

Problem 8.14

Which bond is more polar in the following pairs of molecules: (a) $\text{H}_3\text{C}-\text{H}$, $\text{H}_3\text{C}-\text{Br}$ (b) $\text{H}_3\text{C}-\text{NH}_2$, $\text{H}_3\text{C}-\text{OH}$ (c) $\text{H}_3\text{C}-\text{OH}$, $\text{H}_3\text{C}-\text{SH}$

Solution

(a) $\text{C}-\text{Br}$, since Br is more electronegative than H, (b) $\text{C}-\text{O}$, (c) $\text{C}-\text{O}$

Problem 8.15

In which $\text{C}-\text{C}$ bond of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$, the inductive effect is expected to be the least?

Solution

Magnitude of inductive effect diminishes as the number of intervening bonds increases. Hence, the effect is least in the bond between carbon-3 and hydrogen.

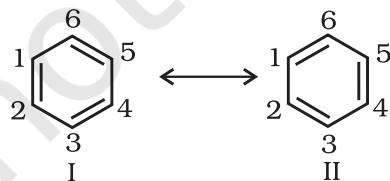
8.7.6 Resonance Structure

There are many organic molecules whose behaviour cannot be explained by a single Lewis structure. An example is that of benzene. Its cyclic structure containing alternating $\text{C}-\text{C}$ single and $\text{C}=\text{C}$ double bonds shown is inadequate for explaining its characteristic properties.



Benzene

As per the above representation, benzene should exhibit two different bond lengths, due to $\text{C}-\text{C}$ single and $\text{C}=\text{C}$ double bonds. However, as determined experimentally benzene has a uniform $\text{C}-\text{C}$ bond distances of 139 pm, a value intermediate between the $\text{C}-\text{C}$ single (154 pm) and $\text{C}=\text{C}$ double (134 pm) bonds. Thus, the structure of benzene cannot be represented adequately by the above structure. Further, benzene can be represented equally well by the energetically identical structures I and II.



Therefore, according to the resonance theory (Unit 4) the actual structure of

benzene cannot be adequately represented by any of these structures, rather it is a hybrid of the two structures (I and II) called *resonance structures*. **The resonance structures (canonical structures or contributing structures) are hypothetical and individually do not represent any real molecule.** They contribute to the actual structure in proportion to their stability.

Another example of resonance is provided by nitromethane (CH_3NO_2) which can be represented by two Lewis structures, (I and II). There are two types of $\text{N}-\text{O}$ bonds in these structures.



However, it is known that the two $\text{N}-\text{O}$ bonds of nitromethane are of the same length (intermediate between a $\text{N}-\text{O}$ single bond and a $\text{N}=\text{O}$ double bond). The actual structure of nitromethane is therefore a resonance hybrid of the two canonical forms I and II.

The energy of actual structure of the molecule (the resonance hybrid) is lower than that of any of the canonical structures. The difference in energy between the actual structure and the lowest energy resonance structure is called the **resonance stabilisation energy** or simply the **resonance energy**. The more the number of important contributing structures, the more is the resonance energy. Resonance is particularly important when the contributing structures are equivalent in energy.

The following rules are applied while writing resonance structures:

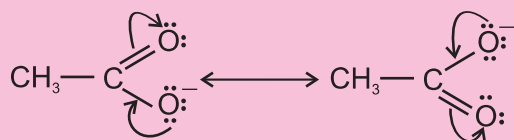
The resonance structures have (i) the same positions of nuclei and (ii) the same number of unpaired electrons. Among the resonance structures, the one which has more number of covalent bonds, all the atoms with octet of electrons (except hydrogen which has a duplet), less separation of opposite charges, (a negative charge if any on more electronegative atom, a positive charge if any on more electropositive atom) and more dispersal of charge, is more stable than others.

Problem 8.16

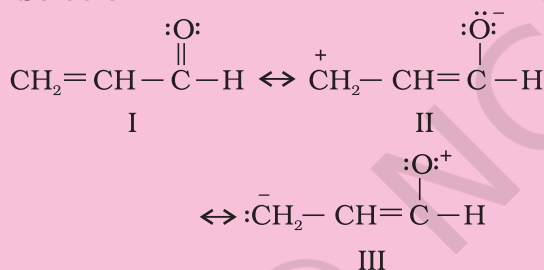
Write resonance structures of CH_3COO^- and show the movement of electrons by curved arrows.

Solution

First, write the structure and put unshared pairs of valence electrons on appropriate atoms. Then draw the arrows one at a time moving the electrons to get the other structures.

**Problem 8.17**

Write resonance structures of $\text{CH}_2=\text{CH}-\text{CHO}$. Indicate relative stability of the contributing structures.

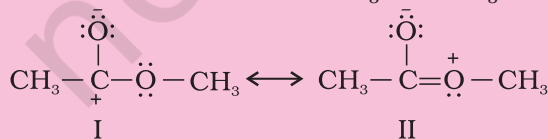
Solution

Stability: I > II > III

[I: Most stable, more number of covalent bonds, each carbon and oxygen atom has an octet and no separation of opposite charge II: negative charge on more electronegative atom and positive charge on more electropositive atom; III: does not contribute as oxygen has positive charge and carbon has negative charge, hence least stable].

Problem 8.18

Explain why the following two structures, I and II cannot be the major contributors to the real structure of $\text{CH}_3\text{COOCH}_3$.

**Solution**

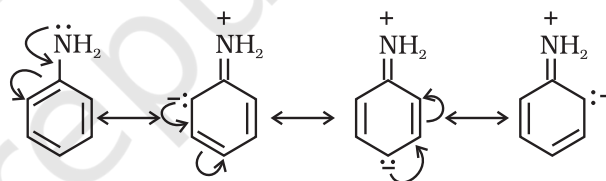
The two structures are less important contributors as they involve charge separation. Additionally, structure I contains a carbon atom with an incomplete octet.

8.7.7 Resonance Effect

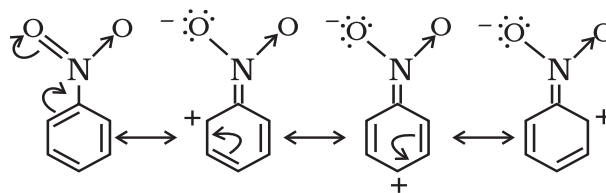
The resonance effect is defined as 'the polarity produced in the molecule by the interaction of two π -bonds or between a π -bond and lone pair of electrons present on an adjacent atom'. The effect is transmitted through the chain. There are two types of resonance or mesomeric effect designated as R or M effect.

(i) Positive Resonance Effect (+R effect)

In this effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system. This electron displacement makes certain positions in the molecule of high electron densities. This effect in aniline is shown as :

**(ii) Negative Resonance Effect (-R effect)**

This effect is observed when the transfer of electrons is towards the atom or substituent group attached to the conjugated system. For example in nitrobenzene this electron displacement can be depicted as :



The atoms or substituent groups, which represent +R or -R electron displacement effects are as follows :

+R effect: - halogen, -OH, -OR, -OCOR, -NH₂, -NHR, -NR₂, -NHCOR,

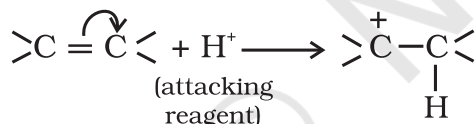
- R effect: - COOH, -CHO, >C=O, - CN, -NO₂

The presence of alternate single and double bonds in an open chain or cyclic system is termed as a conjugated system. These systems often show abnormal behaviour. The examples are 1,3-butadiene, aniline and nitrobenzene etc. In such systems, the π -electrons are delocalised and the system develops polarity.

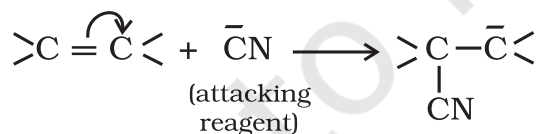
8.7.8 Electromeric Effect (E effect)

It is a temporary effect. The organic compounds having a **multiple bond** (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of π -electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction. It is represented by E and the shifting of the electrons is shown by a curved arrow (\curvearrowright). There are two distinct types of electromeric effect.

(i) **Positive Electromeric Effect (+E effect)** In this effect the π -electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example:



(ii) **Negative Electromeric Effect (–E effect)** In this effect the π -electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example:



When inductive and electromeric effects operate in opposite directions, the electromeric effect predominates.

8.7.9 Hyperconjugation

Hyperconjugation is a general stabilising interaction. It involves delocalisation of σ electrons of C–H bond of an alkyl group directly attached to an atom of unsaturated

system or to an atom with an unshared p orbital. The σ electrons of C–H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p orbital. Hyperconjugation is a permanent effect.

To understand hyperconjugation effect, let us take an example of CH_3CH_2^+ (ethyl cation) in which the positively charged carbon atom has an empty p orbital. One of the C–H bonds of the methyl group can align in the plane of this empty p orbital and the electrons constituting the C–H bond in plane with this p orbital can then be delocalised into the empty p orbital as depicted in Fig. 8.4 (a).

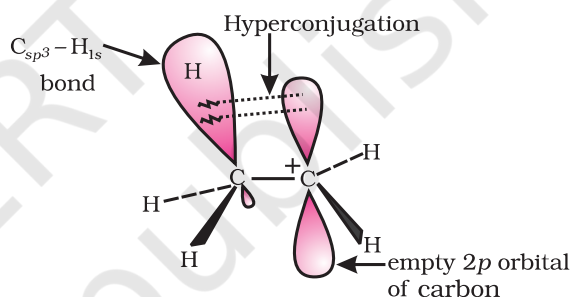
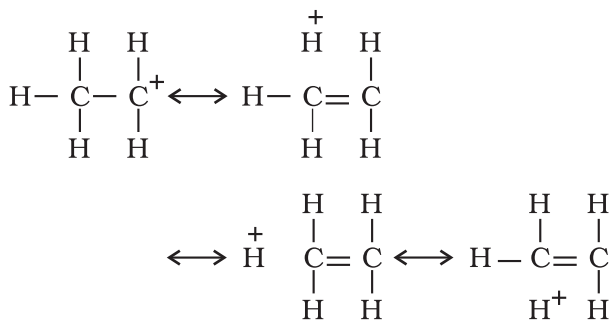
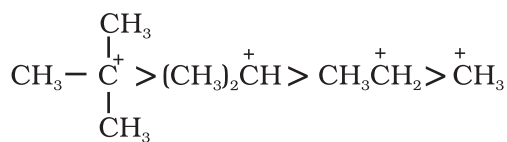


Fig. 8.4(a) Orbital diagram showing hyperconjugation in ethyl cation

This type of overlap stabilises the carbocation because electron density from the adjacent σ bond helps in dispersing the positive charge.



In general, greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilisation of the cation. Thus, we have the following relative stability of carbocations :



Hyperconjugation is also possible in alkenes and alkylarenes.

Delocalisation of electrons by hyperconjugation in the case of alkene can be depicted as in Fig. 8.4(b).

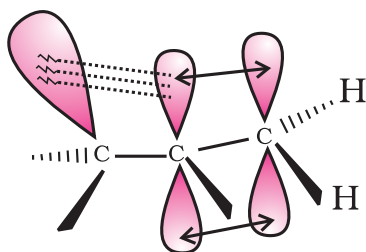
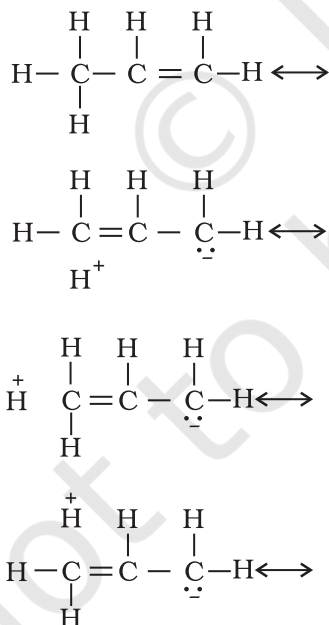


Fig. 8.4(b) Orbital diagram showing hyperconjugation in propene

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 8.19

Explain why $(\text{CH}_3)_3\text{C}^+$ is more stable than CH_3CH_2^+ and CH_3^+ is the least stable cation.

Solution

Hyperconjugation interaction in $(\text{CH}_3)_3\text{C}^+$ is greater than in CH_3CH_2^+ as the $(\text{CH}_3)_3\text{C}^+$ has nine C-H bonds. In CH_3^+ , vacant p orbital is perpendicular to the plane in which C-H bonds lie; hence cannot overlap with it. Thus, CH_3^+ lacks hyperconjugative stability.

8.7.10 Types of Organic Reactions and Mechanisms

Organic reactions can be classified into the following categories:

- Substitution reactions
- Addition reactions
- Elimination reactions
- Rearrangement reactions

You will be studying these reactions in Unit 9 and later in class XII.

8.8 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 :

- Sublimation
- Crystallisation
- Distillation
- Differential extraction and
- 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.

8.8.1 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.

8.8.2 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.

8.8.3 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 8.5). 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.

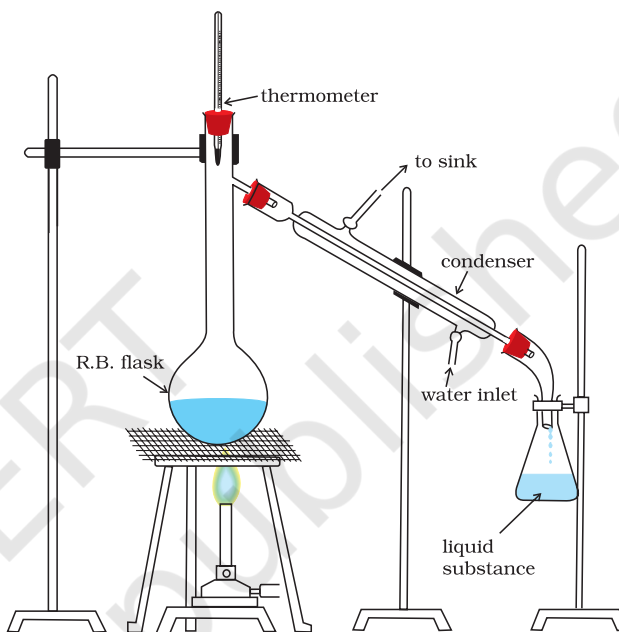


Fig.8.5 Simple distillation. The vapours of a substance formed are condensed and the liquid is collected in conical flask.

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.8.6, page 280).

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

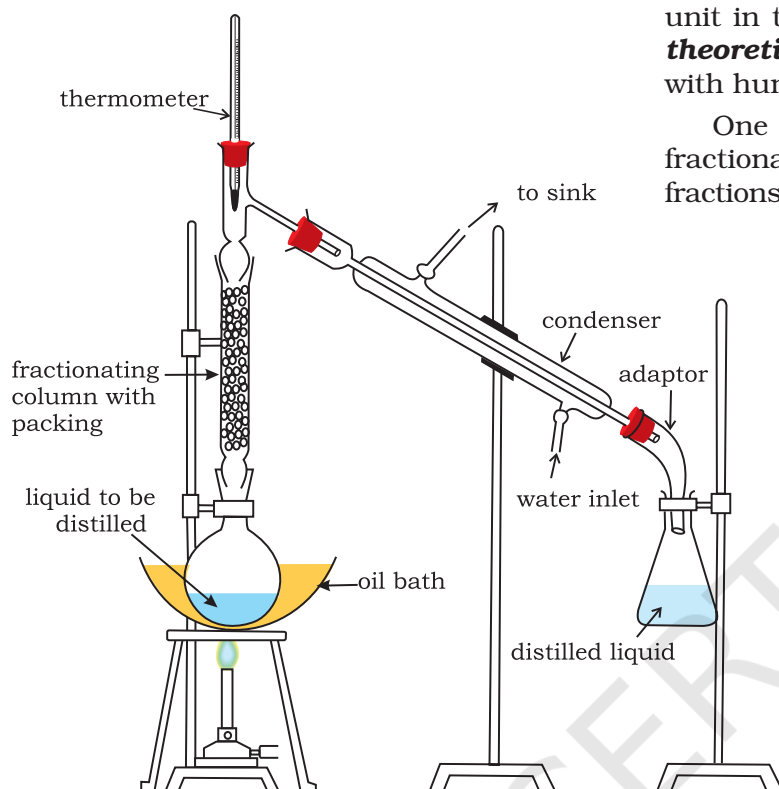


Fig.8.6 Fractional distillation. The vapours of lower boiling fraction reach the top of the column first followed by vapours of higher boiling fractions.

time the 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.8.7. 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 revaporises. 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.8.8). Glycerol can be separated from **spent-lye in soap industry** by using this technique.

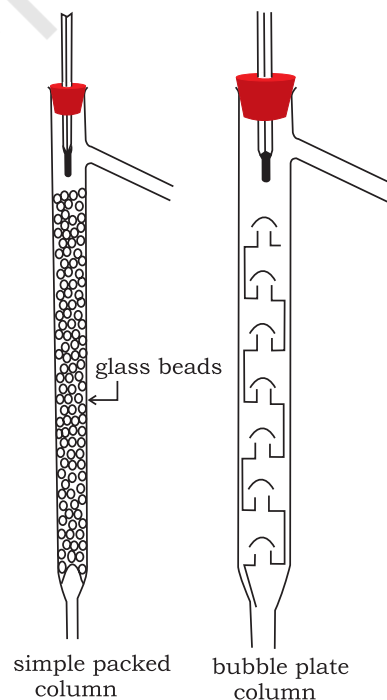


Fig.8.7 Different types of fractionating columns.

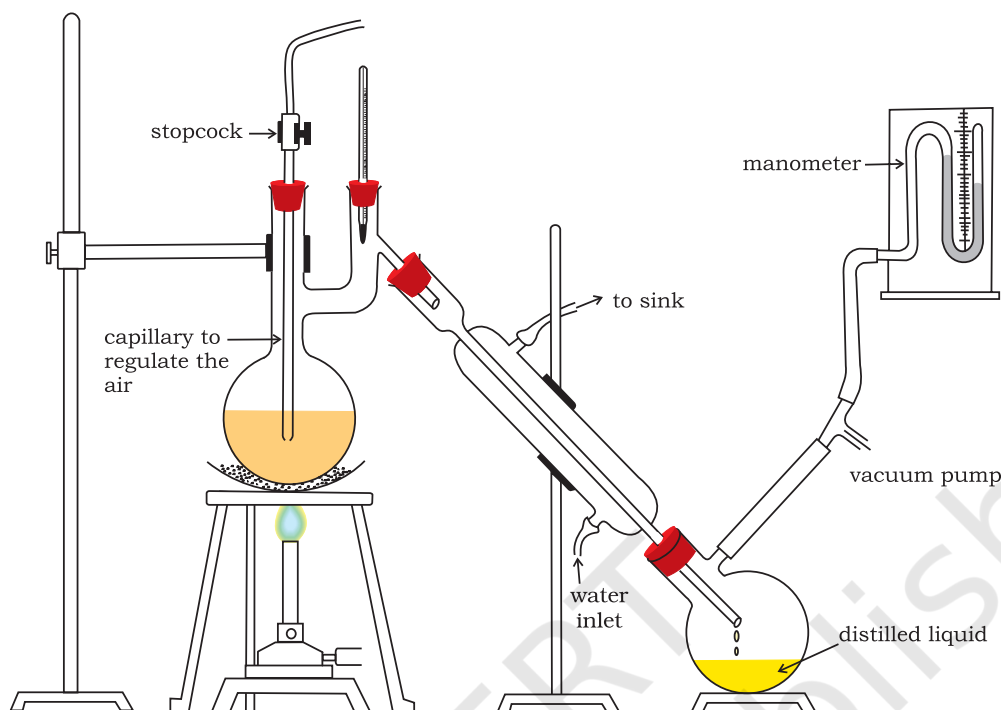


Fig.8.8 Distillation under reduced pressure. A liquid boils at a temperature below its vapour pressure by reducing the pressure.

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.8.9, Page 282).

8.8.4 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. 8.10 (Page 282). 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.

8.8.5 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

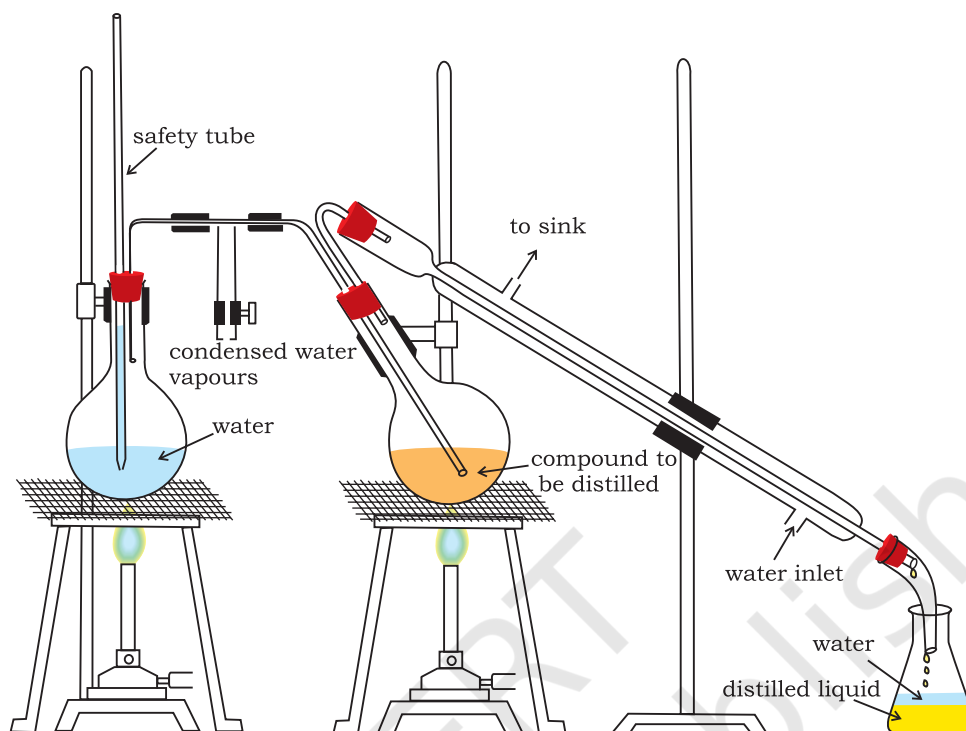


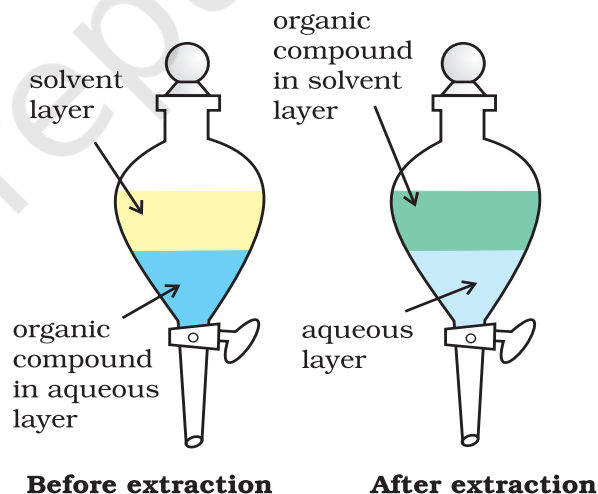
Fig.8.9 Steam distillation. Steam volatile component volatilizes, the vapours condense in the condenser and the liquid collects in conical flask.

name 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



Before extraction **After extraction**
Fig.8.10 Differential extraction. Extraction of compound takes place based on difference in solubility

distances over the stationary phase. Following 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. 8.11). 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. 8.11).

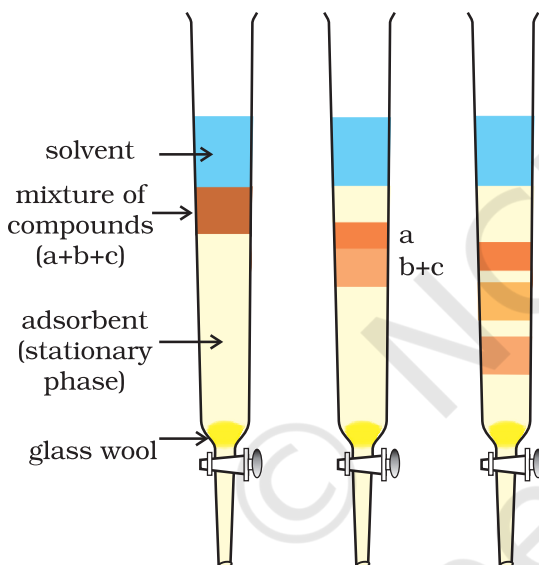


Fig.8.11 Column chromatography. Different stages of separation of components of a mixture.

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. 8.12a). 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. 8.12 b).

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

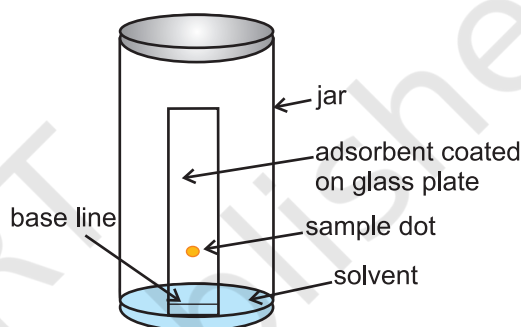


Fig.8.12 (a) Thin layer chromatography. Chromatogram being developed.

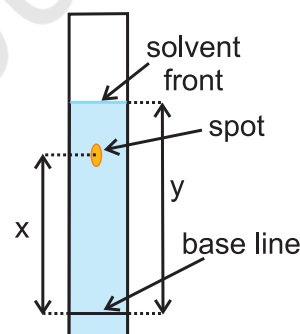


Fig.8.12 (b) Developed chromatogram.

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. 8.12b).

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. 8.13). 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

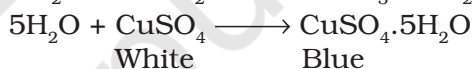
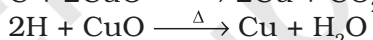
spot on the chromatogram. The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.

8.9 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.

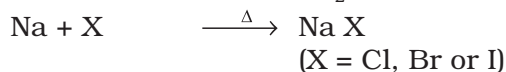
8.9.1 Detection of Carbon and Hydrogen

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).



8.9.2 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:



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

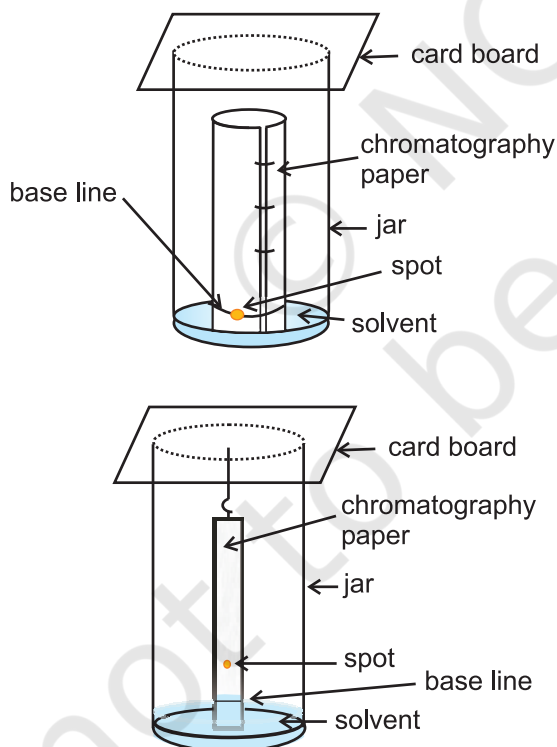


Fig.8.13 Paper chromatography. Chromatography paper in two different shapes.