







Friedrich Wöhler, was a German pioneer in organic chemistry. He is best known for his synthesis of urea an the organic compound from the inorganic compound, ammonium cyanate. This finding went against the mainstream theory of that time called vitalism which stated that organic matter possessed a special force or vital force inherent to all living things. He is also the first to isolate several chemical elements. He is the discoverer of the element aluminum and also the co-discoverer of yttrium, beryllium, and titanium.

Learning Objectives 🥑

After studying this unit students will be able to

- understand the reason for the tetra valency of carbon and shapes of organic molecules
- classify the organic compounds
- name the organic compounds according to IUPAC nomenclature and derive the structure from the IUPAC name
- describe various types of isomerism
- explain the principles of detection and estimation of elements in organic compounds
- describe various techniques used in the purification of organic compounds

### **11.1 Introduction**

Organic chemistry is the study of compounds of carbon. Carbon has a tendency to form more compounds with itself and other atoms (H, O, N, S and halogens) than any other elements. The tendency of an atom to form a chain of bonds with the atoms of the same element is called catenation. The high strength of C-C bond is responsible for its catenation property.

The word 'organic' means 'derived from living organisms'. Organic compounds were thought to be found only in living things. Cell the basic unit of living things, consumes, creates and consists of mainly organic compounds. DNA, the genetic material, the



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lipids, that forms our cell membrane and the glycogen the energy reserve stored in our liver are all organic compounds. Except few inorganic compounds like salt, water etc... all others such as food, medicine, clothing, cosmetics, fuel etc... are compounds of carbon. All the essential biochemical reactions are also organic in nature leading to the fomation of various essential bioorganic molecules such as lipoproteins, phospholipids, glycolipids etc...

Synthesis of acetic acid by kolbe and methane by Berthlot, confirmed that organic compounds can be synthesized in laboratory. Since then, millions of organic compounds were synthesised and characterised. The field of organic chemistry is very vast and its principles find applications in many industries including food, textile, petrochemical, pharmaceutical, dye, polymers, fertilizer, cosmetics etc... Discussing the importance of organic chemistry is just like describing a drop of water in a mighty ocean.

knowledge The of chemical bonding and molecular structure will help in understanding the properties of organic compounds. We know that, the carbon has four valance electrons and its ground state electronic configuration is  $1s^2 2s^2 2p^2$ . An atom can attain noble gas electronic configuration either by transferring or sharing of electrons. It is not possible for the carbon to form either C<sup>4+</sup> or C<sup>4-</sup> ions to attain the nearest noble gas configuration, as it requires large amount of energy. This implies that carbon cannot form ionic bond. Almost in all compounds of carbon, it forms four covalent bonds.

The formation of four covalent bonds can be explained as below. During bond formation, one of the electrons from 2s orbital is promoted to  $2p_z$  orbital. The formation of four sigma bonds by carbon can be explained on the basis of sp<sup>3</sup> hybridisation of carbon. Carbon forms multiple (double and triple) bonds in certain compounds. These can be explained by sp<sup>2</sup> and sp hybridisation of carbon. The carbon forms relatively short bonds which enable the lateral overlap of unhybridised 2p orbitals of sp<sup>2</sup> and sp hybridised carbon to form one and two pi bonds respectively.

Molecular stucture can be derived from the type of hybridisation. An  $sp^3$ hybridised carbon will have a tetrahedral geometry, a  $sp^2$  hybridised carbon will have trigonal planar geometry. and sp hybridised carbon will have a linear geometry.

#### Characteristics of organic compounds:

All organic compounds have the following characteristic properties.

- 1. They are covalent compounds of carbon and generally insoluble in water and readily soluble in organic solvent such as benzene, toluene, ether, chloroform etc...
- Many of the organic compounds are inflammable (except CCl<sub>4</sub>). They possess low boiling and melting points due to their covalent nature
- 3. Organic compounds are characterised by functional groups. A functional group is an atom or a specific combination of bonded atoms that

react in a characteristic way, irrespective of the organic molecule in which it is present. In almost all the cases, the reaction of an organic compound takes place at the functional group. They exhibit isomerism which is a unique phenomenon.

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4. **Homologous series:** A series of organic compounds each containing a characteric functional group and the successive members differ from each other in molecular formula by a CH, group is called homologous series. Eg.

**Alkanes:** Methane  $(CH_4)$ , Ethane  $(C_2H_6)$ , Propane  $(C_3H_8)$  etc.

Alcohols: Methanol (CH<sub>3</sub>OH), Ethanol (C<sub>3</sub>H<sub>5</sub>OH) Propanol (C<sub>3</sub>H<sub>7</sub>OH) etc.)

Compounds of the homologous series are represented by a general formula Alkanes  $C_nH_{2n+2}$ , Alkenes  $C_nH_{2n}$ , Alkynes  $C_nH_{2n-2}$  and can be prepared by general methods. They show regular gradation in physical properties but have almost similar chemical property.

**11.2 Classification of organic compounds** 

The existing large number of organic compounds and ever-increasing number have made it necessary to classify them. They may be classified based on their structure or the functional group.

#### **11.2.1 Classification based on the structure:**



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Based on the above classification let us classify the following compounds.

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1. Classify the following compounds based on the structure

i) 
$$CH \equiv C - CH_2 - C \equiv CH$$

ii) 
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$



Solutions:

- (i) Unsaturated open chain compound
- (ii) saturated open chain compound
- (iii) aromatic benzenoid compound
- (iv) alicyclic compound

### Evaluate Yourself

- 1) Give two examples for each of the following type of organic compounds.
- (i) non-benzonoid aromatic,
- (ii) aromatic heterocyclic,
- (iii) alicyclic and
- (iv) aliphatic open chain.

## 11.2.2 Classification based on functional groups:

# Table 11.1 Class of compounds and their functional group





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| S. No. | Class of<br>compounds     | Functional group        | General formula<br>(R - Alkyl group) |
|--------|---------------------------|-------------------------|--------------------------------------|
| 16     | Cyanide<br>(Nitrile)      | —c≡n                    | R-CN                                 |
| 17     | Isocyanide                | —-NC                    | R-NC                                 |
| 18     | Cyanate                   | —OCN                    | R-OCN                                |
| 19     | Isocyanate                | NCO                     | R-NCO                                |
| 20     | Thiocyanate               | ——SCN                   | R-SCN                                |
| 21     | Isothiocyanate            | — NCS                   | R-NCS                                |
| 23     | Thioalcohols<br>or thiols | ——SH                    | R-SH                                 |
| 24     | Thioethers                | —R                      | R-S-R'                               |
| 25     | Imines                    | ——NH                    | R-CH=NH                              |
| 26     | Nitroso<br>compounds      | NO                      | R-NO                                 |
| 27     | Hydrazines                | ——NH——NH <sub>2</sub>   | R-NH-NH <sub>2</sub>                 |
| 28     | Hydrazo<br>compounds      | —_NH—NH—                | R-NH-NH-R                            |
| 29     | Phenols                   | ОН                      | C <sub>6</sub> H <sub>5</sub> OH     |
| 30     | Imide                     | 0 R 0<br>       <br>CNC | RCON(R')<br> <br>COR"                |

# 11.3 Nomenclature of organic compounds:

The International Union of Pure and Applied Chemistry (IUPAC) is the world authority on chemical nomenclature and terminology, naming of new elements in the periodic table standardized methods for measurement; atomic weights, and many other critically-evaluated data. According to IUPAC recommendations to name any organic compound, it is considered as a derivative of its parent saturated hydrocarbon. The IUPAC name of an organic compound consists of three parts.

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#### prefix + root word + suffix

Root word denotes the number of carbon atoms in the longest continiuous chain in molecules. Prefix denotes the group(s) attached to the main chain which is placed before the root. Suffix denotes the funtional group and is placed after the root word.

# Table 11.2 Number of carbons in parent chain and the corresponding root words

| Chain length(or)<br>no. of carbon atoms | Root word | Chain length(or)<br>no. of carbon atom | Root word   |
|---|-----------|--|-------------|
| C <sub>1</sub>                          | Meth-     | C <sub>17</sub>                        | Heptadec-   |
| C <sub>2</sub>                          | Eth-      | C <sub>18</sub>                        | Octadec-    |
| C <sub>3</sub>                          | Prop-     | C <sub>19</sub>                        | Nonadec-    |
| $C_4$                                   | But-      | C <sub>20</sub>                        | Icos-       |
| C <sub>5</sub>                          | Pent-     | C <sub>21</sub>                        | Henicos     |
| C <sub>6</sub>                          | Hex-      | C <sub>22</sub>                        | Docos       |
| C <sub>7</sub>                          | Hept-     | C <sub>30</sub>                        | Triacont-   |
| C <sub>8</sub>                          | Oct-      | C <sub>31</sub>                        | Hentriacont |
| C <sub>9</sub>                          | Non-      | C <sub>32</sub>                        | Dotriacont  |
| C <sub>10</sub>                         | Dec-      | C <sub>40</sub>                        | Tetracont-  |
| C <sub>11</sub>                         | Undec-    | C <sub>50</sub>                        | Pentacont-  |

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| Chain length(or)<br>no. of carbon atoms | Root word | Chain length(or)<br>no. of carbon atom | Root word  |
|---|-----------|--|------------|
| C <sub>12</sub>                         | Dodec-    | C <sub>60</sub>                        | Hexacont-  |
| C <sub>13</sub>                         | Tridec -  | C <sub>70</sub>                        | Heptacont- |
| C <sub>14</sub>                         | Tetradec- | C <sub>80</sub>                        | Octacont-  |
| C <sub>15</sub>                         | Pentadec- | C <sub>90</sub>                        | Nonacont-  |
| C <sub>16</sub>                         | Hexadec-  | C <sub>100</sub>                       | Hect-      |

**Suffix:** There are two types of suffix. They are primary suffix and secondary suffix

**Primary suffix:** It denotes the saturation/ unsaturation of organic compounds. It is added immediately after the root word. Primary suffix for various saturated and unsaturated carbon chains are as follows:

# Table 11.3 Primary suffix for various saturated and unsaturated carbon chains

| Name & type of carbon<br>chain | Primary<br>suffix |
|--------------------------------|-------------------|
| Saturated, C-C                 | ane               |
| Unsaturated carbon chain       |                   |
| one C=C bond                   | ene               |
| Two C==C bonds                 | diene             |
| Three C=C bonds                | triene            |
| One C≡C bond                   | yne               |
| Two C≡C bonds                  | diyne             |

**Secondary suffix:** It is used to denote the nature of functional group present in the organic compound. It is added to the primary suffix by removig its terminal 'e'. Secondary suffix names for some functional groups is listed below in table 11.4

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# Table 11.4 Secondary suffix and prefixes for some functional groups:

| Class of organic<br>compounds | Functional group             | Prefix              | Secondary suffix   |
|-------------------------------|------------------------------|---------------------|--------------------|
| Alcohols                      | —ОН                          | hydroxy-            | -ol                |
| Thioalco-<br>hols             | ——SH                         | mercapto            | -thiol             |
| Aldehydes                     | о<br>Ш<br>с—н                | formyl-             | -al                |
| Ketones                       | )c=0                         | 0хо-                | -one               |
| Carboxylic<br>acid            | о<br>с_он                    | carboxy-            | -oic acid          |
| Esters                        | O<br>□□<br>C──OR             | Alkoxy–<br>Carbonyl | -oate              |
| Acid<br>chlorids              | о<br>Ш<br>с—сі               | chloro-<br>carbonyl | -oyl<br>chloride   |
| Acid<br>amides                | 0<br>Ⅲ<br>—C—NH <sub>2</sub> | Carbam<br>oyl       | -amide             |
| Amines                        | NH <sub>2</sub>              | amino-              | -amine             |
| Nitriles                      | —c≡n                         | cyano-              | -nitrile           |
| Sulphonic<br>acid             | ——SO <sub>3</sub> H          | sulpho-             | -sulphonic<br>acid |

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**Prefix:** Substituents that are attached to the parent carbon chain are denoted by adding prefix names before the root word. The prefix names for some common substituents are listed below. If the functional groups are not part of the parent chain, they are considered as substituents. In such cases its prefix name is added before the root word. Prefix names for some functional groups mentioned along with their secondary prefix are listed in table 11.4

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# Table 11.5 List of substitutents and their Prefix names

| Substituent group   | Prefix                     |
|---|----------------------------|
| -F  | Fluoro                     |
| -Cl   | Chloro                     |
| -Br   | Bromo                      |
| -I  | Iodo                       |
| -NO <sub>2</sub>  | Nitro                      |
| -NO   | Nitroso                    |
| -N=N-   | Diazo                      |
| -OR   | Alkoxy                     |
| $-OCH_3$ (or) $-OMe$  | Methoxy                    |
| $-OC_2H_5(or) -OEt$   | Ethoxy                     |
| -CH <sub>3</sub> (or) –Me   | Methyl                     |
| $-C_{2}H_{5}(or) -Et$   | Ethyl                      |
| -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>                  | Propyl                     |
| -CH(CH <sub>3</sub> ) <sub>2</sub>                                  | Propan-2-yl<br>(isopropyl) |
| -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> | Butyl                      |

| Substituent group  | Prefix                             |
|--|------------------------------------|
| -CH <sub>2</sub> -CH (CH <sub>3</sub> )-CH <sub>3</sub>                              | 2-methyl propyl<br>(isobutyl)      |
| -C(CH <sub>3</sub> ) <sub>3</sub>  | 2-methylpropan-2-yl<br>(tertbutyl) |
| -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> | Pentyl                             |
| -CH <sub>2</sub> -CH (CH <sub>3</sub> )-CH <sub>2</sub> -CH <sub>3</sub>             | 2-methyl butyl                     |
| -CH <sub>2</sub> -C (CH <sub>3</sub> ) <sub>3</sub>                                  | 2,2-dimethyl propyl<br>(neopentyl) |

# 11.3.1 IUPAC rules for nomenclature of organic compounds

The following steps should be followed for naming an organic compound as per IUPAC nomenclature.

- 1. Choose the longest carbon chain. (Root word). Consider all the other groups attached to this chain as substitutents.
- 2. Numbering of the longest carbon chain
- 3. Naming of the substituents (prefixes or suffixes)
- 4. Arrange the substitutents in the alphabetical order
- 5. Write the name of the compound as below

"prefix + root word + primary suffix + secondary suffix"



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#### The following are guide lines for writing IUPAC of the organic compound.

1. The IUPAC names are always written as single word, with notable exception of organic salts, acids and acid derivatives.

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- 2. Commas are used between two adjacent number or letter symbols, and hypens are used to separate numbers and letter symbol in names Eg: 2,2-Dimethyl-3-hexene N,N-Dimethyl methanamide
- 3. Structural prefix such as, meso-, cis-, trans-, are italicised and joined to the name by a hypen. These prefixes are omitted in alphabetising compound names or in capitalising names at the beginning of a sentence.**Eg:trans-2-Butene**
- 4 .Structural prefixes such as di, tri, tetra are treated as a part of the basic name and therefore are neither italicised nor separated by a hypen. These prefixes are not taken into account in alphabetising compound names **eg: 4- Ethyl -2,2-dimethyl hexane.**
- 5 To name alicyclic compounds , the additional rules should be followed as illustrated in the table 11.6







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- 2) write structural formula for the following compound
- (i) Cyclohexa-1, 4-diene (ii) Ethynyl cyclohexane

#### NOMENCLATURE OF AROMATIC COMPOUNDS:

An aromatic compound consists of two parts nucleus and side chain

(A) **Nucleus:** The benzene ring present in aromatic compound is called nucleus. It is represented as follows

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(B) Side chain: Alkyl or any other aliphatic group attached to the benzene nucleus by replacing one or more hydrogen atom is called the side chain



If one hydrogen atom, (or) two hydrogen atoms or three hydrogen atoms are replaced in the benzene ring by some other groups, they are termed as mono substituted, di substituted or tri substituted derivative respectively.

Example

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If more than one hydrogen atom of benzene ring is replaced by some other atom or group, then their position is mentioned by Arabic numerals 1,2,3 ..... In case of disubstitution, respective position of two groups can also be mentioned as follows.

ortho - adjacent; represented as - o meta - alternate; represented as - m Para - opposite; represented as - p **Aromatic compounds are basically of two types:** 

1. Nuclear substituted aromatic compounds: These are the compounds in which the functional group is directly attached to the benzene ring. They are named as derivatives of benzene.



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2. Side chain substituted aromatic compounds: These are the compounds in which the functional group is present in the side chain of the benzene ring. These are named as phenyl derivatives of the corresponding aliphatic compounds.

#### Side chain substituted



#### Aryl groups

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Selection of parent hydrocarbon out of side chain and benzene ring is based on (more or less) some rule as for the alicyclic compounds.

### Evaluate Yourself

- 3) Write structural formula for the following compounds
- (i) m dinitrobenzene (ii) p-dichloro benzene (iii)1, 3, 5- Trimethyl benzene

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### Table 11.3.1. 2

| Compound Structure and IUPAC Name   | Prefix with position number | Root<br>word | Primary<br>suffix | Secondary<br>suffix |
|---|-----------------------------|--------------|-------------------|---------------------|
| CH <sub>3</sub>   |                             |              |                   |                     |
| CH <sub>3</sub> -CH <sub>2</sub> -CH-CH <sub>2</sub> -CH <sub>3</sub>   | 3-methyl                    | pent         | ane               | -                   |
| 3-methylpentane   |                             |              |                   |                     |
| $CH_{3}$ $CH_{3}-C-CH_{2}-CH_{2}-CH-CH_{3}$ $CH_{3}$ $CH$  | 2,2,5- trimethyl            | Hept         | ane               | _                   |
| $\begin{array}{c} \stackrel{1}{\overset{1}{\text{CH}_{3}-\overset{2}{\text{CH}}-\overset{3}{\text{CH}-\overset{4}{\text{CH}_{2}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{2}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{2}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{2}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{2}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{2}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{2}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{2}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{2}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{2}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{2}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{2}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{3}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{3}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{3}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{3}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{3}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{3}-\overset{5}{\text{CH}_{3}-\overset{5}{\text{CH}_{3}}}}_{(H_{3}-\overset{4}{\text{CH}_{3}-\overset{5}}{\text{CH}_{3}-\overset{5}{\text{CH}_{3}-\overset{5}}{\text{CH}_{3}-\overset{5}}{\text{CH}_{3}-\overset{5}}{\overset{5}}}}}}}}}}}}}}}}}}}}}}}}}}}}}$  | 3-ethyl-<br>-2-methyl       | pent         | ane               | _                   |
| $\begin{array}{c} \begin{array}{c} 2 & 3 & 4 \\ CH_3 - CH - CH_2 - CH_3 \\ 1 \\ CHO \\ 2 - methylbutanal \end{array}$   | 2-methyl                    | but          | an¢               | al                  |
| $\begin{array}{c} \begin{array}{c} \begin{array}{c} 2 \\ CH_{3}-CH_{2}\end{array} \\ - \begin{array}{c} 2 \\ - \begin{array}{c} 2 \\ - \begin{array}{c} 3 \\ - \begin{array}{c} 4 \\ - \begin{array}{c} 4 \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ - \end{array} \\ - \end{array} \\ - \begin{array}{c} 2 \\ - \end{array} \\ \\ - \end{array} \\ \\ - \end{array} \\ - \\ -$ | 2-ethyl                     | but          | en¢               | oic acid            |
| CHO<br>1 $2$ $3$ $4$ $5HOOC -C -C -C H_2 -C H_3 -C H_3 -C H_3 -C H_3 -C H_3 -C H_3 -C -C -C -C -C -C -C -C$   | 2-formyl-2-methyl           | hept         | an¢               | oic acid            |
| $\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} CH_{3} \\ \end{array} \\ HOOC \end{array} \xrightarrow{2} \\ C \\ -C \\ C \\ -C \\ -C \\ -C \\ -C \\ -C $   | 5-hydroxy-2,2-<br>dimethyl  | hept         | an¢               | oic acid            |
| $\begin{array}{c} & & & \\ \hline COOH & \hline COOH \\ & & & \\ \hline H_{3}C-CH_{2} \\ & & \\ \hline CH-CH_{2}-CH \\ & & \\ \hline CH_{2}-CH_{2}-CH_{2}-CH_{3} \\ \hline \\ & & \\ \hline 2-ethyl-4-propylpentanedioic acid \end{array}$  | 2-ethyl-<br>4-propyl        | pent         | an¢               | oic acid            |

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| Compound Structure and IUPAC Name   | Prefix with position number | Root<br>word | Primary<br>suffix | Secondary<br>suffix |
|---|-----------------------------|--------------|-------------------|---------------------|
| $\begin{array}{c} CH_3-CH_2-CH_2-CH-CH_2-CH_3\\ 6 & 5 & 4 & 3 & 2 & 1\\ \hline CH_3\\ 3-methylhexane\end{array}$  | 3-methyl                    | hex          | ane               | -                   |
| $\begin{array}{c} \begin{array}{c} \begin{array}{c} 2 \\ CH_{3} \end{array} \begin{array}{c} 2 \\ CH - CH_{2} - CH_{3} \end{array} \begin{array}{c} 4 \\ H_{2} \end{array} \end{array}$   | 2-Methyl                    | but          | an¢               | al                  |
| $\begin{array}{c} \hline CH_3-CH_2 \\ \hline CH_3-CH_2 \\ \hline CH_1 \\ \hline COOH \\ \hline 2-ethylbut-3-enoic acid \end{array}$   | 2-ethyl                     | but          | 3- en¢            | oic acid            |
| $\begin{array}{c} 6 & 5 & 4 & 3 & 2 & 1 \\ CH_3 - CH_2 - CH - CH_2 - CH_2 CH_2 CN \\ CH_3 \\ 4 - methylhexanenitrile \end{array}$   | 4-methyl                    | hex          | ane               | nitrile             |
| $\begin{array}{c} CH_2=CH\\ 4 & 3 \end{array} - CH - CH_3\\ 2\\ \hline 1CONH_2\\ 2-methylbut-3-enamide\end{array}$  | 2-methyl                    | but          | 3 - en¢           | amide               |
| $CH_{3}-CH-CH_{2}-CH=CH_{4}-CH_{5}$<br>hex-4-en-2-ol  |                             | hex          | 4 - en¢           | 2- ol               |
| $CH_{3} - CH_{2} - CH - CH_{2} - CH - CH_{2} - CH_{3} - CH_{2} - CH_{3} - CH_{2} - CH_{3} - $  | 3-ethyl<br>5- methyl        | hept         | ane               | -                   |
| $\begin{array}{c} CH_{3} \\ 1 \\ CH_{3} - CH - CH - CH_{2} - CH_{2} - CH_{3} \\ \hline C_{2}H_{5} \\ 3 - ethyl-2 - methylhexane \end{array}$  | 3-ethyl-2-methyl            | hex          | ane               | -                   |
| $\begin{array}{c} \hline CH_{3} \hline C_{2}H_{5} \\ \hline CH_{3} - CH_{2} \hline C - CH - CH_{2} - CH_{3} \\ \hline H_{3} \hline CH_{2} - CH_{2} - CH_{3} \\ \hline CH_{2} - CH_{2} - CH_{3} \\ \hline CH_{2} - CH_{2} - CH_{3} \\ \hline SH_{2} - CH_{3} \hline CH_{2} - CH_{3} \\ \hline SH_{2} - CH_{3} \hline CH_{3} - CH_{3} \\ \hline SH_{2} - CH_{3} \hline CH_{3} - CH_{3} \\ \hline SH_{3} - CH_{3} - CH_{3} \hline CH_{3} - CH_{3} \\ \hline SH_{3} - CH_{3} - CH_{3} \hline CH_{3} - CH_{3} \\ \hline SH_{3} - $ | 3,4-diethyl-<br>4-methyl    | hept         | ane               | _                   |
| $CH_{3} - C = CH - CH - CH_{3}$ $CH_{3} - C = CH - CH - CH_{3}$ $CH_{3} - C = CH - CH - CH_{3}$ $CH_{3} - C = CH - CH - CH_{3}$ $CH_{3} - C = CH - CH - CH_{3}$ $CH_{3} - C = CH - CH - CH_{3}$ $CH_{3} - C = CH - CH - CH_{3}$ $CH_{3} - C = CH - CH - CH_{3}$ $CH_{3} - C = CH - CH - CH_{3}$   | 2,4-dimethyl                | pent         | 2 - ene           | _                   |

| Compound Structure and IUPAC Name  | Prefix with position number             | Root<br>word | Primary<br>suffix | Secondary<br>suffix |
|--|---|--------------|-------------------|---------------------|
| ${}^{7}_{CH_{3}}-{}^{6}_{CH}={}^{5}_{CH}-{}^{4}_{CH}={}^{3}_{C}-{}^{2}_{CH}={}^{1}_{CH_{2}}$ $\downarrow \qquad \qquad$ | 3-methyl                                | hept         | 1, 3, 5 - triene  | -                   |
| $CH_3-CH_2-CH_2-C \equiv CH_5 + 4 + 3 + 2 + 1$<br>1-pentyne (or) pent -1- yne  | _                                       | pent         | 1- yne            | _                   |
| $\begin{array}{c} 1 \text{ CH}_{3} \\ \hline \\ H_{3}\text{C} \\ \hline \\ 2 \\ \hline \\ C \\ \hline \\ G \\ \hline \\ OH \\ 3 \text{ CH}_{3} \end{array}$ 2-methyl propan-2-ol   | 2-methyl                                | prop         | an¢               | 2-ol                |
| $\begin{array}{c c} H_{3}C & -CH & -CH_{2} & -CH_{2} \\ \hline H_{3}C & 4 & 2 \\ \hline CH_{3} & 1CH_{2}OH \\ \hline 4 & -methylpentan -1- ol \end{array}$   | 4-methyl                                | pent         | an¢               | 1-ol                |
| $H_3^3C \xrightarrow{CH_3}_{1} H_2OH$<br>2,2-dimethyl propan -1- ol  | 2,2-dimethyl                            | prop         | an¢               | 1-ol                |
| $CH_{3} - CH_{2} - C - OH$<br>propanoic acid   |   | prop         | an¢               | oic acid            |
| $\begin{array}{c} 2 & 1 & 5 \\ 3 & -4 & -CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 \\ 3 & -4 & -CH_3 \\ 3 - methyl-5 - (1, 3 - dimethylcyclobutyl) pentanal \end{array}$  | 3-methyl-5-<br>(1,3-dimethylcyclobutyl) | pent         | an¢               | al                  |
| <sup>3</sup> <sub>CH<sub>3</sub></sub> - <sup>2</sup> <sub>CH</sub> - <sup>1</sup> <sub>CHO</sub><br>2-cyclopentylpropanal   | 2-cyclopentyl                           | prop         | an¢               | al                  |
| $^{3}$ CH <sub>3</sub> -CH-CHO<br>$^{2}$ 2-(cyclobut-2-enyl)propanal   | 2-(cyclobut-<br>2-enyl)                 | prop         | an¢               | al                  |

an¢

3 - one

pent

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 $\begin{array}{c} 1 & 2 \\ CH_3 \cdot CH_2 - \boxed{3} & 4 & 5 \\ C & -CH_2 \cdot CH_3 \\ \parallel \\ O \end{array}$ 

pentan-3-one

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| Compound Structure and IUPAC Name   | Prefix with position number      | Root<br>word | Primary<br>suffix | Secondary<br>suffix |
|---|----------------------------------|--------------|-------------------|---------------------|
| $ \begin{array}{c} 5\\ CH_{3}C = CH_{3} \\ CH_{3} \\ 4-methylpent-3-en-2-one \end{array} $  | 4-methyl                         | pent         | 3- en¢            | 2-one               |
| $5 \\ CH_3 - CH_2 - 3 \\ CH_2 - C = CH \\ C = CH$<br>pent-1-yn-3-one  | _                                | pent         | 1- yn¢            | 3- one              |
| CH=CH-COOH<br>3<br>3-phenyl prop -2-enoicacid   | 3-phenyl                         | prop         | 2- en¢            | oic acid            |
| $\begin{array}{c} CH_3 - CH_2 - CH_2 - OH - CH_3\\ 3 & 2 & 1\\ N - methyl propan - 1 - amine \end{array}$   | N-methyl                         | prop         | an¢               | 1-amine             |
| $\begin{array}{c} 1\\ CH_{3}\\ CH_{3}-CH-NH-CH_{3}\\ 3 2 \end{array}$   | N-methyl                         | prop         | an¢               | 2-amine             |
| N-methylpropan-2-amine<br>$CH_3$<br>$CH_3$<br>$CH_3$ - $CH_2$ - $CH_2$ - $N$ ( $CH_3$ )<br>N,N-dimethylpropan-1-amine   | N,N-dimethyl                     | prop         | an¢               | 1-amine             |
| $\begin{array}{c} \begin{array}{c} CH_{3} \\ CH_{3} - CH_{2} - CH_{2} - N - CH_{2} - CH_{3} \\ CH_{3} - CH_{2} - CH_{2} - N - CH_{2} - CH_{3} \\ \end{array}$<br>N-ethyl-N-methylpropan-1-amine   | N-ethyl-<br>N-methyl             | prop         | an¢               | 1-amine             |
| N(CH <sub>3</sub> ) <sub>2</sub><br>N,N-dimethylbenzenamine   | N,N-dimethyl                     | benzen¢      |                   | amine               |
| $\begin{array}{c} & & & \\ & &$ | 4-hydroxy-3-<br>(2-hydroxyethyl) | hexa         | an¢               | oic acid            |

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# 11.4 Structural representation of organic compounds

Molecular formula of a compound is the simplest, least informative representation, showing the ratio of atoms present. The structure of an organic compound can be represented using any one of the below mentioned methods.

- 1. Lewis structure or dot structure,
- 2. Dash structure or line bond structure,
- 3. Condensed structure
- 4. Bond line structure

We know how to draw the Lewis structure for a molecule. The line bond structure is obtained by representing the two electron covalent bond by a dash or line (-) in a Lewis structure. A single line or dash represents single  $\sigma$  covalent bond, double line represents double bond (1 $\sigma$  bond, 1 $\pi$  bond) and a triple line represents

triple bond (1 $\sigma$  bond, 2 $\pi$  bond). Lone pair of electrons on heteroatoms may or may not be shown. This represents the complete structural formula.

This structural formula can be further abbreviated by omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a condensed structural formula.

For further simplification, organic chemists use another way of representing the structures in which only lines are used. In this type of representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are shown in a zigzag fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc. These representations can be easily understood by the following illustration.

| Molecular<br>forumula                                     | Complete structural<br>formula (dash line<br>structure)   | Condensed<br>Structure                                | Bond line<br>Structure |
|---|---|---|------------------------|
| n-propanol<br>C <sub>3</sub> H <sub>8</sub> O             | $ \begin{array}{ccccc} H & H & H \\   &   &   \\ H - C - C - C - C - OH \\   &   &   \\ H & H & H \end{array} $ | CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH | ОН                     |
| 1,3-butadiene $C_4H_6$                                    | H H H H H $         $ $H - C = C - C = C - H$   | CH <sub>2</sub> =CH-CH=CH <sub>2</sub>                |                        |
| t-butyl chlo-<br>ride<br>C <sub>4</sub> H <sub>9</sub> Cl | H H H H C C C C C C C C C C C C C C C C   | $CH_{3} - CH_{3} - CI$                                | Cl                     |



#### **Molecular models**



Fig 11.3 Methane - Molecular Models

Molecular models are physical devices that are used for a better visualisation and perception of three dimensional shapes of organic molecules. These are made of wood, plastic or metal and are commercially available. (i) Frame work model (ii) Ball and stick model & (iii) space filling model. In the frame work model only the bonds connecting the atoms themselves are shown. This model emphasizes the pattern of bonds of a molecule while ignoring the size of the atom. In the ball and stick model, both the atoms and the bonds are shown. Ball represent atoms and the stick a bond. Compounds containing C=C can be best represented by using springs in place of sticks and this model is termed as ball and spring model. The space filling model emphasizes the relative size of each atom based on its vander-waals radius.

#### Three dimensional representation of organic molecules:

The simplest convention is solid and dashed wedge formula in which 3-D image of a molecule can be perceived from two dimensional picture. In this representation a tetrahedral molecule with four atoms or group a,b,c and d bonded to it can be represented by a wedge formula as follows. A solid wedge ( \_\_\_\_\_ ) (or a heavy line) is used to indicate a bond projecting

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#### Fisher projection formula:

This is a method of representing three dimensional structures in two dimension. In this method, the chiral atom(s) lies in the plane of paper. The horizontal substituents are pointing towards the observer and the vertical substituents are away from the observer. Fisher projection formula for tartaric acid is given below.



#### Sawhorse projection formula:

Here the bond between two carbon atoms is drawn diagonally and slightly elongated. The lower left hand carbon is considered lying towards the front and the upper right hand carbon towards the back. The Fischer projection inadequately portrays the spatial relationship between ligands attached to adjacent atoms. The sawhorse projection attempts to clarify the relative location of the groups.



#### Newman projection formula:

In this method the molecules are viewed from the front along the carboncarbon bond axis. The two carbon atom forming the  $\sigma$  bond is represented by two circles. One behind the other so that only the front carbon is seen. The front carbon atom is shown by a point where as the carbon lying further from the eye is represented by the origin of the circle. Therefore, the C-H bonds of the front carbon are depicted from the circle while C-H bonds of the back carbon are drawn from the circumference of the circle with an angle of 120° to each other.



# 11.5. Isomerism in organic compounds:

The term 'isomerism' was given by Berzelius, and its represents of existence

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of two or more compounds with the same molecular formula but different structure and properties (physical, chemical, or both). Compounds exhibiting this isomerism are called isomers. The difference in properties of two isomers is due to difference in (bond connectivity or spatial arrangement) the arrangement of atoms within their molecules. Isomerism is broadly divided into two types. i. Constitutional isomerism, ii. stereoisomerism.



### 11.5.1 Constitutional isomers (Formerly structural isomers):

This type of isomers have same molecular formula but differ in their bonding sequence. Structural or constitutional isomerism is further classified into following types.

### (a) Chain or nuclear or skeletal isomerism:

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These isomers differ in the way in which the carbon atoms are bonded to each other in a carbon chain or in other words isomers have similar molecular formula but differ in the nature of the carbon skeleton (ie. Straight or branched)



#### (b) Position isomerism:

If different compounds belonging to same homologous series with the same molecular formula and carbon skeleton, but differ in the position of substituent or functional group or an unsaturated linkage are said to exhibit position isomerism.

#### **Example:**

(i) Molecular formula 
$$C_5H_{10}$$
  
 $CH_3 - CH_2 - CH_2 - CH = CH_2$   
Pent-1-ene  
and  
 $CH_3 - CH_2 - CH = CH - CH_3$   
Pent-2-ene

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#### (c) Functional isomerism:

Different compounds having same molecular formula but different functional groups are said to exhibit functional isomerism.

#### Example:

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(i) 
$$C_{3}H_{6}O$$
  $CH_{3}$ — $CH_{2}$ ·CHO  
Propanal  
(aldehyde group)  
O  
 $CH_{3}$ — $C$ — $CH_{3}$   
Propanone  
(keto group)  
(ii)  $C_{3}H_{6}O_{2}$   $CH_{3}$ — $CH_{2}$ — $COOH$   
Propanoic acid  
acid group  
 $CH_{3}$ — $COOCH_{3}$   
Methyl acetate  
(ester group)

(d) Metamerism: This type of isomerism is a special kind of structural isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group or different alkyl groups attached to the either side of the same functional group and having same molecular formula. This isomerism is shown by compounds having functional group such as ethers, ketones, esters and secondary amines between two alkyl groups.



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(e) Tautomerism: It is a special type of functional isomerism in which a single compound exists in two readily inter convertible structures that differ markedly in the relative position of atleast one atomic nucleus, generally hydrogen. The two different structures are known as tautomers. There are several types of tautomerism and the two important types are dyad and triad systems.

(i) **Dyad system:** In this system hydrogen atom oscillates between two directly linked polyvalent atoms. Eg:



In this example hydrogen atom oscillates between carbon & nitrogen atom

### Evaluate Yourself

4) Write all the possible isomers of molecular formula  $C_4H_{10}O$  and identify the isomerisms found in them.

(ii) Triad system: In this system hydrogen atom oscillates between three polyvalent atoms. It involves 1,3 migration of hydrogen atom from one polyvalent atom to other within the molecule. The most important type of triad system is keto-enol tautomerism and the two groups of tautomers are ketoform and enol-form. The polyvalent atoms involved are one oxygen and two carbon atoms. Enolisation is a process in which keto-form is converted to enol form. Both tautomeric forms are not equally stable. The less stable form is known as labile form

#### Example:

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#### Nitro-aci tautomerism.



(f) **Ring chain isomerism:** In this type of isomerism, compounds having same molecular formula but differ in terms of bonding of carbon atom to form open chain and cyclic structures for eg:



#### 11.5.2 Stereoisomerism:

The isomers which have same bond connectivity but different arrangement of groups or atoms in space are known as stereoisomers. This branch of chemistry dealing with the study of three-dimensional nature (spactial arrangement) of molecules is known as stereo chemistry. The metabolic activities in living organisms, natural synthesis and drug synthesis involve various stereoisomers.

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#### Steroisomerism:

#### 11.5.3 Geometrical isomerism:

Geometrical isomers are the stereoisomers which have different arrangement of groups or atoms around a rigid frame work of double bonds. This type of isomerism occurs due to restricted rotation of double bonds, or about single bonds in cyclic compounds.

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In alkenes, the carbon-carbon double bond is sp<sup>2</sup> hybridized. The carbon-carbon double bond consists of a  $\sigma$  bond and a  $\pi$  bond. The  $\sigma$  bond is formed by the head on overlap of sp<sup>2</sup> hybrid orbitals. The  $\pi$  bond is formed by the side wise overlap of 'p' orbitals. The presence of the  $\pi$  bond lock the molecule in one position. Hence, rotation around C=C bond is not possible. This restriction of rotation about C-C double bond is responsible for geometrical isomerism in alkenes.



These two compounds are termed as geometrical isomers and are distinguished from each other by the terms cis and trans. The cis isomer is one in which two similar groups are on the same side of the double bond. The trans isomers is that in which the two similar groups are on the opposite side of the double bond, hence this type of isomerism is often called cis-trans isomerism.

The cis-isomer can be converted to trans isomer or vice versa is only if either isomer is heated to a high temperature or absorbs light. The heat supplies the energy (about 62kcal/ mole) to break the  $\pi$  bond so that rotation about  $\sigma$  bond becomes possible. Upon cooling, the reformation of the  $\pi$  bond can take place in two ways giving a mixture both cis and trans forms of trans-2-butene and cis-2-butene.





Generally the trans isomer is more stable than the corresponding *cis* isomers. This is because in the cis isomer, the bulky groups are on the same side of the double bond. The steric repulsion of the groups makes the cis isomers less stable than the trans isomers in which bulky groups are on the opposite side. These cis and trans isomers have different chemical property is. They can be separated by fractional distillation, gas chromatography etc., All alkenes with identical substrate do not show geometrical isomerism. Geometrical isomerism is possible only when each double bonded C atom is attached to two different atoms or groups eg. In propene no geometrical isomers are possible because one of the double bonded carbon has two identical H atoms.

Cis-trans isomerism is also seen around single bond. For eg: 1,3-butadiene has two double bonds in conjugation.  $CH_2=CH-CH=CH_2$ . It can exist in infinite number of conformations, but the following two extreme conformations are important.

#### ii) Oximes and azo compounds:

Restricted rotation around C=N (oximes) gives rise to geometrical isomerism in oximes. Here 'syn' and 'anti' are used instead of cis and trans respectively. In the syn isomer the H atom of a doubly bonded carbon and –OH group of doubly bonded nitrogen lie on the same side of the double bond, while in the anti isomer, they lie on the opposite side of the double bond. For eg:



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#### 11.5.4 Optical Isomerism

Compounds having same physical and chemical property but differ only in the rotation of plane of the polarized light are known as optical isomers and the phenomenon is known as optical isomerism.

Some organic compounds such as glucose have the ability to rotate the plane of the plane polarized light and they are said to be optically active compounds and this property of a compound is called optical activity. The optical isomer, which rotates the plane of the plane polarised light to the right or in clockwise direction is said to be dextro rotatary (dexter means right) denoted by the sign (+), whereas the compound which rotates to the left or anticlockwise is said to be leavo rotatary (leavues means left) denoted by sign(-). Dextrorotatory compounds are represented as 'd' or by sign (+) and lavorotatory compounds are represented as 'l' or by sign (-).

#### Enantiomerism and optical activity

An optically active substance may exist in two or more isomeric forms which have same physical and chemical properties but differ in terms of direction of rotation of plane polarized light, such optical isomers which rotate the plane of polarized light with equal angle but in opposite direction are known as enantiomers and the phenomenon is known as enantiomerism. Isomers which are non-super imposable mirror images of each other are called enantiomers.

## Conditions for enantiomerism or optical isomerism

A carbon atom whose tetra valency

is satisfied by four different substituents (atoms or groups) is called asymmetric carbon or chiral carbon. It is indicated by an asterisk as C\*. A molecule possessing chiral carbon atom and non-super imposable to its own mirror image is said to be a chiral molecule or asymmetric, and the property is called chirality or dissymmetry.



# 11.6 Detection of elements in organic compounds

#### Introduction

The first step in the analysis of an organic compound is the detection of elements present in it. The principal elements are carbon, hydrogen and oxygen In addition to these they may contain nitrogen, sulphur and halogens. Phosphorous. Metals like Li, Mg, Zn are present in certain organometalic compounds.

#### Detection of carbon and hydrogen

If the compound under investigation is 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 like  $CCl_4$ ,  $CS_2$  all organic compounds also contain hydrogen. The presence of both these elements is confirmed by the following common test.

**Copper(II)oxide test:** The organic substance is mixed with about three times its weight of dry copper oxide by grinding. The mixture is then placed in a hard glass test tube fitted with a bent delivery tube. The other end of which is dipping into lime water in an another test tube. The mixture is heated strongly and the following reaction take place.

$$C + 2CuO \longrightarrow CO_2 + 2Cu$$
$$2H + CuO \longrightarrow H_2O + Cu$$

Thus if carbon is present, it is oxidized to  $CO_2$  which turns lime water milky. If hydrogen is also present, it will be oxidized to water which condenses in small droplets on the cooler wall of the test tube and inside the bulb. Water is collected on anhydrous  $CuSO_4$  which turns anhydrous  $CuSO_4$  blue. This confirms the presence of C and H in the compound.

Detection of nitrogen by lassaigne sodium fusion test: This is a good test for the detection of nitrogen in all classes of nitrogenous compound and it involves the preparation of sodium fusion extract

This method involves the conversion of covalently bonded N, S or halogen present in the organic compounds to corresponding water soluble ions in the form of sodium salts For this purpose a small piece of Na dried by pressing between the folds of a filter paper is taken in a fusion tube and it is gently heated. When it melts to a shining globule, put a pinch of the organic compound on it. Heat the tube till reaction ceases and becomes red hot. Plunge it in about 50 mL of distilled water taken in a china dish and break the bottom of the tube by striking against the dish. Boil the contents of the dish for about 10 mts and filter. This filtrate is known as lassaignes extract or sodium fusion extract and it used for detection of nitrogen, sulfur and halogens present in organic compounds.

ii) Test for Nitrogen: If nitrogen is present it gets converted to sodium cyanide which reacts with freshly prepared ferrous sulphate and ferric ion followed by conc. HCl and gives a Prussian blue color or green colour or precipitate. It confirms the presence of nitrogen. HCl is added to dissolve the greenish precipitate of ferrous hydroxide produced by the excess of NaOH on FeSO<sub>4</sub> which would otherwise mark the Prussian blue precipitate. The following reaction takes part in the formation of Prussian blue.

Na + C + N 
$$\longrightarrow$$
 NaCN  
from organic compounds  
FeSO<sub>4</sub> + 2NaOH  $\longrightarrow$  Fe(OH)<sub>2</sub> + Na<sub>2</sub>SO<sub>4</sub>  
(from excess of sodium)

$$6NaCN + Fe(OH)_{2} \longrightarrow Na_{4} [Fe(CN)_{6}]$$
  
sod.ferrocyanide  
+ 2NaOH  
$$3Na_{4} [Fe(CN)_{6}] + 4FeCl_{3} \longrightarrow Fe_{4} [Fe(CN)_{6}]_{3}$$
  
ferric ferrocyanide  
Prussian blue or green ppt  
+ 12 NaCl

Incase if both N & S are present, a blood red colour is obtained due to the following reactions.



#### iii) Test for sulphur:

 a) To a portion of the lassaigne's extract, add freshly prepared sodium nitro prusside solution. A deep violet or purple colouration is obtained. This test is also used to detect S<sup>2-</sup> in inorganic salt analysis

 $Na_2S+Na_2$  [Fe (CN<sub>5</sub>) NO]→Na4 [Fe (CN<sub>5</sub>) NOS] sodium nitro prusside

 b) Acidify another portion of lassaigne's extract with acetic acid and add lead acetate solution. A black precipitate is obtained.

$$(CH_{3}COO)_{2}Pb + Na_{2}S \xrightarrow{PbS} + 2CH_{3}COONa$$

c) **Oxidation test:** The organic substances are fused with a mixture of  $KNO_3$  and  $Na_2CO_3$ . The sulphur, if present is oxidized to sulphate.

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

The fused mass is extracted with water, acidified with HCl and then  $BaCl_2$  solution is added to it. A white precipitate indicates the presence of sulphur.

 $BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2NaCl$ 

iv) Test for halogens: To another portion of the lassaigne's filtrate add dil HNO<sub>3</sub> warm gently and add AgNO<sub>3</sub> solution. a) Appearance of curdy white precipitate soluble in ammonia solution indicates the presence of chlorine.

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- b) Appearance of pale yellow precipitate sparingly soluble in ammonia solution indicates the presence of bromine.
- c) Appearance of a yellow precipitate insoluble in ammonia solution indicates the presence of iodine.

| $Na + X \xrightarrow{heat} NaX$<br>$from \\ organic \\ compound$ (Where | x= Cl, Br, I) |
|---|---------------|
| $Nax + AgNO_3 \longrightarrow AgX + NaNO_3$                             |               |

If N or S is present in the compound along with the halogen, we might obtain NaCN and Na<sub>2</sub>S in the solution, which interfere with the detection of the halogen in the AgNO<sub>3</sub> test Therefore we boil the lassaignes extract with HNO<sub>3</sub> which decomposes NaCN and Na<sub>2</sub>S as

NaCN + HNO<sub>3</sub> 
$$\bigtriangleup$$
 NaNO<sub>3</sub> + HCN   
Na<sub>2</sub>S + 2HNO<sub>3</sub>  $\Longrightarrow$  2NaNO<sub>3</sub> + H<sub>2</sub>S   
further  
NaCN + AgNO<sub>3</sub>  $\longrightarrow$  AgCN + NaNO<sub>3</sub>  
white ppt confusing with AgCl  
Na<sub>2</sub>S + AgNO<sub>3</sub>  $\longrightarrow$  Ag<sub>2</sub>S  $\downarrow$  + NaNO<sub>3</sub>  
black ppt

V) Test for phosphorous: A solid compound is strongly heated with a mixture of Na<sub>2</sub>CO<sub>3</sub> & KNO<sub>3</sub>. phosphorous present in the compound is oxidized to sodium phosphate. The residue is extracted with water and boiled with Conc. HNO<sub>3</sub>. A solution of ammonium molybdate is added to the above solution. A canary yellow coloration or precipitate shows the presence of phosphorous.

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#### **11.7 Estimation of elements**

After detecting the various elements present in a given organic compound by qualitative analysis it is necessary to determine their composition by weight. The estimation of carbon, hydrogen, nitrogen, sulphur halogens are discussed here. No dependable method is however available for determination oxygen and hence its amount is always determined by difference.

#### Estimation of carbon and hydrogen:

Both carbon and hydrogen are estimated by the same method. A known weight of the organic substance is burnt in excess of oxygen and the carbon and hydrogen present in it are oxidized to carbon dioxide and water, respectively.

$$C_x H_y + O_2 \longrightarrow xCO_2 + \frac{y}{2} H_2O$$

The weight of carbon dioxide and water thus formed are determined and the amount of carbon and hydrogen in the organic substance is calculated.

The apparatus employed for the purpose consists of three units (i) oxygen

supply (2) combustion tube (3) absorption apparatus. (see Fig. 11.2)

- (1) Oxygen supply: To remove the moisture from oxygen it is allowed to bubble through sulphuric acid and then passed through a U-tube containing sodalime to remove  $CO_2$ . The oxygen gas free from moisture and carbondioxide enters the combustion tube.
- (2) Combustion tube: A hard glass tube open at both ends is used for the combustion of the organic substance. It contains (i) an oxidized copper gauze to prevent the backward diffusion of the products of combustion (ii) a porcelain boat containing a known weight of the organic substance (iii) coarse copper oxide on either side and (iv) an oxidized copper gauze placed towards the end of the combustion tube. The combustion tube is heated by a gas burner.
- (3) Absorption Apparatus: The combustion products containing moisture and carbon-dioxide are then passed through the absorption apparatus which consists of (1) a weighed U-tube



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packed with pumice soaked in Conc.  $H_2SO_4$  to absorb water (ii) a set of bulbs containing a strong solution of KOH to absorb CO<sub>2</sub> and finally (iii) a guard tube filled with anhydrous CaCl<sub>2</sub> to prevent the entry of moisture from atmosphere.

**Procedure:** The combustion tube is heated strongly to dry its content. It is then cooled slightly and connected to the absorption apparatus. The other end of the combustion tube is open for a while and the boat containing weighed organic substance is introduced. The tube is again heated strongly till the substance in the boat is burnt away. This takes about 2 hours. Finally, a strong current of oxygen is passed through the combustion tube to sweap away any traces of carbon dioxide or moisture which may be left in it. The U-tube and the potash bulbs are then detached and the increase in weight of each of them is determined.

#### **Calculation:**

Weight of the organic substance taken = w g

Increase in weight of  $H_2O$  = x g

Increase in weight of  $CO_2$  = y g

18 g of H<sub>2</sub>O contains 2g of hydrogen

 $\therefore x \text{ g of H}_2\text{O contains}\left(\frac{2}{18}x\right)\text{g of hydrogen}$ 

Percentage of hydrogen= $\left(\frac{2}{18} \times \frac{x}{w} \times 100\right)$ %

44g of  $CO_2$  contains 12g of carbon

$$\therefore y \text{ g of CO}_2 \text{ contains } \left(\frac{12}{44}y\right) \text{ g of carbon}$$

Percentage of Carbon= $\left(\frac{12}{44} \times \frac{y}{w} \times 100\right)\%$ 

#### Note:

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- 1. If the organic substance under investigation also contain N, it will produce oxides of nitrogen on combustion. A spiral of copper is introduced at the combustion tube, to reduce the oxides of nitrogen to nitrogen which escapes unabsorbed.
- 2. If the compound contains halogen as well, a spiral of silver is also introduced in the combustion tube. It converts halogen into silver halide.
- 3. In case if the substance also contains sulphur, the copper oxide in the combustion tube is replaced by lead chromate. The  $SO_2$  formed during combustion is thus converted to lead sulphate and prevented from passing into the absorption unit.

#### Worked out example: 1

0.26g of an organic compound gave 0.039 g of water and 0.245 g of carbon dioxide on combustion. Calculate the percentage of C & H

Weight of organic compound = 0.26g

Weight of water = 0.039g

Weight of  $CO_2 = 0.245g$ 

#### Percentage of hydrogen

18 g of water contain 2 g of hydrogen

0.039 g of water contain  $\frac{2}{18} \times \frac{0.039}{0.26}$ % of hydrogen =  $\frac{0.039}{0.26} \times \frac{2}{18} \times 100 = 1.66\%$  ۲

#### Percentage of carbon

44 g of CO<sub>2</sub> contain 12 g of C 0.245 g of CO<sub>2</sub> contains  $\frac{12}{44} \times \frac{0.245}{0.26}$  g of C % of Carbon =  $\frac{12}{44} \times \frac{0.245}{0.26} \times 100 = 25.69$  %

### Evaluate Yourself

5) 0.2346g of an organic compound containing C, H & O, on combustion gives 0.2754g of  $H_2O$  and 0.4488g  $CO_2$ . Calculate the % composition of C, H & O in the organic compound [C=52.17, H = 13.04, O = 34.79]

#### **Estimation of sulphur:**

**Carius method:** A known mass of the organic substance is heated strongly with fuming  $HNO_3$ . C & H get oxidized to  $CO_2$  &  $H_2O$ while sulphur is oxidized to sulphuric acid as per the following reaction.

$$C \xrightarrow{\text{fum. HNO}_3} CO_2$$

$$2H \xrightarrow{\text{fum. HNO}_3} H_2O$$

$$S \xrightarrow{SO_2} O + H_2O H_2SO_4$$

The resulting solution is treated with excess of  $BaCl_2$  solution  $H_2SO_4$  present in the solution in quantitatively converted into  $BaSO_4$ , from the mass of  $BaSO_4$ , the mass of sulphur and hence the percentage of sulphur in the compound can be calculated.

#### **Procedure:**

A known mass of the organic compound is taken in clean carius tube and

added a few mL of fuming  $HNO_3$ . The tube is the sealed. It is then placed in an iron tube and heated for about 5 hours. The tube is allowed to cool to room temperature and a small hole is made to allow gases produced inside to escape. The carius tube is broken and the content collected in a beaker. Excess of BaCl<sub>2</sub> is added to the beaker contains  $H_2SO_4$  acid as a result of the reaction is converted to BaSO<sub>4</sub>. The precipitate of BaSO<sub>4</sub> is filtered, washed, dried and weighed. From the mass of BaSO<sub>4</sub>, percentage of S is found.

Mass of the organic compound = w g

Mass of the  $BaSO_4$  formed = x g

233g of  $BaSO_4$  contains 32 g of Sulphur

 $\therefore x \text{ g of BaSO}_4 \text{ contains } \left(\frac{32}{233}x\right) \text{g of S}$ Percentage of Sulphur =  $\left(\frac{32}{233} \times \frac{x}{W} \times 100\right) \%$ 

#### Example -2

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In an estimation of sulphur by carius method, 0.2175 g of the substance gave 0.5825 g of  $BaSO_4$  calculate the percentage composition of S in the compound.

Weight of organic compound 0.2175 g

Weight of BaSO<sub>4</sub> 0.5825 g

233 g of  $BaSO_4$  contains 32 g of S

0.5825 g of BaSO<sub>4</sub> contains  $\frac{32}{233} \times \frac{0.5825}{0.2175}$ Percentage of S= $\frac{32}{233} \times \frac{0.5825}{0.2175} \times 100$ = 36.78 %

### Evaluate Yourself

6) 0.16 g of an organic compound was heated in a carius tube and  $H_2SO_4$  acid formed was precipitated with  $BaCl_2$ . The mass of  $BaSO_4$  was 0.35g. Find the percentage of sulphur

**Estimation of halogens: carius method:** A known mass of the organic compound is heated with fuming  $HNO_3$  and  $AgNO_3$ . C,H &S get oxidized to  $CO_2$ ,  $H_2O \& SO_2$  and halogen combines with  $AgNO_3$  to form a precipitate of silver halide.



The ppt of AgX is filtered,

washed, dried and weighed. From the mass of AgX and the mass of the organic compound taken, percentage of halogens are calculated.

A known mass of the substance is taken along with fuming HNO<sub>3</sub> and AgNO<sub>3</sub> is taken in a clean carius tube. The open end of the Carius tube is sealed and placed in a iron tube for 5 hours in the range at 530-540 K Then the tube is allowed to cool and a small hole is made in the tube to allow gases produced to escape. The tube is broken and the ppt is filtered, washed, dried and weighed. From the mass of AgX obtained, percentage of halogen in the organic compound is calculated.

Weight of the organic compound: w g

Weight of AgCl precipitate = a g

143.5 g of AgCl contains 35.5 g of Cl

 $\therefore$  a g of AgCl contains  $\frac{35.5}{143.5} \times a$ 

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w g Organic compound gives a g AgCl

Percentage of Cl in w g =  $\left(\frac{35.5}{143.5} \times \frac{a}{w} \times 100\right)$ % organic compound

Let Weight of silver Bromide be 'b'g

188g of AgBr contains 80 g of Br

: b g of AgBr contains  $\left(\frac{80}{188} \text{ b}\right)$  g of Br

w g Organic compound gives b g AgBr

Percentage of Br in w g =  $\left(\frac{80}{188} \times \frac{b}{w} \times 100\right)$ % organic compound

Let Weight of silver Iodide be 'c'g

235g of AgI contains 127 g of I

 $\therefore$  C g of AgI contains  $\left(\frac{127}{235} c\right)$  g of I

w g Organic compound gives c g AgI

Percentage of I in w g =  $\left(\frac{127}{235} \times \frac{c}{w} \times 100\right)$ % organic compound

**EXAMPLE :** 0.284 g of an organic substance gave 0.287 g AgCl in a carius method for the estimation of halogen. Find the Percentage of Cl in the compound.

Weight of the organic substance = 0.284 g Weight of AgCl is = 0.287 g

143.5 g of AgCl contains 35.5 g of chlorine

0.287 g of AgCl contains  $\frac{35.5}{143.5} \times \frac{0.287}{0.284}$ % of chlorine is  $\frac{35.5}{143.5} \times \frac{0.287}{0.284} \times 100 = 24.98\%$ 

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### Evaluate Yourself



7) 0.185 g of an organic compound when treated with Conc. HNO<sub>3</sub> and silver nitrate gave 0.320 g of silver bromide. Calculate the % of bromine in the compound. (Ag =108, Br = 80) Ans: 73.6

8) 0.40 g of an iodo-substituted organic compound gave 0.235 g of AgI by carius method. Calculate the percentage of iodine in the compound. (Ag = 108, I = 127 (Ans = 31.75)

#### **Estimation of phosphorus:**

Carius method: A known mass of the compound organic (w) containing phosphorous is heated with fuming HNO<sub>3</sub> in a sealed tube where C is converted into CO<sub>2</sub> and H to H<sub>2</sub>O. phosphorous present in organic compound is oxidized to phosphoric acid which is precipitated, as ammonium phosphomolybdate by heating with Conc. HNO<sub>3</sub> and then adding ammonium molybdate.

 $\begin{array}{c} H_{3}PO_{4} + 12 \ (NH_{4})_{2} \ MoO_{4} + 21 \ HNO_{3} \\ & \checkmark \\ heat \\ (NH_{4})_{3} \ PO_{4}.12MoO_{3} + 21NH_{4} \ NO_{3} + 12 \ H_{2}O \end{array}$ 

The precipitate of ammonium phosphomolybdate thus formed is filtered washed, dried and weighed.

In an alternative method, the phosphoric acid is precipitated as magnesium-ammonium phosphate by adding magnesia mixture (a mixture containing MgCl<sub>2</sub>, NH<sub>4</sub>Cl and ammonia) This ppt is washed, dried and ignited to get magnesium pyrophosphate which is washed, dried a weighed. The following are the reaction that takes place.

By knowing the mass of the organic compound and the mass of ammonium phosphomolybdate or magnesium pyrophosphate formed, the percentage of P is calculated.

Mass of organic compound is wg

Weight of ammonium

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phosphomolybdate хg

Weight of magnesium pyrophosphate = y g

Mole mass of  $(NH_4)_3PO_4.12MoO_3$  is =1877g

[3 x(14 + 4) + 31 + 4(16)] + 12 (96 + 3x16)

Molar mass of Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> is 222 g

(2x24) + (31x2) + (7x16)

 $1877g of (NH_4)_3 PO_4.12MoO_3 contains 31g of P$ 

xg of  $(NH_4)_3PO_4.12$  MoO<sub>3</sub> in w g of organic compound contains  $\frac{31}{1877} \times \frac{x}{w}$  of phosphorous

Percentage of Phosphorous= $\frac{31}{1877} \times \frac{x}{w} \times 100\%$ 

(or)

227 of Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> contains 62 g of P Y g of of  $Mg_2P_2O_7$  in w g of Organic compound contains  $\frac{62}{222} \times \frac{y}{w}$  of P.

Percentage Phosphorous =  $\frac{62}{222} \times \frac{y}{w} \times 100\%$ 

Example 4: 0.24 g of organic compound containing phosphorous gave 0.66 g of  $Mg_2P_2O_7$ by the usual analysis. Calculate the percentage of phosphorous in the compound

Weight of an organic compound = 0.24 g Weight of  $Mg_2P_2O_7$ = 0.66 g

222 g of Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub> contains 62 g of P 0.66 g contains  $\left(\frac{62}{222} \times 0.66\right)$  g of P Percentage of P $\frac{62}{222} \times \frac{0.66}{0.24} \times 100 = 76.80 \%$ Evaluate Yourself

9) 0.33 g of an organic compound containing phosphorous gave 0.397 g of  $Mg_2P_2O_7$  by the analysis. Calculate the percentage of P in the compound (Ans: 23.21) (MFW of  $Mg_2P_2O_7$  is 222 P = 31)

**Estimation of nitrogen:** There are two methods for the estimation of nitrogen in an organic compound. They are 1. Dumas method 2. Kjeldahls method

#### 1. Dumas method:

This method is based upon the fact that nitrogenous compound when heated with cupric oxide in an atmosphere of  $CO_2$  yields free nitrogen. Thus

 $C_{x} H_{y} N_{z} + (2x + y/2) CuO \implies x CO_{2} + y/2 H_{2}O + z/2 N_{2} + (2x + y/2) Cu$ 

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



Fig 11.4 Dumas Method

The apparatus used in Dumas method consists of  $CO_2$  generator, combustion tube, Schiffs nitrometer. (See Fig. 11.4)

#### CO<sub>2</sub> generator:

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 $CO_2$  needed in this process is prepared by heating magnetite or sodium bicarbonate contained in a hard glass tube or by the action of dil. HCl on marble in a kipps apparatus. The gas is passed through the combustion tube after being dried by bubbling through Conc. H<sub>2</sub>SO<sub>4</sub>.

**Combustion Tube:** The combustion tube is heated in a furnace is charged with a) A roll of oxidized copper gauze to prevent the back diffusion of the products of combustion and to heat the organic substance mixed with CuO by radiation b) a weighed amount of the organic substance mixed with excess of CuO, C) a layer of course CuO packed in about 2/3 of the entire length of the tube and kept in position by loose asbestos plug on either side; this oxidizes the organic vapors passing through it, and d) a reduced copper spiral which reduces any oxides of nitrogen formed during combustion to nitrogen.

Schiff's nitro meter: The nitrogen gas obtained by the decomposition of the substance in the combustion tube is mixed with considerable excess of  $CO_2$  It is estimated by passing nitrometer when  $CO_2$  is absorbed by KOH and the nitrogen gets collected in the upper part of graduated tube.

**Procedure:** To start with the tap of nitro meter is left open.  $CO_2$  is passed through the combustion tube to expel the air in it. When the gas bubbles rising through, the

potash solution fails to reach the top of it and is completely absorbed it shows that only CO<sub>2</sub> is coming and that all air has been expelled from the combustion tube. The nitrometer is then filled with KOH solution by lowering the reservoir and the tap is closed. The combustion tube is now heated in the furnace and the temperature rises gradually. The nitrogen set free form the compound collects in the nitro meter. When the combustion is complete a strong current of CO<sub>2</sub> is sent through, the apparatus in order to sweep the last trace of nitrogen from it. The volume of the gas gets collected is noted after adjusting the reservoir so that the solution in it and the graduated tube is the same. The atmospheric pressure and the temperature are also recorded.

#### **Calculations:**

Weight of the substance taken = wg

Volume of nitrogen =  $V_1 L$ 

Room Temperature =  $T_1 K$ 

Atmospheric Pressure = P mm of Hg

Aqueous tension at

room temperature =  $P^1$  mm of Hg

Pressure of dry nitrogen =  $(P-P^1) = P_1 mm$  of Hg.

Let  $p_0 V_0$  and  $T_0$  be the pressure, Volume and temperature respectively of dry nitrogen at STP,

Then, 
$$\frac{P_0 V_0}{T_0} = \frac{P_1 V_1}{T_1}$$

$$\therefore V_0 = \frac{P_1 V_1}{T_1} \times \frac{T_0}{P_0}$$
$$V_0 = \left(\frac{P_1 V_1}{T_1} \times \frac{273K}{760}\right) \text{mmHg}$$

Calculation of percentage of nitrogen.  $22.4 \text{ L of N}_{2}$  at STP weigh 28gof N<sub>2</sub>

$$\therefore$$
 V<sub>0</sub> L of N<sub>2</sub> at S.T.P weigh  $\frac{28}{22.4} \times$  V<sub>0</sub>

Wg of Organic compound contain  $\left(\frac{28}{22.4} \times \frac{V_0}{W}\right)$ g of nitrogen

:. Percentage of nitrogen =

 $( \mathbf{0} )$ 

$$\left(\frac{28}{22.4} \times \frac{\mathrm{V}_{0}}{\mathrm{W}}\right) \times 100$$

**Problem:** 0.1688 g when analyzed by the Dumas method yield 31.7 mL of moist nitrogen measured at  $14^{\circ}$  C and 758 mm mercury pressure. Determine the % of N in the substance (Aqueous tension at  $14^{\circ}$  C =12 mm)

Weight of Organic compound = 0.168g Volume of moist nitrogen  $(V_1) = 31.7 \text{mL}$   $= 31.7 \times 10^{-3} \text{ L}$ Temperature  $(T_1) = 14^{\circ}\text{C}$  = 14 + 273 = 287KPressure of Moist nitrogen (P) = 758 mm Hg Aqueous tension at 14°C = 14°C = 12 mm of Hg  $\therefore$  Pressure of dry nitrogen = (P-P<sup>1</sup>) = 758 - 12= 746 mm of

Hg

$$\frac{P_1V_1}{T_1} = \frac{P_0V_0}{T_0}$$
  

$$\therefore V_0 = \frac{746 \times 31.7 \times 10^{-3}}{287} \times \frac{273}{760}$$
  

$$V_0 = 29.58 \times 10^{-3} L$$

### Percentage of nitrogen= $\left(\frac{28}{22.4} \times \frac{V_0}{W}\right) \times 100$ = $\frac{28}{22.4} \times \frac{29.58 \times 10^{-3}}{0.1688} \times 100$

= 21.90%



#### Kjeldahls method:

This method is carried much more easily than the Dumas method. It is used largely in the analysis of foods and fertilizers. Kjeldahls method is based on the fact that when an organic compound containing nitrogen is heated with Conc.  $H_2SO_4$ , the nitrogen in it is quantitatively converted to ammonium sulphate. The resultant liquid is then treated with excess of alkali and then liberated ammonia gas absorbed in excess of standard acid. The amount of ammonia (and hence nitrogen) is determined by finding the amount of acid neutralized by back titration with same standard alkali.

#### **Procedure:**

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A weighed quantity of the substance (0.3 to 0.5 g) is placed in a special long – necked Kjeldahl flask made of pyrex glass. About 25 mL of Conc. H<sub>2</sub>SO<sub>4</sub> together with a little K<sub>2</sub>SO<sub>4</sub> and CuSO<sub>4</sub> (catalyst) are added to it the flask is loosely stoppered by a glass bulb and heated gently in an inclined position. The heating is continued till the brown color of the liquid first produced, disappears leaving the contents clear as before. At this point all the nitrogen in the substance is converted to  $(NH_{4})_{2}SO_{4}$ . The Kjeldahl flask is then cooled and its contents are diluted with distilled water and then carefully transferred into a 1 lit round bottom flask. An excess NaOH solution is poured down the side of the flask and it is fitted with a Kjeldahl trap and a water condenser. The lower end of the

condenser dips in a measured volume of excess the  $\frac{N}{20}$  H<sub>2</sub>SO<sub>4</sub> solution. The liquid in the round bottom flask is then heated and the liberated ammonia is distilled into sulphuric acid. The Kjeldahl trap serves to retain any alkali splashed up on vigorous boiling. (See Fig. 11.3)



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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 alkali, using phenolphthalein as the indicator.

#### **Calculation:**

Weight of the substance = Wg.

Volume of  $H_2SO_4$  required for the complete neutralisation of evolved  $NH_3 = V mL$ .

Strength of  $H_2SO_4$  used to neutralise  $NH_3 = N$ 

Let the Volume and the strength of NH<sub>3</sub> formed are V<sub>1</sub> and N<sub>1</sub> respectively

we know that  $V_1N_1 = VN$ 

The amount of nitrogen present in the w g of Organic Compound =  $\frac{14 \times NV}{1 \times 1000 \times w}$ 

Percentage of Nitrogen = 
$$\left(\frac{14 \times NV}{1000 \times w}\right) \times 100\%$$

**Example :** 0.6 g of an organic compound was Kjeldalised and NH<sub>3</sub> evolved was absorbed into 50 mL of semi-normal solution of  $H_2SO_4$ . The residual acid solution was diluted with distilled water and the volume made up to 150 mL. 20 mL of this diluted solution required 35 mL of  $\frac{N}{20}$ NaOH solution for complete neutralization. Calculate the % of N in the compound.

Weight of Organic compound = 0.6g Volume of sulphuric acid taken= 50mL Strength of sulphuric acid taken= 0.5 N 20 ml of diluted solution of unreacted sulphuric acid was neutralised by 35 mL of 0.05 N Sodium hydroxide

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Strength of the diluted sulphuric acid = \frac{35 \times 0.05}{20}
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= 0.0875 N

Volume of the sulphuric acid remaining after reaction with =  $V_1 mL$ Organic compound Strength of  $H_2SO_4 = 0.5N$ Volume of the diluted  $H_2SO_4 = 150 mL$ Strength of the diluted sulphuric acid = 0.0875 N

$$V_1 = \frac{150 \times 0.087}{0.5} = 26.25 \text{ mL}$$

Volume of  $H_2SO_4$  consumed by ammonia = 50 - 26.25

= 23.75 mL

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23.75 mL of 0.5 N  $H_2SO_4 \equiv 23.75$  mL of 0.5 N N $H_3$ 

The amount of Nitrogen present in the 0.6 =  $\frac{14g}{1000 \text{ mL} \times 1 \text{ N}} \times 23.75 \times 0.5 \text{N}$ = 0.166g

Percentage of Nitrogen =  $\frac{0.166}{0.6} \times 100$ = 27.66 %

### Evaluate Yourself

10) 0.3 g of an organic compound on kjeldahl's analysis gave enough ammonia to just neutralize 30 mL of  $0.1N H_2SO_4$ . Calculate the percentage of nitrogen in the compound.

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# 11.8 Purification of organic compounds

#### Need for purification:

In order to study the structure, physical properties, chemical properties and biological properties of organic compounds they must be in the pure state. There are several methods by which organic compounds can be purified. The methods employed for purification depend upon the nature of impurity and the nature of organic compound. The most widely used technique for the separation and purification of organic compounds are: (a) Crystallisation, Sublimation (c) Distillation (d) (b) Fractional distillation (e) Steam distillation (f) Azeotropic distillation (g) Differential extraction and (h) Chromatography.



#### **11.8.1 Sublimation:**

Few substances like benzoic acid, naphthalene and camphor when heated pass directly from solid to vapor without melting (ie liquid). On cooling the vapours will give back solids. Such phenomenon is called sublimation. It is a useful technique to separate volatile and non-volatile solid. It has limited application because only a few substance will sublime.

Substances to be purified is taken in a beaker. It is covered with a watch glass. The beaker is heated for a while and the resulting vapours condense on the bottom of the watch glass. Then the watch glass is removed and the crystals are collected. This method is applicable for organic substance which has high vapour pressure at temperature below their melting point. Substances like naphthalene, benzoic acid can be sublimed quickly. Substance which has very small vapour pressure will decompose upon heating are purified by sublimation under reduced pressure. This apparatus consists of large heating and large cooling surface with small distance in between because the amount of the substance in the vapour phase is much too small in case of a substance with low vapour pressure.

#### **11.8.2 Crystallization:**

It is the most widely used method for the purification of solid organic compound. This process is carried out in by the following step

Selection of solvent: Most of the **(i)** organic substances being covalent do not dissolve in polar solvents like water, hence selection of solvent (suitable) becomes necessary. Hence the powdered organic substance is taken in a test tube and the solvent is added little by little with constant stirring and heating, till the amount added is just sufficient to dissolve the solute(ie) organic compound. If the solid dissolves upon heating and throws out maximum crystals on cooling, then the solvent is suitable. This process is repeated with other solvents like benzene, ether, acetone and alcohol till the most suitably one is sorted out.

(ii) **Preparation of solution:** The organic substance is dissolved in a minimum quantity of suitable solvent. Small amount of animal charcoal can be added to decolorize any colored substance. The heating may be done over a wire gauze or water bath depending upon the nature of liquid (ie) whether the solvent is low boiling or high boiling.

(iii) Filtration of hot solution: The hot solution so obtained is filtered through a fluted filter paper placed in a funnel.

(iv) Crystallization: The hot filtrate is then allowed to cool. Most of the impurities are removed on the filter paper, the pure solid substance separate as crystal. When copious amount of crystal has been obtained, then the crystallization is complete. If the rate of crystallization is slow, it is induced either by scratching the walls of the beaker with a glass rod or by adding a few crystals of the pure compounds to the solution.

(v) Isolation and drying of crystals: The crystals are separated from the mother liquor by filtration. Filtration is done under reduced pressure using a Bucher funnel. When the whole of the mother liquor has been drained into the filtration flask, the crystals are washed with small quantities of the pure cold solvent and then dried.

#### 11.8.3 Distillation:

This method is to purify liquids from non-volatile impurities, and used for separating the constituents of a liquid mixture which differ in their boiling points. There are various methods of distillation depending upon the difference in the boiling points of the constituents. The methods are (i) simple distillation (ii) fractional distillation and (iii) steam distillation. The process of distillation involves the impure liquid when boiled gives out vapour and the vapour so formed is collected and condensed to give back the pure liquid in the receiver. This method is called simple distillation. Liquids with large difference in boiling point (about 40k) and do not decompose under ordinary pressure can be purified by simply distillation eg. The mixture of  $C_6H_5NO_2$  (b.p 484k) &  $C_6H_6(354k)$  and mixture of diethyl ether (b.p 308k) and ethyl alcohol (b.p 351k)

Fractional distillation: This is one method to purify and separate liquids present in the mixture having their boiling point close to each other. In the fractional distillation, a fractionating column is fitted with distillation flask and a condenser. A thermometer is fitted in the fractionating column near the mouth of the condenser. This will enable to record the temperature of vapour passing over the condenser. The process of separation of the components in a liquid mixture at their respective boiling points in the form of vapours and the subsequent condensation of those vapours is called fractional distillation. The process of fractional distillation is repeated, if necessary. This method finds a remarkable application in distillation of petroleum, coal-tar and crude oil.

#### 11.8.4 Steam distillation:

This method is applicable for solids and liquids. If the compound to be steam distilled the it should not decompose at the steam temperature, should have a fairly high vapour pressure at 373k, it should be insoluble in water and the impurities present should be non-volatile.



The impure liquid along with little water is taken in a round-bottom flask which is connected to a boiler on one side and water condenser on the other side, the flask is kept in a slanting position so that no droplets of the mixture will enter into the condenser on the brisk boiling and bubbling of steam. The mixture in the flask is heated and then a current of steam passed in to it. The vapours of the compound mix up with steam and escape into the condenser. The condensate obtained is a mixture of water and organic compound which can be separated. This method is used to recover essential oils from plants and flowers, also in the manufacture of aniline and turpentine oil. (see Fig. 11.4)

#### 11.8.5 Azeotropic Distillation

These are the mixture of liquids that cannot be separated by fractional distillation. The mixtures that can be purified only by azeotropic distillation are called as azeotropes. These azeotropes are constant boiling mixtures, which distil as a single component at a fixed temperature. For example ethanol and water in the ratio of 95.87:4.13.

In this method the presence of a third component like  $C_6H_6$ ,  $CCl_4$ , ether, glycerol, glycol which act as a dehydrating agent depress the partial pressure of one component of azeotropic mixture and raises

the boiling point of that component and thus other component will distil over.

Subtances like  $C_6H_6$ ,  $CCl_4$  have low boiling points and reduce the partial vapour pressure of alcohol more than that of water while subtances like glycerol & glycol etc. have high boiling point and reduce the partial vapour pressure of water more than that of alcohol.

#### 11.8.6 Differential extraction:

The process of removing a substance from its aqueous solution by shaking with a suitable organic solvent is termed extraction. When an organic substance present as solution in water can be recovered from the solution by means of a separating funnel. The aqueous solution is taken in a separating funnel with little quantity of ether or chloroform (CHCl<sub>2</sub>). The organic solvent immiscible with water will form a separate layer and the contents are shaken gently. The solute being more soluble in the organic solvent is transfered to it. The solvent layer is then separated by opening the tap of the separating funnel, and the substance is recovered.

#### 11.8.7 Chromatography:

The most valuable method for the separation and purification of small quantity of mixtures. As name implies chroma-colour and graphed writing it was first applied to separation of different colored constituents of chlorophyll in 1906 by M.S Tswett, a Russian botanist. He achieved it by passing a petroleum ether solution of chlorophyll present in leaves through a column of CaCO<sub>3</sub> firmly packed into a narrow glass tube. Different components of the pigments got separated into land or zones of different

colors and now this technique is equally well applied to separation of colorless substances.

The principle behind chromatography is selective distribution of the mixture of organic substances between two phases - a stationary phase and a moving phase. The stationary phase can be a solid or liquid, while the moving phase is a liquid or a gas. When the stationary phase is a solid, the moving phase is a liquid or a gas. If the stationary phase is solid, the basis is adsorption, and when it is a liquid, the basis is partition. So the Chromatography is defined as a technique for the separation of a mixture brought about by differential movement of the individual compound through porous medium under the influence of moving solvent. The various methods of chromatography are

- 1. Column chromatography (CC)
- 2. Thin layer chromatography (TLC)
- 3. Paper chromatography (PC)
- 4. Gas-liquid chromatography (GLC)
- 5. Ion-exchange chromatography

chromatography: Adsorption The principle involved is different compounds adsorbed on adsorbent are an to different degree. Silica gel and alumina are the commonly used adsorbent. The components of the mixture move by varying distances over the stationary phase. Column chromatography and thin layer chromatography are the techniques based on the principle of differential adsorption.

**Column chromatography:** This is the simplest chromatographic method carried out in long glass column having a stop cock

near the lower end. This method involves separation of a mixture over a column of adsorbent (Stationery phase) packed in a column. In the column a plug of cotton or glass wool is placed at the lower end of the column to support the adsorbent powder. The tube is uniformLy packed with suitable absorbent constitute the stationary phase. (Activated aluminum oxides (alumina), Magnesium oxide, starch are also used as absorbents).



Fig 11.5 Column Chromatography

The mixture to be separated is placed on the top of the adsorbent column. Eluent which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Different components are eluted depending upon the degree to which the components are adsorbed and complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column.

layer chromatography: Thin This method is an another type of adsorption chromatography with this method it is possible to separate even minute quantities of mixtures. A sheet of a glass is coated with a thin layer of adsorbent (cellulose, silica gel or alumina). This sheet of glass is called chromoplate or thin layer chromatography plate. After drying the plate, a drop of the mixture is placed just above one edge and the plate is then placed in a closed jar containing eluent (solvent). The eluent is drawn up the adsorbent layer by capillary action. The components of the mixture move up along with the eluent to different distances depending upon their degree of adsorption of each component of the mixture. It is expressed in terms of its retention factor (ie) R<sub>f</sub> value

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

base line (y)

The spots of colored compounds are visible on TLC plate due to their original color. The colorless compounds are viewed under uv light or in another method using iodine crystals or by using appropriate reagent.

**Partition chromatography:** Paper chromatography (PC) is an example of partition chromatography. The same procedure is followed as in thin layer chromatography except that a strip of paper acts as an adsorbent. This method involves continues differential portioning of components of a mixture between stationary and mobile phase. In paper chromatography, a special quality paper known as chromatography paper is used. This paper act as a stationary phase.

A strip of chromatographic paper spotted at the base with the solution of the mixture is suspended in a suitable solvent which act as the mobile phase. The solvent rises up and flows over the spot. The paper selectively retains different components according to their different partition in the two phases where a chromatogram is developed. The spots of the separated colored compounds are visible at different heights from the position of initial spots on the chromatogram. The spots of the separated colorless compounds may be observed either under ultraviolent light or by the use of an appropriate spray reagent.

### Evaluation

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#### I. Choose the best answer.

- 1. Select the molecule which has only one  $\pi$  bond.
  - a) CH<sub>3</sub>- CH = CH CH<sub>3</sub> b) CH<sub>3</sub>- CH = CH - CHO
  - c)  $CH_3 CH = CH COOH$

d) All of these

- 2. In the hydrocarbon  ${}^{7}_{CH_{3}}$ - ${}^{6}_{CH_{2}}$ - ${}^{5}_{CH}$ = ${}^{4}_{CH_{-}}$ - ${}^{3}_{CH_{2}}$ - ${}^{2}_{C}$ = ${}^{1}_{CH}$  the state of hybridisation of carbon 1,2,3,4 and 7 are in the following sequence.
  - a) sp, sp, sp<sup>3</sup>, sp<sup>2</sup>, sp<sup>3</sup>
    b) sp<sup>2</sup>, sp, sp<sup>3</sup>, sp<sup>2</sup>, sp<sup>3</sup>
    c) sp, sp, sp<sup>2</sup>, sp, sp<sup>3</sup>
    d) none of these
  - u) none of these
- 3. The general formula for alkadiene is
  - a)  $C_n H_{2n}$ b)  $C_n H_{2n-1}$ c)  $C_n H_{2n-2}$ d)  $C_n H_{n-2}$

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4. Structure of the compound whose IUPAC name is 5,6 - dimethylhept - 2 - ene is





5. The IUPAC name of the Compound is



- a) 2,3 Diemethylheptane
- b) 3- Methyl -4- ethyloctane
- c) 5-ethyl -6-methyloctane
- d) 4-Ethyl -3 methyloctane.
- 6. Which one of the following names does not fit a real name?
  - a) 3 Methyl –3–hexanone
  - b) 4-Methyl -3- hexanone
  - c) 3– Methyl –3– hexanol
  - d) 2– Methyl cyclo hexanone.
- 7. The IUPAC name of the compound  $CH_3-CH=CH-C\equiv CH$  is
  - a) Pent 4 yn-2-ene
  - b) Pent -3-en-l-yne
  - c) pent 2– en 4 yne
  - d) Pent 1 yn –3 –ene

8. IUPAC name of 
$$CH_3 - C_4H_9$$
  
 $C_2H_5$   $C - CH_3$  is

- a) 3,4,4 Trimethylheptane
- b) 2 Ethyl –3, 3– dimethyl heptane

c) 3, 4,4 – Trimethyloctane

 $( \mathbf{0} )$ 

d) 2 – Butyl -2 –methyl – 3 – ethyl-butane.

- 9. TheIUPACnameofH<sub>3</sub>C- $\begin{array}{c}CH_{3}\\I\\C-C-CH=C(CH_{3})_{2}\\CH_{3}\end{array}$ 
  - a) 2,4,4 Trimethylpent -2-ene
  - b) 2,4,4 Trimethylpent -3-ene
  - c) 2,2,4 Trimethylpent -3-ene
  - d) 2,2,4 Trimethylpent -2-ene
- 10. The IUPAC name of the compound  $CH_3-CH = C - CH_2 - CH_3$   $CH_2 - CH_2 - CH_3$  is
  - a) 3 Ethyl -2– hexene
  - b) 3 Propyl -3– hexene
  - c) 4 Ethyl 4 hexene
  - d) 3 Propyl -2-hexene
- 11. The IUPAC name of the compound  $CH_3$ -CH COOH is | OH
  - a) 2 Hydroxypropionic acid
  - b) 2 Hydroxy Propanoic acid
  - c) Propan 2– ol –1 oic acid
  - d) 1 Carboxyethanol.

12. The IUPAC name of  

$$CH_3$$
  $CH - CH - COOH$  is  
Br  $|_{CH_3}$   
a) 2 - Bromo -3 - methyl butanoic acid

- b) 2 methyl 3- bromobutanoic acid
- c) 3 Bromo 2 methylbutanoic acid
- d) 3 Bromo 2, 3 dimethyl propanoic acid.
- 13. The structure of isobutyl group in an organic compound is

a) 
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2$$

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- 14. The number of stereoisomers of 1, 2 dihydroxycyclopentane
  - a) 1 b)2 c) 3 d) 4
- 15. Which of the following is optically active?
  - a) 3 Chloropentane
  - b) 2 Chloro propane
  - c) Meso tartaric acid
  - d) Glucose
- 16. The isomer of ethanol is
  - a) acetaldehydeb) dimethyletherc) acetoned) methyl carbinol
- 17. How many cyclic and acyclic isomers are possible for the molecular formula  $C_3H_6O$ ?

a) 4 b) 5 c) 9 d) 10

- 18. Which one of the following shows functional isomerism?
  - a) ethylene b) Propane
  - c) ethanol d)  $CH_2Cl_2$
- 19.  $\overset{\bigcirc}{\operatorname{CH}}_2 \overset{\frown}{\operatorname{C-CH}}_3$  and  $\operatorname{CH}_2 = \overset{\frown}{\operatorname{C-CH}}_3$  are O
  - a) resonating structureb) tautomersc) Optical isomersd) Conformers.
- 20. Nitrogen detection in an organic compound is carried out by Lassaigne's test. The blue colour formed is due to the formation of.
  - a)  $\operatorname{Fe}_{3}[\operatorname{Fe}(\operatorname{CN})_{6}]_{2}$
  - b)  $\operatorname{Fe}_{4}[\operatorname{Fe}(\operatorname{CN})_{6}]_{3}$
  - c)  $\operatorname{Fe}_{4}[\operatorname{Fe}(\operatorname{CN})_{6}]_{2}$
  - d)  $\operatorname{Fe}_{3}[\operatorname{Fe}(\operatorname{CN})_{6}]_{3}$

21. Lassaigne's test for the detection of nitrogen fails in

a) H<sub>2</sub>N – CO– NH.NH<sub>2</sub>.HCl b) NH<sub>2</sub> – NH<sub>2</sub>. HCl

c)  $C_6H_5 - NH - NH_2$ . HCl

d) C<sub>6</sub>H<sub>5</sub> CONH<sub>2</sub>

 $( \mathbf{0} )$ 

- 22. Connect pair of compounds which give blue colouration / precipitate and white precipitate respectively, when their Lassaigne's test is separately done.
  - a) NH<sub>2</sub> NH<sub>2</sub> HCl and ClCH<sub>2</sub>-CHO
    b) NH<sub>2</sub> CS NH<sub>2</sub> and CH<sub>3</sub> CH<sub>2</sub>Cl
    c) NH<sub>2</sub> CH<sub>2</sub> COOH and NH<sub>2</sub> CONH<sub>2</sub>
    d) C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> and ClCH<sub>2</sub> CHO.
- 23. Sodium nitropruside reacts with sulphide ion to give a purple colour due to the formation of

a)  $[Fe(CN)_5 NO]^{3-1}$ 

- b)  $[Fe(NO)_{5} CN]^{+}$
- c) [Fe(CN)<sub>c</sub>NOS]<sup>4-</sup>
- d) [Fe (CN)<sub>5</sub> NOS]<sup>3-</sup>
- 24. An organic Compound weighing 0.15g gave on carius estimation, 0.12g of silver bromide. The percentage of bromine in the Compound will be close to

| a) 46%  | b) 34%  |
|---------|---------|
| c) 3.4% | d) 4.6% |

- 25. A sample of 0.5g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50mL of 0.5M  $H_2SO_4$ . The remaining acid after neutralisation by ammonia consumed 80mL of 0.5 MNaOH, The percentage of nitrogen in the organic compound is.
  - a) 14%
  - b) 28%
  - c) 42%
  - d) 56%

26. In an organic compound, phosphorus is estimated as

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- a)  $Mg_2P_2O_7$  b)  $Mg_3(PO_4)_2$ c)  $H_3PO_4$  d)  $P_2O_5$
- 27. Ortho and para-nitro phenol can be separated by
  - a) azeotropic distillation
  - b) destructive distillation
  - c) steam distillation
  - d) cannot be separated
- 28. The purity of an organic compound is determined by
  - a) Chromatography
  - b) Crystallisation
  - c) melting or boiling point
  - d) both (a) and (c)
- 29. A liquid which decomposes at its boiling point can be purified by
  - a) distillation at atmospheric pressure
  - b) distillation under reduced pressure
  - c) fractional distillation
  - d) steam distillation.

30. Assertion:  $CH_3 - C = CH - COOH$  is

 $COOC_2H_5$ 

3- carbethoxy -2- butenoicacid.

**Reason:** The principal functional group gets lowest number followed by double bond (or) triple bond.

(a) both the assertion and reason are true and the reason is the correct explanation of assertion.

(b) both assertion and reason are true and the reason is not the correct explanation of assertion.

- (c) assertion is true but reason is false
- (d) both the assertion and reason are false.

### II. Write brief answer to the following questions.

- 31. Give the general characteristics of organic compounds?
- 32. Describe the classification of organic compounds based on their structure.
- 33. Write a note on homologous series.
- 34. What is meant by a functional group? Identify the functional group in the following compounds.
  - (a) acetaldehyde (b) oxalic acid
  - (c) di methyl ether (d) methylamine
- 35. Give the general formula for the following classes of organic compounds
  - (a) Aliphatic monohydric alcohol
  - (b) Aliphatic ketones.
  - (c) Aliphatic amines.
- 36. Write the molecular formula of the first six members of homologous series of nitro alkanes.
- 37. Write the molecular and possible structural formula of the first four members of homologous series of carboxylic acids.
- 38. Give the IUPAC names of the following compounds.
  - (i)  $(CH_3)_2CH-CH_2-CH(CH_3)-CH(CH_3)_2$

(iii) CH<sub>3</sub>-O-CH<sub>3</sub>

(v) 
$$CH_2 = CH-CH=CH$$

Η Η H<sub>3</sub>C. (vii) H Br Ĥ 0  $\cap$ (viii) HO (ix) (x)  $\mathbf{NH}_{2}$ (xi) C<sub>6</sub>H<sub>5</sub> CN (xii) || 0



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- 39) Give the structure for the following compound.
  - (i) 3- ethyl 2 methyl -1-pentene
  - (ii) 1,3,5- Trimethyl cyclohex 1 -ene
  - (iii) tertiary butyl iodide
  - (iv) 3 Chlorobutanal
  - (v) 3 Chlorobutanol
  - (vi) 2 Chloro 2- methyl propane
  - (vii) 2,2-dimethyl-1-chloropropane
  - (viii) 3 methylbut -1- ene
  - (ix) Butan 2, 2 diol
  - (x) Octane 1,3- diene
  - (xi) 1,3- Dimethylcyclohexane
  - (xii) 3-Chlorobut 1 ene
  - (xiii) 3 methylbutan 2 ol
  - (xiv) acetaldehyde
- 40) Describe the reactions involved in the detection of nitrogen in an organic compound by Lassaigne method.



(xiii)

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41) Give the principle involved in the estimation of halogen in an organic compound by carius method. 6

- 42) Give a brief description of the principles of
  - i) Fractional distillation
  - ii) Column Chromatography
- 43) Explain paper chromatography
- 44) Explain varions types of constitutional isomerism (structural isomerism) in organic compounds
- 45) Describe optical isomerism with suitable example.
- 46) Briefly explain geometrical isomerism in alkene by considering 2- butene as an example.
- 47) 0.30 g of a substance gives 0.88 g of carbon dioxide and 0.54 g of water calculate the percentage of carbon and hydrogen in it.

- 48) The ammonia evolved form 0.20 g of an organic compound by kjeldahl method neutralised 15ml of N/20 sulphare acid solution. Calculate the percentage of Nitrogen.
- 49) 0.32 g of an organic compound, after heating with fuming nitric acid and barium nitrate crystals is a sealed tube game 0.466 g of barium sulphate. Determine the percentage of sulphur in the compound.
- 50) 0.24g of an organic compound gave 0.287 g of silver chloride in the carius method. Calculate the percentage of chlorine in the compound.
- 51) In the estimation of nitrogen present in an organic compound by Dumas method 0.35 g yielded 20.7 mL of nitrogen at 150 C and 760 mm pressure. Calculate the percentage of nitrogen in the compound

