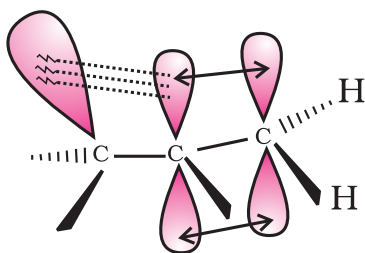


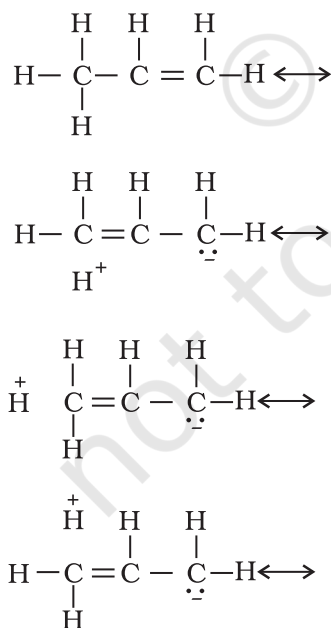
Hyperconjugation is also possible in alkenes and alkylarenes.

Delocalisation of electrons by hyperconjugation in the case of alkene can be depicted as in Fig. 12.4(b).



**Fig. 12.4(b)** Orbital diagram showing hyperconjugation in propene

There are various ways of looking at the hyperconjugative effect. One of the way is to regard C—H bond as possessing partial ionic character due to resonance.



The hyperconjugation may also be regarded as no bond resonance.

### Problem 12.19

Explain why  $(\text{CH}_3)_3\overset{\text{H}}{\text{C}^+}$  is more stable than  $\text{CH}_3\overset{\text{H}}{\text{C}^+}$  and  $\overset{\text{H}}{\text{C}^+}$  is the least stable cation.

### Solution

Hyperconjugation interaction in  $(\text{CH}_3)_3\overset{\text{H}}{\text{C}^+}$  is greater than in  $\text{CH}_3\overset{\text{H}}{\text{C}^+}$  as the  $(\text{CH}_3)_3\overset{\text{H}}{\text{C}^+}$  has nine C-H bonds. In  $\overset{\text{H}}{\text{C}^+}$ , vacant  $p$  orbital is perpendicular to the plane in which C-H bonds lie; hence cannot overlap with it. Thus,  $\overset{\text{H}}{\text{C}^+}$  lacks hyperconjugative stability.

### 12.7.10 Types of Organic Reactions and Mechanisms

Organic reactions can be classified into the following categories:

- (i) Substitution reactions
- (ii) Addition reactions
- (iii) Elimination reactions
- (iv) Rearrangement reactions

You will be studying these reactions in Unit 13 and later in class XII.

### 12.8 METHODS OF PURIFICATION OF ORGANIC COMPOUNDS

Once an organic compound is extracted from a natural source or synthesised in the laboratory, it is essential to purify it. Various methods used for the purification of organic compounds are based on the nature of the compound and the impurity present in it.

The common techniques used for purification are as follows :

- (i) Sublimation
- (ii) Crystallisation
- (iii) Distillation
- (iv) Differential extraction and
- (v) Chromatography

Finally, the purity of a compound is ascertained by determining its melting or boiling point. Most of the pure compounds have sharp melting points and boiling points. New methods of checking the purity of an organic compound are based on different types

of chromatographic and spectroscopic techniques.

### 12.8.1 Sublimation

You have learnt earlier that on heating, some solid substances change from solid to vapour state without passing through liquid state. The purification technique based on the above principle is known as sublimation and is used to separate sublimable compounds from non-sublimable impurities.

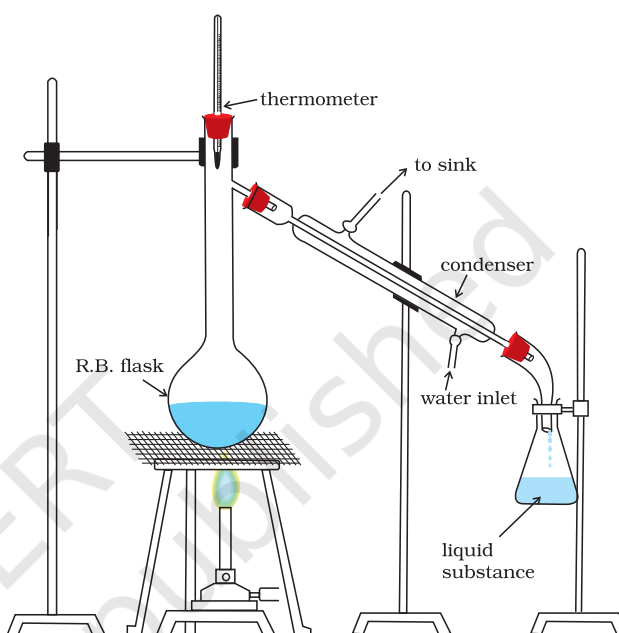
### 12.8.2 Crystallisation

This is one of the most commonly used techniques for the purification of solid organic compounds. It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. The impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to get a nearly saturated solution. On cooling the solution, pure compound crystallises out and is removed by filtration. The filtrate (mother liquor) contains impurities and small quantity of the compound. If the compound is highly soluble in one solvent and very little soluble in another solvent, crystallisation can be satisfactorily carried out in a mixture of these solvents. Impurities, which impart colour to the solution are removed by adsorbing over activated charcoal. Repeated crystallisation becomes necessary for the purification of compounds containing impurities of comparable solubilities.

### 12.8.3 Distillation

This important method is used to separate (i) volatile liquids from nonvolatile impurities and (ii) the liquids having sufficient difference in their boiling points. Liquids having different boiling points vaporise at different temperatures. The vapours are cooled and the liquids so formed are collected separately. Chloroform (b.p. 334 K) and aniline (b.p. 457 K) are easily separated by the technique of distillation (Fig. 12.5). The liquid mixture is taken in a round bottom flask and heated

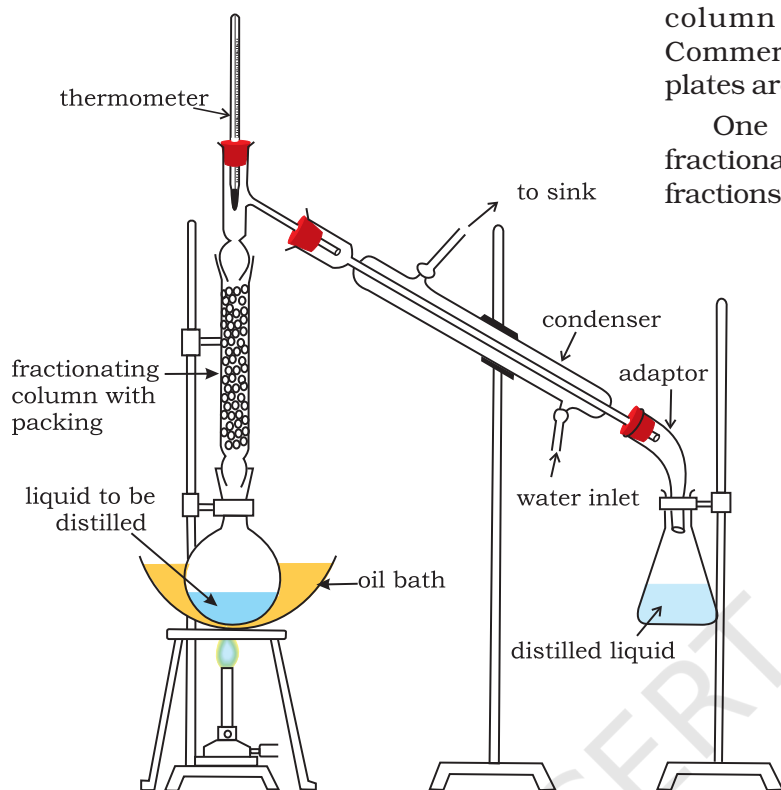
carefully. On boiling, the vapours of lower boiling component are formed first. The vapours are condensed by using a condenser and the liquid is collected in a receiver. The vapours of higher boiling component form later and the liquid can be collected separately.



**Fig. 12.5** Simple distillation. The vapours of a substance formed are condensed and the liquid is collected in conical flask.

**Fractional Distillation:** If the difference in boiling points of two liquids is not much, simple distillation cannot be used to separate them. The vapours of such liquids are formed within the same temperature range and are condensed simultaneously. The technique of fractional distillation is used in such cases. In this technique, vapours of a liquid mixture are passed through a fractionating column before condensation. The fractionating column is fitted over the mouth of the round bottom flask (Fig. 12.6, page 358).

Vapours of the liquid with higher boiling point condense before the vapours of the liquid with lower boiling point. The vapours rising up in the fractionating column become richer in more volatile component. By the time the



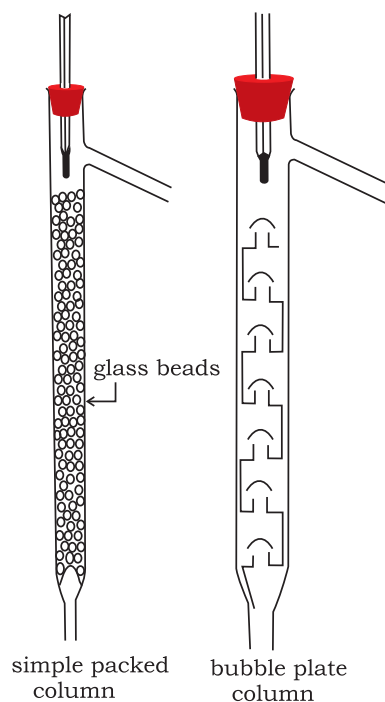
**Fig.12.6** Fractional distillation. The vapours of lower boiling fraction reach the top of the column first followed by vapours of higher boiling fractions.

vapours reach to the top of the fractionating column, these are rich in the more volatile component. Fractionating columns are available in various sizes and designs as shown in Fig.12.7. A fractionating column provides many surfaces for heat exchange between the ascending vapours and the descending condensed liquid. Some of the condensing liquid in the fractionating column obtains heat from the ascending vapours and re-vaporises. The vapours thus become richer in low boiling component. The vapours of low boiling component ascend to the top of the column. On reaching the top, the vapours become pure in low boiling component and pass through the condenser and the pure liquid is collected in a receiver. After a series of successive distillations, the remaining liquid in the distillation flask gets enriched in high boiling component. Each successive condensation and vaporisation unit in the fractionating

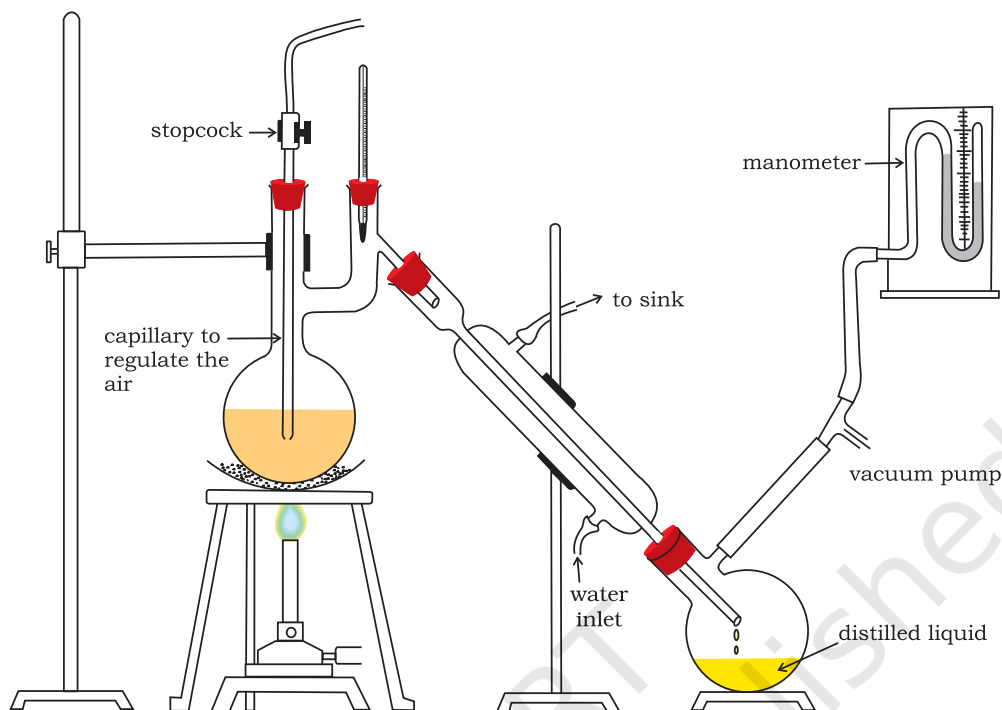
column is called a **theoretical plate**. Commercially, columns with hundreds of plates are available.

One of the technological applications of fractional distillation is to separate different fractions of **crude oil in petroleum industry**.

**Distillation under reduced pressure:** This method is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Such liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surface. A liquid boils at a temperature at which its vapour pressure is equal to the external pressure. The pressure is reduced with the help of a water pump or vacuum pump (Fig.12.8). Glycerol can be separated from **spent-lye in soap industry** by using this technique.



**Fig.12.7** Different types of fractionating columns.



**Fig.12.8** Distillation under reduced pressure. A liquid boils at a temperature below its vapour pressure by reducing the pressure.

**Steam Distillation:** This technique is applied to separate substances which are steam volatile and are immiscible with water. In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic compound is condensed and collected. The compound is later separated from water using a separating funnel. In steam distillation, the liquid boils when the sum of vapour pressures due to the organic liquid ( $p_1$ ) and that due to water ( $p_2$ ) becomes equal to the atmospheric pressure ( $p$ ), i.e.  $p = p_1 + p_2$ . Since  $p_1$  is lower than  $p$ , the organic liquid vaporises at lower temperature than its boiling point.

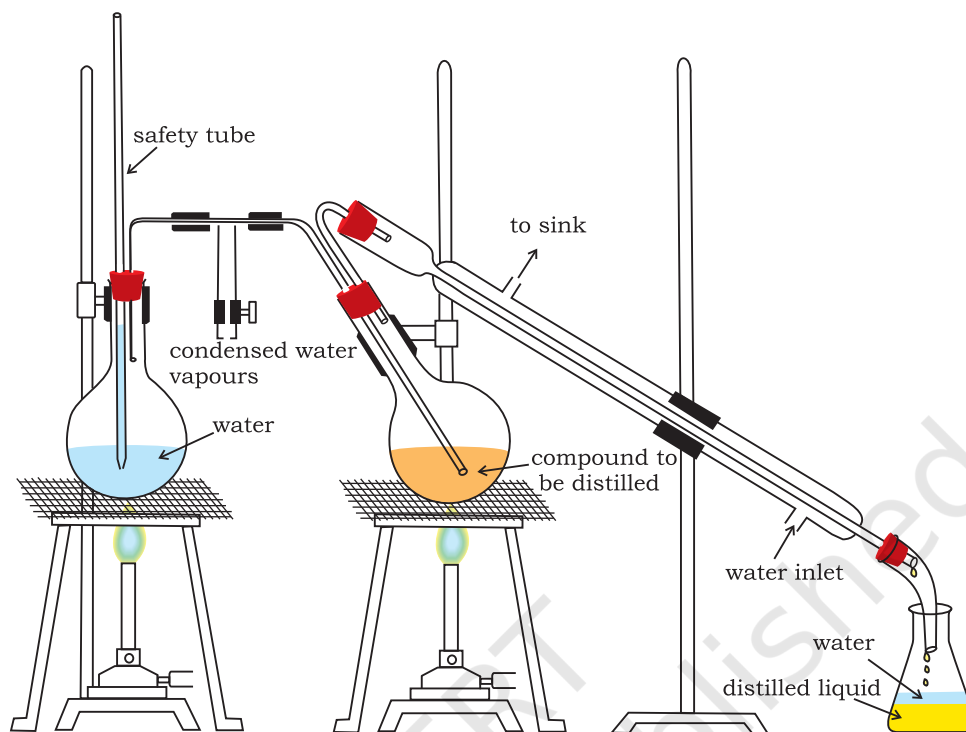
Thus, if one of the substances in the mixture is water and the other, a water insoluble substance, then the mixture will boil close to but below, 373K. A mixture of water and the substance is obtained which can be separated by using a separating funnel. Aniline is separated by this technique from aniline – water mixture (Fig.12.9, Page 360).

#### 12.8.4 Differential Extraction

When an organic compound is present in an aqueous medium, it is separated by shaking it with an organic solvent in which it is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they form two distinct layers which can be separated by separatory funnel. The organic solvent is later removed by distillation or by evaporation to get back the compound. Differential extraction is carried out in a separatory funnel as shown in Fig. 12.10 (Page 360). If the organic compound is less soluble in the organic solvent, a very large quantity of solvent would be required to extract even a very small quantity of the compound. The technique of **continuous extraction** is employed in such cases. In this technique same solvent is repeatedly used for extraction of the compound.

#### 12.8.5 Chromatography

Chromatography is an important technique extensively used to separate mixtures into their components, purify compounds and also to test the purity of compounds. The name



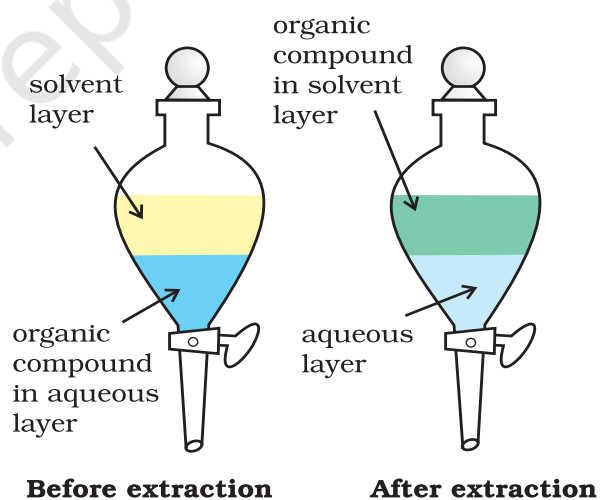
**Fig.12.9** Steam distillation. Steam volatile component volatilizes, the vapours con-

chromatography is based on the Greek word *chroma*, for colour since the method was first used for the separation of coloured substances found in plants. In this technique, the mixture of substances is applied onto a stationary phase, which may be a solid or a liquid. A pure solvent, a mixture of solvents, or a gas is allowed to move slowly over the stationary phase. The components of the mixture get gradually separated from one another. The moving phase is called the mobile phase.

Based on the principle involved, chromatography is classified into different categories. Two of these are:

- Adsorption chromatography, and
- Partition chromatography.

**a) Adsorption Chromatography:** Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase. Following

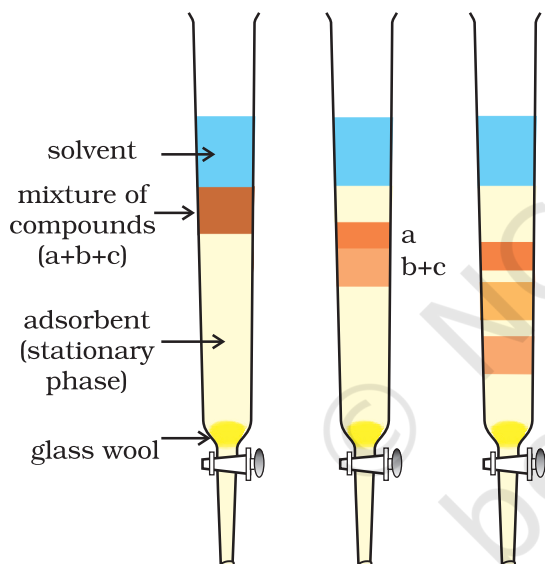


**Fig.12.10** Differential extraction. Extraction of compound takes place based on difference in solubility

are two main types of chromatographic techniques based on the principle of differential adsorption.

- Column chromatography, and
- Thin layer chromatography.

**Column Chromatography:** Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end (Fig. 12.11). The mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube. An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column (Fig. 12.11).

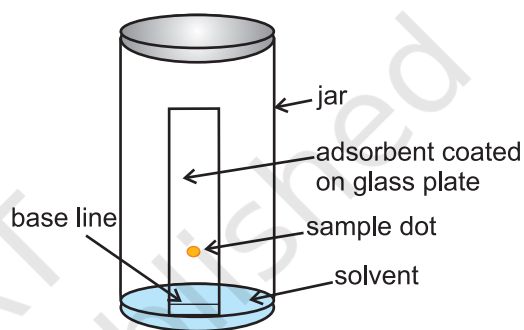


**Fig.12.11** Column chromatography. Different stages of separation of components of a mixture.

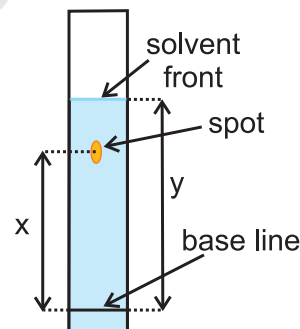
**Thin Layer Chromatography:** Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate. A thin layer (about 0.2mm thick) of an adsorbent (silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as *thin layer chromatography plate or chromaplate*. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate. The glass

plate is then placed in a closed jar containing the eluant (Fig. 12.12a). As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its **retardation factor** i.e.  **$R_f$  value** (Fig. 12.12 b).

$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$



**Fig.12.12 (a)** Thin layer chromatography. Chromatogram being developed.

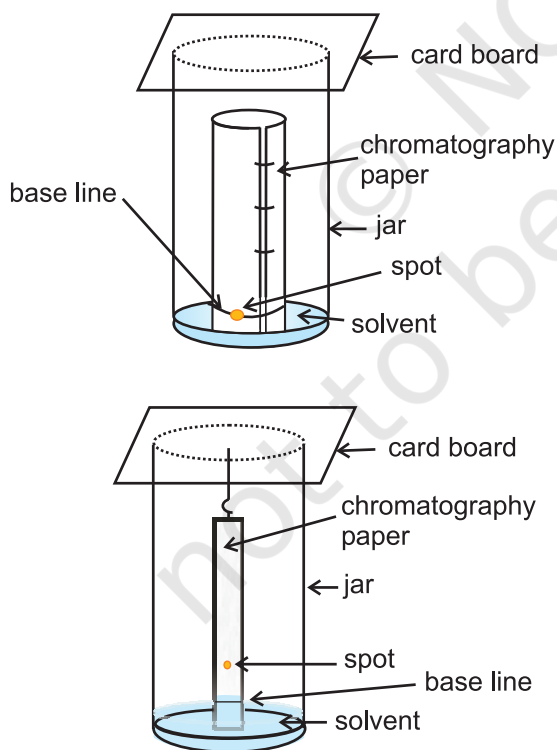


**Fig.12.12 (b)** Developed chromatogram.

The spots of coloured compounds are visible on TLC plate due to their original colour. The spots of colourless compounds, which are invisible to the eye but fluoresce in ultraviolet light, can be detected by putting the plate under ultraviolet light. Another detection technique is to place the plate in a covered jar containing a few crystals of iodine. Spots of compounds, which adsorb iodine, will show up as brown spots. Sometimes an appropriate reagent may also be sprayed on the plate. For example, amino acids may be detected by spraying the plate with ninhydrin solution (Fig. 12.12b).

**Partition Chromatography:** Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper known as chromatography paper is used. Chromatography paper contains water trapped in it, which acts as the stationary phase.

A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents (Fig. 12.13). This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram.



**Fig.12.13** Paper chromatography. Chromatography paper in two different shapes.

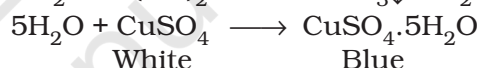
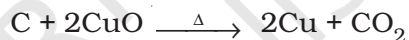
The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.

## 12.9 QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The elements present in organic compounds are carbon and hydrogen. In addition to these, they may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

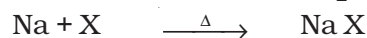
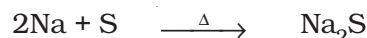
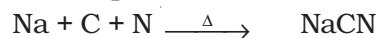
### 12.9.1 Detection of Carbon and Hydrogen

Carbon and hydrogen are detected by heating the compound with copper(II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).



### 12.9.2 Detection of Other Elements

Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by "**Lassaigne's test**". The elements present in the compound are converted from covalent form into the ionic form by fusing the compound with sodium metal. Following reactions take place:



(X = Cl, Br or I)

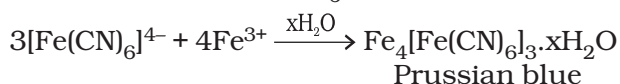
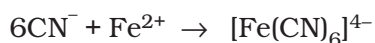
C, N, S and X come from organic compound.

Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract.

#### (A) Test for Nitrogen

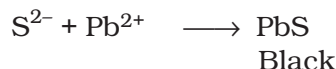
The sodium fusion extract is boiled with iron(II) sulphate and then acidified with

concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen. Sodium cyanide first reacts with iron(II) sulphate and forms sodium hexacyanidoferrate(II). On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanidoferrate(II) to produce iron(III) hexacyanidoferrate(II) (ferriferrocyanide) which is Prussian blue in colour.

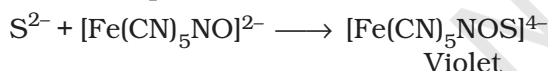


### (B) Test for Sulphur

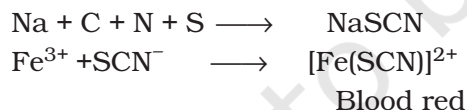
- (a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.



- (b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur.



In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no Prussian blue since there are no free cyanide ions.



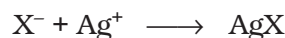
If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.



### (C) Test for Halogens

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and

a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

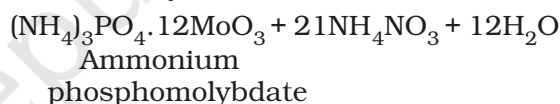
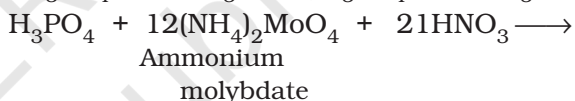


X represents a halogen – Cl, Br or I.

If nitrogen or sulphur is also present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens.

### (D) Test for Phosphorus

The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.



## 12.10 QUANTITATIVE ANALYSIS

Quantitative analysis of compounds is very important in organic chemistry. It helps chemists in the determination of mass per cent of elements present in a compound. You have learnt in Unit-1 that mass per cent of elements is required for the determination of empirical and molecular formula.

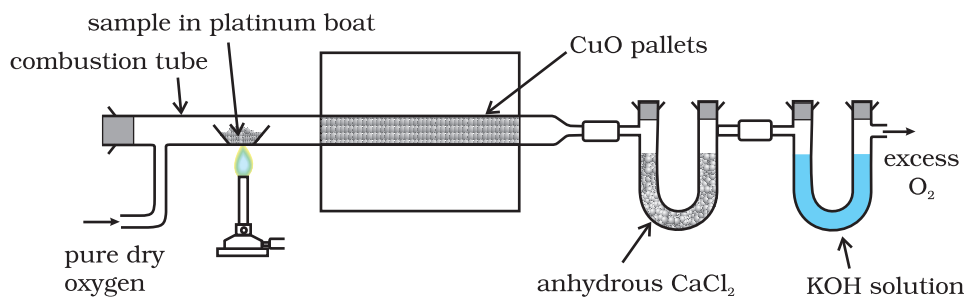
The percentage composition of elements present in an organic compound is determined by the following methods:

### 12.10.1 Carbon and Hydrogen

Both carbon and hydrogen are estimated in one experiment. A known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide. Carbon and hydrogen in the compound are oxidised to carbon dioxide and water respectively.







**Fig.12.14** Estimation of carbon and hydrogen. Water and carbon dioxide formed on oxidation of substance are absorbed in anhydrous calcium chloride and potassium hydroxide solutions respectively contained in U tubes.

The mass of water produced is determined by passing the mixture through a weighed U-tube containing anhydrous calcium chloride. Carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide. These tubes are connected in series (Fig. 12.14). The increase in masses of calcium chloride and potassium hydroxide gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated.

Let the mass of organic compound be  $m$  g, mass of water and carbon dioxide produced be  $m_1$  and  $m_2$  g respectively;

$$\text{Percentage of carbon} = \frac{12 \times m_2 \times 100}{44 \times m}$$

$$\text{Percentage of hydrogen} = \frac{2 \times m_1 \times 100}{18 \times m}$$

#### Problem 12.20

On complete combustion, 0.246 g of an organic compound gave 0.198g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound.

#### Solution

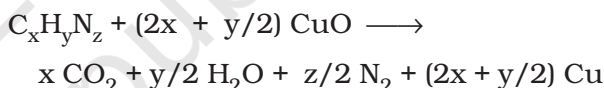
$$\begin{aligned} \text{Percentage of carbon} &= \frac{12 \times 0.198 \times 100}{44 \times 0.246} \\ &= 21.95\% \end{aligned}$$

$$\begin{aligned} \text{Percentage of hydrogen} &= \frac{2 \times 0.1014 \times 100}{18 \times 0.246} \\ &= 4.58\% \end{aligned}$$

#### 12.10.2 Nitrogen

There are two methods for estimation of nitrogen: (i) Dumas method and (ii) Kjeldahl's method.

**(i) Dumas method:** The nitrogen containing organic compound, when heated with copper oxide in an atmosphere of carbon dioxide, yields free nitrogen in addition to carbon dioxide and water.



Traces of nitrogen oxides formed, if any, are reduced to nitrogen by passing the gaseous mixture over a heated copper gauze. The mixture of gases so produced is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide. Nitrogen is collected in the upper part of the graduated tube (Fig. 12.15).

Let the mass of organic compound =  $m$  g

Volume of nitrogen collected =  $V_1$  mL

Room temperature =  $T_1$  K

$$\text{Volume of nitrogen at STP} = \frac{p_1 V_1 \times 273}{760 \times T_1}$$

(Let it be  $V$  mL)

Where  $p_1$  and  $V_1$  are the pressure and volume of nitrogen,  $p_1$  is different from the atmospheric pressure at which nitrogen gas is collected. The value of  $p_1$  is obtained by the relation;

$p_1 = \text{Atmospheric pressure} - \text{Aqueous tension}$   
22400 mL  $\text{N}_2$  at STP weighs 28 g.