# ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

Organic chemistry is a subdiscipline within chemistry involving the scientific study of the structure, properties, and reactions of organic compounds and organic materials, i.e., matter in its various forms that contain carbon atoms. Study of structure determines their structural formula. Study of properties includes physical and chemical properties, and evaluation of chemical reactivity to understand their behavior. The study of organic reactions includes the chemical synthesis of natural products, drugs, and polymers, and study of individual organic molecules in the laboratory and via theoretical (in silico) study.

The range of chemicals studied in organic chemistry includes hydrocarbons (compounds containing only carbon and hydrogen) as well as compounds based on carbon, but also containing other elements, especially oxygen, nitrogen, sulfur, phosphorus (included in many biochemicals) and the halogens. Organometallic chemistry is the study of compounds containing carbon–metal bonds. In addition, contemporary research focuses on organic chemistry involving other organometallics including the lanthanides, but especially the transition metals zinc, copper, palladium, nickel, cobalt, titanium and chromium. Organic compounds form the basis of all earthly life and constitute the majority of known chemicals. The bonding patterns of carbon, with its valence of four—formal single, double, and triple bonds, plus structures with delocalized electrons—make the array of organic compounds structurally diverse, and their range of applications enormous. They form the basis of, or are constituents of, many commercial products including pharmaceuticals; petrochemicals and agrichemicals, and products made from them including lubricants, solvents; plastics; fuels and explosives. The study of organic chemistry overlaps organometallic chemistry and biochemistry, but also with medicinal chemistry, polymer chemistry, and materials science.

Science of organic chemistry is about two hundred years old. Around the year 1780, chemists began to distinguish between organic compounds obtained from plants and animals and inorganic compounds prepared from mineral sources. Berzilius, a Swedish chemist proposed that a 'vital force' was responsible for the formation of organic compounds. However, this notion was rejected in 1828 when F. Wohler synthesised an organic compound, urea from an inorganic compound, ammonium cyanate. The development of electronic theory of covalent bonding ushered organic chemistry into its modern shape.

$$NH_4CNO \xrightarrow{\text{Heat}} NH_2CONH_2$$
Ammonium cyanate   Urea
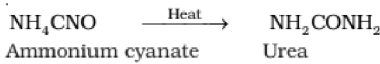
TETRAVALENCE OF CARBON:SHAPES OF ORGANIC COMPOUNDS: We know that tetravalence of carbon and the formation of covalent bonds by it are explained in terms of its electronic configuration and the hybridisation of s and p orbitals. It may be recalled that formation and the shapes of molecules like methane (CH_4), ethene (C_2H_4), ethyne (C_2H_2) are explained in terms of the use of sp^3, sp^2 and sp hybrid orbitals by carbon atoms in the respective molecules. Hybridisation influences the bond length and bond enthalpy (strength) in organic compounds. The sp hybrid orbital contains more s character and hence it is closer to its nucleus and forms shorter and stronger bonds than the sp^3 hybrid orbital. The sp^2 hybrid orbital is intermediate in s character between sp and sp^3 and, hence, the length and enthalpy of the bonds it forms, are also intermediate between them. The change in hybridisation affects the electronegativity of carbon. The greater the s character of the hybrid orbitals, the greater is the electronegativity. Thus, a carbon atom having an sp hybrid orbital with 50% s character is more electronegative than that possessing sp^2 or sp^3 hybridised orbitals. This relative electronegativity is reflected in several physical and chemical properties of the molecules.

Hybridization:

In chemistry, orbital hybridisation (or hybridization) is the concept of mixing atomic orbitals to form new hybrid orbitals (with different energies, shapes, etc., than the component atomic orbitals) suitable for the pairing of electrons to form chemical bonds in valence bond theory. For example, in a carbon atom which forms four single bonds the valence-shell s orbital combines with three valence-shell p orbitals to form four equivalent sp^3 mixtures in a tetrahedral arrangement around the carbon to bond to four different atoms. Hybrid orbitals are useful in the explanation of molecular geometry and atomic bonding properties and are symmetrically disposed in space. Usually hybrid orbitals are formed by mixing atomic orbitals of comparable energies.

Types of hybridisation:
sp^3 hybridisation:
Hybridisation describes the bonding of atoms from an atom's point of view. For a tetrahedrally coordinated carbon (e.g., methane CH_4), the carbon should have 4 orbitals directed towards the 4 hydrogen atoms.Carbon's ground state configuration is $1s^2\ 2s^2\ 2p^2$ or more easily read:


C 1s 2s 2p 2p 2p

109.5°
Four sp^3 orbitals.

The carbon atom can use its two singly occupied p-type orbitals to form two covalent bonds with two hydrogen atoms,[contradictory] yielding the singlet methylene CH_2, the simplest carbene. The carbon atom can also bond to four hydrogen atoms by an excitation (or promotion) of an electron from the doubly occupied 2s orbital to the empty 2p orbital, producing four singly occupied orbitals.

C* 1s 2s 2p 2p 2p

The energy released by the formation of two additional bonds more than compensates for the excitation energy required, energetically favoring the formation of four C-H bonds.
Quantum mechanically, the lowest energy is obtained if the four bonds are equivalent, which requires that they are formed from equivalent orbitals on the carbon. A set of four equivalent orbitals can be obtained that are linear combinations of the valence-shell (core orbitals are almost never involved in bonding) s and p wave functions, which are the four sp^3 hybrids.

C* 1s sp^3 sp^3 sp^3 sp^3
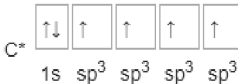
In CH_4, four sp^3 hybrid orbitals are overlapped by hydrogen 1s orbitals, yielding four σ (sigma) bonds (that is, four single covalent bonds) of equal length and strength.


sp^2 hybridisation:

120°
Three sp^2 orbitals.
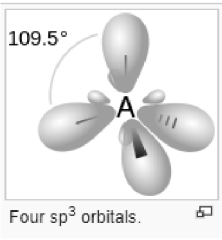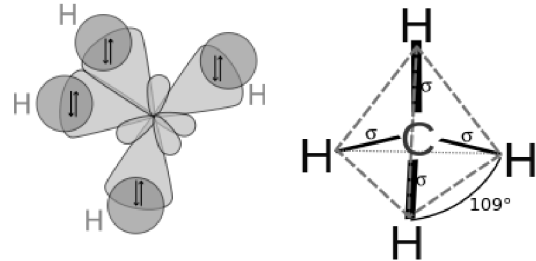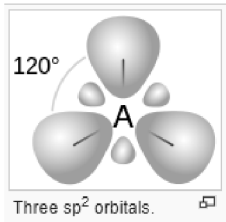
Ethene (C_2H_4) has a double bond between the carbons. For this molecule, carbon sp^2 hybridises, because one π(pi) bond is required for the double bond between the carbons and only three σ bonds are formed per carbon atom. In sp^2 hybridisation the 2s orbital is mixed with only two of the three available 2p orbitals, usually denoted $2p_x$ and $2p_y$. The third 2p orbital ($2p_z$) remains unhybridised.

C* 1s sp^2 sp^2 sp^2 2p
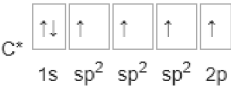
Forming a total of three sp^2 orbitals with one remaining p orbital. In ethene, the two carbon atoms form a σ bond by overlapping one sp^2 orbital from each carbon atom. The π bond between the carbon atoms perpendicular to the molecular plane is formed by 2p–2p overlap. Each carbon atom forms covalent C–H bonds with two hydrogens by s–sp^2 overlap, all with 120° bond angles. The hydrogen–carbon bonds are all of equal strength and length, in agreement with experimental data.

Ethene structure

sp hybridisation:
The chemical bonding in compounds such as alkynes with triple bonds is explained by sp hybridization. In this model, the 2s orbital is mixed with only one of the three p orbitals,resulting in two sp orbitals and two remaining p orbitals.

C* 1s sp sp 2p 2p

180°
Two sp orbitals.
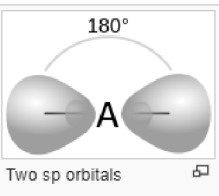
The chemical bonding in acetylene (ethyne) (C_2H_2) consists of sp–sp overlap between the two carbon atoms forming a σ bond and two additional π bonds formed by p–p overlap. Each carbon also bonds to hydrogen in a σ s–sp overlap at 180° angles.

STRUCTURAL REPRESENTATIONS OF ORGANIC COMPOUNDS:
Complete, Condensed and Bond-line Structural Formulas:

The structures of organic compounds are represented in several ways. The most important of these is the Lewis structure. However, if we were to write many compounds with their Lewis structure then definitely it would be very time consuming. Moreover, the bigger the size of the compound, the more painful writing its Lewis structure is. To overcome this problem, some other methods have been introduced.

Complete structural formulae:
The Lewis structures can be simplified by representing the two-electron covalent bond by a dash. Such a structural formula focuses on the electrons involved in bond formation.A single dash represents a single bond, a double dash represents a double bond and a triple dash represents a triple bond. Lone pairs of electrons on heteroatoms (e.g. oxygen, halogens etc) may or may not be shown.

Ethane   Ethene   Ethyne
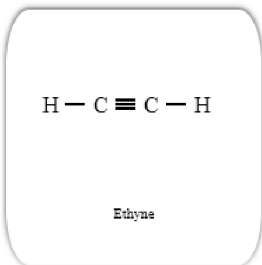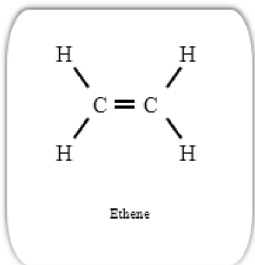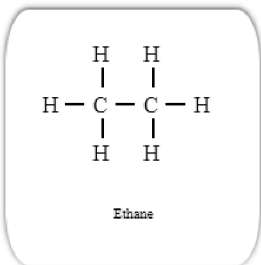
Condensed structural formulae:
Complete structural formulae can be further abbreviated by omitting some or all the dashes representing covalent bonds.

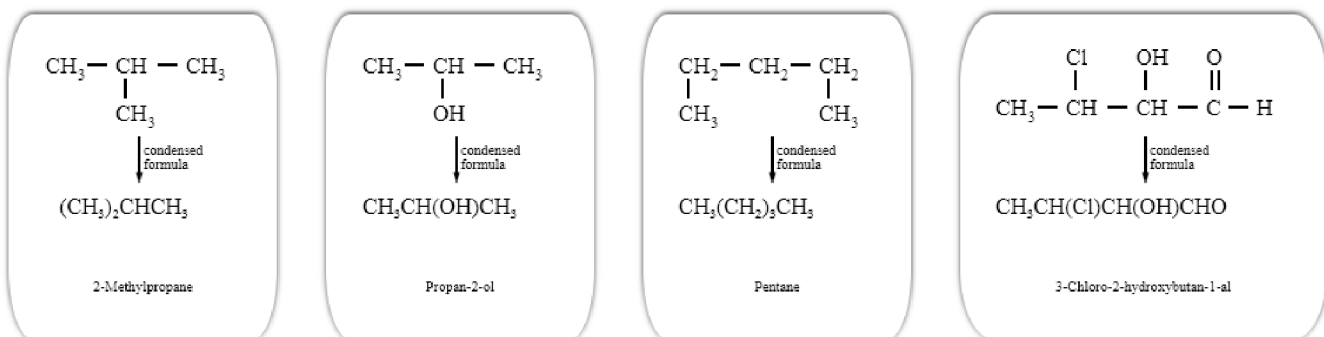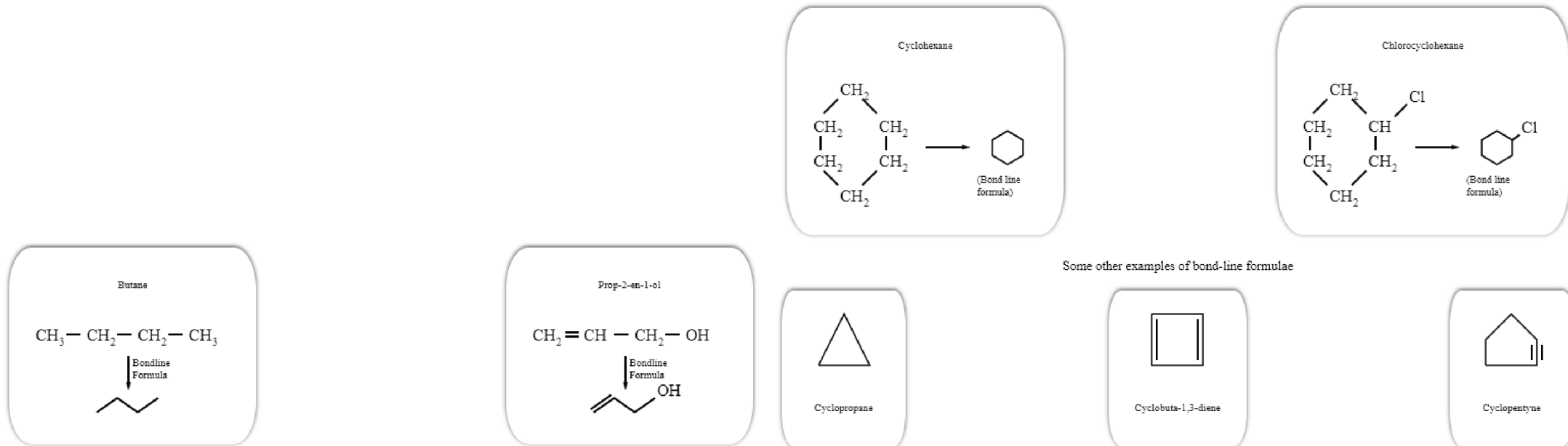CH₃CH₃ → CH_3CH_3

Ethane

$CH_2 = CH_2$

Ethene

$CH \equiv CH$

Ethyne
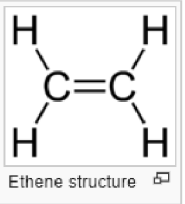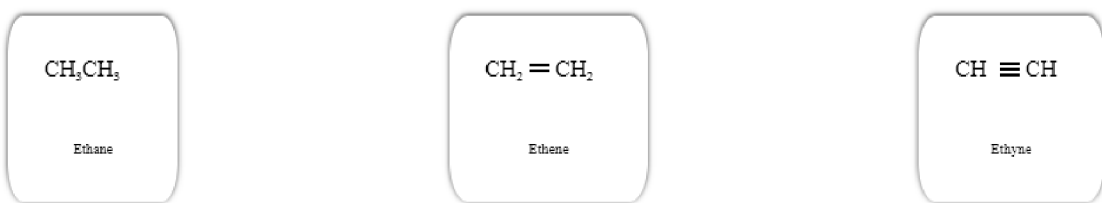
Identical repetitive units are put in parenthesis and subscripts are used to indicate their repetition. For example, $CH_3CH_2CH_2CH_2CH_2CH_3$ can be further condensed to $CH_3(CH_2)_4CH_3$. The role of parantheses is very important in condensed structural formulae. Study the following examples carefully :

Some other examples of condensed structural formulae

$CH_3 - CH - CH_3$
|
CH_3

condensed formula ↓

$(CH_3)_2CHCH_3$

2-Methylpropane

$CH_3 - CH - CH_3$
|
OH

condensed formula ↓

$CH_3CH(OH)CH_3$

Propan-2-ol

$CH_2 - CH_2 - CH_2$
| |
CH_3 CH_3

condensed formula ↓

$CH_3(CH_2)_3CH_3$

Pentane

Cl   OH   O
| | ‖
$CH_3 - CH - CH - C - H$

condensed formula ↓

$CH_3CH(Cl)CH(OH)CHO$

3-Chloro-2-hydroxybutan-1-al

Bond-line structural representation:
In Bond-line structural representation, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a zig-zag fashion. Only heteroatoms are written in bond line representation.
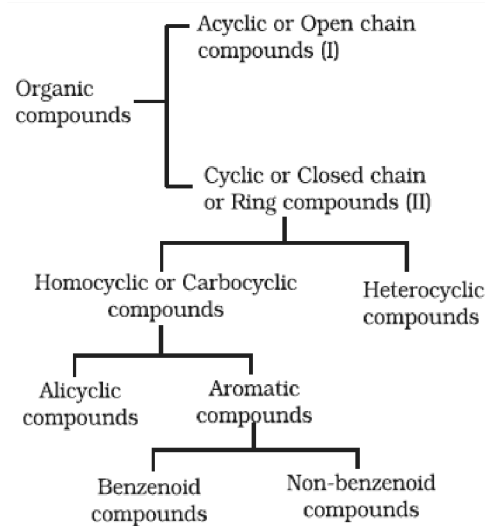
Cyclohexane

→ (Bond line formula)

Chlorocyclohexane

→ (Bond line formula)

Butane

$CH_3 - CH_2 - CH_2 - CH_3$

Bondline Formula ↓

Prop-2-en-1-ol

$CH_2 = CH - CH_2 - OH$

Bondline Formula ↓

OH

Some other examples of bond-line formulae

Cyclopropane

Cyclobuta-1,3-diene

Cyclopentyne

Three-Dimensional Representation of Organic Molecules:
The three-dimensional (3-D) structure of organic molecules can be represented on paper by using certain conventions. For example, by using solid ( ) and dashed ( ) wedge formula, the 3-D image of a molecule from a two-dimensional picture can be perceived. In these formulas the solid-wedge is used to indicate a bond projecting out of the plane of paper, towards the observer. The dashed-wedge is used to depict the bond projecting out of the plane of the paper and away from the observer. Wedges are shown in such a way that the broad end of the wedge is towards the observer. The bonds lying in plane of the paper are depicted by using a normal line (—). 3-D representation of methane molecule on paper has been shown in the following figure:

dashed wedge (bond away from observer)

bonds in the plane of paper

H

C—H

H

H

solid wedge (bond towards observer)
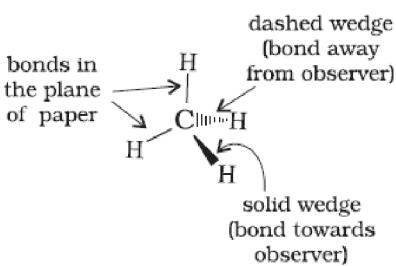
CLASSIFICATION OF ORGANIC COMPOUNDS: Organic Compounds are broadly classified as follows:

Organic compounds
— Acyclic or Open chain compounds (I)
— Cyclic or Closed chain or Ring compounds (II)

Homocyclic or Carbocyclic compounds — Heterocyclic compounds

Alicyclic compounds — Aromatic compounds

Benzenoid compounds — Non-benzenoid compounds

Acyclic compound or open-chain compound
In chemistry, an open-chain compound or acyclic compound is a compound with a linear structure, rather than a cyclic one. An open-chain compound having no side groups is called a straight-chain compound . For those with 4 or more carbons, the linear forms can have straight-chain or branched-chain isomers. The lowercase prefix n- denotes the straight-chain isomer; for example, n-butane is straight-chain butane, whereas i-butane is isobutane. Straight-chain molecules are often not literally straight, in the sense that their bond angles are often not 180°, but the name reflects that they are schematically straight, as the models below show.

branched-chain | straight-chain | n-nonane

open-chain
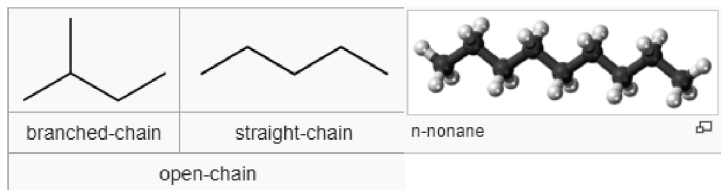
Alicyclic or closed chain or ring compounds:
In organic chemistry, an alicyclic compound contains one or more all-carbon rings which may be either saturated or unsaturated, but do not have aromatic character. Sometimes atoms other than carbon are also present in the ring (heterocyclic). Alicyclic compounds may have one or more aliphatic side chains attached.
The simplest alicyclic compounds are the monocyclic cycloalkanes: cyclopropane, cyclobutane, cyclopentane, cyclohexane, cycloheptane, cyclooctane, and so on. Bicyclic alkanes include bicycloundecane, decalin, and housane. Polycyclic alkanes include cubane, basketane, and tetrahedrane.

Cyclopropane   Cyclohexane

Cyclohexene   Tetrahydrofuran
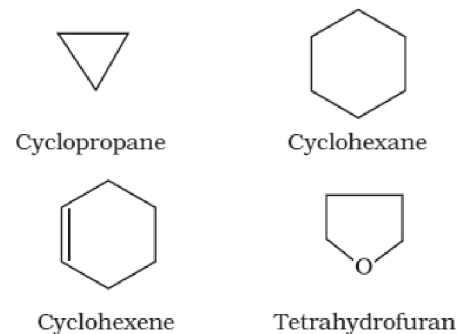
Aromatic compounds:
Aromatic compounds are special types of compounds.These include benzene and other related ring compounds (benzenoid). Like alicyclic compounds,aromatic comounds may also have hetero atom in the ring. Such compounds are called hetrocyclic aromatic compounds.
**Benzenoids:** Benzenoids are organic compounds with at least one benzene ring in their structure. The resonance in the benzene rings adds to the stability of the organic compound and makes them ineffective to changes, until and unless favourable conditions are met. They have three pi and three sigma bonds arranged alternatively inside the benzene ring structure. This pattern is also called the conjugated pi system.

Benzene   Aniline   Naphthalene
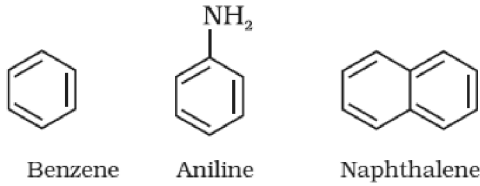
Non-Benzenoids: Non-Benzenoids are organic compounds that do not have a benzene ring. They are devoid of any kind of benzene rings and have a different structure. They have a conjugated pi system, irrespective of the absence of the benzene rings. They contain 5 – 7 carbon atoms in the ring structures. The conjugated pi system imparts the aromatic nature to these compounds. Some most common examples are azulenes, Tropolone etc.

Tropolone
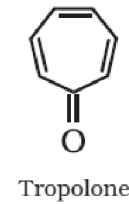
Heterocyclic aromatic compounds: A heterocyclic compound is an organic compound in which one or more of the carbon atoms in the backbone of the molecule has been replaced by an atom other than carbon. Typical hetero atoms include nitrogen, oxygen, and sulfur.

pyridine   pyrrole   furan   thiophene
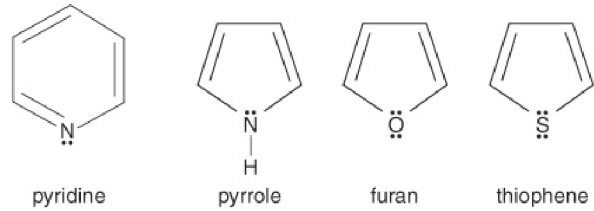
Functional Group:
A functional group is a group of atoms in a molecule with distinctive chemical properties, that causes the molecule's characteristic chemical reactions. The same functional group will undergo the same or similar chemical reactions regardless of the rest of the molecule's composition.
The examples are hydroxyl group (–OH), aldehyde group (–CHO) and carboxylic acid group (–COOH) etc.

Homologous Series:
A group or a series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called homologues. The members of a homologous series can be represented by general molecular formula and the successive members differ from each other in molecular formula by a –CH$_2$ unit. There are a number of homologous series of organic compounds. Some of these are alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals, alkanones, alkanoic acids, amines etc.
Within that series, many physical properties such as boiling point gradually change with increasing mass. For example, ethane (C$_2$H$_6$), has a higher boiling point than methane (CH$_4$). This is because the London dispersion forces between ethane molecules are higher than that between methane molecules, resulting in stronger forces of intermolecular attraction, raising the boiling point.

IUPAC Nomenclature of Alkanes:
IUPAC nomenclature of organic chemistry is a method of naming organic chemical compounds as recommended by the International Union of Pure and Applied Chemistry (IUPAC). It is published in the Nomenclature of Organic Chemistry (informally called the Blue Book). Ideally, every possible organic compound should have a name from which an unambiguous structural formula can be created.
According to the Guidelines set by IUPAC, the nomenclature of compounds must follow these steps:
The Longest Chain Rule: The parent hydrocarbon must be identified and subsequently named. The parent chain belonging to the compound in question is generally the longest chain of carbon atoms, be it in the form of a straight chain or a chain of any other shape.
The Lowest Set of Locants: The carbon atoms belonging to the parent hydrocarbon chain must be numbered using natural numbers and beginning from the end in which the lowest number is assigned to the carbon atom which carries the substituents.
Multiple instances of the same substituent: Prefixes which indicate the total number of the same substituent in the given organic compounds are given, such as di, tri, etc.
Naming of different substituents: In the organic compounds containing multiple substituents, the corresponding substituents are arranged in alphabetical order of names in the IUPAC nomenclature of organic compounds in question. The naming of different substituents present at the same positions: In the scenario wherein two differing substituent groups are present at the same position of the organic compound, the substituents are named in ascending alphabetical order.
Naming Complex Substituents: Complex substituents of organic compounds having branched structures must be named as substituted alkyl groups whereas the carbon which is attached to the substituent group is numbered as one. These branched and complex substituents must be written in brackets in the IUPAC nomenclature of the corresponding compounds.
The format of the IUPAC Name of the Compound can be written as: **Locant + Prefix + Root + Locant + Suffix:**
1. **Root**
The Word root indicates the total number of carbon atoms present in the longest carbon chain belonging to the compound. For example, 'Meth' refers to a chain with 1 carbon atom and 'Pent' refers to a chain with 5 carbon atoms.
2. **Suffix**
The suffix in IUPAC nomenclature is usually a functional group belonging to the molecule which follows the root of the name. It can be further divided into the following types.
A **Primary Suffix**, which is written immediately after the word root as in the case of alkanes, where the suffix is 'ane'.
A **Secondary Suffix**, which is generally written after the primary suffix is written. For example, compounds having an alkane and alcohol group attached to them will be named as alkanol, with 'ol' being the secondary suffix for the alcohol group. In accordance with these norms, the suffix of a compound can be written as a part of the IUPAC name of the given compound.
3. **Prefix**
Prefixes are added prior to the root of the compounds IUPAC nomenclature. Prefixes are very useful since they indicate the presence of side chains or substituent groups in the given organic molecule. These prefixes also offer insight into the cyclic or acyclic natures of the compounds in question.
Primary Prefixes: Indicate the cyclic or acyclic nature of the given compound. The prefix 'cyclo' is used for cyclic compounds, for example.
Secondary Prefixes: Indicate the presence of side chains or substituent groups. An example of these types of prefixes would be the 'CH3' group, which is called the methyl group.

Straight chain hydrocarbons:
The names of such compounds are based on their chain structure, and end with suffix '-ane' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH$_4$ to C$_4$H$_{10}$, where the prefixes are derived from trivial names).

Number of carbon atoms:	1	2	3	4	5	6	7	8	9	10
Prefix:	meth	eth	prop	but	pent	hex	hept	oct	non	dec

Name	Molecular Formula	Condensed Structural Formula
Methane	CH$_4$	CH$_4$
Ethane	C$_2$H$_6$	CH$_3$CH$_3$
Propane	C$_3$H$_8$	CH$_3$CH$_2$CH$_3$
Butane	C$_4$H$_{10}$	CH$_3$(CH$_2$)$_2$CH$_3$
Pentane	C$_5$H$_{12}$	CH$_3$(CH$_2$)$_3$CH$_3$
Hexane	C$_6$H$_{14}$	CH$_3$(CH$_2$)$_4$CH$_3$
Heptane	C$_7$H$_{16}$	CH$_3$(CH$_2$)$_5$CH$_3$
Octane	C$_8$H$_{18}$	CH$_3$(CH$_2$)$_6$CH$_3$
Nonane	C$_9$H$_{20}$	CH$_3$(CH$_2$)$_7$CH$_3$
Decane	C$_{10}$H$_{22}$	CH$_3$(CH$_2$)$_8$CH$_3$

Branched chain hydrocarbons: In a branched chain compound small chains of carbon atoms are attached at one or more carbon atoms of the parent chain. The small carbon chains (branches) are called alkyl groups. For example:
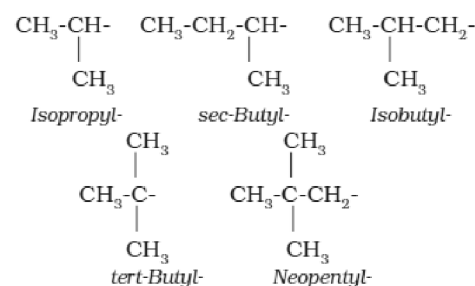

(a)   (b)

In order to name such compounds, the names of alkyl groups are prefixed to the name of parent alkane. An alkyl group is derived from a saturated hydrocarbon by removing a hydrogen atom from carbon. Thus, CH$_4$ becomes -CH$_3$ and is called methyl group. An alkyl group is named by substituting 'yl' for 'ane' in the corresponding alkane. Some alkyl groups are listed in the following Table:
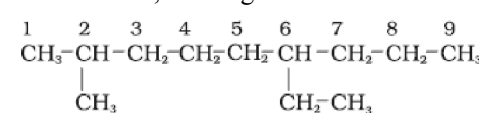
Alkane		Alkyl group	
Molecular formula	Name of alkane	Structural formula	Name of alkyl group
CH$_4$	Methane	-CH$_3$	Methyl
C$_2$H$_6$	Ethane	-CH$_2$CH$_3$	Ethyl
C$_3$H$_8$	Propane	-CH$_2$CH$_2$CH$_3$	Propyl
C$_4$H$_{10}$	Butane	-CH$_2$CH$_2$CH$_2$CH$_3$	Butyl
C$_{10}$H$_{22}$	Decane	-CH$_2$(CH$_2$)$_8$CH$_3$	Decyl

Abbreviations are used for some alkyl groups. For example, methyl is abbreviated as Me, ethyl as Et, propyl as Pr and butyl as Bu. The alkyl groups can be branched also. Thus, propyl and butyl groups can have branched structures as shown below.

CH_3-CH-
|
CH_3
Isopropyl-

CH_3-CH_2-CH-
|
CH_3
sec-Butyl-

$CH_3-CH-CH_2-$
|
CH_3
Isobutyl-

CH_3
|
CH_3-C-
|
CH_3
tert-Butyl-

CH_3
|
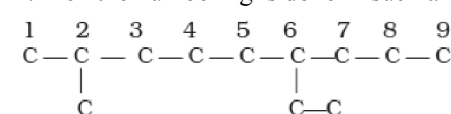CH_3-C-CH_2-
|
CH_3
Neopentyl-

Nomenclature of branched chain alkanes: The rules for naming them are given below :
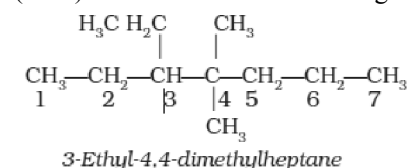1. First of all, the longest carbon chain in the molecule is identified.

1 2 3 4 5 6 7 8 9
$CH_3-CH-CH_2-CH_2-CH_2-CH-CH_2-CH_2-CH_3$
      | |
     CH_3 CH_2-CH_3

2. Then the numbering is done in such a way that the branched carbon atoms get the lowest possible numbers.

1 2 3 4 5 6 7 8 9
$C-C-C-C-C-C-C-C-C$
 | |
   C $C-C$

3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. Thus, name for the compound shown above is: 6-ethyl-2- methylnonane. [Note: the numbers are separated from the groups by hyphens and there is no break between methyl and nonane.]
4. If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however, are not considered. Thus, the following compounds are named as:

   H_3C H_2C CH_3
        | |
$CH_3-CH_2-CH-C-CH_2-CH_2-CH_3$
1   2   3 |4 5   6   7
              CH_3

3-Ethyl-4,4-dimethylheptane

5. If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing

1   2   3   4   5   6   7   8
$CH_3-CH_2-CH-CH_2-CH_2-CH-CH_2-CH_3$
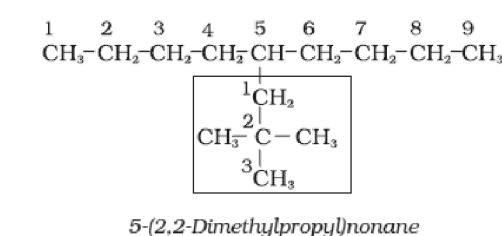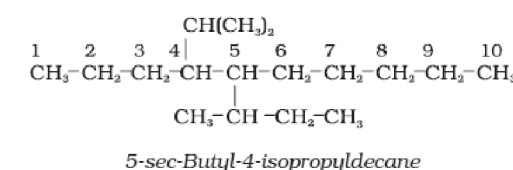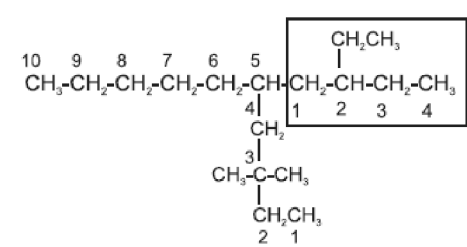 | |
       CH_2CH_3 CH_3
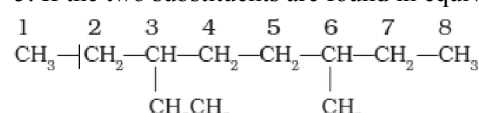
6. The branched alkyl groups can be named by following the above mentioned procedures. However, the carbon atom of the branch that attaches to the root alkane is numbered 1 as exemplified below:

4   3   2   1
$CH_3-CH-CH_2-CH-$
    | |
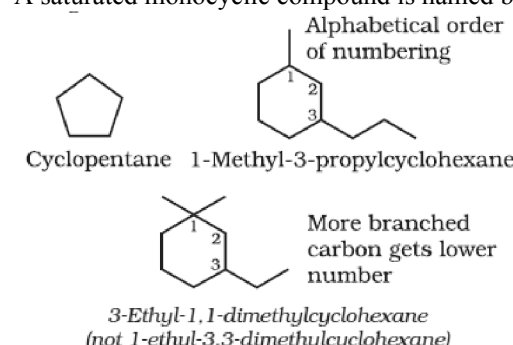 CH_3 CH_3
1,3-Dimethylbutyl-
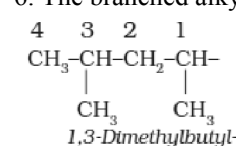
The name of such branched chain alkyl group is placed in parenthesis while naming the compound. While writing the trivial names of substituents' in alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes sec- and tert- are not considered to be the part of the fundamental name. The use of iso and related common prefixes for naming alkyl groups is also allowed by the IUPAC nomenclature as long as these are not further substituted. In multisubstituted compounds, the following rules may aso be remembered:
• If there happens to be two chains of equal size, then that chain is to be selected which contains more number of side chains.
• After selection of the chain, numbering is to be done from the end closer to the substituent.
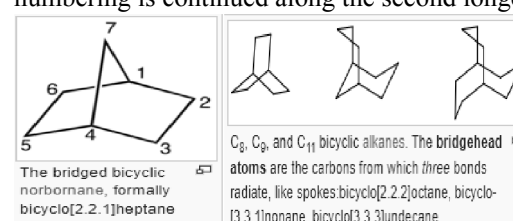

5-(2-Ethylbutyl)-3,3-dimethyldecane

5-sec-Butyl-4-isopropyldecane

5-(2,2-Dimethylpropyl)nonane

Cyclic Compounds:
A saturated monocyclic compound is named by prefixing 'cyclo' to the corresponding straight chain alkane. If side chains are present, then the rules given above are applied. Names of some cyclic compounds are given below.

Cyclopentane   1-Methyl-3-propylcyclohexane

3-Ethyl-1,1-dimethylcyclohexane
(not 1-ethyl-3,3-dimethylcyclohexane)

Bicyclic molecule:
A bicyclic molecule (from bi 'two', and cycle 'ring') is a molecule that features two joined rings. The root of the compound name depends on the total number of atoms in all rings together, possibly followed by a suffix denoting the functional group with the highest priority. Numbering of the carbon chain always begins at one bridgehead atom (where the rings meet) and follows the carbon chain along the longest path, to the next bridgehead atom. Then numbering is continued along the second longest path and so on. Fused and bridged bicyclic compounds get the prefix bicyclo.


The bridged bicyclic norbornane, formally bicyclo[2.2.1]heptane

C_8, C_9, and C_{11} bicyclic alkanes. The bridgehead atoms are the carbons from which three bonds radiate, like spokes.bicyclo[2.2.2]octane, bicyclo-[3.3.1]nonane, bicyclo[3.3.3]undecane.

Spiro molecule:
Here, the two rings are connected with a single atom called spiro atom. Spiro compounds may be fully carbocyclic (all carbon) or heterocyclic (having one or more non-carbon atom).

Spiro Compounds Nomenclature:
• Spiro Compounds have a prefix spiro which represent two rings with a spiro junction.
• Prefix is followed by a square bracket comprising the number of atoms in the smaller ring then the number of atoms in the larger ring, separated by a period, excluding the spiroatom.
• Position-numbering is done by beginning with an atom of the smaller ring which is near to the spiroatom around the atoms of that ring, then the spiroatom itself, then around the atoms of the larger ring.


Spiro[3.4]octane

Spiro[4.5]deca-1,6-diene
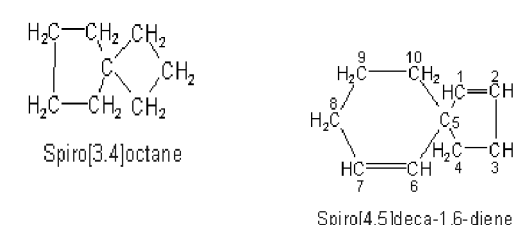
Nomenclature of Organic Compounds having Functional Group(s)
Here, the longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain.

Alkenes:
Alkenes are named for their parent alkane chain with the suffix "-ene" and a numerical root indicating the position of the carbon with the lower number for each double bond in the chain. Multiple double bonds take the form -diene, -triene, etc., with the size prefix of the chain taking an extra "a" Simple cis and trans isomers may be indicated with a prefixed cis- or trans-. However, cis- and trans- are relative descriptors. It is IUPAC convention to describe all alkenes using absolute descriptors of Z- (same side) and E- (opposite) with the Cahn–Ingold–Prelog priority rules.

but-1-ene   buta-1,3-diene

trans-but-2-ene   *cis*-but-2-ene
(E)-but-2-ene   (Z)-but-2-ene
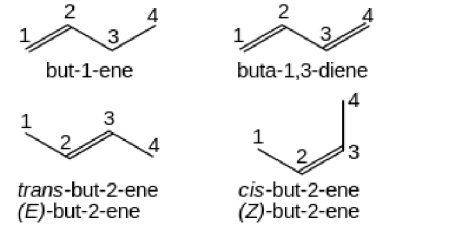
Alkynes:

Alkynes are named using the same system, with the suffix "-yne" indicating a triple bond.


ethyne   propyne
(acetylene)   (methylacetylene)
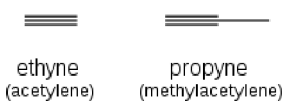
Haloalkanes and haloarenes:

n haloalkanes and haloarenes (R−X), Halogen functional groups are prefixed with the bonding position and take the form of fluoro-, chloro-, bromo-, iodo-, etc., depending on the halogen. Multiple groups are dichloro-, trichloro-, etc., and dissimilar groups are ordered alphabetically as before.
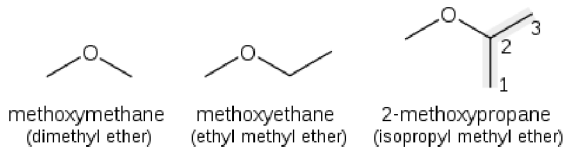

trichloromethane   2-bromo-2-chloro-1,1,1,-trifluoroethane
(chloroform)   (halothane)
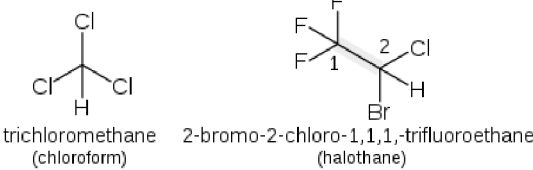
Alcohols:

Alcohols (R−OH) take the suffix "-ol" with a numerical suffix indicating the bonding position. The suffixes -diol, -triol, -tetraol, etc., are used for multiple −OH groups.

ethanol   propan-1-ol   ethane-1,2-diol
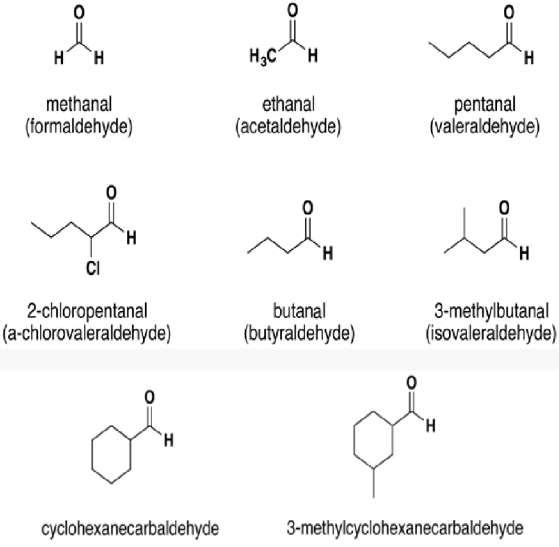(ethyl alcohol) (propyl alcohol)n- (ethylene glycol)
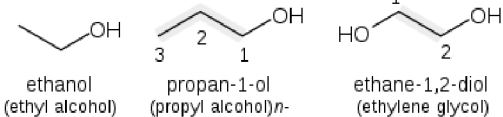
Ethers:

Ethers (R−O−R) consist of an oxygen atom between the two attached carbon chains. The shorter of the two chains becomes the first part of the name with the -ane suffix changed to -oxy, and the longer alkane chain becomes the suffix of the name of the ether. If the oxygen is not attached to the end of the main alkane chain, then the whole shorter alkyl-plus-ether group is treated as a side-chain and prefixed with its bonding position on the main chain.

methoxymethane   methoxyethane   2-methoxypropane
(dimethyl ether) (ethyl methyl ether) (isopropyl methyl ether)

Alternatively, an ether chain can be named as an alkane in which one carbon is replaced by an oxygen, a replacement denoted by the prefix "oxa". For example, $CH_3OCH_2CH_3$ could also be called 2-oxabutane.
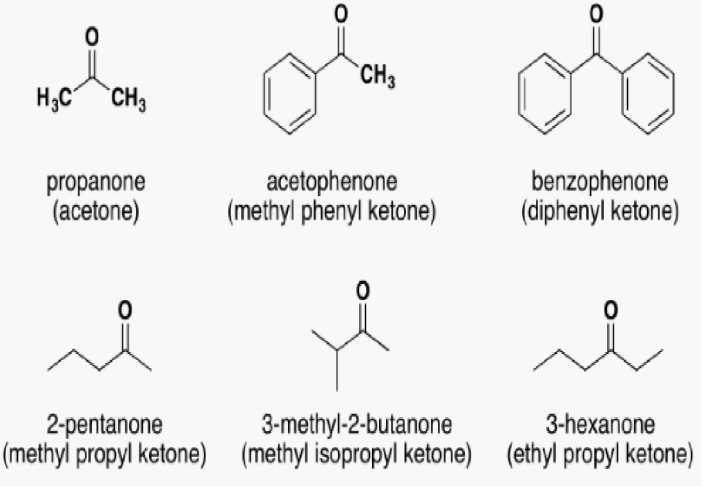
Aldehydes:

Aldehydes (R−CH=O) take the suffix "-al".The aldehyde funtional group is given the #1 numbering location and this number is not included in the name.When the -CHO functional group is attached to a ring the suffix *-carbaldehyde* i added.


methanal   ethanal   pentanal
(formaldehyde) (acetaldehyde)   (valeraldehyde)

2-chloropentanal   butanal   3-methylbutanal
(a-chlorovaleraldehyde) (butyraldehyde) (isovaleraldehyde)

cyclohexanecarbaldehyde   3-methylcyclohexanecarbaldehyde

Ketones:

In general ketones ($R_2C=O$) take the suffix "-one".Some common ketones are known by their generic names.

propanone   acetophenone   benzophenone
(acetone)   (methyl phenyl ketone) (diphenyl ketone)

2-pentanone   3-methyl-2-butanone   3-hexanone
(methyl propyl ketone) (methyl isopropyl ketone) (ethyl propyl ketone)

Carboxylic Acids:

In general, carboxylic acids (R−C(=O)OH) are named with the suffix -oic acid (etymologically a back-formation from benzoic acid). As with aldehydes, the carboxyl functional group must take the "1" position on the main chain and s the locant need not be stated.

Butanoic acid   Propanoic acid


2-Methylpentanoic acid   3-Chloropropanoic acid
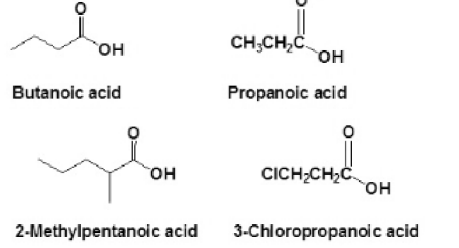
When a carboxyl group is added to a ring the suffix -carboxylic acid is added to the name of the cyclic compound. The ring carbon attached to the carboxyl group is given the #1 location number.

Cyclopentanecarboxylic acid   Cis-2-Bromocyclohexanecarboxylic acid
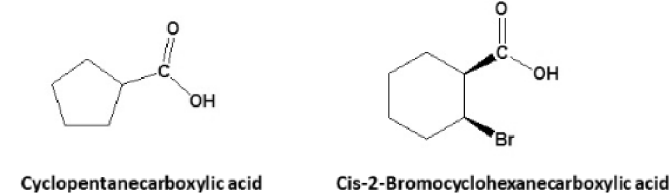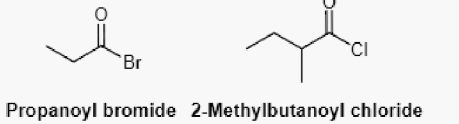
Esters:

Esters (R−C(=O)O−R') are named as alkyl derivatives of carboxylic acids. The alkyl (R') group is named first. The R−C(=O)O part is then named as a separate word based on the carboxylic acid name, with the ending changed from -oic acid to -oate.
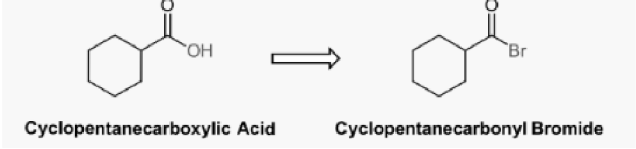

methyl methanoate   methyl ethanoate   ethyl methanoate
(formate)   (acetate)   (ethyl formate)
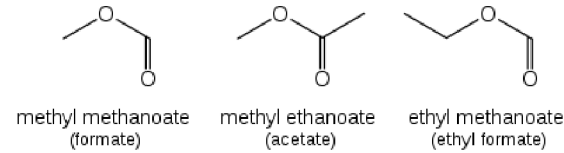
Acid Halides:

The nomenclature of acid halides starts with the name of the corresponding carboxylic acid. If the corresponding carboxylic acid has an –oic acid or –ic acid ending it is removed and replaced with the ending -oyl followed by the first syllable of the name of the halogen along with an –ide ending.

When the corresponding acid includes a -carboxylic acid ending, it is removed and replaced with the ending -carbonyl. This is followed by the first syllable of the name of the halogen along with an –ide ending

Propanoyl bromide 2-Methylbutanoyl chloride

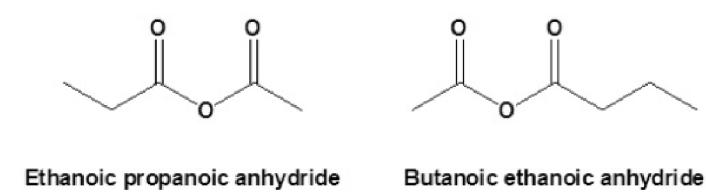Cyclopentanecarboxylic Acid   Cyclopentanecarbonyl Bromide
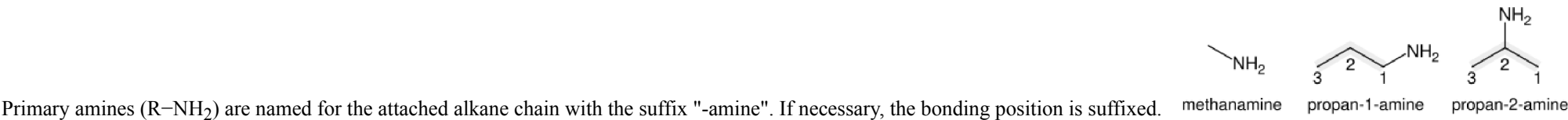
Acid Anhydrides:

he acid anhydride functional group results when two carboxylic acids combine and lose water (anhydride = without water).

Symmetrical acid anhydrides are named like carboxylic acids except the ending -acid is replaced with -anhydride. This is true for both the IUPAC and Common nomenclature.

Propanoic anhydride   Ethanoic anhydride
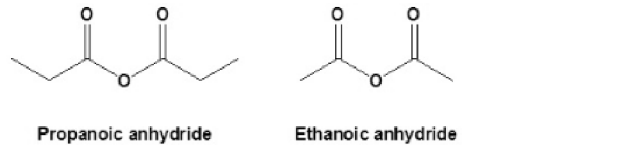
Unsymmetrical acid anhydrides are named by first naming each component carboxylic acid alphabetically arranged (without the word acid) followed by spaces and then the word anhydride.

Ethanoic propanoic anhydride   Butanoic ethanoic anhydride

Amines:

methanamine   propan-1-amine   propan-2-amine

Primary amines (R−NH$_2$) are named for the attached alkane chain with the suffix "-amine". If necessary, the bonding position is suffixed.

For secondary amines (of the form R−NH−R), the longest carbon chain attached to the nitrogen atom becomes the primary name of the amine; the other chain is prefixed as an alkyl group with location prefix given as an italic N. Tertiary amines (R−NR−R) are treated similarly.

N-methylethanamine   *N*-ethyl-*N*-methylpropanamine
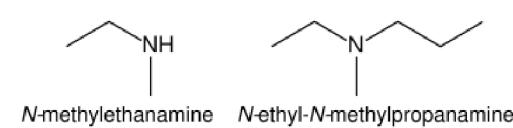
Nitriles:

Name the parent alkane (include the carbon atom of the nitrile as part of the parent) followed with the word -nitrile. The carbon in the nitrile is given the #1 location position. It is not necessary to include the location number in the name because it is assumed that the functional group will be on the end of the parent chain.Cycloalkanes are followed by the word -carbonitrile.

N≡CCH$_2$CH$_2$CH$_3$

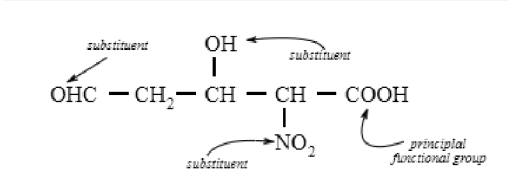Butane nitrile   2-Bromopropane nitrile
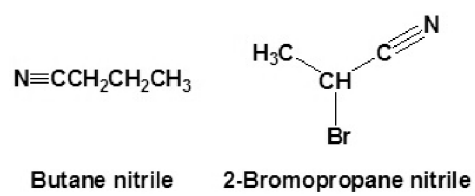
Polyfunctional Group Compounds:

In a polyfunctional compound, one of the functional groups is selected as the principal functional group (used as suffix) while all other functional groups are treated as substituents(used as prefix).

Functional groups according to their priorities are listed in the priority table in decreasing order i.e., Carboxylic acid with the highest priority is placed at the top while alkyne being the least in priority is placed at the bottom. The functional group which has the highest priority among all the functional groups present in an organic compound is selected as the principle functional group.

PRIORITY TABLE [HIGHER to LOWER]	
COMPOUND NAME	FORMULA
Carboxylic acid	-COOH
Sulphonic acid	-SO$_3$H
Ester	-COOR
Acid chloride	-COCl
Acid amides	-CONH$_2$
Nitrile	-CN
Aldehyde	-CHO
Ketone	>C=O
Alcohol	-OH
Phenol	-C$_6$H$_6$O
Thiols	-SH
Amines	-NH$_2$
Ether	-OR
Alkene	>C=C<
Alkyne	-C≡C-

Substituents	
SECONDARY FUNCTIONAL GROUP	PREFIX
-X (F,Cl,Br,I)	Halo (fluoro, chloro, bromo, iodo)
-OH	Hydroxy
-SH	Mercapto
-OR	Alkoxy
-NH$_2$	Amino
-CHO	Formyl or alkanoyl
-C=O	Keto or oxo
-COOH	Carboxy
-COOR	Alkoxycarbonyl or carbalkoxy
-COCl	Halocarbonyl or haloalkanoyl
-CN	Cyano
-CONH$_2$	Carbamoyl or Carboxamido

Examples :

3-Oxobutan-1-oic acid

4-Chloro-3-methoxybutan-1-al

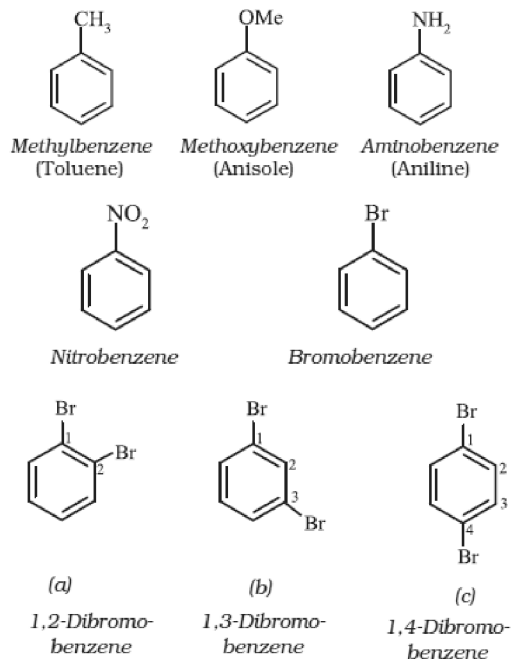

4-Aminopentan-2-ol


2-Amino-5-formyl-3-hydroxypentan-1-oic acid

Nomenclature of Substituted Benzene Compounds:

For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word benzene as shown in the following examples. However,common names (written in bracket below) of many substituted benzene compounds are also universally used.

Methylbenzene (Toluene)   Methoxybenzene (Anisole)   Aminobenzene (Aniline)

Nitrobenzene   Bromobenzene

(a) 1,2-Dibromo-benzene   (b) 1,3-Dibromo-benzene   (c) 1,4-Dibromo-benzene

ISOMERISM:

The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers.The following flow chart shows different types of isomerism.
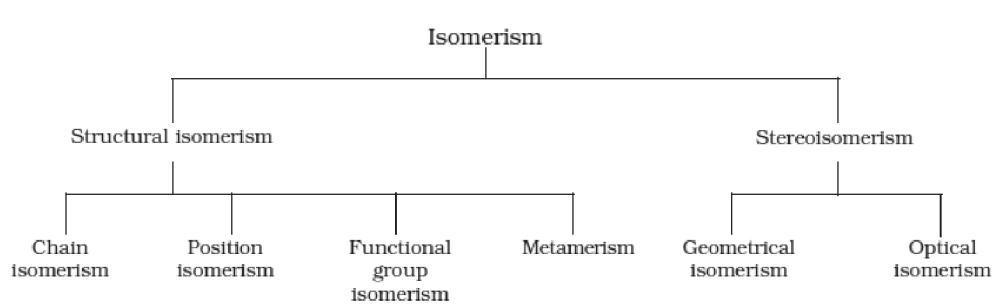

Structural Isomerism:

Compounds having the same molecular formula but different structures (manners in which atoms are linked) are classified as structural isomers. Some typical examples of different types of structural isomerism are given below:

(i) **Chain isomerism:** When two or more compounds have similar molecular formula but different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example, C_5H_{12} represents three compounds:

$CH_3CH_2CH_2CH_2CH_3$
Pentane

Isopentane
(2-Methylbutane)

Neopentane
(2,2-Dimethylpropane)
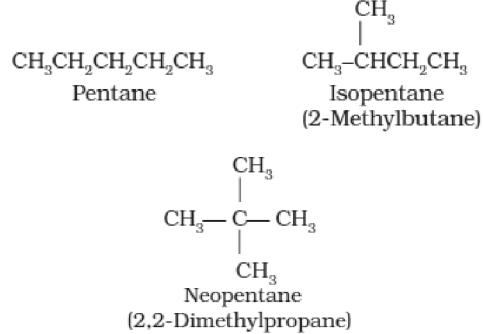
(ii)**Position isomerism:**

When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism.

$CH_3CH_2CH_2OH$
Propan-1-ol

CH_3-CH-CH_3
Propan-2-ol
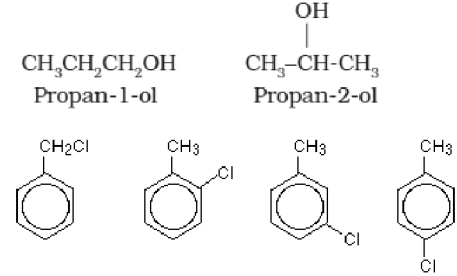
(iii)**Functional group isomerism:**

Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group isomerism.

propanal   propanone

propanoic acid   methyl ethanoate
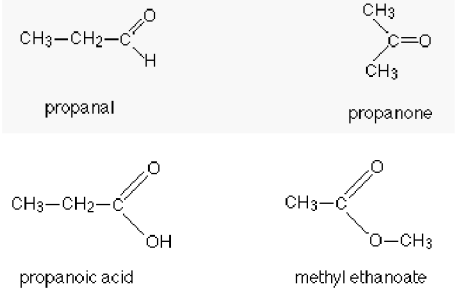
(iv)**Metamerism:**

Compounds having the same molecular formula but the different number of carbon atoms around the functional group are known as metamers of each other and the phenomenon is known as metamerism.

$C_2H_5 - O - C_2H_5$ and $CH_3 - O - CH_2 - CH_2 - CH_3$
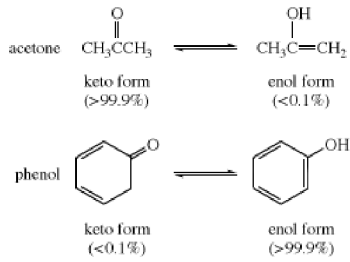diethyl ether   methyl propyl ether
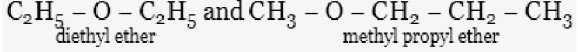
(v)**Tautomerism:**

Tautomerism is a phenomenon where a single chemical compound tends to exist in two or more interconvertible structures that are different in terms of the relative position of one atomic nucleus, which is generally hydrogen.It is also called desmotropism.

Care should be taken not to confuse tautomers with depictions of "contributing structures" in chemical resonance. Tautomers are distinct chemical species that can be distinguished by their differing atomic connectivities, molecular geometries, and physicochemical and spectroscopic properties,[6] whereas resonance forms are merely alternative Lewis structure (valence bond theory) depictions of a single chemical species, whose true structure is a quantum superposition, essentially the "average" of the idealized, hypothetical geometries implied by these resonance forms.

The most common type of tautomerism is that involving carbonyl, or keto, compounds and unsaturated hydroxyl compounds, or enols; the structural change is the shift of a hydrogen atom between atoms of carbon and oxygen, with the rearrangement of bonds as indicated:
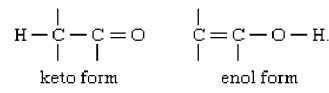
keto form   enol form

In many aliphatic aldehydes and ketones, such as acetaldehyde, the keto form is the predominant one; in phenols, the enol form, which is stabilized by the aromatic character of the benzene ring, is the major component.

acetone CH_3CCH_3
keto form
(>99.9%)

$CH_3C=CH_2$
enol form
(<0.1%)

phenol

keto form
(<0.1%)

enol form
(>99.9%)

Stereoisomerism:

Stereoisomerism, or Spatial isomerism, is a form of isomerism in which molecules have the same molecular formula and sequence of bonded atoms (constitution), but differ in the three-dimensional orientations of their atoms in space.This contrasts with structural isomers, which share the same molecular formula, but the bond connections or their order differs. By definition, molecules that are stereoisomers of each other represent the same structural isomer.

Geometric isomerism(Cis–trans and E-Z isomerism):

Stereoisomerism about double bonds arises because rotation about the double bond is restricted, keeping the substituents fixed relative to each other.[5] If the two substituents on at least one end of a double bond are the same, then there is no stereoisomer and the double bond is not a stereocenter, e.g. propene, $CH_3CH=CH_2$ where the two substituents at one end are both H.

Traditionally, double bond stereochemistry was described as either cis (Latin, on this side) or trans (Latin, across), in reference to the relative position of substituents on either side of a double bond. A simple example of cis-trans isomerism is the 1,2-disubstituted ethenes, like the dichloroethene ($C_2H_2Cl_2$) isomers shown below.
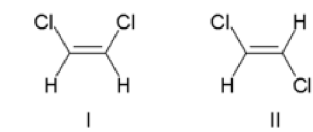
Molecule I is cis-1,2-dichloroethene and molecule II is trans-1,2-dichloroethene. Due to occasional ambiguity, IUPAC adopted a more rigorous system wherein the substituents at each end of the double bond are assigned priority based on their atomic number. If the high-priority substituents are on the same side of the bond, it is assigned Z (Ger. zusammen, together). If they are on opposite sides, it is E (Ger. entgegen, opposite).Since chlorine has a larger atomic number than hydrogen, it is the highest-priority group.Using this notation to name the above pictured molecules, molecule I is (Z)-1,2-dichloroethene and molecule II is (E)-1,2-dichloroethene. It is not the case that Z and cis or E and trans are always interchangeable. Consider the following fluoromethylpentene:
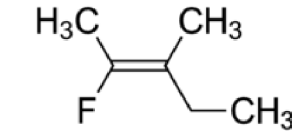

The proper name for this molecule is either trans-2-fluoro-3-methylpent-2-ene because the alkyl groups that form the backbone chain (i.e., methyl and ethyl) reside across the double bond from each other, or (Z)-2-fluoro-3-methylpent-2-ene because the highest-priority groups on each side of the double bond are on the same side of the double bond. Fluoro is the highest-priority group on the left side of the double bond, and ethyl is the highest-priority group on the right side of the molecule.

Difference between cis and trans isomers

cis isomer	trans isomer
Cis isomers are almost always polar.	Trans isomers are not very polar. Many trans isomers are non-polar molecules.
Due to loosely packed molecules, cis isomers have relatively lower melting points than trans isomers.	Due to tightly packed molecules, the melting points of trans isomers are usually higher than those of cis isomers.
The boiling point of cis isomers is high due to the presence of strong forces of attraction between the atoms of the cis isomer.	The boiling point is comparatively low for trans isomers as there are no strong attractive forces.

OPTICAL (CONFIGURATIONAL) ISOMERISM::
Optical isomerism is another class of stereoisomerism. The organic compounds that exhibit optical isomerism must have a unique ability to rotate the plane polarized light either towards left or towards right hand directions. This unique ability is generally known as **optical activity**. Optical activity of any compound is measured by analyzing the sample in an instrument called **Polarimeter**. A solution of known concentration of optically active compound is when exposed to the beam of plane polarized light, the beam of plane polarized light is rotated through a certain number of degrees, either to the clockwise (right) direction or anti-clockwise (left) direction. The compound which rotates the plane polarized light towards clockwise direction is called to be **dextrorotatory (represented by +)**; whereas, the compound which rotates the plane polarized light towards anti-clockwise direction is called to be **levorotatory (represented by -)**. Figure 1 shows the schematic representation of polarimeter.
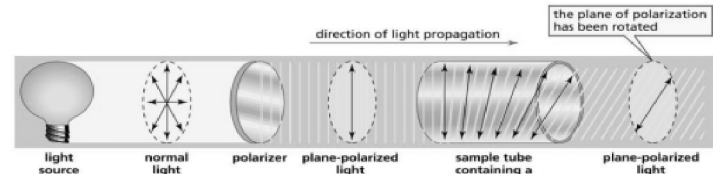
The degree of rotation depends upon the number of the molecules of the compounds falls in the path of beam. To compare the rotating power of different optically active compounds, the specific rotation of each compound is calculated and then comparison should be made. **Specific rotation** is defined as the degree of rotation offered for the given wavelength of plane polarized light at given temperature by a solution of 1g/mL concentration is filled in a 10 cm length sample cell. Specific rotation is represented by and can be calculated as:

$$[\alpha]_\lambda^t = \frac{100\alpha}{lc}$$

Where α is observed angle of rotation; t is the temperature of during experiment; λ is the wavelength of light used; l is the length of the tube in decimeter; and c is the concentration of the compounds per 100 mL of solution.
**ELEMENTS OF SYMMETRY:**All optically active molecules/object are chiral and they exhibit enantiomerism (Figure 2). A chiral molecule is that which cannot be superimposed on its mirror image; however, both the non-super imposable isomers are called enantiomers.Elements of symmetry are a simple tool to identify whether a molecule is chiral or not. The necessary condition for optically active molecule to be chiral is that, the molecule should not possess any kind of symmetry elements. The elements of symmetry are generally categorized as follows:

   i. Simple axis of symmetry (C_n)
   ii. Plane of symmetry (σ)
   iii. Centre of symmetry (C_i)
   iv. Alternating axis of symmetry (S_n)

MOLECULAR CHIRALITY, ENANTIOMERISM: The necessary condition for a molecule to have optical isomerism is that molecule should not have any kind of symmetry elements present in it, in other words the molecule should be **dissymmetric**. Such molecules are called 'Chiral' and the property is called 'molecular chirality'. Optically active chiral molecules which are non-super imposable on their mirror images are called 'enantiomers' and the phenomenon is known as 'enantiomerism'. To exhibit optical isomerism an organic compound must have at least one asymmetric carbon atom. An asymmetric carbon atom is that which is bonded to four different atoms or groups.
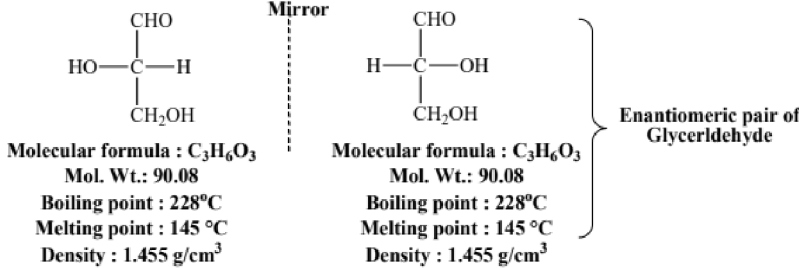
CHIRAL AND ACHIRAL MOLECULES WITH TWO STEREOGENIC CENTRES: Let us consider the stereoisomers of Tartaric acid which has two stereo centers with identical atoms/groups attached to both the stereo centers. The tartaric acid have two stereo centers and can have four stereoisomers out of which two stereoisomers are non-super imposable mirror image of each other called enantiomers and chiral; and rest two are identical to each other and also have plane of symmetry hence it can be divided in to two equal halves, therefore are
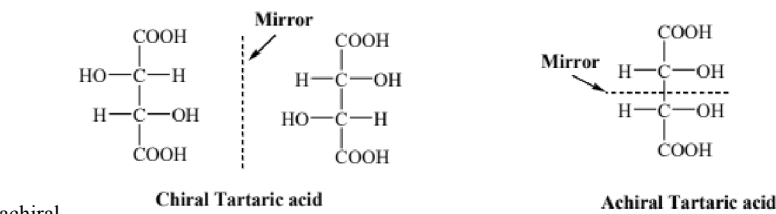
achiral.
DIASTEREOMERS: Diastereomers are those stereoisomers that are not mirror image of each other, in other words you can understand the diastereomers are stereoisomers that are not enantiomers. Diastereomers are non-enantiomeric stereoisomers with two or more stereo centers.

FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM:

In an organic reaction, the organic molecule (also referred as a substrate) reacts with an appropriate attacking reagent and leads to the formation of one or more intermediate(s) and finally product(s).The general reaction is depicted as follows :


In such a reaction a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed. A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism.

Fission of a Covalent Bond:
In chemistry, bond cleavage, or bond fission, is the splitting of chemical bonds. In general, there are two classifications for bond cleavage: homolytic and heterolytic, depending on the nature of the process.
Homolytic cleavage: In homolytic cleavage, or homolysis, the two electrons in a cleaved covalent bond are divided equally between the products. This process is also known as homolytic fission or radical fission.
Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called **free radicals**. Free radicals are very reactive.
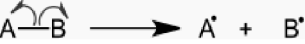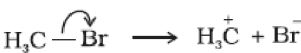

Alkyl radicals are classified as primary,secondary, or tertiary. Alkyl radical stability increases as we proceed from primary to tertiary:
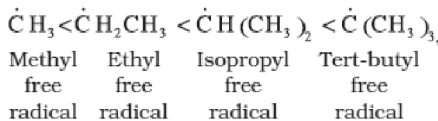
Organic reactions, which proceed by homolytic fission are called free radical or homopolar or nonpolar reactions.
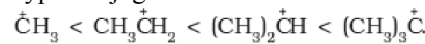**Heterolytic cleavage:**In heterolytic cleavage, or heterolysis, the bond breaks in such a fashion that the originally-shared pair of electrons remain with one of the fragments. Thus, a fragment gains an electron, having both bonding electrons, while the other fragment loses an electron. This process is also known as ionic fission.
After heterolysis, one atom has a sextet electronic structure and a positive charge and the other, a valence octet with at least one lone pair and a negative charge. Thus, heterolytic cleavage of bromomethane will give CH_3^+ and Br^- as shown below.

A species having a carbon atom possessing sextext of electrons and a positive charge is called a carbocation (earlier called carbonium ion).Carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon.Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects.The observed order of carbocation stability is:

$$\overset{+}{C}H_3 < CH_3\overset{+}{C}H_2 < (CH_3)_2\overset{+}{C}H < (CH_3)_3\overset{+}{C}.$$

These carbocations have trigonal planar shape with positively charged carbon being sp^2 hybridised.

The heterolytic cleavage can also give a species in which carbon gets the shared pair of electrons.

$$CH_3 \!\frown\! Z \longrightarrow H_3C\!:^- + Z^+$$
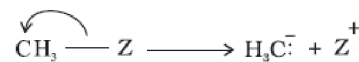
Such a carbon species carrying a negative charge on carbon atom is called carbanion. Carbanions are also unstable and reactive species. The organic reactions which proceed through heterolytic bond cleavage are called ionic or heteropolar or just polar reactions.
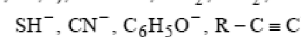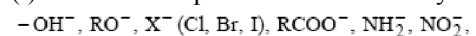
Nucleophiles and Electrophiles:

Nucleophile:A nucleophile is a chemical species that forms bonds by donating an electron pair. All molecules and ions with a free pair of electrons or at least one pi bond can act as nucleophiles. Because nucleophiles donate electrons, they are Lewis bases.

Nucleophilic describes the affinity of a nucleophile to bond with positively charged atomic nuclei. Nucleophilicity, sometimes referred to as nucleophile strength, refers to a substance's nucleophilic character and is often used to compare the affinity of atoms. Neutral nucleophilic reactions with solvents such as alcohols and water are named solvolysis. Nucleophiles may take part in nucleophilic substitution, whereby a nucleophile becomes attracted to a full or partial positive charge, and nucleophilic addition.

Nucleophilicity is closely related to basicity. The difference between the two is, that basicity is a thermodynamic property (i.e. relates to an equilibrium state), but nucleophilicity is a kinetic property, which relates to rates of certain chemical reactions.

Examples:

(i)Electron rich species and have affinity towards nucleus (which is positively charged).

$$-OH^-, RO^-, X^- (Cl, Br, I), RCOO^-, NH_2^-, NO_2^-, :$$
$$SH^-, CN^-, C_6H_5O^-, R-C \equiv C^-$$

(ii)Neutral nucleophiles are capable of donating a pair of electrons e.g.

$$H_2\ddot{O}, R-\ddot{O}-H, \ddot{N}H_3, R-\ddot{S}-H, R\ddot{N}H_2, R-\ddot{O}-R, R-Mg-X$$
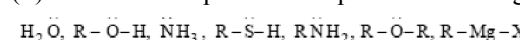
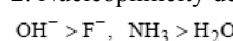**Nucleophilicity:**

1. Species with negative charge are stronger nucleophiles than analogous species without a negative charge.

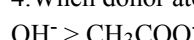$$OH^- > H_2O, \qquad SH^- > H_2S, \qquad NH_2^- > NH_3$$
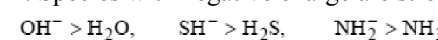
2. Nucleophilicity decreases from left to right across the periodic table eg.

$$OH^- > F^-, \quad NH_3 > H_2O$$

3. Nucleophilicity increases down the periodic table.

$$I^- > Br^- > Cl^- > F^-, \ HSe^- > HS^- > HO^-$$
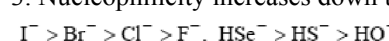
4.When donor atom is identical, then nucleophilicity increases with increase in basic strength.

$$OH^- > CH_3COO^-$$

Electrophile:

an electrophile is a chemical species that forms bonds with nucleophiles by accepting an electron pair.[1] Because electrophiles accept electrons, they are Lewis acids. Most electrophiles are positively charged, have an atom that carries a partial positive charge, or have an atom that does not have an octet of electrons.

Electrophiles mainly interact with nucleophiles through addition and substitution reactions. Frequently seen electrophiles in organic syntheses include

- Cations such as H$^+$ and NO$^+$
- Polarized neutral molecules such as HCl,alkyl halides, acyl halides, and carbonyl compounds,
- Polarizable neutral molecules such as Cl$_2$ and Br$_2$
- oxidizing agents such as organic peracids, chemical species that do not satisfy the octet rule such as carbenes and radicals, and some Lewis acids such as BH$_3$ and DIBAL

Electron Displacement Effects in Covalent Bonds:

The electron displacement in an organic molecule may take place either in the ground state under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent. The electron displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarlisation of the bond. Inductive effect and resonance effects are examples of this type of electron displacements. Temporary electron displacement effects are seen in a molecule when a reagent approaches to attack it. This type of electron displacement is called electromeric effect or polarisability effect. In the following sections we will learn about these types of electronic displacements.

Inductive Effect: *Inductive effect* in a molecule is a local change in the electron density due to electron-withdrawing or electron-donating groups elsewhere in the molecule, resulting in a permanent dipole in a bond.It is present in a σ (sigma) bond, unlike the electromeric effect which is present in a π (pi) bond.The I effect is a permanent effect & generally represented by an arrow on the bond.Moreover, the inductive effect is feeble since it involves the shift of strongly held σ-bond electrons and other stronger factors may overshadow this effect.

The halogen atoms in an alkyl halide are electron withdrawing while the alkyl groups have electron donating tendencies. If the electronegative atom (missing an electron, thus having a positive charge) is then joined to a chain of atoms, usually carbon, the positive charge is relayed to the other atoms in the chain. This is the electron-withdrawing inductive effect, also known as the **-I** effect. In short, alkyl groups tend to donate electrons, leading to the **+I** effect. Its experimental basis is the ionization constant.

Relative inductive effects: Relative inductive effects have been experimentally measured through the resulting pK$_a$ of a nearby carboxylic acid group (see § Carboxylic acids). In increasing order of +I effect or decreasing order of -I effect, common functional groups are:

$$\overset{+}{N}R_3 > \overset{+}{N}H_3 > NO_2 > CN > COOH > F > Cl > Br > I$$
$$> OAr > OR > OH > C \equiv CR > Ar > H$$
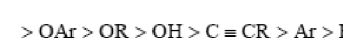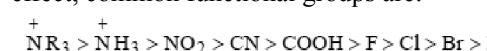
$\longleftarrow$ Increasing $-$ I effect (Electrons attracting)

$$O^- > COO^- > CR_3 > CHR_2 > CH_2R > CH_3 > D > H$$

$\longleftarrow$ Increasing $+$ I effect (electrons repelling)

Hydrogen subsituents also exhibit an isotope effect: relative to the same order, –T > –D > –H, where H is hydrogen, D deuterium, and T tritium. The strength of inductive effect is also dependent on the distance between the substituent group and the main group that react; the longer the distance, the weaker the effect.

Inductive effects can be expressed quantitatively through the *Hammett equation*, which describes the relationship between reaction rates and equilibrium constants with respect to substituent.

Applications of Inductive Effect: The inductive effect also plays a vital role in deciding the acidity and basicity of a molecule. Groups having +I effect (Inductive effect) attached to a molecule increases the overall electron density on the molecule and the molecule is able to donate electrons, making it basic. Similarly, groups having -I effect attached to a molecule decreases the overall electron density on the molecule making it electron deficient which results in its acidity. As the number of -I groups attached to a molecule increases, its acidity increases; as the number of +I groups on a molecule increases, its basicity increases.

Carboxylic acids: The strength of a carboxylic acid depends on the extent of its ionization constant: the more ionized it is, the stronger it is. As an acid becomes stronger, the numerical value of its pKa drops.

In acids, the electron-releasing inductive effect of the alkyl group increases the electron density on oxygen and thus hinders the breaking of the O-H bond, which consequently reduces the ionization. Due to its greater ionization, formic acid (pKa=3.74) is s tronger than acetic acid (pKa=4.76). Monochloroacetic acid (pKa=2.82), though, is stronger than formic acid, due to the electron-withdrawing effect of chlorine promoting ionization.

In benzoic acid, the carbon atoms which are present in the ring are sp^2 hybridised. As a result, benzoic acid (pKa=4.20) is a stronger acid than cyclohexanecarboxylic acid (pKa=4.87). Also, in aromatic carboxylic acids, electron-withdrawing groups substituted at the ortho and para positions can enhance the acid strength.

Since the carboxyl group is itself an electron-withdrawing group, dicarboxylic acids are, in general, stronger acids than their monocarboxyl analogues.

INDUCTOMETRIC EFFECT: Consider the inductive effect in a bond $\overset{\delta+}{A} \longrightarrow \overset{\delta-}{B}$. When some negatively charged ion approaches A, the inductive effect between A − B is temporarily increased which is known as inductometric effect.

RESONANCE: There are many organic molecules whose behaviour cannot be explained by a single Lewis structure. An example is that of benzene.

Benzene

Its cyclic structure containing alternating C–C single and C=C double bonds shown is inadequate for explaining its characteristic properties. As per the above representation, benzene should exhibit two different bond lengths, due to C–C single and C=C double bonds. However, as determined experimentally benzene has a uniform C–C bond distances of 139 pm, a value intermediate between the C–C single(154 pm) and C=C double (134 pm) bonds. Thus, the structure of benzene cannot be represented adequately by the above structure. Further, benzene can be represented equally well by the energetically identical structures I and II.
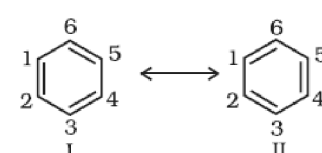
Therefore, according to the resonance theory the actual structure of benzene cannot be adequately represented by any of these structures, rather it is a hybrid of the two structures (I and II) called resonance structures. **The resonance structures (canonical structures or contributing structures) are hypothetical and individually do not represent any real molecule.** They contribute to the actual structure in proportion to their stability.

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

The following rules are applied while writing resonance structures:

The resonance structures have

(i)the same positions of nuclei and

(ii)the same number of unpaired electrons.

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

Resonance Effect or Mesomeric Effect

(i) Positive Resonance Effect (+R effect) In this effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system. This electron displacement makes certain positions in the molecule of high electron density. This effect in aniline is shown as :
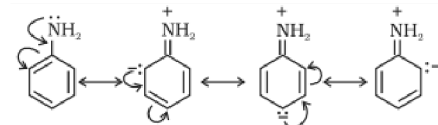
(ii) Negative Resonance Effect (- R effect) This effect is observed when the transfer of electrons is towards the atom or substituent group attached to the conjugated system. For example in nitrobenzene this electron displacement can be depicted as :
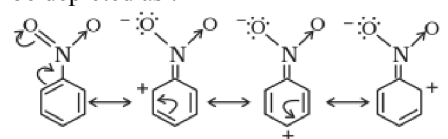
The atoms or substituent groups, which represent +R or –R electron displacement effects are as follows :

+R effect: – halogen, –OH, –OR, –OCOR, –NH$_2$, –NHR, –NR$_2$, –NHCOR,
– R effect: – COOH, –CHO, >C=O, – CN, –NO$_2$

The presence of alternate single and double bonds in an open chain or cyclic system is termed as a conjugated system. These systems often show abnormal behaviour. The examples are 1,3- butadiene, aniline and nitrobenzene etc. In such systems, the π-electrons are delocalised and the system develops polarity.
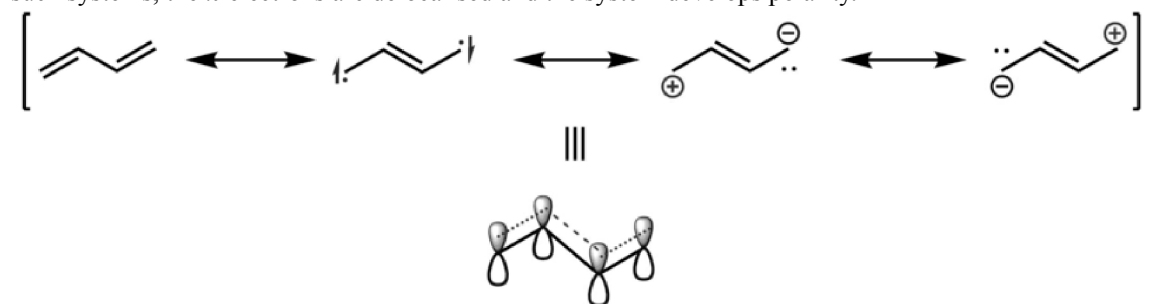
Electromeric Effect (E effect) It is a temporary effect. The organic compounds having a multiple bond (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of π-electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction. It is represented by E and the shifting of the electrons is shown by a curved arrow ( ). There are two distinct types of electromeric effect.
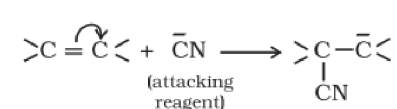**(i) Positive Eelctromeric Effect (+E effect)**
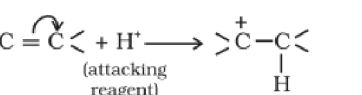
In this effect the π−electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :
**(ii) Negative Electromeric Effect (–E effect)**
In this effect the π - electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example:
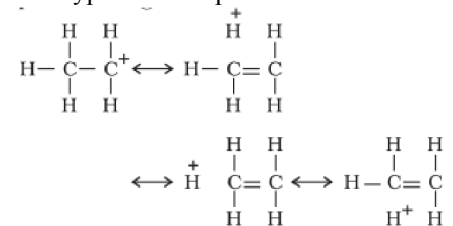

Hyperconjugation Hyperconjugation is a general stabilising interaction. It involves delocalisation of σ electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared p orbital. The σ electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p orbital. Hyperconjugation is a **permanent effect**.
To understand hyperconjugation effect, let us take an example of CH$_3$ CH$_2^+$ (ethyl cation) in which the positively charged carbon atom has an empty p orbital. One of the C-H bonds of the methyl group can align in the plane of this empty p orbital and the electrons constituting the C-H bond in plane with this p orbital can then be delocalised into the empty p orbital as depicted in Fig.
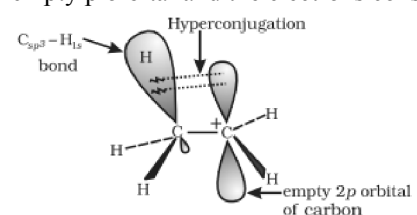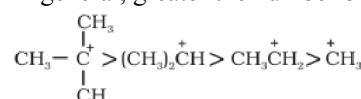

Orbital diagram showing hyperconjugation in ethyl cation

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


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


Hyperconjugation is also possible in alkenes and alkylarenes.
Delocalisation of electrons by hyperconjugation in the case of alkene can be depicted as in Fig.
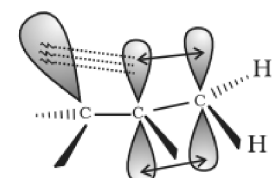
Orbital diagram showing hyperconjugation in propene

There are various ways of looking at the hyperconjugative effect. One of the way is to regard C—H bond as possessing partial ionic character due to resonance.
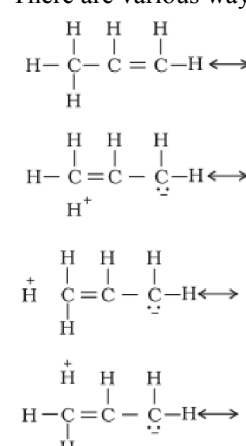
The hyperconjugation may also be regarded as **no bond resonance**.

Types of Organic Reactions and Mechanisms
Organic reactions can be classified into the following categories:
(i) Substitution reactions
(ii) Addition reactions
(iii) Elimination reactions
(iv) Rearrangement reactions

METHODS OF PURIFICATION OF ORGANIC COMPOUNDS
Once an organic compound is extracted from a natural source or synthesised in the laboratory, it is essential to purify it. Various methods used for the purification of organic compounds are based on the nature of the compound and the impurity present in it.
The common techniques used for purification are as follows :
(i) Sublimation
(ii) Crystallisation
(iii) Distillation
(iv) Differential extraction and
(v) Chromatography
Finally, the purity of a compound is ascertained by determining its melting or boiling point. Most of the pure compounds have sharp melting points and boiling points New methods of checking the purity of an organic compound are based on different types of chromatographic and spectroscopic techniques.

Sublimation
We know that on heating, some solid substances change from solid to vapour state without passing through liquid state. The purification technique based on the above principle is known as sublimation and is used to separate sublimable compounds from nonsublimable impurities.

Crystallisation This is one of the most commonly used techniques for the purification of solid organic compounds. It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. The impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to get a nearly saturated solution. On cooling the solution, pure compound crystallises out and is removed by filtration. The filtrate (mother liquor) contains impurities and small quantity of the compound. If the compound is highly soluble in one solvent and very little soluble in another solvent,

crystallisation can be satisfactorily carried out in a mixture of these solvents. Impurities, which impart colour to the solution are removed by adsorbing over activated charcoal. Repeated crystallisation becomes necessary for the purification of compounds containing impurities of comparable solubilities

Simple Distillation This important method is used to separate (i) volatile liquids from nonvolatile impurities and (ii) the liquids having sufficient difference in their boiling points. Liquids having different boiling points vaporise at different temperatures. The vapours are cooled and the liquids so formed are collected separately. Chloroform (b.p 334 K) and aniline (b.p. 457 K) are easily separated by the technique of distillation (as shown in the following figure) .
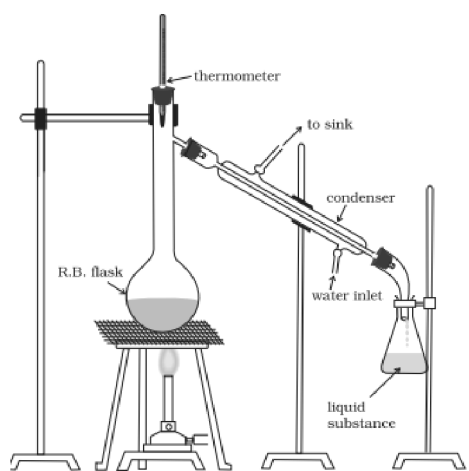

The liquid mixture is taken in a round bottom flask and heated carefully. On boiling, the vapours of lower boiling component are formed first. The vapours are condensed by using a condenser and the liquid is collected in a receiver. The vapours of higher boiling component form later and the liquid can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

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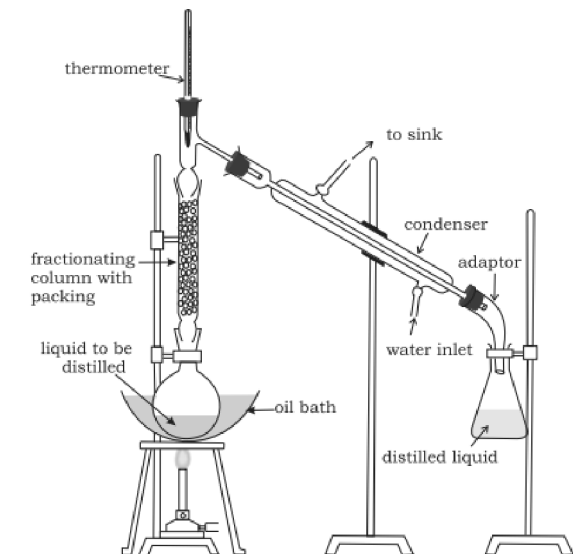

Vapours of the liquid with higher boiling point condense before the vapours of the liquid with lower boiling point. The vapours rising up in the fractionating column become richer in more volatile component. By the time the vapours reach to the top of the fractionating column, these are rich in the more volatile component. Fractionating columns are available in various sizes and designs as shown in the figure. A fractionating column provides many surfaces for heat exchange between the ascending vapours and the descending condensed liquid. Some of the condensing liquid in the fractionating column obtains heat from the ascending vapours and revaporises. The vapours thus become richer in low boiling component. The vapours of low boiling component ascend to the top of the column. On reaching the top, the vapours become pure in low boiling component and pass through the condenser and the pure liquid is collected in a receiver. After a series of successive distillations, the remaining liquid in the distillation flask gets enriched in high boiling component. Each successive condensation and vaporisation unit in the fractionating column is called a theoretical plate. Commercially, columns with hundreds of plates are available. One of the technological applications of fractional distillation is to separate different fractions of crude oil in petroleum industry. Distillation under reduced pressure: This method is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Such liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surface. A liquid boils at a temperature at which its vapour pressure is equal to the external pressure. The pressure is reduced with the help of a water pump or vacuum pump . Glycerol can be separated from spent-lye in soap industry by using this technique.

Steam Distillation: This technique is applied to separate substances which are steam volatile and are immiscible with water. In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic compound is condensed and collected. The compound is later separated from water using a separating funnel(as shown in figure).
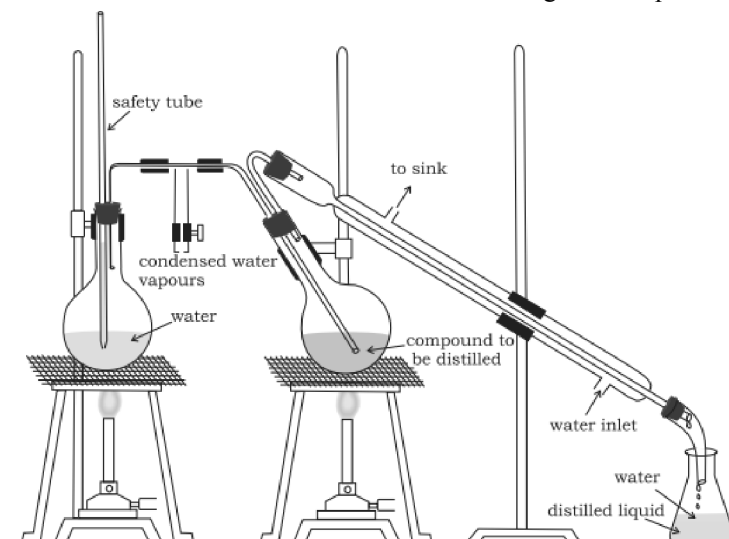
In steam distillation, the liquid boils when the sum of vapour pressures due to the organic liquid (p_1) and that due to water (p_2) becomes equal to the atmospheric pressure (p), i.e. $p = p_1 + p_2$. Since p_1 is lower than p, the organic liquid vaporises at lower temperature than its boiling point. Thus, if one of the substances in the mixture is water and the other, a water insoluble substance, then the mixture will boil close to but below, 373K. A mixture of water and the substance is obtained which can be separated by using a separating funnel. Aniline is separated by this technique from aniline – water mixture .

Differential Extraction When an organic compound is present in an aqueous medium, it is separated by shaking it with an organic solvent in which it is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they form two distinct layers which can be separated by separatory funnel. The organic solvent is later removed by distillation or by evaporation to get back the compound. Differential extraction is carried out in a separatory funnel as shown in the following figure.


Before extraction   **After extraction**
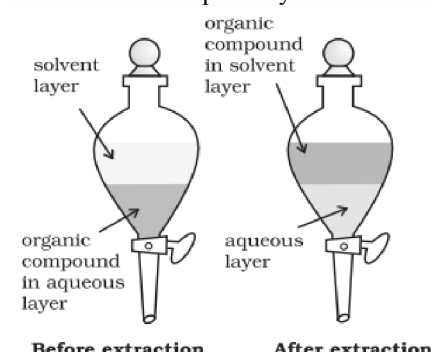
If the organic compound is less soluble in the organic solvent, a very large quantity of solvent would be required to extract even a very small quantity of the compound. The technique of continuous extraction is employed in such cases. In this technique same solvent is repeatedly used for extraction of the compound.

Chromatography: Chromatography is an important technique extensively used to separate mixtures into their components, purify compounds and also to test the purity of compounds. The name chromatography is based on the Greek word chroma, for colour since the method was first used for the separation of coloured substances found in plants. In this technique, the mixture of substances is applied onto a stationary phase, which may be a solid or a liquid. A pure solvent, a mixture of solvents, or a gas is allowed to move slowly over the stationary phase. The components of the mixture get gradually separated from one another. The moving phase is called the mobile phase. Based on the principle involved, chromatography is classified into different categories. Two of these are:
(a) Adsorption chromatography, and
(b) Partition chromatography.
Column Chromatography: Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end.
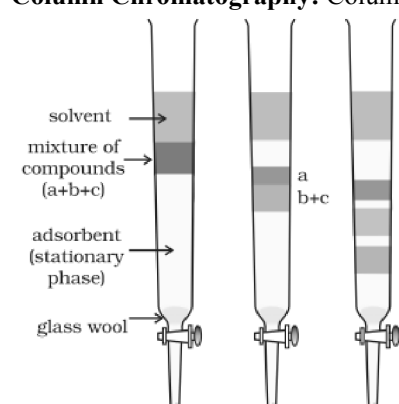
The mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube. An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column

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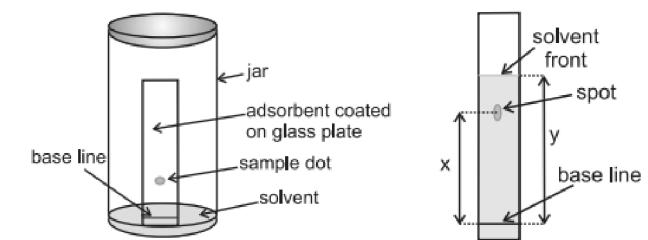

As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e. Rf value

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

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

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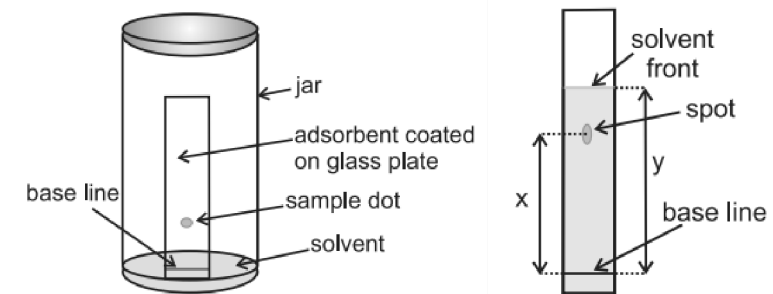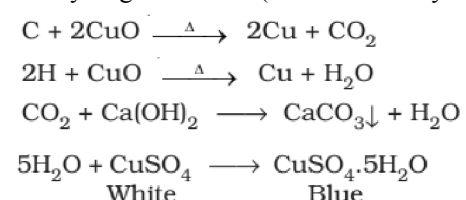

A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents . This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram. The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography.

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

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

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$
$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$
$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O$$
$$\underset{\text{White}}{5H_2O + CuSO_4} \longrightarrow \underset{\text{Blue}}{CuSO_4.5H_2O}$$

Detection of Other Elements: Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by "Lassaigne's test". The elements present in the compound are converted from covalent form into the ionic

$$Na + C + N \xrightarrow{\Delta} NaCN$$
$$2Na + S \xrightarrow{\Delta} Na_2S$$
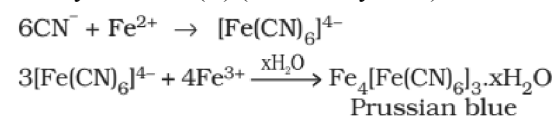$$Na + X \xrightarrow{\Delta} Na X$$
$$(X = Cl, Br \text{ or } I)$$
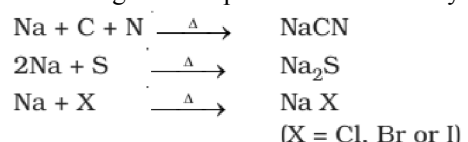
form by fusing the compound with sodium metal. Following reactions take place:
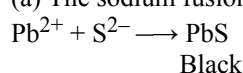C, N, S and X come from organic compound.
Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract.

(I) Test for Nitrogen: The sodium fusion extract is boiled with iron(II) sulphate and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen. Sodium cyanide first reacts with iron(II) sulphate and forms sodium hexacyanoferrate(II). On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanoferrate(II) to produce iron(III) hexacyanoferrate(II) (ferriferrocyanide) which is Prussian blue in colour.

$$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$
$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3.xH_2O}$$
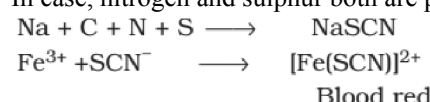
(II) Test for Sulphur:
(a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.
$$Pb^{2+} + S^{2-} \longrightarrow \underset{\text{Black}}{PbS}$$
(b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur.
$$S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow \underset{\text{Violet}}{[Fe(CN)_5NOS]^{4-}}$$
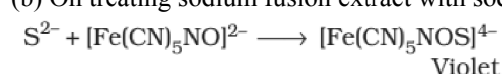
In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no Prussian blue since there are no free cyanide ions.
$$Na + C + N + S \longrightarrow NaSCN$$
$$Fe^{3+} + SCN^- \longrightarrow \underset{\text{Blood red}}{[Fe(SCN)]^{2+}}$$
If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.
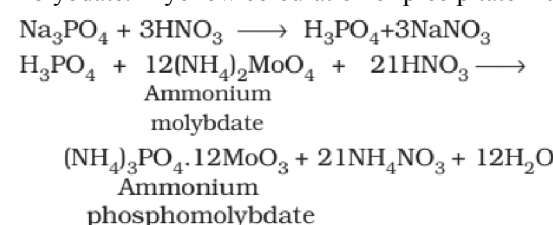$$NaSCN + 2Na \longrightarrow NaCN + Na_2S$$
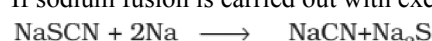
(III) Test for Halogens: The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.
$$X^- + Ag^+ \longrightarrow AgX$$
X represents a halogen – Cl, Br or I.
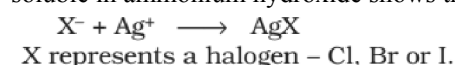
If nitrogen or sulphur is also present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens.

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

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$
$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow$$
$$\underset{\text{Ammonium molybdate}}{}$$
$$\underset{\text{Ammonium phosphomolybdate}}{(NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O}$$

QUANTITATIVE ANALYSIS:
The percentage composition of elements present in an organic compound is determined by the methods based on the following principles:

Carbon and Hydrogen: Both carbon and hydrogen are estimated in one experiment. A known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide. Carbon and hydrogen in the compound are oxidised to carbon dioxide and water respectively.
$$C_xH_y + (x + y/4) O_2 \longrightarrow x CO_2 + (y/2) H_2O$$
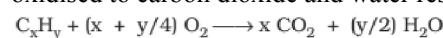
The mass of water produced is determined by passing the mixture through a weighed U-tube containing anhydrous calcium chloride. Carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide. These tubes are connected in series .
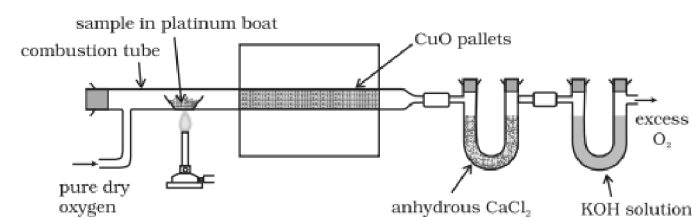
increase in masses of calcium chloride and potassium hydroxide gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated.

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

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

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

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

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

$C_xH_yN_z + (2x + y/2)\, CuO \longrightarrow$

$x\, CO_2 + y/2\, H_2O + z/2\, N_2 + (2x + y/2)\, Cu$
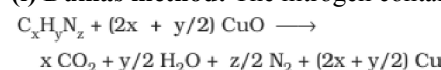
Traces of nitrogen oxides formed, if any, are reduced to nitrogen by passing the gaseous mixture over a heated copper gauze. The mixture of gases so produced is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide. Nitrogen is collected in the upper part of the graduated tube
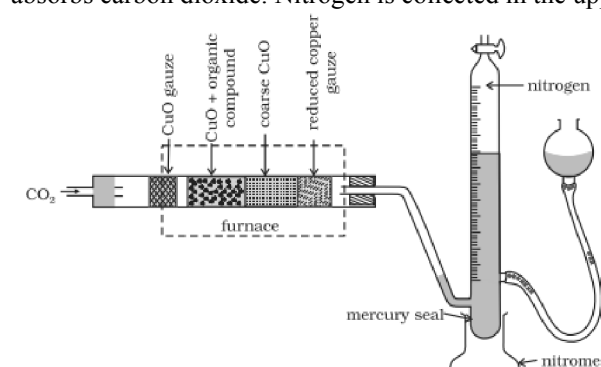
Let the mass of organic compound $= m$ g
Volume of nitrogen collected $= V_1$ mL
Room temperature $= T_1$ K

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

(Let it be V mL)

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

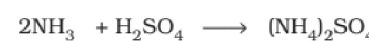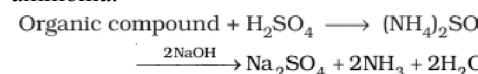$p_1 =$ Atmospheric pressure – Aqueous tension

22400 mL N_2 at STP weighs 28 g.

V mL N_2 at STP weighs $= \dfrac{28 \times V}{22400}$ g

Percentage of nitrogen $= \dfrac{28 \times V \times 100}{22400 \times m}$

(ii) Kjeldahl's method: The compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate . The resulting acid mixture is then heated with excess of sodium hydroxide.
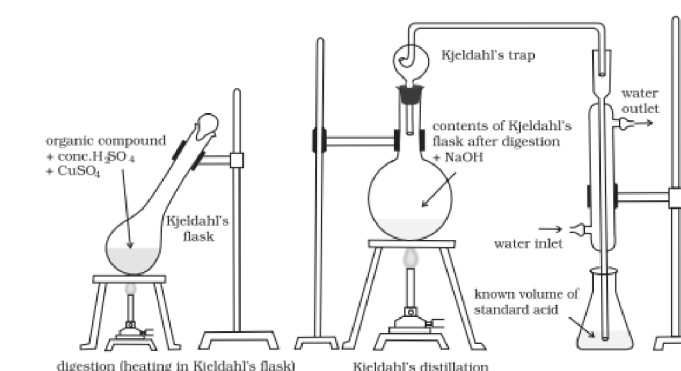
The liberated ammonia gas is absorbed in an excess of standard solution of sulphuric acid. The amount of ammonia produced is determined by estimating the amount of sulphuric acid consumed in the reaction. It is done by estimating unreacted sulphuric acid left after the absorption of ammonia by titrating it with standard alkali solution. The difference between the initial amount of acid taken and that left after the reaction gives the amount of acid reacted with ammonia.

Organic compound $+ H_2SO_4 \longrightarrow (NH_4)_2SO_4$

$\xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$

$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$

Let the mass of organic compound taken $= m$ g
Volume of H2SO4 of molarity. M.
taken $= V$ mL
Volume of NaOH of molarity. M, used for
titration of excess of $H_2SO_4 = V_1$ mL
V_1 mL of NaOH of molarity M

$= V_1/2$ mL of H_2SO_4 of molarity M
Volume of H_2SO_4 of molarity M unused
$= (V - V_1/2)$ mL
$(V - V_1/2)$ mL of H_2SO_4 of molarity M

$= 2(V - V_1/2)$ mL of NH_3 solution of
molarity M.
1000 mL of 1 M NH_3 solution contains 17 g
NH_3 or 14 g of N
$2(V - V_1/2)$ mL of NH_3 solution of molarity M
contains:

$\dfrac{14 \times M \times 2(V - V_1/2)}{1000}$ g N

Percentage of N $= \dfrac{14 \times M \times 2(V - V_1/2)}{1000} \times \dfrac{100}{m}$

$= \dfrac{1.4 \times M \times 2(V - V_1/2)}{m}$

Kjeldahl method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulphate under these conditions.

Halogens:
Carius method: A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as Carius tube, in a furnace. Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed. Let the mass of organic

Let the mass of organic
compound taken $= m$ g
Mass of AgX formed $= m_1$ g
1 mol of AgX contains 1 mol of X
Mass of halogen in m_1 g of AgX

$= \dfrac{\text{atomic mass of X} \times m_1 \text{g}}{\text{molecular mass of AgX}}$

Percentage of halogen

$= \dfrac{\text{atomic mass of X} \times m_1 \times 100}{\text{molecular mass of AgX} \times m}$

Sulphur: A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid. Sulphur present in the compound is oxidised to sulphuric acid. It is precipitated as barium sulphate by adding excess of barium chloride solution in water. The precipitate is filtered, washed, dried and weighed. The percentage of sulphur can be calculated from the mass of barium sulphate.
Let the mass of organic compound taken $= m$ g and the mass of barium sulphate formed $= m_1$ g

1 mol of $BaSO_4 = 233$ g $BaSO_4 = 32$ g sulphur

m_1 g $BaSO_4$ contains $\dfrac{32 \times m_1}{233}$ g sulphur

Percentage of sulphur $= \dfrac{32 \times m_1 \times 100}{233 \times m}$

Phosphorus: A known mass of an organic compound is heated with fuming nitric acid whereupon phosphorus present in the compound is oxidised to phosphoric acid. It is precipitated as ammonium phosphomolybdate, $(NH_4)_3PO_4.12MoO_3$, by adding ammonia and ammonium molybdate. Alternatively, phosphoric acid may be precipitated as $MgNH_4PO_4$ by adding magnesia mixture which on ignition yields $Mg_2P_2O_7$.

Let the mass of organic compound taken
= m g and mass of ammonium phospho
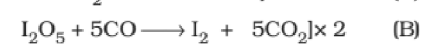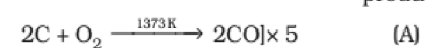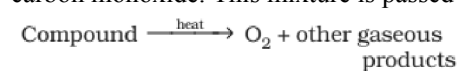molydate = m_1g

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

Percentage of phosphorus = $\dfrac{31 \times m_1 \times 100}{1877 \times m}$ %

If phosphorus is estimated as $Mg_2P_2O_7$,

Percentage of phosphorus = $\dfrac{62 \times m_1 \times 100}{222 \times m}$ %

where, 222 u is the molar mass of $Mg_2P_2O_7$,
m, the mass of organic compound taken, m_1,
the mass of $Mg_2P_2O_7$ formed and 62, the mass
of two phosphorus atoms present in the
compound $Mg_2P_2O_7$.

Oxygen: The percentage of oxygen in an organic compound is usually found by difference between the total percentage composition (100) and the sum of the percentages of all other elements. However, oxygen can also be estimated directly as follows: A definite mass of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide. This mixture is passed through warm iodine pentoxide (I_2O_5) when carbon monoxide is oxidised to carbon dioxide producing iodine.

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

$2C + O_2 \xrightarrow{1373K} 2CO] \times 5$ (A)

$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2] \times 2$ (B)

equation (B) by multiplying the equations (A) and (B) by 5 and 2 respectively; we find that each mole of oxygen liberated from the compound will produce two moles of carbondioxide.

Thus 88 g carbon dioxide is obtained if 32 g oxygen is liberated.

Let the mass of organic compound taken be m g Mass of carbon dioxide produced be m_1 g

$\therefore$ m_1 g carbon dioxide is obtained from

$\dfrac{32 \quad m_1}{88}$ g O_2

$\therefore$ Percentage of oxygen = $\dfrac{32 \quad m_1 \quad 100}{88 \quad m}$ %

The percentage of oxygen can be derived from the amount of iodine produced also.

Presently, the estimation of elements in an organic compound is carried out by using microquantities of substances and automatic experimental techniques. The elements, carbon, hydrogen and nitrogen present in a compound are determined by an apparatus known as CHN elemental analyser. The analyser requires only a very small amount of the substance (1-3 mg) and displays the values on a screen within a short time.