determined by difference.

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.



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.

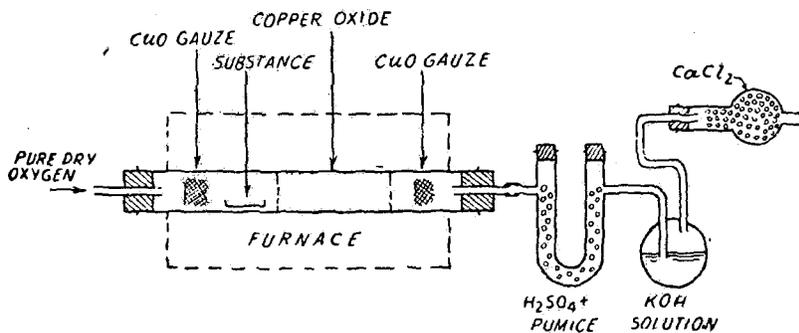


Fig. 3-4. Apparatus for the estimation of C and H.

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 soda-lime. 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 $\frac{1}{4}$ inch in diameter, and open at both ends is used for the combustion of the organic substance. It is filled as shown 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 gm.) 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 grams
Increase in weight of U-tube (H_2O)	= y grams
Increase in weight of potash bulbs (CO_2)	= z grams
Since 18 grams of water contain hydrogen	= 2 grams
y grams of water contain hydrogen	= $\frac{2}{18} \times y$ grams
Also, 44 grams of CO_2 contain carbon	= 12 grams
z " " " "	= $\frac{12}{44} \times z$ grams

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 gm. of an organic substance gave on combustion 0.4950 gm. of carbon dioxide and 0.2025 gm. of water. Calculate the percentage of carbon and hydrogen in it.

Weight of the substance taken = 0.2475 gm.

Weight of CO_2 formed = 0.4950 gm.

Weight of H_2O formed = 0.2025 gm.

Now, we know, $\text{CO}_2 \equiv \text{C}$ and $\text{H}_2\text{O} \equiv 2\text{H}$
 $\frac{44}{12}$ $\frac{18}{2}$

Weight of C in 0.4950 gm. of CO_2 = $\frac{0.4950 \times 12}{44}$ gm.

Weight of H in 0.2025 gm. of H_2O = $\frac{0.2025 \times 2}{18}$ gm.

$$\text{Hence, percentage of C} = \frac{0.4950 \times 12}{44} \times \frac{100}{0.2475}$$

$$= 54.54$$

$$\text{and percentage of H} = \frac{0.2025 \times 2}{18} \times \frac{100}{0.2475}$$

$$= 9.00$$

Example 2. 0.2346 gm. 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 gm. and 0.4488 gm. respectively. Determine the percentage composition of the compound.

Wt. of CO_2 (increase in wt. of potash bulbs) = 0.4488 gm.

Wt. of H_2O (increase in wt. of U-tube) = 0.2754 gm.

Since we know that $\text{CO}_2 \equiv \text{C}$ and $\text{H}_2\text{O} \equiv 2\text{H}$
 $\frac{44}{12}$ $\frac{18}{2}$

Wt. of C in 0.4488 gm. of CO_2 = $\frac{0.4488 \times 12}{44}$ gm.

Wt. of H in 0.2754 gm. of H_2O = $\frac{0.2754 \times 2}{18}$ gm.

But the wt. of the compound taken for analysis = 0.2346 gm.

$$\therefore \text{Percentage of C in it} = \frac{0.4488 \times 12}{44} \times \frac{100}{0.2346} = 52.18$$

$$\text{Percentage of H} = \frac{0.2754 \times 2}{18} \times \frac{100}{0.2346} = 13.04$$

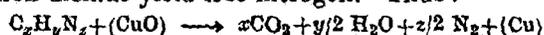
Percentage of O (difference) = 34.78;

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's 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 :



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 Dumas' method consists of :

- (i) *CO₂ generator*,
(ii) *Combustion tube*,
and (iii) *Schiff's nitrometer*.

CO₂ GENERATOR. The carbon dioxide needed in this process is prepared by heating magnesite or sodium bicarbonate contained in

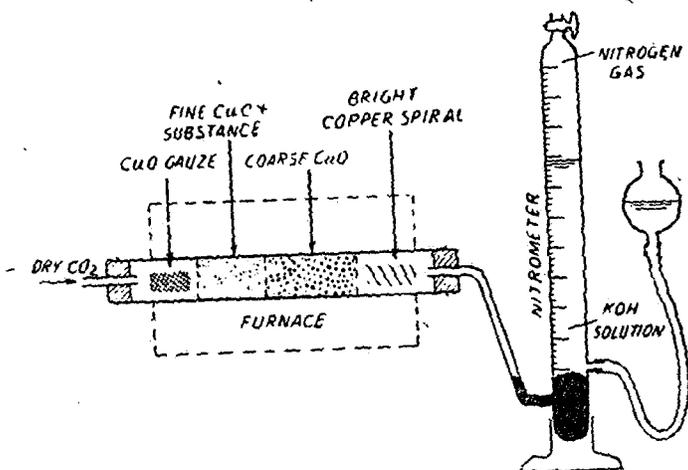


Fig. 3-5. Dumas' method for nitrogen estimation.

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 cms. 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 gm.) 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 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 mls.

t = room temperature in $^{\circ}C$

B = barometric pressure in mm. of mercury

b = aq. tension at room temperature ($t^{\circ}C$)

$$\begin{aligned} \text{Volume of } N_2 \text{ at N.T.P.} &= \frac{v(B-b)}{t+273} \times \frac{273}{760} \\ &= V \text{ mls. (say)} \end{aligned}$$

Now, 22,400 mls. of N_2 at N.T.P. weigh = 28 gms.

$$V \text{ mls.} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad = \frac{28}{22400} \times V \text{ gms.}$$

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

Example 3. 0.1877 gm. of an organic substance when analysed by the Dumas' method yield 31.7 mls. of moist nitrogen measured at $14^\circ C$ and 758 mm. mercury pressure. Determine the percentage of nitrogen in the substance. (Aqueous tension at $14^\circ C = 12$ mm.)

$$\text{Volume of } N_2 \text{ at N.T.P.} \quad = \frac{v(B-b)}{t+273} \times \frac{273}{760} = V \text{ mls.}$$

Substituting the various values in the above equation,

$$V = \frac{31.7(758-12)}{14+273} \times \frac{273}{760} = 29.6 \text{ mls}$$

$$\text{Weight of 29.6 mls. of nitrogen} = \frac{28}{22400} \times 29.6 \text{ gms.}$$

$$\therefore \text{Percentage of nitrogen} \quad = \frac{28 \times 29.6}{22400} \times \frac{100}{0.1877}$$

$$= 19.72$$

Example 4. In the estimation of nitrogen present in an organic compound by Dumas' method, 0.200 gm. yielded 20.7 mls. of nitrogen at $15^\circ C$ and 760 mm. pressure. Calculate the percentage of nitrogen in the compound.

$$\text{Volume of } N_2 \text{ at N.T.P.} \quad = \frac{v \times B}{t+273} \times \frac{273}{760} = V \text{ mls.}$$

Substituting the various values in the above equation,

$$V = \frac{20.7 \times 760}{288} \times \frac{273}{760} = 19.63 \text{ mls.}$$

$$\text{Weight of 19.63 mls. of nitrogen} = \frac{28}{22400} \times 19.63 \text{ gms.}$$

$$\therefore \text{Percentage of nitrogen} \quad = \frac{28}{22400} \times 19.63 \times \frac{100}{0.2}$$

$$= 12.27$$

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

Kjeldahl's 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 gm.) is placed in a special long-necked 'Kjeldahl flask' made of resistant glass. About 25 mls. of concentrated sulphuric acid to-

gether 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

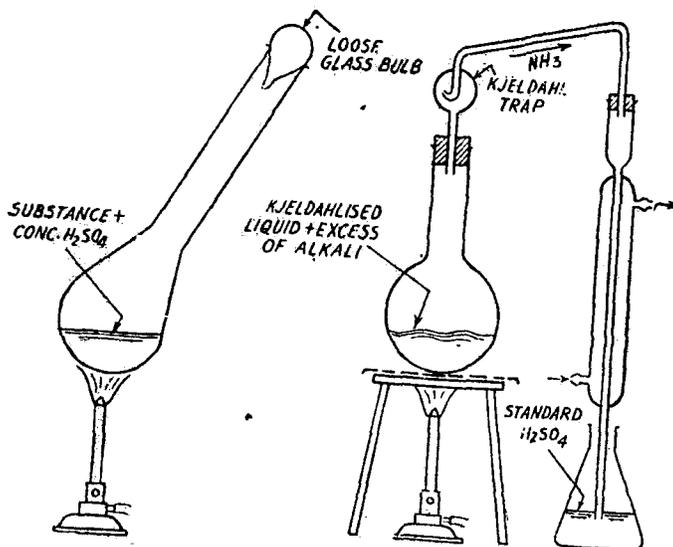


Fig. 3-6. Kjeldahl flask.

Fig. 3-7. Distillation of ammonia.

contents diluted with some distilled water, and then carefully transferred into a one-litre round-bottomed 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-bottomed 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 gms. and V mls. of N. HCl is required for complete neutralisation of ammonia evolved.

$$V \text{ ml. N. HCl} \equiv V \text{ ml. of N. NH}_3$$

1000 mls. of N. NH_3 contain 17 gms. of ammonia or 14 gms. of nitrogen.

Amount of nitrogen present in V mls. of N. NH_3

$$= \frac{14}{1000} \times V \times N \text{ gm.}$$

$$\begin{aligned} \text{Percentage of nitrogen} &= \text{Wt. of nitrogen} \times \frac{100}{\text{Wt. of substance}} \\ &= \frac{14}{1000} \times V \times N \times \frac{100}{x} \\ &= \frac{1.4VN}{x} \end{aligned}$$

where N stands for normality of the acid used

V stands for volume of the acid used up

and x stands for the substance kjeldahlised.

Example 5. 0.257 gm. 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 mls. of N/10 hydrochloric acid which required 23.2 mls. of N/10 NaOH for neutralisation at the end of the operation. Determine the percentage of nitrogen in the substance.

$$\begin{aligned} \text{Volume of N/10 HCl neutralised by ammonia} &= 50 - 23.2 \\ &= 26.8 \text{ mls.} \end{aligned}$$

$$\begin{aligned} \text{Now, } 26.8 \text{ mls. of N/10 HCl} &\equiv 26.8 \text{ mls. of N/10 NH}_3 \\ &\equiv 26.8 \text{ mls. of N/10 N (combined)} \end{aligned}$$

$$26.8 \text{ mls. of N/10 N solution contains } \frac{14}{10} \times \frac{26.8}{1000} \text{ gms. of nitrogen}$$

This weight of nitrogen was originally present in 0.257 gm. of the organic substance.

$$\therefore \text{Percentage of nitrogen} = \frac{14 \times 26.8}{10 \times 1000} \times \frac{100}{0.257} = 14.6.$$

Example 6. 0.4 gm. of an organic compound was kjeldahlised and ammonia evolved was absorbed into 50 mls. of semi-normal solution of sulphuric acid. The residual acid solution was diluted with distilled water and the volume was made up to 150 mls. 20 mls. of this diluted solution required 31 mls. of N/20 NaOH solution for complete neutralisation. Calculate the percentage of nitrogen in the compound.

(i) CALCULATION OF ACID USED BY AMMONIA.

$$\text{Volume of } \frac{N}{2} \text{ H}_2\text{SO}_4 \text{ taken} = 50 \text{ mls.}$$

Let the volume of N/2 H₂SO₄ left unused by ammonia = V mls.

V mls. of this acid solution was diluted to 150 mls. and titrated against N/20 NaOH.

$$20 \text{ mls. of diluted solution} \equiv 31 \text{ mls. of N/20 NaOH.}$$

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

$$\text{Normality of 150 mls. of acid solution} = \frac{31}{400} \text{ N}$$

$$\text{i.e., } V \text{ mls. of } \frac{N}{2} \text{ H}_2\text{SO}_4 \equiv 150 \text{ mls. of } \frac{31}{400} \text{ N diluted acid}$$

$$V = 150 \times \frac{31}{400} \times \frac{2}{1} = 23.25 \text{ mls.}$$

$$\text{Volume of } \frac{N}{2} \text{H}_2\text{SO}_4 \text{ left} = 23.25 \text{ mls.}$$

∴ Volume of acid used up by ammonia = $50 - 23.25 = 26.75$ mls.

(ii) CALCULATION OF PERCENTAGE OF N.

$$\begin{aligned} 26.75 \text{ mls. of } N/2 \text{H}_2\text{SO}_4 &\equiv 26.75 \text{ mls. of } N/2 \text{NH}_3 \text{ solution} \\ &\equiv 26.75 \text{ mls. of } N/2 \text{ N (combined in solution)} \end{aligned}$$

∴ Wt. of nitrogen in 26.75 mls. of N/2 solution

$$= \frac{14}{2} \times \frac{1}{1000} \times 26.75 \text{ gms.}$$

This wt. of nitrogen was originally present in 0.4 gm. of the substance.

$$\therefore \text{Percentage of nitrogen} = \frac{14}{2} \times \frac{1}{1000} \times 26.75 \times \frac{100}{0.4} = 46.81.$$

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 cms. length and closed at one end. About 5 mls. of fuming nitric acid together with 2 to 2.5 gms. 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.

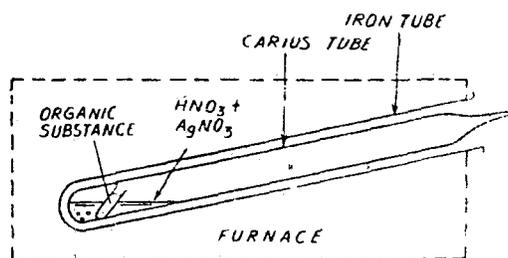


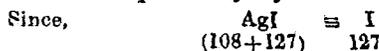
Fig. 3.8. Heating the bomb tube in a furnace (Carius Method).

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.

Let w gms. of the organic substance give x gms. of the silver halide.

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

Example 7. 0.197 gm. of an organic substance when heated with excess of strong nitric acid and silver nitrate gave 0.3525 gm. of silver iodide. Find the percentage of iodine in the compound.

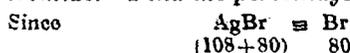


In this case 0.197 gm. of the compound gave 0.3525 gm. of AgI

$$\equiv \frac{0.3525 \times 127}{235} \text{ gm. iodine}$$

$$\therefore \text{ the percentage of iodine} = \frac{0.3525 \times 127}{235} \times \frac{100}{0.197} \\ = 96.68.$$

Example 8. 0.2562 gm. of an organic substance when heated with excess of strong nitric acid and silver nitrate gave 0.3066 gm. of silver bromide. Find the percentage of bromine in the compound.



Here, 0.2562 gm. of the substance gave 0.3066 gm. of AgBr

$$= \frac{0.3066 \times 80}{188} \text{ gm. bromine}$$

$$\therefore \text{ the percentage of bromine} \\ = \frac{0.3066 \times 80}{188} \times \frac{100}{0.2562} = 50.93$$

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

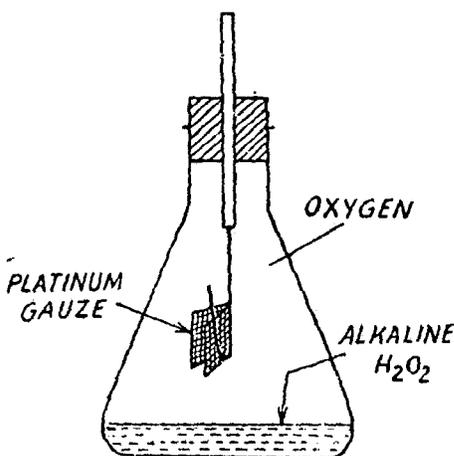


Fig. 3-9. Estimation of halogens by oxygen flask method.

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.

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 gms. and V mls. of N silver nitrate is required to reach the end point, the percentage of chlorine can be calculated.

Since $\text{Cl} \equiv \text{AgNO}_3$

V mls. of N $\text{AgNO}_3 \equiv V$ mls. of N chlorine (Cl)

But 1000 mls. of N chlorine (Cl) solution contains Cl
 $= 35.5$ gm.

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

$$= \frac{35.5}{1000} \times N \times V \text{ gm.}$$

Hence percentage of Cl in sample

$$= \frac{35.5}{1000} \times N \times V \times \frac{100}{x}$$

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.



If x gm. of the sample require V mls. of N sodium thio-sulphate,

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

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, $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$, by the addition of ammonia and ammonium molybdate solution, which is then separated, dried and weighed.

Example 9. In an estimation of sulphur by the Carius method 0.2175 gm. of the substance gave 0.5825 gm. of barium sulphate. Calculate the percentage of sulphur in the substance.

We know, $\text{BaSO}_4 \equiv \text{S}$
(137 + 32 + 64) 32

Or, 233 gms. of BaSO_4 contain 32 gms. of sulphur.

0.5825 " " " $\frac{32}{233} \times 0.5825$ gm. of sulphur.

This is the weight of sulphur present in 0.2175 gm. of the substance.

Hence, percentage of S = $\frac{32 \times 0.5825}{233} \times \frac{100}{0.2175} = 36.77$.

Example 10. 0.395 gm. of an organic compound by Carius method for the estimation of sulphur gave 0.582 gm. of BaSO_4 . Find the percentage of sulphur in the compound.

We know, $\text{BaSO}_4 \equiv \text{S}$
233 32

i.e., 233 gms. of BaSO_4 contains 32 gms. of sulphur.

∴ 0.582 " " " $\frac{32}{233} \times 0.582$ gm. of sulphur.

This is the weight of sulphur present in 0.395 gm. of the substance.

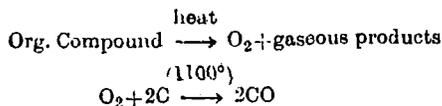
Hence, the percentage of sulphur

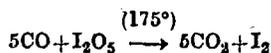
$$= \frac{32}{233} \times 0.582 \times \frac{100}{0.395} \\ = 20.23.$$

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.





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.

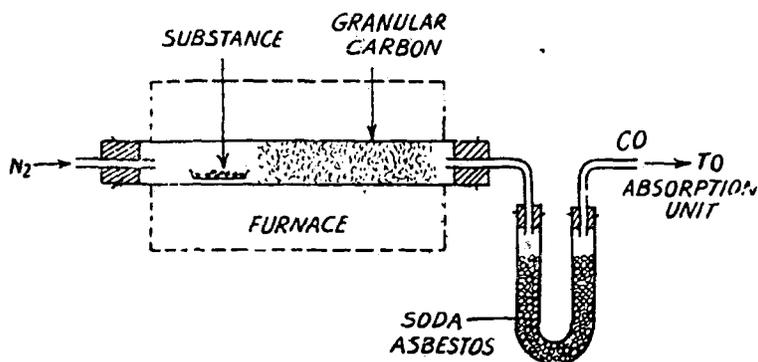


Fig. 3-10. Pyrolysis unit of the apparatus used for the estimation of oxygen.

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.

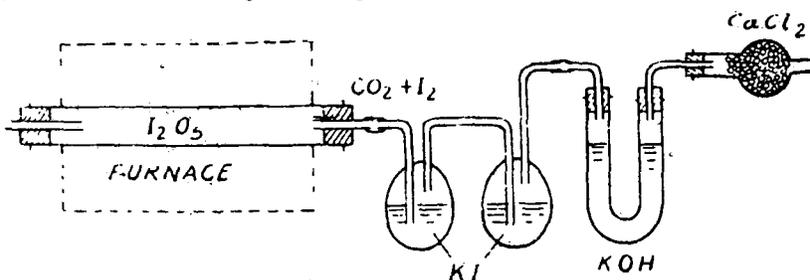


Fig. 3-11. Absorption unit.

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-ash tube where CO_2 is retained. The soda-ash 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 gms.

Increase in the weight of KOH tube = y gms.

Since $\text{O} \equiv \text{CO} \equiv \text{CO}_2$

16 gms. of oxygen present in the substance can form 44 grams of CO_2 .

\therefore 44 gms of CO_2 are obtained from oxygen
= 16 gms.

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

Hence the weight of oxygen in the weight of sample taken

$$= \frac{16}{44} \times y \text{ gms.}$$

\therefore the percentage of oxygen

$$= \frac{16}{44} \times \frac{y}{x} \times 100$$

QUESTIONS

1. Give an account of the methods by which the presence of nitrogen, chlorine and sulphur is tested in organic solids.

2. How would you test for the presence of chlorine in an organic compound? Describe how it is qualitatively determined.

3. How can you identify halogens and nitrogen when they occur together in an organic compound?

4. Explain briefly with a diagram of the apparatus employed in the method of determining the percentage of carbon and hydrogen in an organic compound containing carbon, hydrogen and nitrogen only.

5. Describe fully how you would detect the presence of (a) nitrogen, (b) sulphur, (c) phosphorus in an organic substance, explaining as far as possible the reactions involved by means of equations. How would you determine one of these elements quantitatively?

6. Describe with essential details the various methods available for the quantitative estimation of nitrogen in an organic compound.

0.8 gm. of a substance was digested with sulphuric acid and then dissolved with an excess of caustic soda. The ammonia gas evolved was passed through 100 c.c. of 1 N sulphuric acid. The excess of acid required 80 c.c. of 1 N caustic soda solution for its complete neutralisation. Calculate the percentage of nitrogen in the compound. [Ans. 35%] (Nagpur B.Sc., 1960)

7. How is nitrogen detected and estimated in an organic compound? 0.2 gm. of an organic substance on Kjeldahl's analysis gave enough ammonia to just neutralise 20 c.c. of decinormal sulphuric acid. Calculate the percentage of nitrogen in the compound. [Ans. 14.0%] (Annamalai B.Sc., 1961)

8. Describe the method of estimation of sulphur in an organic compound.

Three isomeric compounds have vapour density 29.5 and contain C = 61.02%, H = 16.25% and N = 23.73%. Assign structural formulae to them and suggest a method to distinguish them.

(Atomic weights : H=1, C=12, N=14)

(Ans. $C_3H_7NH_2$; $CH_3NHC_2H_5$; $(CH_3)_3N$) (Baroda B.Sc., 1962)

9. How do you detect the presence of nitrogen, sulphur and halogen in organic compounds? Explain the chemical reactions involved. How are organic compounds purified? (Osmania B.Sc. Part II, 1963)

10. How would you estimate nitrogen in a nitrogenous organic compound? Give all details and discuss the reactions involved. (Nagpur B.Sc. II, 1964)

11. Describe fully Kjeldahl's method for the estimation of nitrogen in an organic compound. What are its limitations? (Calcutta B.Sc., 1964)

12. How can you estimate nitrogen quantitatively in an organic compound? (Dibrugarh B.Sc., 1967)

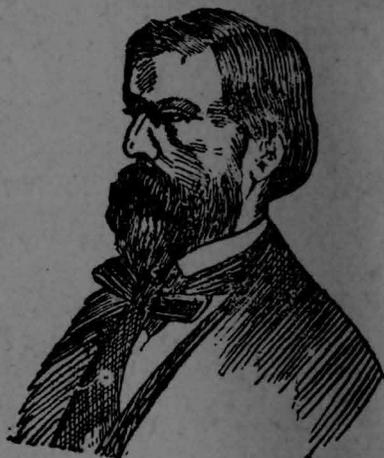
13. Give a brief account of (a) the detection and (b) a method for the estimation of nitrogen and sulphur in an organic compound. (Osmania B.Sc., 1968)

14. How are nitrogen and sulphur detected in an organic compound? How is nitrogen estimated? (Mumbai B.Sc., 1968)

15. How can you detect the presence of nitrogen, sulphur and halogens in an organic compound? (Dibrugarh B.Sc., 1968)

4

Empirical and Molecular formulae. Determination of Molecular Weights



Victor Meyer
(1848-1897)

German chemist. He investigated nitroalkanes. He gave a method for the determination of vapour density which bears his name.

I. 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 (H.C.F.), so as to give 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 weights.

<i>Carbon</i>	<i>Hydrogen</i>	<i>Chlorine</i>
$\frac{10.06}{12} = 0.84$	$\frac{0.84}{1} = 0.84$	$\frac{89.10}{35.5} = 2.51$

Step 2. Divide these numbers by the smallest number (in this case 0.84).

$\frac{0.84}{0.84} = 1$	$\frac{0.84}{0.84} = 1$	$\frac{2.51}{0.84} = 3$
-------------------------	-------------------------	-------------------------

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	H.C.F.	Atoms present
C	14.5	12	$1.21 \div 1.20 = 1.0$	1.0	$1 \times 2 = 2$
H	1.8	1	$1.8 \div 1.20 = 1.5$	1.5	$1.5 \times 2 = 3$
Cl	64.46	35.5	$1.81 \div 1.20 = 1.5$	1.5	$1.5 \times 2 = 3$
O	19.24	16	$1.20 \div 1.20 = 1.0$	1.0	$1 \times 2 = 2$

In this case, the final figures representing the number of atoms of each element are multiplied by 2 so as to 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 gram of an organic substance yielded : (i) 0.147 gram of carbon dioxide and 0.12 gm. water and (ii) 74.6 mls. of nitrogen gas at S.T.P. Find the simplest formula of the substance.

CALCULATION OF PERCENTAGE OF ELEMENTS

Since $CO_2 \equiv C$; $H_2O \equiv 2H$, 22,400 mls. $N_2 = 28$ gms

$$\text{Percentage of carbon} = \frac{0.147 \times 12}{44} \times \frac{100}{0.2} = 20.04$$

$$\text{,, ,, hydrogen} = \frac{0.12 \times 2}{18} \times \frac{100}{0.2} = 6.66$$

$$\text{,, ,, nitrogen} = \frac{74.6 \times 28}{22400} \times \frac{100}{0.2} = 46.63$$

$$\text{,, ,, oxygen (by difference)} = 26.77$$

CALCULATION OF EMPIRICAL FORMULA

	%age	At. Wt.	Atomic Ratio	H.C.F.	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 $\text{CH}_4\text{N}_2\text{O}$.

Example 4. 0.21 gram of an organic substance containing C, H, O and N only, gave on combustion 0.462 gram carbon dioxide and 0.1215 gram water. 0.104 gram of it when distilled with caustic soda evolved ammonia which was neutralised by 15 mls. of $\text{N}/20$ H_2SO_4 . Calculate the empirical formula.

CALCULATION OF PERCENTAGE COMPOSITION:

Percentage of nitrogen :—

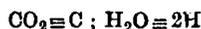
$$15 \text{ mls. of } \frac{\text{N}}{20} \text{ H}_2\text{SO}_4 \equiv 15 \text{ mls. of } \frac{\text{N}}{20} \text{ NH}_3 \equiv 15 \text{ mls. of } \frac{\text{N}}{20} \text{ N} \quad (\text{combined})$$

$$\therefore \text{ wt. of nitrogen in 0.104 gm. substance} = 15 \times \frac{14}{20} \times \frac{1}{1000} \text{ gm.} \\ = 0.0105 \text{ gm.}$$

$$\% \text{age of the nitrogen} = \frac{0.0105}{0.104} \times 100 = 10.09$$

Percentage of C and H :—

Since



$$\% \text{age of C} = \frac{0.462 \times 12}{44} \times \frac{100}{0.21} = 60.0$$

$$\text{H} = \frac{0.1215 \times 2}{18} \times \frac{100}{0.21} = 6.43$$

Percentage of oxygen (by difference) = 23.48

CALCULATION OF EMPIRICAL FORMULA

	%age	At. Wt.	Atomic Ratio	H.C.F.	Atoms present
C	60 ÷	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 $\text{C}_7\text{H}_9\text{NO}_2$.

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 $(\text{CH}_4)_1$
Ethylene	CH_2	C_2H_4 or $(\text{CH}_2)_2$
Acetic acid	CH_2O	$\text{C}_2\text{H}_4\text{O}_2$ or $(\text{CH}_2\text{O})_2$
Glucose	CH_2O	$\text{C}_6\text{H}_{12}\text{O}_6$ or $(\text{CH}_2\text{O})_6$

Thus we can write :

$$\text{Molecular Formula} = (\text{Empirical Formula})_n$$

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

$$M. \text{Wt.} = \text{Emp. formula Wt.} \times n$$

whence

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

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, ($\text{C}=12$; $\text{H}=1$; $\text{O}=16$).

$$\text{Molecular formula} = (\text{Empirical formula})_n$$

But

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

In this case, M. Wt. = 90

$$\text{Emp. F. Wt.} = 12 + 2 + 16 = 30$$

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

Hence, the molecular formula = $(\text{CH}_2\text{O})_3$ or $\text{C}_3\text{H}_6\text{O}_3$.

Example 6. An organic liquid contains 12.8 per cent carbon, 2.1 per cent hydrogen and 85.1 per cent bromine. 0.188 gram of it in a Victor Meyer experiment, displaced 24.2 mls. of moist air measured at 14°C and 752 mm. pressure. Find the molecular formula of the substance. (Aq. tension at $14^\circ\text{C}=12$ mm.)

CALCULATION OF MOLECULAR WEIGHT :

$$\text{Volume of dry air replaced at N.T.P.} = \frac{24.2(752-12)}{287} \times \frac{273}{760}$$

$$= 22.42 \text{ mls.}$$

Now, the wt. of 22.42 mls. of vapour of substance = 0.188 gm.

$$\begin{aligned} \text{,, ,, 22400 ,, ,, ,,} &= \frac{0.188}{22.42} \times 22400 \\ &= 187.9 \text{ gms.} \end{aligned}$$

Molecular weight of the substance = 187.9.

CALCULATION OF EMPIRICAL FORMULA :

	%age		At. Wt.		Atomic ratio		H.C.F.		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 $(\text{CH}_2\text{Br})_n$

But

$$n = \frac{M. \text{Wt.}}{\text{Emp. F. Wt.}} = \frac{187.9}{12 + 2 + 80} = 2$$

∴ Molecular formula = $\text{C}_2\text{H}_4\text{Br}_2$.

5611

Example 7. An organic dibasic acid contains C=17.39 ; H=1.45, and Br=57.97 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 $\text{R}(\text{C}_2\text{H}_5)_2$.

Molecular weight of ethyl ester = $2 \times \text{V.D.} = 2 \times 166 = 332$

Thus $\text{R}(\text{C}_2\text{H}_5)_2 = \text{R} + 2(24 + 5) = 332$

Whence $\text{R} = 274$

\therefore Molecular weight of the acid $\text{RH}_2 = 274 + 2 = 276$.

CALCULATION OF EMPIRICAL FORMULA :

Percentage of oxygen = $100 - (17.39 + 1.45 + 57.97) = 23.19$

	%age	At. wt.	=	Atomic Ratio	÷	H.C.F.	=	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 $\text{C}_2\text{H}_2\text{BrO}_2$.

Let the molecular formula of the acid be $(\text{C}_2\text{H}_2\text{BrO}_2)_n$.

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

\therefore Molecular formula is $\text{C}_4\text{H}_4\text{Br}_2\text{O}_4$.

Example 8. 0.20 gm. of anhydrous organic acid gave on combustion 0.40 gm. water and 0.195 gm. carbon dioxide. The acid is found to be dibasic and 0.5 gm. of its silver salt leaves on ignition 0.355 gm. silver. What is the molecular formula of the acid ?

CALCULATION OF MOLECULAR WEIGHT :

$$\frac{\text{M. Wt. of silver salt}}{2 \times 108} = \frac{0.5}{0.355}$$

$$\text{M. Wt. of silver salt} = \frac{0.5}{0.355} \times 2 \times 108 = 304.2$$

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

$$\begin{aligned} \text{But } \text{RH}_2 &= \text{RAg}_2 - 2\text{Ag} + 2\text{H} \\ &= 304.2 - 216 + 2 = 90.2. \end{aligned}$$

CALCULATION OF EMPIRICAL FORMULA :

$$\text{Percentage of C} = \frac{0.195 \times 12}{44} \times \frac{100}{0.2} = 26.59$$

$$\text{Percentage of H} = \frac{0.40 \times 2}{18} \times \frac{100}{0.2} = 2.22$$

$$\text{Percentage of O (by difference)} = 71.19.$$

	%age	At. Wt.	=	Atomic ratio	÷	H.C.F.	=	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

$$\text{Let it be } (\text{CHO}_2)_n ; n = \frac{\text{M. Wt.}}{\text{Emp. F. Wt.}} = \frac{90.2}{12 + 1 + 32} = 2$$

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 gm. of the acid required 20 mls. of $N/10$ NaOH for complete neutralisation.

Deduce the empirical and the molecular formulae of the acid.

CALCULATION OF MOLECULAR WEIGHT :

$$20 \text{ mls. } \frac{N}{10} \text{ NaOH} \equiv 20 \text{ ml. } \frac{N}{10} \text{ acid} \equiv \frac{20}{100} \times \frac{N}{10} \text{ gm. acid}$$

$$\text{Thus : } \frac{20}{1000} \times \frac{N}{10} = 0.272$$

$$\text{Whence } N = 500 \times 0.272 = 136$$

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

CALCULATION OF EMPIRICAL FORMULA :

	At. Wt.		Atomic ratio		H.C.F.		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 $(C_4H_4O)_n$

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

Hence, molecular formula is $C_8H_8O_2$.

Example 10. A mono-acid organic base gave the following results on analysis :—

- (i) 0.100 gm. gave 0.2882 gm. CO_2 and 0.0756 gm. H_2O .
- (ii) 0.200 gm. gave 21.8 mls. nitrogen at $15^\circ C$ and 750 mm.
- (iii) 0.400 gm. of the platinichloride, left on ignition, 0.125 gm. of Pt.

What is the molecular formula of the base ?

CALCULATION OF MOLECULAR WEIGHT :

$$\begin{aligned} \text{M. Wt. of platinichloride} &= 195 \times \frac{\text{Wt. of salt taken}}{\text{Wt. of Pt left}} \\ &= 195 \times \frac{0.4}{0.125} = 624 \\ B &= \frac{B_2H_2PtCl_6 - H_2PtCl_6}{2} \\ &= \frac{624 - 410}{2} = 107 \end{aligned}$$

∴ Molecular weight of the base is 107.

CALCULATION OF EMPIRICAL FORMULA :

$$\text{Volume of nitrogen at N.T.P.} = 21.8 \times \frac{273}{288} = 20.66 \text{ mls.}$$

$$\text{Percentage of C} = \frac{0.2882 \times 12}{44} \times \frac{100}{0.1} = 78.6$$

$$\text{Percentage of H} = \frac{0.0756 \times 2}{18} \times \frac{100}{0.1} = 8.4$$

$$\text{Percentage of N} = \frac{20.66 \times 28}{22400} \times \frac{100}{0.2} = 12.91$$

Element	% age	At. weight	At. ratio	H.C.F.	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 :

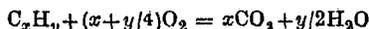
Let the molecular formula be $(C_7H_9N)_n$

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

∴ 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 its 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



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

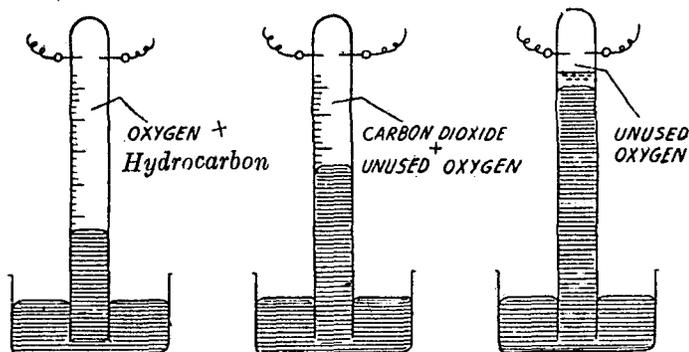


Fig. 4.1. Explosion of gaseous hydrocarbons in eudiometer tube.

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 $(V_1 - V_2)$.

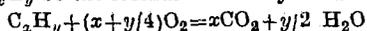
The molecular formula of the hydrocarbon is then found by the application of Avogadro Law.

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

Volume of oxygen used = $100 - 70 = 30$ mls.

“ “ carbon dioxide formed = $90 - 70 = 20$ mls.

If C_xH_y be the formula of the hydrocarbon,



Applying the converse of Avogadro Law,

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

or 10 mls. $C_xH_y + 10(x + y/4)$ mls. $O_2 = 10x$ mls. $CO_2 + 10y/2$ mls. 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 .

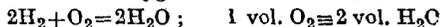
Alternative Solution :

Total oxygen used (for CO_2 and H_2O) = 30 mls.



Hence for 20 mls. CO_2 formed, volume of oxygen used = 20 mls.

\therefore Volume of oxygen used for water alone = $30 - 20 = 10$ mls.



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

Now, 10 mls. hydrocarbon + 30 mls. O_2 + 20 mls. CO_2 + 20 mls. H_2O

or 1 ml. “ + 3 mls. $O_2 = 2$ mls. CO_2 + 2 mls. H_2O

Applying Avogadro's 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	CHEMICAL
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	

1. 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.

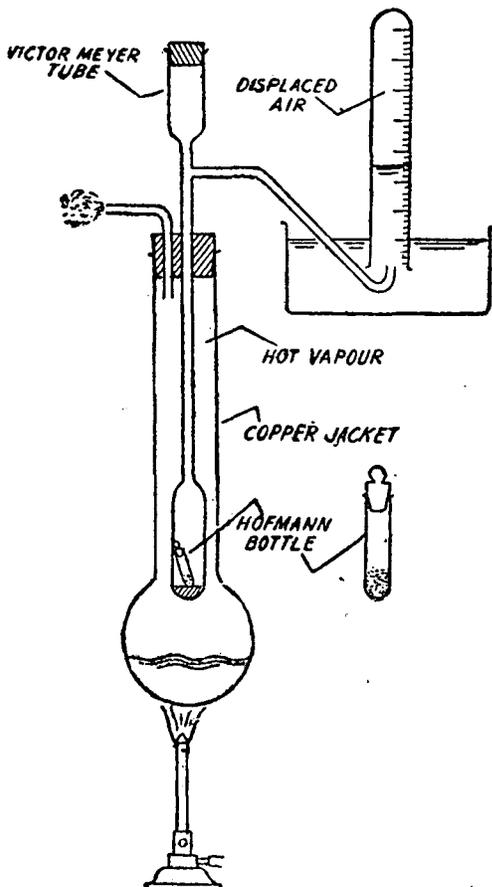


Fig. 4-2. Victor Meyer method for Mol. Wt. determination.

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 gm.) 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

S.T.P. and the weight of 22.4 litres of vapour calculated. This is numerically equal to the molecular weight of the substance.

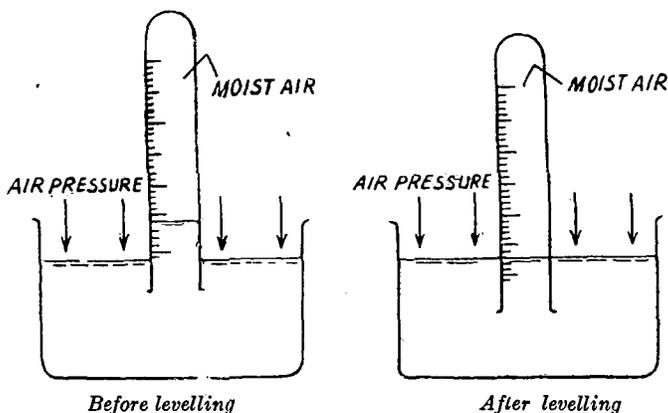


Fig. 4.3. After levelling the pressure of moist air collected is equal to the atmospheric pressure.

Example 1. In a Victor Meyer determination of molecular weight 0.1 gm. of the substance displaced 27 mls. 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, $V_{15} = 27$ mls.

Atmospheric temperature = 15°C or on absolute scale

$$T_{15} = 273 + 15 = 288^\circ$$

Pressure of dry air, $P_{15} = 745 - 12.7 = 732.3$ mm.

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

$$\begin{aligned} \text{Hence, volume of displaced air at N.T.P.} &= \frac{732.3 \times 27 \times 273}{288 \times 760} \\ &= 24.67 \text{ mls.} \end{aligned}$$

Thus the weight of 24.67 mls. of vapour of the substance = 0.1 gm.

$$\begin{aligned} \text{'' '' 22400 '' '' ''} &= \frac{0.1 \times 22400}{24.67} \\ &= 90.80 \text{ (mol. wt.)} \end{aligned}$$

Example 2. 0.22 gm. of a substance when vaporised by Victor Meyer's method displaced 45.0 mls. 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 N.T.P.

	<i>Initial Conditions</i>	<i>Final Conditions</i>
Volume	$(V_1) = 45$ mls.	Volume = V_2
Pressure	$(P_1) = 755 - 17.4$ = 737.6 mm.	Pressure = 760 mm.
Temperature	$(T_1) = 20 + 273$ = 293°A.	Temperature = 273°A

Applying the General Gas Equation

$$\frac{760 \times V_2}{273} = \frac{45 \times 737.6}{293}$$

$$\therefore V_2 = \frac{45 \times 737.6}{293} \times \frac{273}{760}$$

$$= 40.70 \text{ mls.}$$

(ii) CALCULATION OF M. WT.

Wt. of 40.7 mls. of vapours at N.T.P. = 0.22 gm.

\(\therefore\) Wt. of 22400 mls. of vapours at N.T.P.

$$= \frac{0.22}{40.7} \times 22400 = 121.1$$

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 substance is then calculated as described under Victor Meyer method.

CRYOSCOPIC METHOD OR FREEZING POINT METHOD

The molecular weight of a non-volatile 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.

$$m = \frac{100Kw}{\Delta T W}$$

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 100 grams of the solvent. Its value is usually given in ready-reference tables.

VALUES OF K FOR SOME SOLVENTS

Water	18.6°C	Acetic acid	38.2°C
Benzene	51.2°C	Phenol	73°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 0.01°C and a platinum stirrer; (ii) the *outer air-jacket* which surrounds 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.

In an actual determination 15.20 grams 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 gm.) 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 gram of an organic substance when dissolved in 2.5 grams of water lowered its freezing point by 0.19°C . Calculate the molecular weight of substance. (Molecular depression constant for water is 18.5).

Substituting the values in the expression

$$m = \frac{100Kw}{\Delta T W} = \frac{100 \times 18.5 \times 0.512}{0.19 \times 2.5} = 199.5$$

Example 2. 1.355 gms. of a substance dissolved in 55 gms. of acetic acid 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 gms.) is 38.5°C .

$$\begin{aligned} \text{Depression of freezing point} &= 0.618^{\circ} \\ \text{Weight of solute} &= 1.355 \text{ gms.} \\ \text{Weight of solvent} &= 55 \text{ gms.} \end{aligned}$$

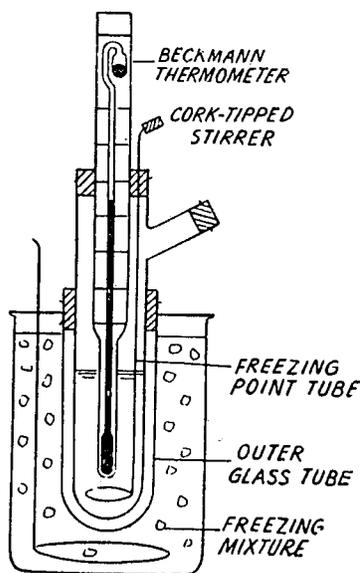


Fig. 4.4. Determination of depression of freezing point.

Substituting the values in the expression

$$m = \frac{100Kw}{\Delta TW} = \frac{100 \times 38.5 \times 1.355}{0.618 \times 55} = 153.5.$$

EBULLIOSCOPIC METHOD OR BOILING POINT METHOD

The molecular weight of a non-volatile 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.

$$m = \frac{100Kw}{\Delta TW}$$

m = Molecular weight of the dissolved compound,

K = Molecular elevation constant,

w = Weight of dissolved substance,

W = Weight of solvent,

T = 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-molecule of the solute in 100 grams of the solvent. Its value is generally given in ready-reference tables.

VALUES OF K FOR SOME SOLVENTS

Water	5.2°C	Benzene	26.7°C
Ethyl alcohol	11.5°C	Ether	21.0°C
Acetone	16.7°C	Acetic acid	25.3°C

Determination of Elevation of boiling point. The apparatus now commonly used for the determination of the elevation of

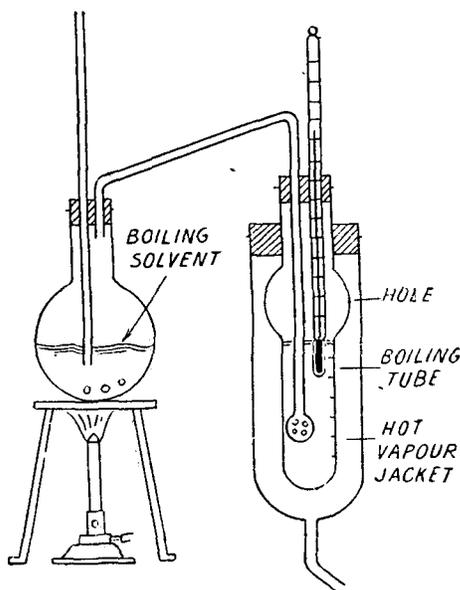


Fig. 4-5. Determination of elevation of boiling point by Landsberger's method.

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 mls. It is fitted with a thermometer reading up to 0.1°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 hole H. This forms a

protecting jacket round the boiling-tube and prevents the loss of heat due to radiation.

In an actual determination 5.7 mls. 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 gram) 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 gram 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 16.7°.*

$$\begin{aligned} \text{Elevation in boiling point} &= 56.88 - 56.38 \\ &= 0.50^\circ. \end{aligned}$$

Substituting the given values in the expression

$$m = \frac{100Kw}{\Delta TW}$$

we have

$$\begin{aligned} m &= \frac{100 \times 16.7 \times 0.717}{0.50 \times 10} \\ &= 239.4 \end{aligned}$$

Example 2. *A solution made by dissolving 1.5126 gms. of a substance in 21.01 gms. 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 gms. benzene is 25.70.

$$\text{Elevation of boiling point} = 1.05^\circ\text{C}$$

Substituting the given values in the expression

$$\begin{aligned} m &= \frac{100Kw}{\Delta TW} \\ &= \frac{100 \times 25.7 \times 1.5126}{1.05 \times 21.01} \\ &= 176.2. \end{aligned}$$

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 gm. 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 gms. and the weight of the residue of metallic silver be a gms.

The weight of silver salt that would leave 108 gms. (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 gm. of the silver salt of a dibasic organic acid was ignited, when a residue of 0.463 gm. of metallic silver was left. Calculate the molecular weight of the acid.

Weight of silver salt taken = 0.759 gm.

Weight of silver left as residue = 0.463 gm.

∴ The weight of silver salt that would leave 108 gms. of silver

$$= \frac{0.759}{0.463} \times 108 = 177.05$$

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

$$= 70.05 \times 2 \text{ (basicity)}$$

$$= 140.1.$$

Example 4. When heated cautiously in a crucible, 0.3652 gram of silver benzoate gave 0.1720 gram silver. Find the molecular weight of benzoic acid.

The weight of silver benzoate that would leave 108 gms. of silver

$$= \frac{0.3652}{0.1720} \times 108$$

$$= 229.2 \text{ gms.}$$

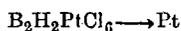
∴ Equivalent weight of benzoic acid

$$= 229.2 - 108 + 1 = 122.2$$

Since benzoic acid is a monobasic acid, its molecular weight
 $= 122 \cdot 2 \times 1 = 122 \cdot 2$

PLATINICHLORIDE METHOD FOR BASES

Most organic bases (amines) combine with hydrochloro-platinic 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.



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

Let x gms. be the weight of the platinichloride taken and a gms. 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 gms. of platinum will be left by 1 gm. molecular weight of the platinichloride.

But a gms. of platinum is left by x gms. platinichloride

$$\therefore 195 \text{ gms.} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{x}{a} \times 195 \text{ gms. ,,}$$

Hence Mol. Wt. of platinichloride

$$= \frac{x}{a} \times 195$$

(2) The equivalent weight of the base, B

$$\begin{aligned} &= \frac{B_2H_2PtCl_6 - H_2PtCl_6}{2} \\ &= \frac{\text{M.Wt. of platinichloride} - 410}{2} \\ &= \frac{\frac{x}{a} \times 195 - 410}{2} \end{aligned}$$

(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 gm. of the platinichloride of a monoacid base on ignition gave 0.209 gm. of platinum. Find the molecular weight of the base. ($Pt=195$).

(i) 0.209 gm. platinum is left by 0.6387 gm. of platinichloride

$$\therefore 195 \text{ gms.} \quad \text{,,} \quad \text{,,} \quad \text{,,} \quad \frac{0.6387}{0.209} \times 195 \text{ gms. ,,}$$

$$\text{Hence Mol. Wt. of the platinichloride} = \frac{0.6387}{0.209} \times 195 = 596.0$$

$$(i) \text{ Eq. Wt. of base} = \frac{\text{Mt. Wt. of platinichloride} - 410}{2}$$

$$= \frac{596 - 410}{2} = 93.0$$

$$(ii) \text{ Mol. Wt. of base} = \text{Eq. Wt.} \times \text{Acidity}$$

$$= 93.0 \times 1 = 93.0$$

Example 6. 0.98 gm. of the platinichloride of a diacid base left on ignition 0.3585 gm. of platinum. Find the molecular weight of the base.

(i) 0.3585 gm. Pt is left by 0.98 gm. platinichloride

$$195 \text{ gms.} \quad \text{,,} \quad \text{,,} \quad \frac{0.98}{0.3585} \times 195 \text{ gms.} \quad \text{,,}$$

$$\therefore \text{ M. Wt. of platinichloride} = \frac{0.98}{0.3585} \times 195 = 533$$

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

$$= \frac{533 - 410}{2} = \frac{123}{2}$$

$$(iii) \text{ M. Wt. of base} = \text{Eq. Wt.} \times \text{Acidity}$$

$$= \frac{123}{2} \times 2 = 123.$$

VOLUMETRIC METHOD FOR ACIDS AND BASES

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

Suppose V mls. of N/10 alkali neutralise x gms. acid

$$\therefore 1000 \text{ mls. ,, } 1N \quad \text{,,} \quad \text{,,} \quad \frac{x}{V} \times 1000 \times 10 \text{ gms. acid}$$

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

$$\text{the Eq. Wt. of acid} = \frac{x}{V} \times 1000 \times 10$$

$$\text{and Mol. Wt. of acid} = \text{Eq. Wt.} \times \text{Basicity.}$$

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 :

$$\text{Mol. Wt.} = \text{Eq. Wt.} \times \text{Acidity}$$

Example 7 0.183 gm. of an aromatic monobasic acid required 15 mls. of N/10 sodium hydroxide solution for exact neutralisation. Calculate the molecular weight of the acid.

15 mls. N/10 NaOH solution \equiv 0.183 gm. acid

$$1000 \text{ mls. } 1N \text{ NaOH solution} \equiv 0.183 \times \frac{1000}{15} \times 10 \text{ gms. acid.}$$

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

$$\therefore \text{ Eq. Wt. of acid} = 0.183 \times \frac{1000}{15} \times 10$$

$$= 122.$$

$$\begin{aligned} \text{Mol. Wt. of solid} &= \text{Eq. Wt.} \times \text{Basicity} \\ &= 122 \times 1 = 122. \end{aligned}$$

Example 8. 0.25 gm. of a dibasic organic acid were dissolved in water and the volume made to 100 mls. 10 mls. of this solution required 12.3 mls. of N/30 sodium hydroxide solution for complex neutralisation. Find the molecular weight of the acid.

$$\begin{aligned} 12.3 \text{ mls. N/30 NaOH solution} &\equiv 10 \text{ mls. of acid} \\ 123 \text{ mls. N/30 NaOH solution} &\equiv 100 \text{ mls. of acid} \\ &\equiv 0.25 \text{ gm. acid} \\ 1000 \text{ mls. 1 N NaOH solution} &\equiv \frac{0.25}{123} \times 1000 \times 30 \text{ gms.} \\ \therefore \text{Eq. Wt. of acid} &= \frac{0.25}{123} \times 1000 \times 30 = 61.0 \\ \text{Mol. Wt. of acid} &= \text{Eq. Wt.} \times \text{Basicity} \\ &= 60.96 \times 2 = 121.92. \end{aligned}$$

Example 9. 0.20 gm. of a diacid base required 25 mls. of N/8 HCl for exact neutralisation. What is the molecular weight of the base?

$$\begin{aligned} 25 \text{ mls. of N/8 HCl} &\equiv 0.20 \text{ gm. of the base} \\ 1000 \text{ mls. of N HCl} &\equiv \frac{0.20}{25} \times 1000 \times 8 \text{ gms. of base} \end{aligned}$$

But 1000 mls. of N HCl contain 1 gm. equivalent of acid and will neutralise 1 gm. equivalent of the base.

$$\begin{aligned} \therefore \text{Eq. Wt. of base} &= \frac{0.20}{25} \times 1000 \times 8 \\ &= 64 \\ \text{Mol. Wt. of base} &= \text{Eq. Wt.} \times \text{Acidity} \\ &= 64 \times 2 = 128. \end{aligned}$$

QUESTIONS

1. On analysis an organic compound was found to contain C=43.98%, Cl=37.18%, H=2.09%. Calculate the empirical formula. Given that the compound is a monobasic acid, write the molecular formula.
2. The organic liquids each containing 54.5 per cent carbon and 9.0 per cent hydrogen and having vapour density 44 gives different results on hydrolysis. One of them yields methyl alcohol and the other ethyl alcohol; while the saline residue in the former case on acidification yields propionic acid and in the latter acetic acid. Establish the identity of the two.
3. An organic substance A gave the following analysis: 0.123 gm. gave 0.284 gm. of carbon dioxide and 0.045 gm. of water.
0.1845 gm. of it gave 16.8 c.c. of nitrogen at N.T.P.
When it was treated with tin and hydrochloric acid it gave a substance B containing 77.41% carbon, 7.63% hydrogen and 15.05% nitrogen.
The substance B when diazotised and heated in presence of water gave a compound C which on distillation with zinc dust gave benzene.
Assign structural formulæ to A, B and C.
4. An organic compound contains 81.55 per cent carbon, 4.8 per cent hydrogen and 13.6 per cent nitrogen and has the vapour density 51.5. It evolves ammonia when heated with caustic potash and on reduction with sodium and

alcohol forms a base which reacts with nitrous acid giving off nitrogen and yielding alcohol. The alcohol can be oxidised to benzoic acid. What is the original substance and how is it prepared? Explain the above changes.

5. An aromatic dibasic acid gave the following results on analysis: —

(i) 0.219 gm. of the dibasic acid gave on combustion 0.528 gm. carbon dioxide and 0.081 gm. water.

(ii) 1.9 gms. of the silver salt of the dibasic acid gave 1.08 gms. of silver on ignition.

(iii) On nitration, the acid gave only one mono-nitro derivative. Assign structural formula to the acid and describe one method of preparing it.

(H=1; C=12; O=16; Ag=108).

6. An organic compound X gave the following results on analysis: C, 16.27%; H, 0.68%; O, 10.83% and Cl, 72.20%. It reduced Fehling's solution and the vapour density was found to be 73.8. On heating with alkali it gave a pleasant smelling liquid Y.

X could also be prepared by the action of chlorine on ethyl alcohol.

What is the nature of the compound X and what is the liquid Y?

7. An organic compound (A) has the molecular formula $C_7H_5NO_4$. Tin and HCl reduce it to a compound (B) having the formula $C_7H_7NO_2$. The compound (B) on boiling with $NaNO_2$ and HCl gives a compound (C) with molecular formula $C_7H_5O_3$. The compound (C) gives the following reactions:

(a) It is acidic and evolves CO_2 with $NaHCO_3$. (b) Ferric chloride gives a deep violet colour. (c) On heating with soda lime, it loses CO_2 and gives phenol.

Assign structures to A, B and C, and explain all the reactions.

(Agra B.Sc. II, 1967)

8. An organic compound (A) containing 76.6% C and 6.38% H, gave a mixture of two isomers (B) and (C); when an alkaline solution of (A) was refluxed with chloroform at 60°C. B, being steam volatile, was separated by steam distillation. B, on oxidation gave an acid (D) containing 60.87% C and 4.34% H. The (D) acid was also obtained by heating sodium salt of (A) with CO_2 at 120–140°C under pressure. Assign structures to A, B, C and D and explain the reaction involved.

(Banaras B.Sc. II, 1967)

9. An organic compound (A), containing 40% of C, 6.67% of hydrogen and vapour density 15, restored the colour of Schiff's reagent. On treatment with caustic potash, it gave an alcohol (B) that could be obtained by the reduction of (A) and an acid (C) which could be obtained by the oxidation of (A). What was the compound (A)? Explain these reactions.

(Gorakhpur B.Sc., 1967)

10. A neutral organic compound (X) contains C=65.3%, H=3.4% and N=9.5%. On heating with sodalime, it evolved ammonia but does not undergo diazotisation or react with acetyl chloride. On reaction with sodium hypobromite it gave an acid (Y) $C_7H_7O_2N$ which dissolves in acids as well as in alkalis. What are compounds (X) and (Y) and explain the reactions involved? Give one method for the preparation of the compound (X).

(Allahabad B.Sc. II, 1967)

11. An organic compound containing 58.53% carbon, 4.065% hydrogen and 11.39% nitrogen, gave on reduction a product which on subsequent acetylation formed acetamide. Assign the structural formulae to the compound and explain the reactions involved.

(Agra B.Sc. III, 1967)

12. (i) 0.2905 gm. of a solid organic acid on combustion gave 0.6160 gm. of CO_2 and 0.0945 gm. of H_2O . (ii) On heating with sodalime, its sodium salt gave benzene. (iii) It forms two series of salts and two series of esters and (iv) It furnishes an anhydride on simple heating. From the above facts about the acid, find out its structural formula and explain the reactions.

(Agra B.Sc. III, 1967)

13. An aromatic organic compound containing 58.53% of carbon, 4.07% of hydrogen, 11.39% of nitrogen and 26.01% of oxygen was found to have a molecular weight 123. On reduction it gave a monoacid organic base. What structural formula would you assign to it ?
(Indore B.Sc. III, 1967)

14. An organic compound A on analysis was found to contain C=16.271%, H=0.677% and Cl=72.203%. It reduced Fehling's solution and on oxidation gave a monocarboxylic acid B having C=14.679, H=0.612 and Cl=65.137. On distillation with sodalime, B gave a sweet smelling liquid C containing 89.12% chlorine and which can also be obtained by heating A with alkali. What structural formulae would you assign to A, B and C? Explain the above reactions.
(Udaipur B.Sc., 1968)

15. An aromatic substance A contains 77.8% carbon and 7.4% hydrogen and forms an ester 'B' with acetyl chloride. 'A' on treatment with phosphorus pentachloride gives a product 'C' containing 28.0% chlorine. On oxidation with nitric acid 'A' gives a monocarboxylic acid 'D'. Explain the above reactions and suggest suitable structures for A, B, C and D.
(Osmania B.Sc., 1960)

16. A compound, $C_6H_{12}O$ (A), reacted with hydroxylamine but not with Fehling's solution. On catalytic hydrogenation A gave $C_6H_{14}O$ (B). The compound B when passed over hot alumina, yielded C_6H_{12} (C). The compound C on ozonolysis furnished two compounds. One of which gave a negative Tollen's test and a positive Iodoform test. The other gave a positive Tollen's test and a negative Iodoform reaction. Suggest structures for the compounds A, B and C.
(Jadavpur B.Sc., 1968)

17. A compound on analysis, is found to possess the following percentage composition :

$$C=66.4, \quad H=5.53 \quad \text{and} \quad Cl=28.06$$

When the compound is oxidised with potassium permanganate an acid is obtained which contains 68.8% carbon and 4.9% hydrogen. In another experiment when the compound is treated with sodium hydroxide a new compound is produced which contains 77.8% carbon and 7.4% hydrogen.

Explain these reactions and determine the structural formula of the compound.
(Ujjain B.Sc., 1968)

18. 0.106 gm. of an aromatic hydrocarbon of mol. wt. 106 gave on combustion 0.352 gm. CO_2 and 0.090 gm. H_2O . Calculate the molecular formula and write all the possible structures. Discuss how you would distinguish between them.
(Kurukshetra B.Sc., 1968)

19. An organic compound containing 65.45 per cent of carbon, 9.09 per cent of hydrogen and the rest nitrogen was found to have vapour density 27.5. On boiling with dilute sulphuric acid it gave a monobasic organic acid which on distillation with soda lime gave ethane. But on treatment with tin and hydrochloric acid it gave a monoacid base which gave propyl alcohol with nitrous acid. What is the formula of the compound? Explain these reactions.

20. How is chlorine in an organic compound detected and estimated?

Two different volatile substances gave the following identical results on analysis C=52.2%, H=13.0% and the rest is oxygen. The vapour density of both the compounds was the same and found to be 23. Assign the structural formulae to the two substances and describe the action of boiling HI on each of them.
(Bangalore B.Sc., 1969)

21. How is nitrogen detected in an organic compound? 2.0 gm. of an organic compound containing C, H and O gave on combustion 2.93 gm. of CO_2 and 1.2 gm. of water? Its molecular weight is 180. What is its molecular formula?
(Bangalore B.Sc., 1969)

22. A hydrocarbon (A) of formula $C_{15}H_{14}$ takes up readily one mole of hydrogen or one mole of Bromine. Oxidation converts it into benzoic acid and other acid (B) of molecular formula $C_8H_8O_2$. More vigorous oxidation of hydrocarbon (A) gives benzoic acid and phthalic acid. What is the structure of hydrocarbon (A) and the acid (B)? Write their names.
(Udaipur B.Sc., 1969)

23. The organic compounds A and B contain C=40% and hydrogen=6.66%. The vapour density of A was 15 and that of B was 30. A reduced

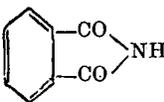
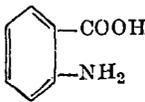
Fehling's solution but did not react with sodium carbonate, while B did not reduce Fehling solution but produced effervescence with sodium carbonate. Deduce the structural formulae of A and B and explain the above reactions. (Udaipur B.Sc., 1969)

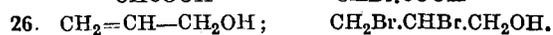
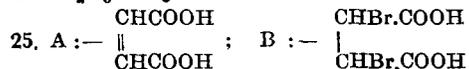
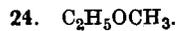
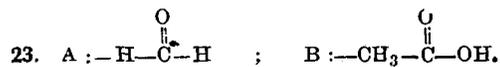
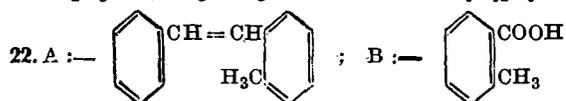
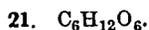
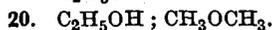
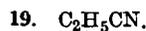
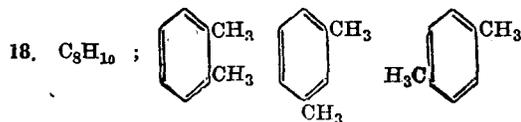
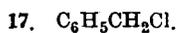
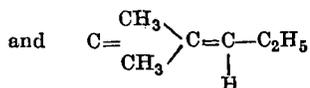
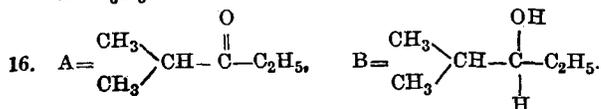
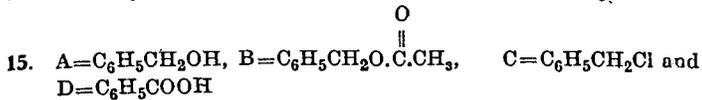
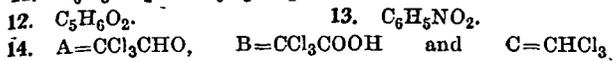
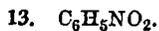
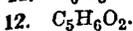
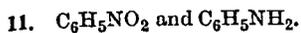
24. An organic compound gave the following results on analysis. 0.2115 gm. on combustion gave 0.4655 gm. CO_2 and 0.2533 gm. water. The vapour density of the substance was 29.7. When treated with potassium dichromate and dilute H_2SO_4 it produced a substance which gave the Iodoform test. What was the original compound. (Panjab B.Sc., 1969)

25. A dibasic organic acid (A) contains C=41.38% and H=3.45%. It reacts with bromine and gives a bromoacid (B) containing Bromine=57.9%. Suggest structural formulae for the acids (A) and (B). (Kurukshestra B.Sc., 1969)

26. A primary alcohol with a vapour density 29 contained C=62.17%, H=10.3% and reacted with bromine to give a derivative which contained carbon=16.5, H=2.7 and Br=73.4%. Determine the structural formula of the compound and its derivative. (Meerut B.Sc., 1969)

ANSWERS

- $\text{C}_6\text{H}_3\text{Cl}_2\text{COOH}$.
- $\text{C}_2\text{H}_5\text{COOCH}_3$, methyl propionate ;
 $\text{CH}_3\text{COOC}_2\text{H}_5$, ethyl acetate.
- A = $\text{C}_6\text{H}_5\text{NO}_2$, B = $\text{C}_6\text{H}_5\text{NH}_2$, C = $\text{C}_6\text{H}_5\text{OH}$.
- $\text{C}_6\text{H}_5\text{CN}$.
- C_6H_4
 $\begin{cases} \text{COOH} \\ \text{COOH} \end{cases}$ Phthalic acid
- (A) $\text{C}_6\text{H}_5\text{CH}_3$; (B) C_6H_4
 $\begin{cases} \text{CH}_3 \\ \text{Cl} \end{cases}$ ortho; (C) C_6H_4
 $\begin{cases} \text{CH}_3 \\ \text{Cl} \end{cases}$ meta;
(D) C_6H_4
 $\begin{cases} \text{CH}_3 \\ \text{Cl} \end{cases}$ para.
- $\text{C}_3\text{H}_5\text{N}$; $\text{C}_3\text{H}_6\text{O}_2$.
- $\text{HOOCCH}=\text{CHCOOH}$;
A = maleic acid and
B = fumaric acid.
- $\text{C}_6\text{H}_4(\text{CH}_3)\text{COOH}$ ortho-toluic acid.
- (A) HCHO ; (B) CH_3COOH .
- $\text{C}_2\text{H}_5\text{COOH}$.
- (A) CCl_3CHO ; (B) CCl_3COOH ; CCl_3H .
- $\text{C}_3\text{H}_5\text{COONH}_4$.
- $\text{C}_3\text{H}_6\text{O}$.
- A = C_8H_6 ; B = $\text{C}_7\text{H}_6\text{O}_2$; C = $\text{C}_8\text{H}_6\text{Cl}_2$
- $\text{CH}_3\text{CH}_2\text{CONH}_2$.
- $\text{C}_6\text{H}_4(\text{CH}_3)_2$.
- $\text{C}_2\text{H}_4\text{Cl}_2$.
- CH_3CONH_2 .
- (A) $\text{C}_6\text{H}_4(\text{COOH})_2$ Phthalic acid ;
(B) $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ Phthalic anhydride ;
(C) $\text{C}_6\text{H}_4(\text{CO})_2\text{NH}$ Phthalimide ;
(D) $\text{C}_6\text{H}_4(\text{NH}_2)\text{COONa}$ sod. o-aminobenzoate.
- 93.07 ; aniline.
- $\text{CH}_3\text{CH}_2\text{NH}_2$.
- (A) $\text{C}_6\text{H}_4(\text{NO}_2)\text{COOH}$; (B) $\text{C}_6\text{H}_4(\text{NH}_2)\text{COOH}$;
(C) $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$.
- (A) $\text{C}_6\text{H}_5\text{OH}$; (B) $\text{C}_6\text{H}_4(\text{OH})\text{CHO}$, ortho ;
(C) $\text{C}_6\text{H}_4(\text{OH})\text{CHO}$, para ; (D) $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$, ortho ;
- (A) HCHO ; (B) CH_3OH ; (C) HCOOH .
- (x)  ; (y) 



5

Structure of Organic Molecules. Classical Concept



Joseph A. Le Bel

ATOMIC STRUCTURE AND VALENCY

The views on the atomic structure which are accepted today have developed from the classical Rutherford Bohr Theory. According to this theory, the atom is made 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 one unit negative charge and negligible weight. The number of protons and electrons in an atom being equal, it is electrically neutral.

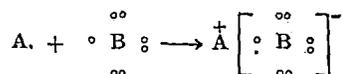
The extra nuclear electrons are said to revolve round the nucleus in fixed orbits or 'energy levels'. While the electron moves in such a level, it possesses a definite quantity of energy and it neither emits nor absorbs energy. The electrons are arranged in the outer orbits so that the maximum number of electrons in the various orbits starting from the first one is 2, 8, 18, 32, 18, 8. The outermost orbit of electrons in different atoms (except those of inert gases) is incomplete and the electrons in it are known as **valency electrons**.

HOW ATOMS JOIN TO FORM MOLECULES ?

The classical concept of formation of molecules, proposed by **Lewis and Kossel**, is based upon the electronic structure of atoms. 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. G.N. Lewis proposed that *it is the urge of atoms to complete their outermost orbits of electrons as in the inert gases, which is responsible for chemical combination*. In other words, chemical union between two atoms results from the redistribution of electrons between them so that both the atoms complete their last orbits or acquire stable configuration possessed by the inert gases. The chemical linkages are of three types :

- (i) *Electrovalent Linkage ;*
- (ii) *Covalent Linkage , and*
- (iii) *Co-ordinate Linkage.*

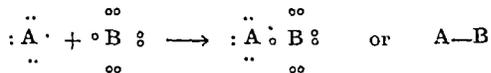
Electrovalent Linkage. The type of linkage unites two atoms one of which has excess electrons than the stable number (2 or 8), and the other is short of electrons. Thus :



Here, the atom A transfers its excess electron to B, and thus both complete their last orbit of electrons. The atoms A and B become positive and negative respectively, and are thus bound by electrostatic lines of force. This type of linkage occurs commonly in inorganic compounds.

Electrovalent compounds are non-volatile, soluble in water and possess high melting points. Their aqueous solutions conduct electric current.

Covalent Linkage. This type of linkage binds two atoms, both of which are short of electrons. The two atoms contribute one electron each and then share the resulting pair of electrons.

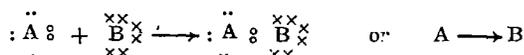


This linkage, signified by a single line, is termed **Covalent Linkage** (*Co-joint*). It is commonly found in organic compounds.

Covalent compounds are volatile, generally insoluble in water but soluble in organic solvents, and possess low melting and boiling points. Their solutions do not conduct electric current.

Co-ordinate Linkage. A co-ordinate linkage connects two atoms, one of which has a spare pair of electrons and the other is short of a pair of electrons. The first atom (*donor atom*) contributes

its pair (*lone pair*) of electrons and the second atom (*acceptor atom*) accepts.



After the formation of the linkage, the lone pair of electrons is held in common and fills the last orbit of A as well as B. The linkage is represented by an arrow, pointing away from the donor atom.

Co-ordinate compounds resemble covalent compounds in respect of their physical properties.

VALENCY OF CARBON ATOM

The atomic number of carbon is 6 and its atomic weight 12. Its electronic structure can be represented as shown in Fig. 5-1. It has four electrons in the last orbit and tends to gain four more electrons by forming four covalent bonds with other H atoms. Thus, the structural formula of the simplest hydrocarbon methane (CH_4) can be written as :

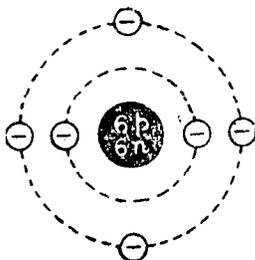
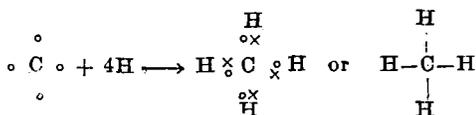


Fig. 5-1. Atomic structure of carbon.



Similarly in all organic molecules carbon atom is tetra-covalent.

According to Le Bel and van't Hoff, the four valencies of the carbon atom are not lying in one plane but instead these are sym-

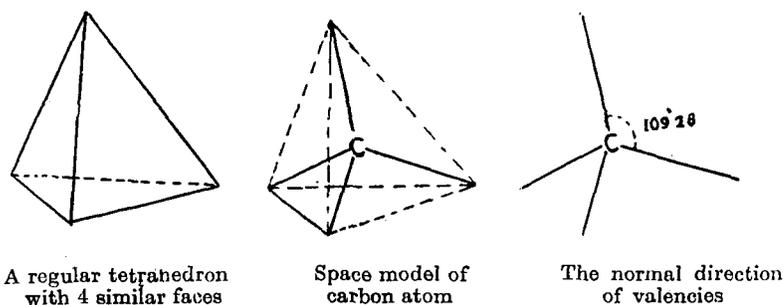


Fig. 5-2.

metrically distributed in space so that the angle contained between any two valency bonds is $109^\circ 28'$.

It will be instructive for the student to construct model of a tetrahedron from a sheet of paper as follows :

Cut out the paper along the solid lines around the edges. Then fold the other solid lines over a foot-rule, and glue the faces of the tetrahedron together with the aid of the three glue flaps. If the centre of this tetrahedron is taken to represent a carbon atom, the vertices will show the direction of the four valencies.

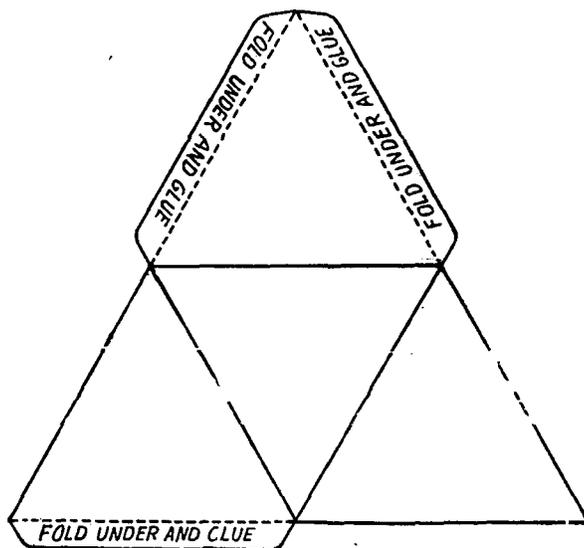
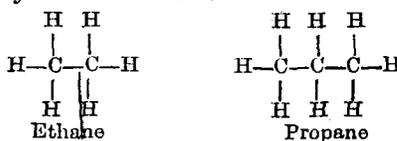


Fig. 5.3. How to make a paper tetrahedron.

SINGLE CARBON-TO-CARBON BOND

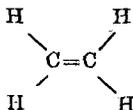
A carbon atom has the wonderful instinct of uniting with other carbon atoms through covalent bonds. This serves to construct the carbon structure of organic molecules. Thus the molecules of hydrocarbons, ethane and propane contain two and three carbon atoms respectively linked by covalent bonds.



Single carbon-to-carbon bond is usually strong and is not easily broken during chemical changes.

DOUBLE BOND OR ETHYLENIC LINKAGE

In certain compounds, two of the valencies of a carbon atom may be satisfied by union with the two valencies of another carbon atom. Thus in ethylene molecule the two carbon atoms are linked by two covalent bonds.



Such a union involving two covalent bonds between the adjacent carbon atoms is spoken of as **Double Bond** or *Ethylenic Linkage*, since it occurs in ethylene molecule. The two valency bonds of each of the carbon atoms while they join to form a double bond have been much distorted from their normal direction and are consequently under strain. Therefore, a **double bond is weak** and is easily ruptured by oxidation, or is reduced to a stable single bond during chemical reaction.

TRIPLE BOND OR ACETYLENIC LINKAGE

Sometimes, two adjacent carbon atoms are linked together by three covalent bonds. Thus, acetylene molecule is represented as

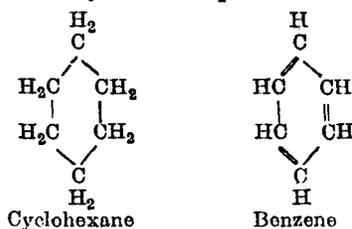


Such a linkage involving triple union between adjacent carbon atoms is called a **Triple Bond** or *Acetylenic Linkage* as it occurs in acetylene molecule.

Like a double bond, a triple bond also signifies a great strain in the molecule. In fact, *a triple bond is weaker than even the double bond*. It is readily ruptured by oxidation, or reduced to a double bond and then to a single bond during chemical reactions.

RING STRUCTURES

We have given above some examples of substances where the molecules consist of carbon atoms joined together in chains that are free at both ends. There are also numerous compounds known where carbon atoms join to form closed rings. These are termed **Ring Compounds** or **Cyclic Compounds**. Thus we have :

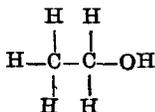


STRUCTURAL FORMULA

We have seen that a *molecular formula* states the number and kind of atoms in the molecule. Thus ethyl alcohol has molecular formula $\text{C}_2\text{H}_6\text{O}$ which implies that a molecule of the compound is made of two carbon atoms, six hydrogen atoms and one oxygen atom. A molecular formula remains silent as to how these atoms of various elements are joined in the molecule.

*A formula showing a complete picture as to how the various atoms are linked to each other in the molecule, is known as a **Structural formula**.*

For example ethyl alcohol having molecular formula $\text{C}_2\text{H}_6\text{O}$ has structural formula



Thus a structural formula shows clearly as to which atom is bonded to which atom in the molecule. It may be recalled here that the valency bonds of carbon atoms are distributed symmetrically in space. Therefore, a structural formula written in the plane of the paper is not an exact picture of the molecular structure.

A model of the molecule is often useful to facilitate our thinking about the structure of a molecule. One simple kind of a model to represent structure of a molecule consists of coloured balls and sticks or pegs of metal wire. This is called **ball-and-stick model** or **ball-and-peg model**. The following model of methane (CH_4) shows that it has a three dimensional structure.

The model shows the exact angle between the bonds. Hence models are very helpful in telling us as to how the various atoms of the molecule are arranged in space.

It is true that the beginning student finds it useful to construct models of organic compounds. In this way he can visualise their shapes better. But it is inconvenient to draw a three dimensional sketch each time. Since we must write on a 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 following models of methylene chloride (CH_2Cl_2). We should not forget despite the appearance of the projection formulae that the carbon bond angles are not 90° and the molecules are not flat. Or, that the formulae really do not represent the models.

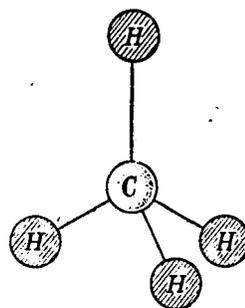


Fig. 5-4. Model of methane.

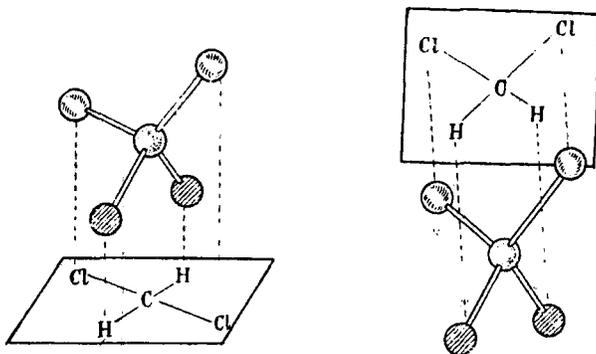


Fig. 5-5. Projections of CH_2Cl_2 molecular models give formulae on the plane paper.

We have discussed above the ball-and-stick models of organic substances. These models consist of coloured wooden 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 bond angles, the size of individual atoms is ignored. This defect has been overcome in the **Stuart models**.

In these models the ball 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.

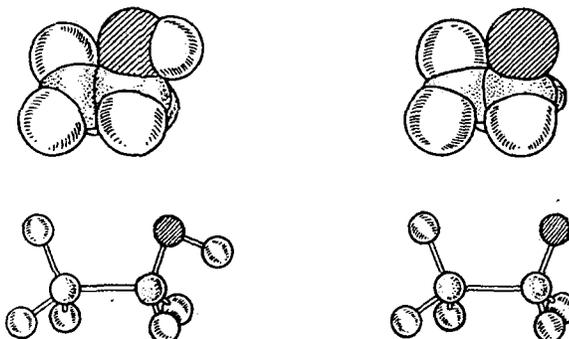


Fig. 5-6. Stuart and ball-and-stick models of ethyl alcohol and chloroethane.

In the space-filling or Stuart models, the spheres representing atoms in the molecule are designed so as to indicate sharing of electron clouds.

Writing structural formulae. We have seen that real molecules are three dimensional as shown by the models. Usually the chemists write formulae in the plane of the paper and indicate the angles between valencies of carbon atoms as right angles. This is only for convenience, otherwise valency bonds of carbon lie in a zig-zag way.

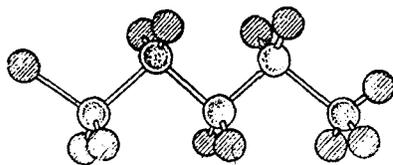
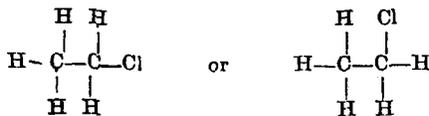


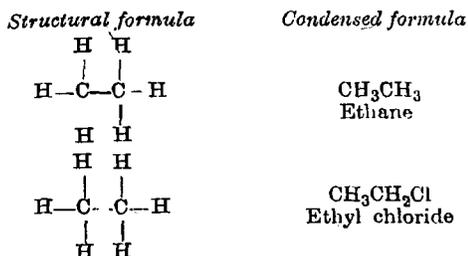
Fig. 5-7. Valency bonds of carbon atoms in pentane lie in a zig-zag way.

Thus the structural formulae written on paper simply indicate the order in which the various atoms are joined and do not give any idea of their disposition in space. In other words, they only depict the structural representation of a molecule and the valency bonds may be put in any direction. Thus ethyl 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. For this reason chemists often write what we call 'condensed structural formulae'. These can be written more rapidly and in less space.

In a condensed formula all atoms linked to a given carbon atom are given after the 'C' and in the same line but their bonds are not shown.



It may be noted that atoms other than hydrogen are written after the hydrogen atom in the condensed structural formulae.

Skeletal formulae. Sometime skeletal formulae are used for brevity or to make the differences in the carbon chains more apparent. A skeletal formula shows all atoms in a molecule except hydrogen. Thus skeletal formula of ethane and propane would be



It is assumed that all the remaining valencies of carbon atom are filled by hydrogen atoms. The skeletal formulae of the two butanes may be written as



BOND LENGTHS

When two atoms are linked by a covalent bond, the distance between the centre of the two atomic nuclei is called the **Bond Length**. There are several methods available for the measurement of bond lengths (or bond distances) which include X-ray diffraction, electron diffraction and molecular spectroscopy but the description of these belongs to Physical Chemistry. The concept of bond lengths and their measurement is of considerable interest in Organic Chemistry. The unit length here is an Angstrom (symbol Å) which is equal to 10^{-8} cm.

Bond lengths of certain pairs of atoms involved in organic molecules are given in the table below :

BOND	BOND LENGTH (Å)	BOND	BOND LENGTH Å
C—H (Alkanes)	1.07	C—Br (Bromoalkane)	1.94
N—H (Amines)	1.00	C—I (Iodoalkane)	2.14
O—H (Alcohols)	0.96	C=C (Alkenes)	1.35
C—C (Alkanes)	1.54	C=O (Ketones)	1.22
C—N (Amines)	1.47	C≡C (Alkynes)	1.20
C—O (Alcohols)	1.48	C≡N (Nitriles)	1.16
C—Cl (Chloroalkanes)	1.76	C=C (Benzene)	1.39

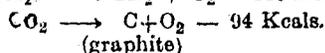
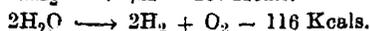
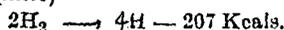
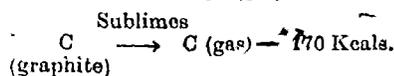
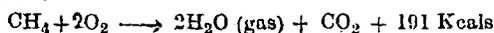
BOND ENERGIES

The bond C—H, or any other chemical bond is characterised by a **bond energy** which is the energy needed to break that bond in any compound in which it exists. The value of bond energy can be calculated from the bond spectrum of the molecule concerned.

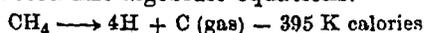
For molecules containing three or more atoms, *i.e.*, two or more bonds, the heat of formation of the molecule from the atoms can be regarded as the sum of all the bond energies. Thus the heat of formation of the water molecule from hydrogen and oxygen atoms is twice the bond energy of O—H bond. This can be easily calculated from the heat of formation of steam (from molecular hydrogen and oxygen) and the known dissociation energies of the O₂ and H₂ molecules by application of Hess's law of Constant Heat Summation (*see a Text-book of Physical Chemistry*).

The bond energies of C—H, C—C, C=C and C≡C bonds can be calculated in a similar manner, using known heats of combustion of hydrocarbons and the heats of combustion of carbon and hydrogen.

Example. Find the bond energy of the C—H bond from the following data :



Solution. By Hess's law, thermochemical equations can be added and subtracted like algebraic equations.



This naturally involves the breaking of four C—H bonds.

∴ The average value for the C—H bond energy is 99 Kilo-calories.

A list of bond energies of important bonds is given below :

BOND	BOND ENERGY (KCAL/MOLE)	BOND	BOND ENERGY (KCAL/MOLE)
C—H	98.7	C—C	82.6
C—Cl	80.0	C=C	145.8
C—Br	69.0	C≡C	199.6
C—I	55.0	C—O	85.0
		C=O	178.0
		O—H	110.6

Bond energies provide a very useful indication of the strengths of the various chemical bonds. The bond energies of carbon-to-carbon single, double and triple bonds show that the order of their strength is $—>=>≡$.

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 examination 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 7.5×10^{-5} cm. to 4×10^{-5} cm., a monochromatic source gives a single wavelength component.

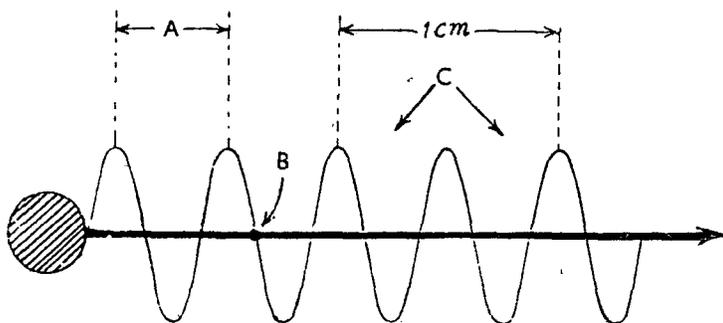


Fig. 5.8.

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 7.5×10^{-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} cm.) than the visible light.

RADIATION	WAVELENGTH (cm)	WAVE NUMBER (cm^{-1})	ENERGY (ergs)
1. Infrared	3×10^{-2} to 7×10^{-5}	33 to 1.4×10^4	66 to 2.8×10^{-12}
2. Visible	7.5×10^{-5} to 4×10^{-5}	1.0×10^4 to 2.5×10^4	2.7×10^{-12} to 5×10^{-12}
3. Ultraviolet	4×10^{-5} to 10^{-5}	2.5×10^4 to 10^5	5×10^{-12} to 2.8×10^{-12}

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. 5-9.

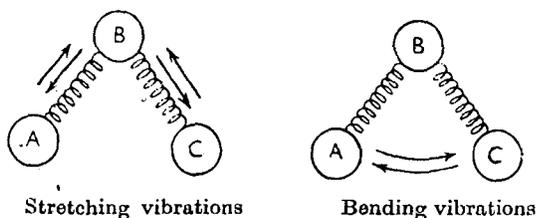


Fig. 5-9. Vibratory motion in a molecule.

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.

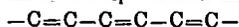
Ultraviolet and visible absorption spectra. It is one of the earliest physical methods of elucidating the structure of organic molecules. Absorption of visible and ultraviolet light produces changes in the energy of electrons, in atoms of the molecule from a stable to an unstable orbital. The significant 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 2.17×10^{-5} cm while β carotene (having 11 conjugated double bonds) absorbs strongly at 4.5×10^{-5} cm. The following table bears out the statement that value of λ_{max} increases with increased conjugation.

COMPOUND	$\lambda_{max} \times 10^{-5}$ 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.

*A conjugated system of multiple bonds may be as



—the one which contains (here) a double bond and single bond alternately in the carbon chain.

Infrared spectra. Unlike the situation obtaining in visible and ultraviolet absorption spectra, all organic molecules absorb light in the infra-red 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 (I.R.) absorption spectra. Just as fingerprints are taken as a characteristic of identity of every individual, the bands in I.R. spectra are also characteristic of a compound. In other words, the bands in the spectra of a molecule can be regarded as its 'molecular fingerprints' leading to its recognition.

The I.R. spectra 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 I.R. spectra are compared with I.R. spectra 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.

A particular functional group gives rise to characteristic absorption bands in the infrared spectra. In other words a particular group strongly absorbs light of certain wavelength no matter to which compound it belongs to. From example a carbonyl group ($>C=O$) strongly absorbs the radiation in the region 6×10^{-4} cm. while a carbon hydrogen bond absorbs near 3.4×10^{-4} cm. The maximum absorption bands in the accompanying plot of I.R. spectrum of acetone show absorptions at 5.9×10^{-4} cm. and 3.45×10^{-4} cm. indicating the presence of a carbonyl group and carbon hydrogen bonds of the methyl group.

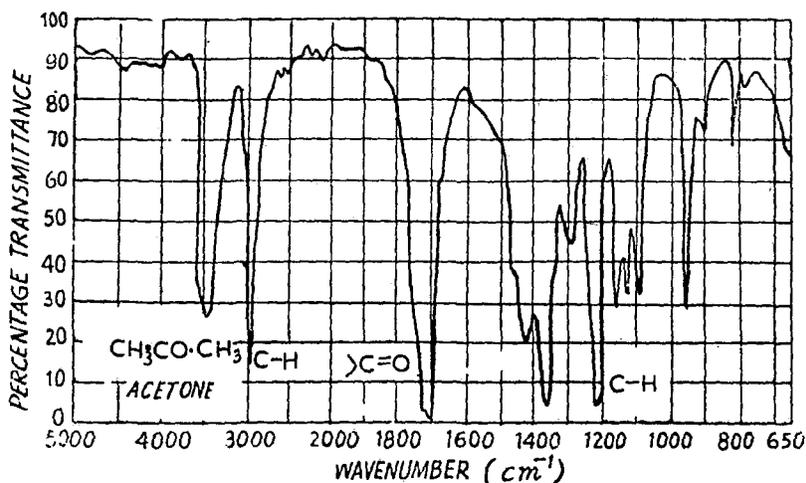


Fig. 5-10. Infrared spectrum of acetone.

Sufficient information can be derived from I.R. 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 mgms.) which too can be recovered unchanged after the required measurements have been made.

TABLE : Some Characteristic Infrared Absorption Frequencies

BOND	TYPE OF COMPOUND	WAVELENGTH cm^{-1}
$\begin{array}{c} \\ -C-H \\ \end{array}$	Alkanes	2850 - 2960
$\begin{array}{c} \\ =C-H \\ \end{array}$	Alkenes	3010 - 3100
$\equiv C-H$	Alkynes	3300
$\begin{array}{c} \quad \\ -C-C- \\ \quad \end{array}$	Alkanes	600 - 1500
$\begin{array}{c} \diagup \quad \diagdown \\ C=C \\ \diagdown \quad \diagup \end{array}$	Alkenes	1620 - 1680
$-C \equiv C-$	Alkynes	2100 - 2260
$\begin{array}{c} \diagup \\ C=O \end{array}$	Aldehydes	1720 - 1740
$\begin{array}{c} \diagdown \\ C=O \end{array}$	Ketones	1705 - 1725
$\begin{array}{c} \diagup \\ C=O \end{array}$	Acids	1700 - 1750
$-OH$	Alcohols	3590 - 3650
$-NH_2$	Amines	3300 - 3500

QUESTIONS

1. How do you explain the urge of the atoms for chemical union? Name the three types of linkages and give examples to illustrate their mode of formation between atoms.
2. Write the structure of carbon atom and show that carbon is tetra-valent in organic molecules.
3. What is meant by covalent and electrovalent linkages, and which of these linkages generally occur in organic compounds? Give the electronic formula of methane.
4. On what conception regarding the structure of carbon atom, is the graphic formula of an organic compound based? Point out its limitations. Describe the electronic structure of a carbon atom and write down the electronic formulae of the following :

Methane, Ethane, Chloroform and Carbon tetrachloride.

5. Write notes on : Single carbon-to-carbon linkage, double bond, triple bond. How is it that a single bond is the strongest of all ?

6. What do you understand by the structural formula of a compound ? Mention its significance.

7. (a) Explain the terms 'electrovalency' and 'covalency'.

(b) Discuss the following statement :

'The existence of the organic compounds is consequent on the tendency of carbon atoms to form covalent linkages with one another and with atoms of other elements.'

Illustrate your answer by referring to simple organic substances.

8. What do you understand by the expression 'Tetra-covalency of Carbon' ? Explain the significance of a 'single bond', 'double bond' and a 'triple bond'. Arrange them in the order of their strengths giving reasons for your answer. Give at least one example of the substances containing (i) 'single' bonds only, (ii) at least one 'double' bond and (iii) at least one 'triple' bond.

9. How will you make a paper tetrahedron? Also construct ball-and-peg model of methane.

10. Define a structural formula. Write structural formulae of propane, ethyl alcohol and dichloroethane.

11. How ball-and-stick models are helpful in understanding the structure of organic molecules. What are the limitations of such models and in what way Stuart models are an improvement over ball-and-stick models.

12. How do you write the structural formulae of organic compounds in the plane of the paper ?

13. What is a 'Condensed structural formula' and a 'Skeletal formula' ? Give examples and say why these are commonly used in organic chemistry ?

14. What do you understand by absorption spectra of organic compound? How is infrared spectrum utilized for ascertaining the structure of an organic compound ?

15. Write an essay on spectroscopy of organic compounds.

16. How is infrared spectrum caused ? What changes are brought about as a result of absorption of infrared radiations ?

6

Structure of Organic Molecules. Modern Concepts



Niels Bohr

The classical theory given by Lewis and Kossel proved very profitable in interpreting the nature of chemical bonds. The electronic formulas of organic compounds explained in a satisfactory way the reactions and behaviour of a large number of them.

The orbital theory of chemical bonding based on the modern concepts of atomic structure is more sound and has stood the test of time. It has proved to be much more useful in interpreting and predicting the behaviour of most of the organic compounds. These concepts undoubtedly have their origin in the wave-mechanical treatment of atoms and molecules; it would be perfectly alright for the present to dispense with any mathematical treatment, and to discuss the theory in a general way.

THE STRUCTURE OF ATOMS

The views on atomic structure which are accepted today have developed from the classical Rutherford-Bohr theory. Thus an atom is made of a positively charged nucleus surrounded by one or more electrons. The stability of such an atom is due to the electrostatic attraction between the positive nucleus and the negative electrons.

The nucleus of an atom consists of protons and neutrons. A *proton* carries one positive charge and has unit mass, while a *neutron* has the same mass but carries no charge. Thus the positive charge of the nucleus of an atom is equal to the number of protons present in the nucleus and is called its **Atomic Number**. An electron carries a unit negative charge and has negligible mass. Since atom is electrically neutral, the atomic number of an atom is also equal to the number of extra-nuclear electrons.

Let us consider the simplest atom, hydrogen. It consists of the nucleus made of one proton and a single outer electron. Next comes helium with atomic number two and, therefore, having two outer electrons. Carbon, the most important element in organic chemistry, has the atomic number of six, and hence possesses six extra-nuclear electrons.

Although nearly the entire mass of the atom is concentrated in the nucleus, the formation of chemical bonds is concerned with extra-

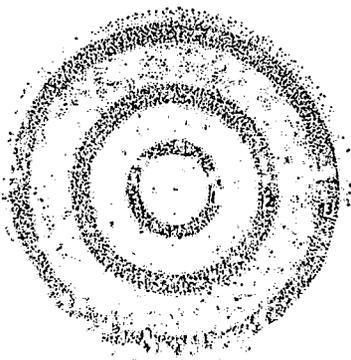


Fig. 6.1. How shells would appear if probability of finding electrons is represented by shading.

nuclear electrons only. According to the theory of quantum mechanics, the electron is executing a back and forth motion about the nucleus rather than moving around it 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 and thus offers the appearance of a spherical *cloud*. While the extra-nuclear electrons are free to move about in the cloud, on mathematical calculations it has been noted that they have a greater tendency to align themselves in concentric spherical **shells** placed one above the other around the nucleus, thus giving a structure something like that of an onion. Since the electron when present in a certain shell is associated with a definite amount of energy, the shells are also termed **Energy levels**. Starting from the shell or energy level nearest the nucleus, these are designated as 1, 2, 3, 4, 5, 6, 7. The maximum number of electrons which the various shells can hold is 2, 8, 18, 32, 18, 8 respectively. The increasing number of shells or energy levels implies higher energy of the electrons present in these.

The electrons present in each principal shell or energy level are divided into **subshells** or **sublevels**, as many as the number of the shell. The four subshells are denoted by the letters *s*, *p*, *d* and *f* whose energies increase in the order named. Thus the first shell

nuclear electrons only. According to the theory of quantum mechanics, the electron is executing a back and forth motion about the nucleus rather than moving around it 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 and thus offers the appearance of a spherical *cloud*. While the extra-nuclear electrons are free to move about in the cloud, on mathematical calculations it has been noted that they have a greater tendency to align themselves in concentric spherical **shells** placed one above

has single subshell designated as $1s$; the second shell has two subshells designated as $2s$ and $2p$, the third shell has three subshells designated as $3s$, $3p$, $3d$ and the fourth shell has four subshells— $4s$, $4p$, $4d$ and $4f$.

The subshells are further divided into smaller units called the **orbitals** which the electrons occupy. An s subshell is made of one orbital, a p subshell, three orbitals; a d subshell, 5 orbitals; and f subshell, 7 orbitals. Since each orbital can hold two electrons, the maximum number of electrons in the subshells s , p , d and f is 2, 6, 10 and 14 respectively. Some time the principal shell numbers are also designated by the letters K, L, M, N etc. but the numbers are used in preference. The following diagram (Fig. 6.2) depicts beautifully the concept of shells, subshells, as also the maximum number of electrons which could fill these.

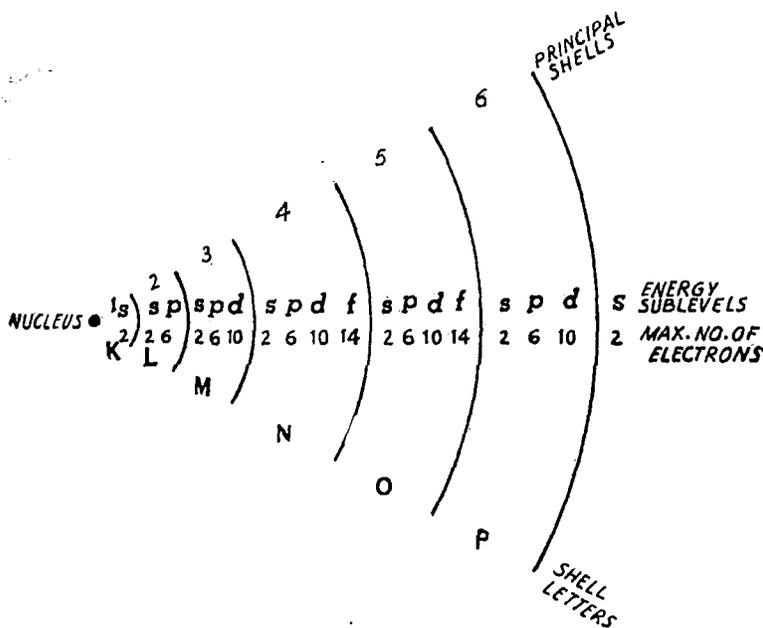


Fig. 6.2. Electron shells of an atom, indicating the number of electrons that can be accommodated in various energy levels.

The maximum number of electrons which occupy the various shells is also being given in the table below. It may be noted that in case of subshells, the number in front indicates the principal shell number and the superscripts give the number of electrons in that particular subshell.

TABLE: Distribution of electrons in shells and sub-shells

PRINCIPAL SHELL No.	MAX. NO. OF ELECTRONS	SUBSHELL AND THE MAX. NO. OF ELECTRONS IN EACH			
1 (K)	2	$1s^2$			
2 (L)	8	$2s^2$	$2p^6$		
3 (M)	18	$3s^2$	$3p^6$	$3d^{10}$	
4 (N)	32	$4s^2$	$4p^6$	$4d^{10}$	$4f^{14}$
5 (O)	32	$5s^2$	$5p^6$	$5d^{10}$	$5f^{14}$
6 (P)	18	$6s^2$	$6p^6$		
7 (Q)	8	$7s^2$	$7p^6$		

THE NATURE OF ATOMIC ORBITALS

As already discussed, electrons in each energy level are visualised as tiny particles executing rapid back and forth motion. By and large this movement takes place in a certain region in space. This region in the atom to which an electron is confined and which has a geometrical shape, is termed the **Atomic Orbital** or **Orbital**. It may be clearly understood that the term orbital has no association with the term 'orbit' which defines a particular path of movement. It only implies that the electron at any moment is found at any place of the orbital, although it may spend more time in certain parts than in others. Furthermore, not more than two electrons can occupy one orbital. All electrons in orbitals spin clockwise or anti-clockwise, and the two 'coupled' electrons of a given orbital must have opposite spins in order to be accommodated in the same orbital. By the same argument, two electrons with the same spin will go to different orbitals.

THE GOOMETRICAL FORM OF THE *s* AND *p* ORBITALS

The first ten elements (At. Nos. 1 to 10) of the periodic table include Hydrogen, Carbon and Oxygen which occur most often in organic compounds. The maximum number of extra-nuclear electrons in the atoms of these elements is 10 (Ne, At. No. 10). Two of these could be present in the first shell and eight in the second. Thus, the first shell is made of one subshell ($1s$) or one orbital called the ' s orbital'. The second principal shell consists of two subshells— $2s$ subshell which has two electrons or one ' s orbital', and the $2p$ subshell which may have six electrons or three ' p orbitals'. Thus for study of organic compounds, we will confine our discussion to the discussion of the shapes of s and p orbitals.

According to mathematical derivations, the s **Orbital** has a *spherical shape* with the atomic nucleus lying at its centre which is indicated by a plus (+) charge. As discussed earlier, we have one s orbital at each principal shell, its size being larger with the higher shell number. Hence the $1s$ orbital lies completely within the $2s$

orbital which is surrounded by the 3s orbital, and so on. It may be noted that there is no bar against two or more orbitals occupying the same space.

The *p* orbitals are considerably different from the *s* orbitals. They are not spherical but have dumb-bell shape.

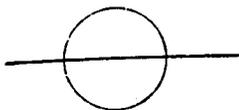


Fig. 6.3. *s* orbital has spherical shape.



Fig. 6.4. *p* orbital has dumb-bell shape and direction along the central axis.

The two lobes of the orbital have a position concentric with the nucleus, termed a *node*, where the probability of finding an electron becomes zero and the plane passing through this point is termed a *nodal plane*. This type of orbital has a shape as well as direction about the nucleus.

As we have already observed, the possible number of electron in a shell is six and since not more than two electrons can occupy an orbital, there are three *p* orbitals. These exist perpendicular to each other along the three axes (named *x*, *y*, *z*) and are designated as p_x , p_y , p_z .

The subscripts do not imply any different energy, but simply indicate the direction of the orbital. The principal shell number to

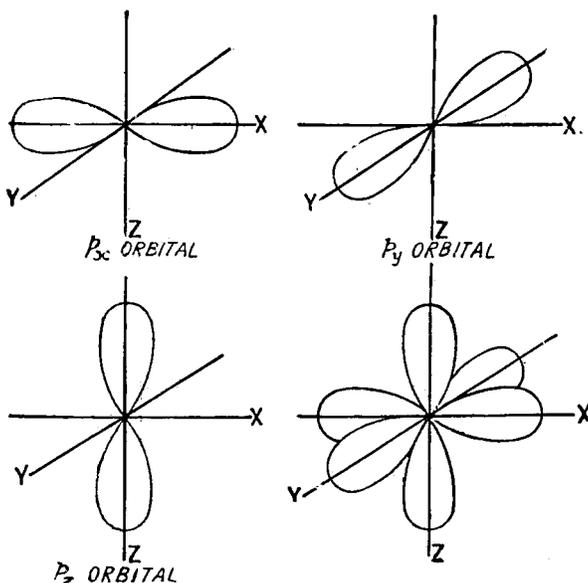


Fig. 3.5. The three *p* orbitals are dumb-bell shaped and arranged at right angles to each other, the nucleus of the atom lying at the intersection of the axes.

which a p electron belongs is generally prefixed and thus the three p electrons in the second shell are written as $2p_x, 2p_y, 2p_z$.

Electronic Configuration. We have already stated that extranuclear electrons are distributed in shells or energy levels around the nucleus which are divided into subshells (or energy sub-levels) and these are made of orbitals.

(1) The principal shells are numbered as 1, 2, 3, etc. which is also the order of their increasing energy.

(2) The number of sub-shells in a particular shell is given by its number. Thus shell (1) has one sub-shell (s), the shell (2) has two sub-shells (s, p), and so on.

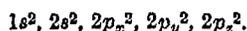
(3) The square of the number of a principal shell gives the number of orbitals in that shell. Thus shell (1) has ($1^2 = 1$) one orbital; the shell (2) has ($2^2 = 4$) four orbitals.



Fig. 6-6. Electrons with opposite spin.

(4) No more than two electrons can occupy the same orbital and these must have opposite spins which are indicated by arrows in opposite directions.

According to the above principles, the first principal shell has one sub-shell s and one orbital (s orbital). The second principal shell has two sub-shells— s and p , the s sub-shell being made of one orbital only, while p sub-shell of three orbitals (p -orbitals). The atom of neon (At. No. 10) has ten electrons arranged in two shells; the first shell having two electrons and the second shell eight. It stands to reason that neon atom has all the orbitals in the two shells completely filled. The configuration of neon in 'short hand' notation could be written as



Here, letters indicate the type of orbital, the prefix stands for the principal shell number and the superscripts show the number of electrons in the orbital. The beryllium atom (At. No. 4) has four electrons, two of these occupy the $1s$ orbital and remaining two will go to the $2s$ orbital. The remaining elements B, C, N, O, F, Ne (At. Nos. 5 to 10) each have two $1s$ electrons, two $2s$ electrons, and the rest of the electrons go into the p -orbitals.

The boron atom (At. No. 5) has five electrons which are placed—two in $1s$ orbital, two in $2s$ orbital, and one in $2p_x$ orbital. Carbon (At. No. 6) has six electrons, and the sixth electron goes into $2p_y$ orbital. Proceeding similarly, the seventh electron in Nitrogen will go into $2p_z$ orbital. Now since each p orbital has one electron, the eighth, ninth and tenth electron of Oxygen, Fluorine and Nitrogen will go to fill the $p_x, p_y,$ and p_z orbitals respectively. The complete configurations of the first ten elements are summarized 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	$1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2$

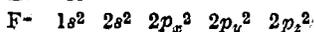
CHEMICAL BONDING

After this brief review of the atomic orbital theory, let us now extend this concept to interpret chemical bonding.

In the table given above, it may be noted that He and Ne have all available orbitals filled and are chemically stable. The rest of the atoms H, Li, Be, B, C, N, O and F have partially filled orbitals and are chemically active or unstable. The inert gases He and Ne being stable possess lowest energy, while the rest of the atoms mentioned above tend to become stable by combination with other atoms which results in a lowering of their energy. Thus in general, *atoms tend to combine with other atoms to form molecules and in this process there is a lowering of their energy, for the most stable condition is that with the lowest energy.*

It may also be noted that He and Ne have completely filled orbitals (two electrons to each), while the other atoms like H, Li, Be etc. have certain half-filled orbitals (one electron each). Hence it stands to reason that orbitals containing one electron only can cause chemical combination so that the atoms in the resulting molecule come to possess orbitals which are completely filled. This is accompanied by a lowering of energy.

Electrovalent Bond. The formation of an electrovalent bond takes place by the transfer of an electron from the partially filled orbital of an electropositive atom to the partially filled orbital of an electronegative atom which now will have a pair of electrons. Thus Li transfers its lone electron from the $2s$ orbital to the $2p_x$ orbital of F, to form Li^+ and F^- ions.



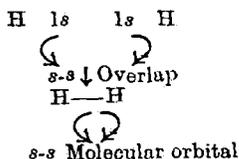
The Li^+ and F^- ions due to electrostatic attraction are bonded to give Li^+F^- molecule. It may be seen that all orbitals in Li^+ and F^- ions possess two electrons each and thus acquire stability (lowest energy).

Covalent Bond. A covalent bond is formed when two half-filled orbitals belonging to different atoms overlap in space and merge to form a new bigger orbital which is known as **molecular orbital**. The molecular orbital surrounds the atomic nuclei of both atoms and marks the region in which the pair of electrons will be found. The new orbital provides a greater freedom of movement to the 'paired' electrons which now belong to both the nuclei. It might be expected, from logical reasoning, that larger the region of movement allowed to an electron lower will be its energy. Thus the greater freedom enjoyed by the electrons in the molecular orbital, results in a decrease of energy (increase in stability). The molecule formed in this way is more stable than the isolated atoms.

Molecular Orbitals (*M.O.*).

As already stated, a molecular orbital is formed when two atomic orbitals overlap so that the electrons come to occupy the common orbital which surrounds two nuclei. This may involve *s* and *s* orbitals; *s* and *p* orbitals; or *p* and *p* orbitals.

***s-s* Molecular Orbitals.** A molecular orbital formed by the overlap of *s* orbitals of two atoms are called *s-s* molecular orbitals. Let us consider the bond formation in hydrogen molecule from two individual hydrogen atoms. As the atoms are brought together, their *1s* orbitals overlap and merge to form an *s-s* molecular orbital.



This may be pictorially represented as follows :

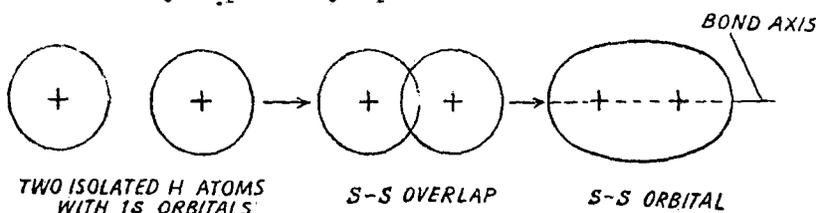


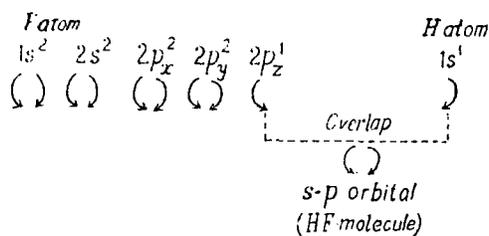
Fig. 6-7. Formation of *s-s* orbital in Hydrogen molecule.

The boundary of the *s-s* orbital in space, which in this case is ovoid, defines the region which the two electrons now occupy jointly. We call this orbital a **Sigma Orbital** (from the Greek letter σ corresponding to *s*) since it is completely symmetrical about the bond axis passing through the two nuclei. Although electrons may be present anywhere in this orbital, the probability of finding electrons

is maximum between the two nuclei, for they are attracted equally by both the nuclei.

The bond established by the overlap of two s orbitals, is called a **Sigma bond** or σ -**bond**. Since an s orbital is spherically symmetrical, the overlap may take place equally well in any direction and hence there is no direction to such a bond.

s - p Orbitals. An s orbital and p orbital may overlap, even though the atomic orbitals in the two atoms lie in different principal shells. The molecular orbital thus formed is known as s - p **Orbital**. The combination of Hydrogen atom and Fluorine atom giving a molecule of hydrogen fluoride affords an example of this type. There is one $1s$ bonding orbital on hydrogen and one such half-filled $2p$ orbital on Fluorine atom, while the rest of the Fluorine orbitals are completely filled and not available for overlap and entering into bond formation.



Here the orbital overlap consists in an attack of $1s$ orbital on hydrogen atom at a dumbbell shaped half-empty $2p$ orbital of fluorine. The resulting molecular orbital (σ orbital) may be depicted to have been formed as in Fig. 6-8.

The s - p overlap of orbitals between H and F forms a *sigma bond*, yielding HF molecule. It is noteworthy that in the σ orbital here, the nodal plane stands at right angles to the nuclear axis.

p - p Orbitals. We have already studied that the three dumbbell shaped p orbitals are directed along the three axes x , y and z which are at right angles to each other. For each of the three orbitals

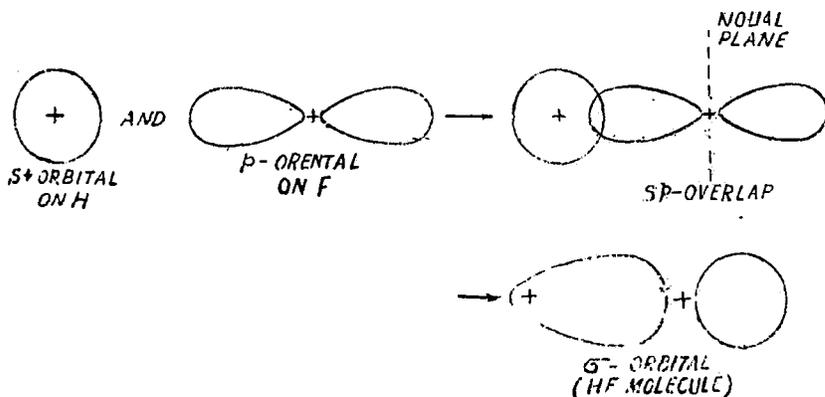


Fig. 6-8. Formation of HF molecule.

p_x , p_y , p_z there is a nodal plane dividing the p orbitals into two lobes.

The overlap of p orbital of one atom with p orbital of another atom may take place to form a p - p molecular orbital in two ways.

(a) *Head-on Overlap*: Let us consider two p_x orbitals approaching for an overlap by pointing directly 'heads' towards one another. This head-on overlap, as we call it, ensures so much lowering of energy that the new orbital is very stable and has a direction in relation to other p orbitals in the atom. The orbital thus generated being symmetrical about the nuclear axis, is designated a **Sigma orbital** and the bond so established a **Sigma bond**.

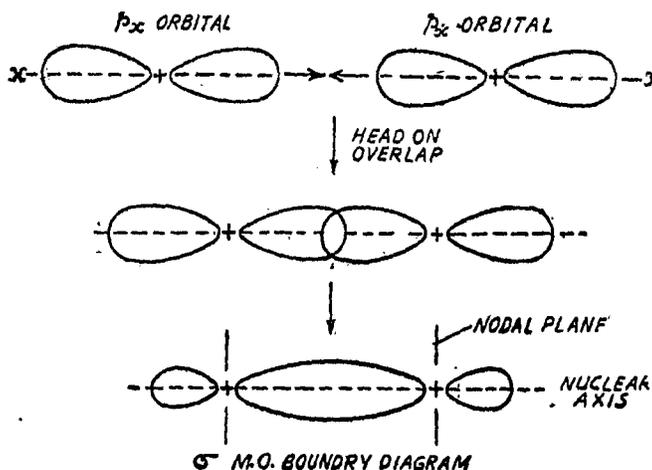
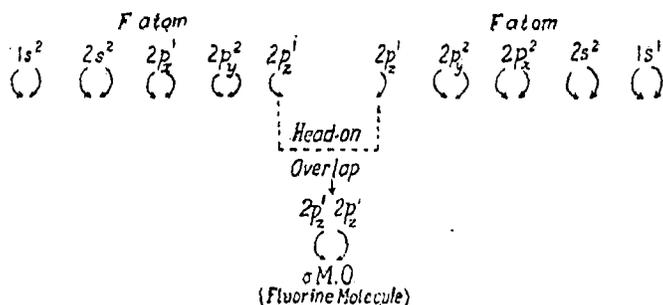


Fig. 6-9.

In the M.O. shown above there are two nodal planes that are perpendicular to the nuclear axis (a characteristic of σ M.O.)

Formation of molecules of fluorine, chlorine and bromine offer common examples of this type of bonding. Thus :



(b) *Side-wise Overlap*. When two p orbitals approach each other side-wise as shown below, the overlap takes place at both their lobes simultaneously. The extent of overlap in this case is relatively small (compared to head-on overlap) and the molecular orbital thus

formed is oriented above and below the nodal plane which contains the nuclear axis. As indicated by the boundary diagram, this molecular orbital has sausage-like regions parallel to the nodal plane passing through the two nuclei.

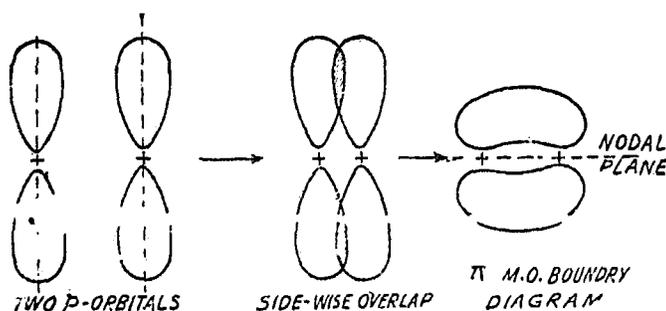


Fig. 6-10. Formation of π M.O. orbital.

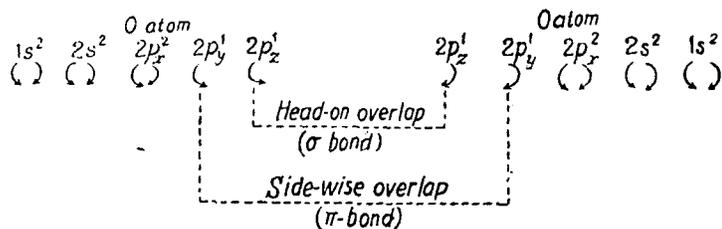
Such a molecular orbital generated by the side-wise overlap of the two half-filled p orbitals and having only one nodal plane containing the nuclear axis is called a π M.O. or **Pi Molecular Orbital**.

For recapitulation it may be re-stated that unlike π M.O., σ M.O. has a nodal plane which is perpendicular to the nuclear axis.

A covalent bond established as a result of π M.O. formation is called a π (**Pi**) **bond**. There are two important characteristics of a π bond. Firstly, it is weaker than a σ bond since the extent of overlap is relatively smaller and hence there is a lesser decrease in energy of the system. Secondly, it is not possible to rotate the atoms constituting a π bond relative to one another. If an attempt is made to do so, the p orbital lobes of the two atoms will no longer be coplanar, their overlap will be decreased and the energy of the system increased. In other words, the rotation around 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 Geometrical isomerism.

Formation of Oxygen molecule - Double bond. We have seen that a single covalent bond results from the overlap of two s orbitals, one s orbital and one p orbital, or two p orbitals. All these bonds called σ bonds possess symmetry about the bond axis. In general, all single bonds are σ bonds.

Now let us proceed to discuss the formation of oxygen molecule (O_2) which is known to contain a double bond. In this case the oxygen atoms happen to possess two bonding p orbitals on each atom. The $2p_x$ and $2p_z$ half-filled orbitals oriented at right angles, on each of the oxygen atoms experience a head-on and a side-wise overlap respectively resulting in a σ and a π orbital simultaneously.



Thus the two atoms in oxygen molecule are linked by one σ and one π bond.

The following diagram depicts the formation of molecular orbitals in oxygen molecule.

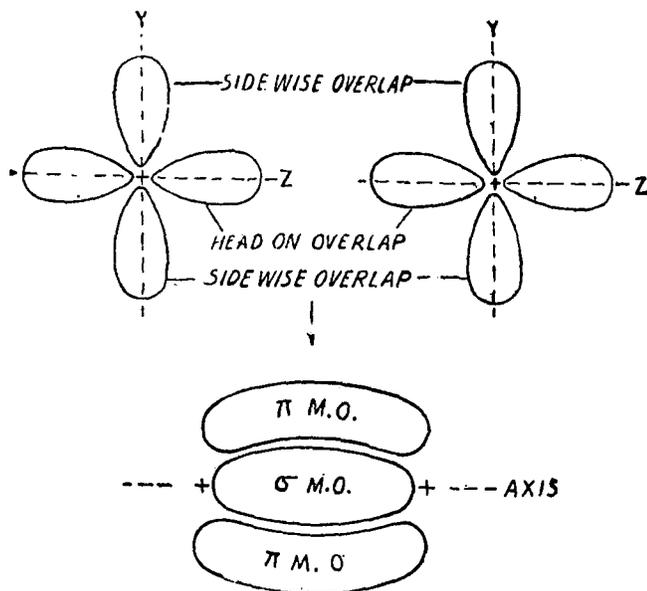


Fig. 6-11. M.O. boundary diagram for σ and π bonds in oxygen molecule.

As is clear from the above considerations the double bond in oxygen is made of one *sigma* bond and one *pi* bond.

Formation of Nitrogen molecule—Triple bond. Here the nitrogen atoms forming the N_2 molecule possess three bonding p orbitals each. The $2p_x$, $2p_y$, $2p_z$ half-filled orbitals are oriented along the three axes at right angles. $2p_y$ orbitals of two nitrogen atoms form a σ M.O. by head-on overlap, while $2p_x$ and $2p_z$ orbitals form two π M.O.'s by side-wise overlap.

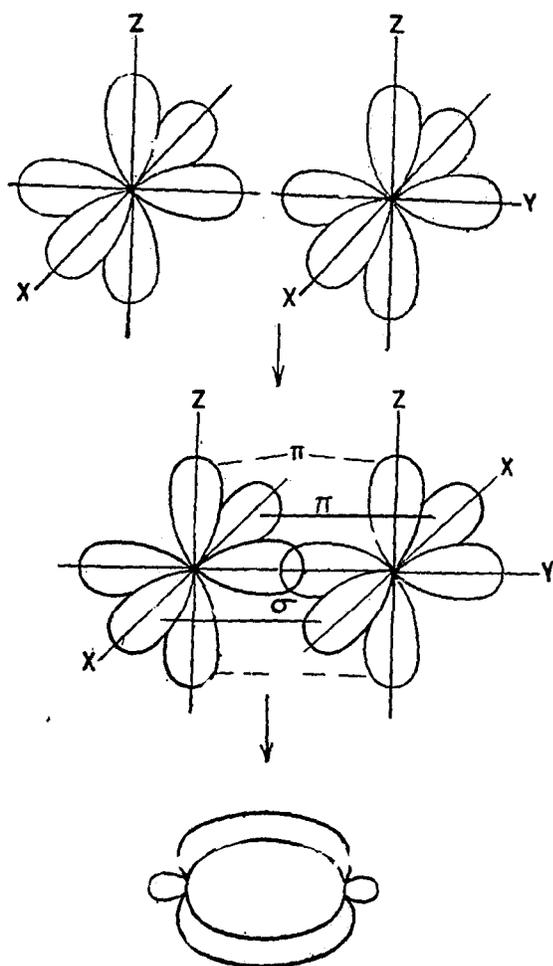
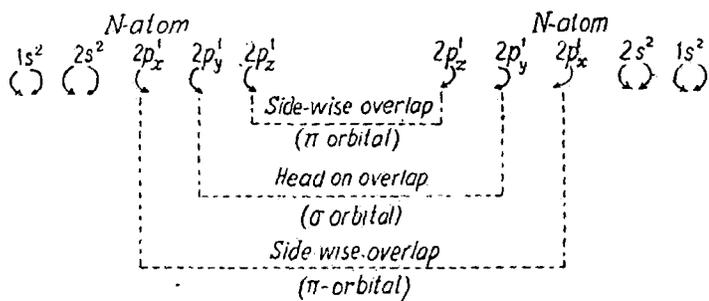


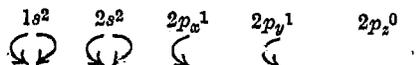
Fig. 6.12. The two "sausage clouds" of two Molecular orbitals.

The preceding diagram (Fig. 6.12) depicts the formation of Nitrogen molecule.

Thus in the classical line structure of nitrogen molecule ($\text{N}\equiv\text{N}$), one line represents a σ bond and the other two π bonds

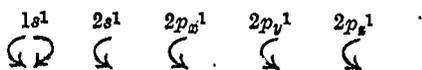
HYBRIDIZATION AND TETRACOVALENCY OF CARBON

Experiment tells us that carbon atom forms four covalent bonds. But when we examine the electronic structure of carbon



we find that it has only two unpaired $2p$ orbitals which can presumably form two σ bonds.

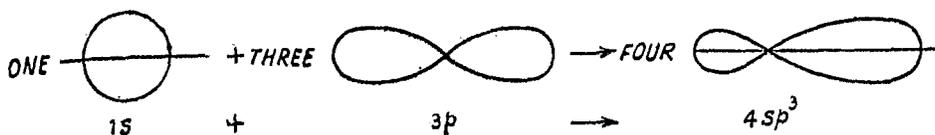
To provide an explanation for the tetra-covalency of carbon in methane (CH_4) and its relatives, it may be assumed that the two $2s$ electrons uncouple themselves and one of these is 'promoted' to the vacant $2p_z$ orbital which will now have higher energy and less stability. The electronic configuration of the 'excited' carbon atom could be written as



Now we have four half-filled orbitals which could possibly overlap with the four $1s$ orbitals of hydrogen atoms to form four σ bonds which would result in the lowering of energy. It stands to reason that the lowering of energy thus caused by the formation of two additional σ bonds of carbon is more than that necessary to promote an electron from a $2s$ orbital to a $2p$ orbital. It follows that although the isolated carbon atom is most stable with $2s$ and $2p$ electrons, the stabler compounds of carbon result when all four electrons in second energy level are in separate orbitals and form four covalent bonds.

We have seen that an excited carbon atom has four available orbitals in the second energy level—one s and three p orbitals. On overlapping with $1s$ orbitals of hydrogen atoms to form methane molecule, there would result one $s-s$ orbital and three $s-p$ orbitals. But we know that the $s-s$ orbital will be different from each of the three $s-p$ orbitals in respect of directional character as well as energy. But this would be contrary to actual facts since experiment shows that the four covalent bonds in methane are equivalent.

To account for the above situation, the concept of hybrid orbitals has been introduced. According to the theory of wave mechanics, orbitals on the same atom which lie close to one another in energy, tend to combine or 'mix' and then redistribute to form equivalent number of new orbitals which are called **hybridised orbitals** and the phenomenon is termed **hybridisation**. Thus in an excited carbon atom, it is assumed that one $2s$ and three $2p$ orbitals combine or mix together and redistribute as four new equivalent hybrid orbitals which are designated as sp^3 orbitals (spoken as "sp three"). Each of the four hybrid orbitals possess three-fourths characteristics of p orbital and one-fourth of s orbital.



The hybridisation of the orbitals of carbon may be pictorially represented as below :

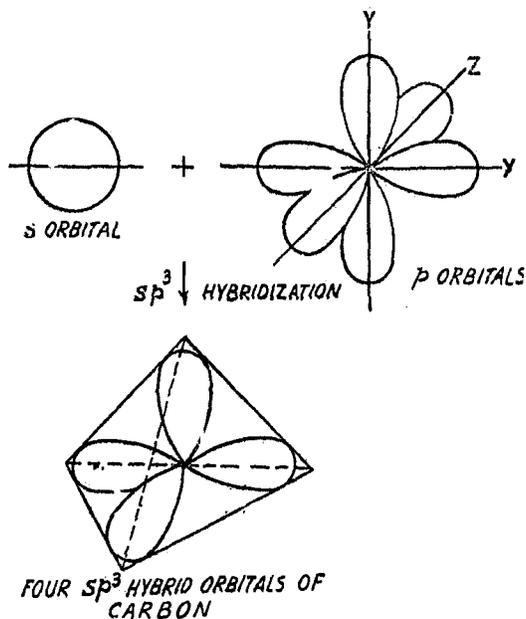


Fig. 6-13. Four sp^3 hybrid orbitals of carbon.

It is noteworthy that the hybrid sp^3 orbital has a new shape which differs somewhat from that of a p orbital, in that the lobe on one side of the node is larger than the lobe on the other side. Overlap with another orbital to form a bond naturally occurs with the larger lobe and for simplifying the molecular orbitals, very often the smaller lobe is not indicated. The most important characteristic of the sp^3 orbitals is that these four are distributed symmetrically in space on account of electronic repulsions keeping them farthest from each other. If the valencies are regarded as radiating from the nucleus of the carbon atom, their directions are towards the corners of a regular tetrahedron and the angles between them are $109^\circ 28'$.

The type of hybridisation involving the mixing of four 'pure' orbitals as described above to give four equivalent sp^3 hybrid orbitals, is called **tetrahedral hybridization**. It is met with in saturated carbon compounds.

Let us now proceed to consider the formation of methane molecule. The four sp^3 hybrid orbitals of the carbon atom are

directed in space towards the four corners of a regular tetrahedron and the $1s$ orbital of four hydrogen atoms should approach its four apexes for the overlap. This would establish four equivalent σ bonds with the carbon atom resulting in the formation of a symmetrical methane molecule. Thus :

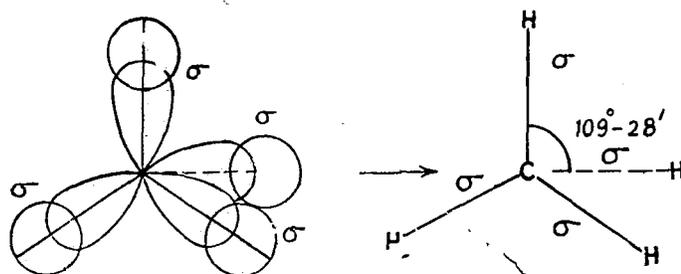


Fig. 6-14. Structure of Methane molecule.

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 σ bonds as in methane molecule. Thus :

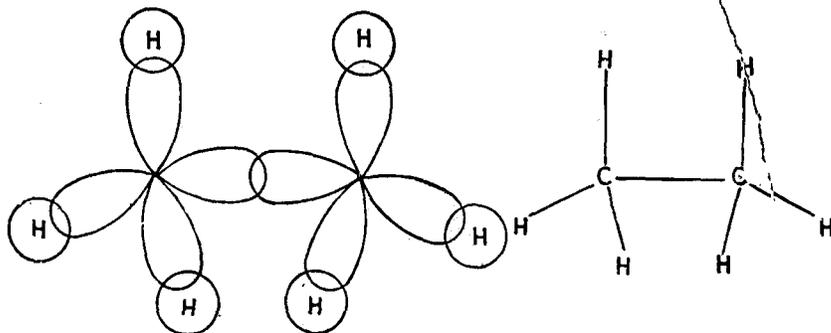
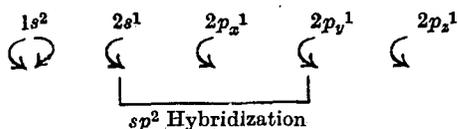


Fig. 6-15. Structure of Ethane molecule.

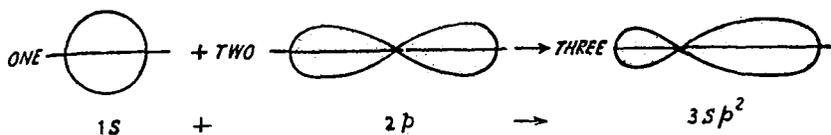
It may be noted how beautifully the sp^3 hybridization of orbitals as illustrated above has theoretically substantiated the Le Bel and van't Hoff's theory of the tetrahedral arrangement of carbon valency bonds in saturated organic molecules.

HYBRIDISATION AND MULTIPLE BONDS

In the classical representation of an ethylenic linkage, >C=C< , no difference can be made out between the two bonds which unite the carbon atoms. Huckel's model of hybridization in doubly bonded carbon atoms demonstrates that the two linkages constituting a double bond are not identical. He assumes that in the case of ethylenic compounds of the four 'pure' atomic orbitals of excited carbon atom only $2s$, and $2p_x$ and $2p_y$ orbitals are hybridised



to give *three equivalent orbitals*. These orbitals formed by the hybridization of one *s* and two *p* orbitals, are called **sp^2 Orbitals** (spoken as "*sp two*").



The three sp^2 orbitals are very much similar in shape to sp^3 orbitals and lie in one plane (XY plane) and are disposed symmetrically at an angle of 120° to one another. This type of hybridization is termed **Trigonal hybridization** and is visualised to take place as follows :

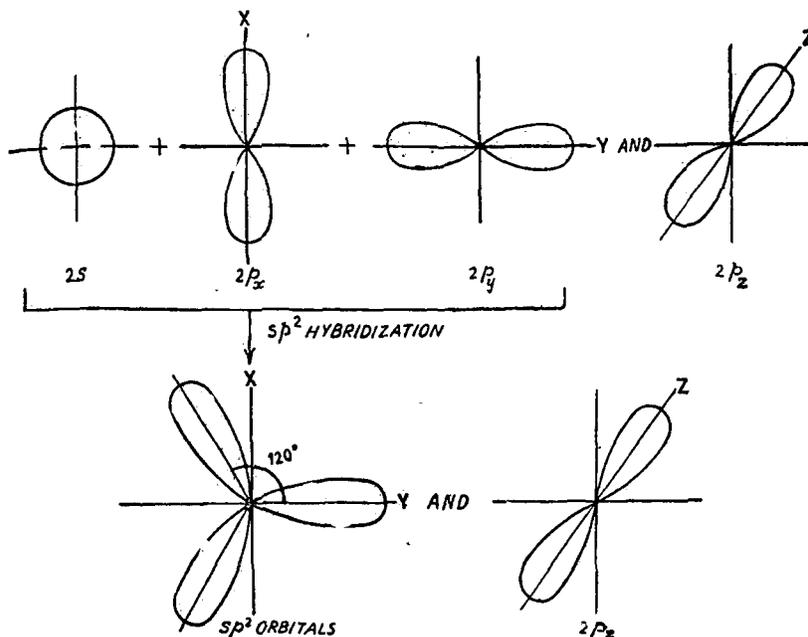


Fig. 6-16. Trigonal Hybridization.

As indicated above, the carbon atoms undergoing trigonal hybridization, undoubtedly possess the third free p_z orbital which has its lobes disposed above and below the plane of hybrid orbitals at right angles to this plane (Fig. 6-17).

Structure of Ethylene molecule. In the formation of ethylene molecule, the two carbon atoms (in sp^2 hybridization state) form

σ bond by the head-on overlap of the two sp^3 orbitals contributed one each by the two carbons. The remaining two sp^2 orbitals of

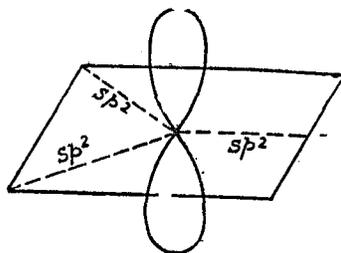


Fig. 6-17.

each carbon form σ bonds with hydrogen atoms. The unhybridized $2p_z$ orbitals of the two carbon atoms undergo a sidewise overlap forming a π bond. Thus the carbon-to-carbon double bond in ethylene is made of one σ and one π bond. Since the energy of a π bond is less than that of a σ bond, the two bonds constituting the ethylenic linkage, are not identical in strength. The π bond being weaker is easily ruptured in addition reactions of ethylene.

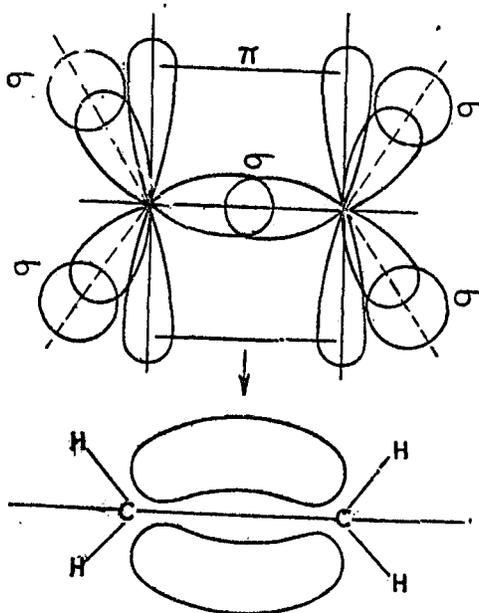
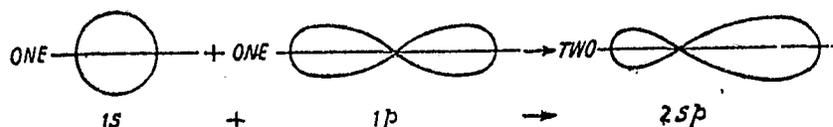


Fig. 6-18. Orbital model for Ethylene.

For the above reason, ethylenic linkage is sometimes represented as >C=C<

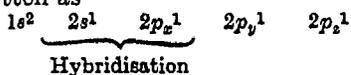
Structure of Acetylene. To interpret the structure of

acetylene molecule we visualise another kind of hybrid orbitals of the carbon atom. Here one s orbital and only one p orbital hybridise to form two equivalent collinear orbitals; the other two p orbitals remaining undisturbed.



This is known as sp hybridization and the new orbitals are termed sp orbitals.

The electronic configuration of each carbon atom in acetylene molecule may be written as



The $2s$ and $2p_x$ orbitals hybridise to give two sp orbitals. One of the two sp hybrid orbitals on each carbon is then used in forming a σ

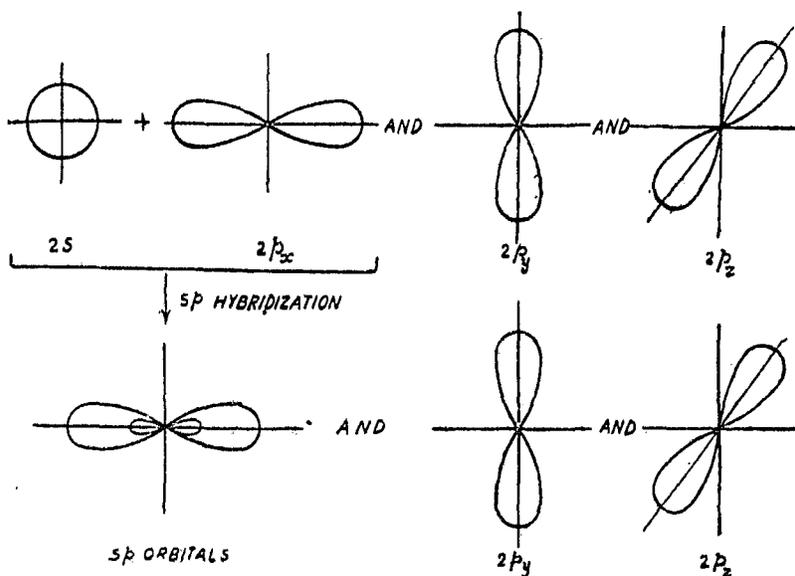


Fig. 6-19.

bond with the other carbon, and the remaining sp orbitals get bonded with a hydrogen atom. This leaves two unhybridised p orbitals ($2p_y$ and $2p_z$) on each carbon atom, both of which are mutually perpendicular to the line of $H-C-C-H$ nuclei. These orbitals are capable of forming two π bonds by the edge-on overlap. Thus :

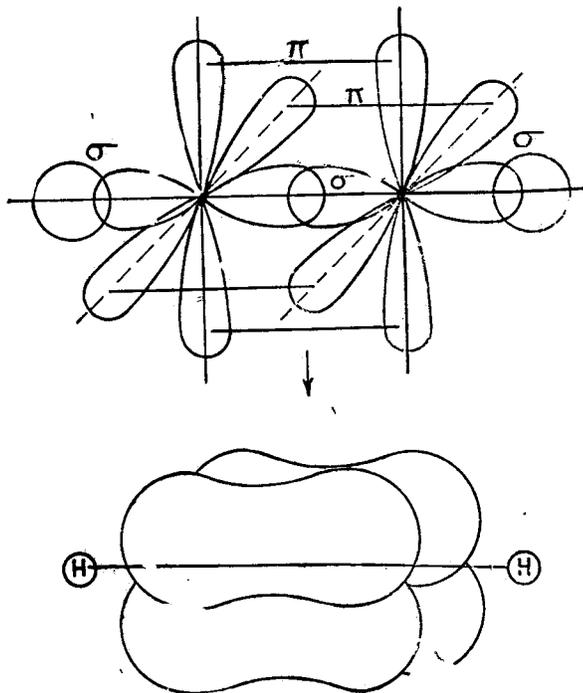
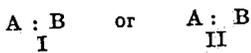


Fig. 6-20. Orbital model for acetylene showing σ and π bonds.

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



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

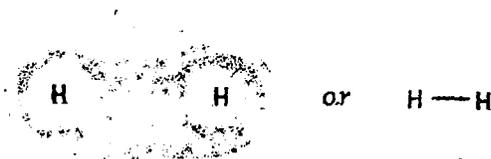
H 2.1						
Li 0.97	Be 1.5	B 2.0	C 2.5	N 3.1	O 3.5	F 4.1
Na 1.0	Mg 1.2	Al 1.5	Si 1.7	P 2.1	S 2.4	Cl 2.8
K 0.90	Ca 1.0	Ga 1.5	Ge 2.0	As 2.2	Se 2.5	Br 2.7
Rb 0.80	Sr 1.0	In 1.5	Sn 1.72	Sb 1.82	Te 2.0	I 2.2
Cs 0.86	Ba 0.97	Tl 1.4	Pb 1.5	Bi 1.7	Po 1.8	At 1.9

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 some electronegativity) exert equal attractive force on the two electrons which are, therefore, symmetrically disposed in the molecular orbital. Thus :

Fig. 6-21. Uniform electron cloud in H_2 molecule.

The covalent bond in hydrogen molecule is, therefore, non-polar.

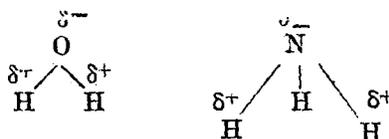
In a molecule having two different atoms joined by a covalent bond, the atom having higher electronegativity will exert a greater attractive pull on the shared pair of electrons. Thus the two electrons will spend more time near this than the other atom, making it slightly negative. Thus in hydrogen fluoride 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. 6-22.

Thus the covalent bond joining H and F atoms develops polarity and is called a **Polar bond**. By and large the covalent bond 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 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

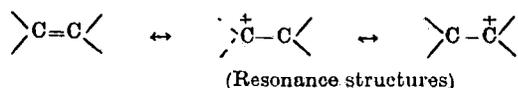
The concept of resonance was forwarded on purely chemical grounds when Kekule structure of benzene was found unsatisfactory to explain its properties in full. Later it was discovered that there are, in fact, numerous substances which like benzene could be assigned two or more structural formulas differing only in the placement of bonds or electrons, and the actual behaviour of the subs-

tance 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 process of hybridisation of two or more covalent bond structures to yield a new stable hybrid form with less energy is termed **Resonance**.

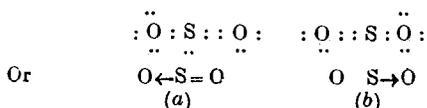
It may be clearly understood that the old concept that two or more structural formulas oscillate between themselves and each of them contribute to the properties of the substance, -is incorrect. Resonance really involves the delocalisation of electrons in the molecule so as to give a new stable form 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 and slightly weaker than a single carbon-to-carbon bond. This is explained by the fact that one of the electron pairs between the two carbons is delocalised or displaced to give a stable resonance hybrid form as follows :

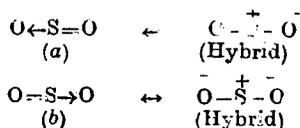


It may be noted that as one electron pair shifts to one or the other carbon atom, the double bond becomes a single bond with polarity developed on it. Therefore, the resonance hybrid form of the double bond in such a case becomes stable as in benzene and possesses a character intermediate between that 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.



None of these formulas can properly account for the properties of sulphur dioxide. These postulate two different types of linkages (one double and one covalent) 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 SO₂ molecule but a new 'hybrid' structure having 'equivalent' S—O bond explains its behaviour. This new hybrid is stable and has independent existence.



Quantum mechanics reveals that the resonance hybrid possesses less energy than those 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 state of the actual structure, the energy diagram assumes the following shape.

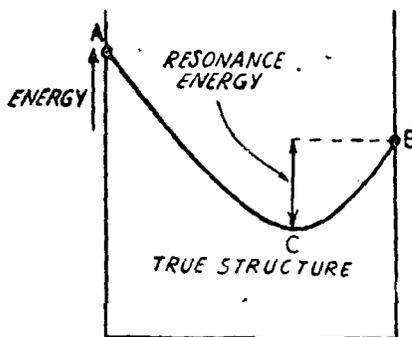
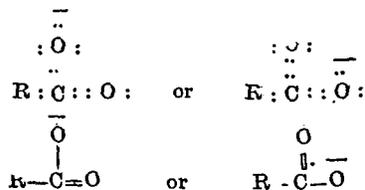


Fig. 6.23.

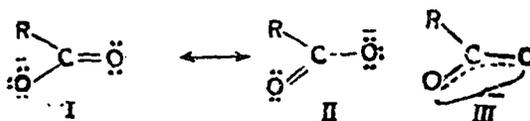
The amount by which the energy of the resonance structure is less than that of the canonical structure, is termed the *Resonance Energy* and this difference of energy is a measure of the added stability conferred by resonance.

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.



The above 'hybrid' form warrants 'equivalence' of the two