

Inorganic Chemistry:-

1. Chemical Calculations2
2. General Introduction to Metallurgy 22
3. Atomic Structure – I.....222
4. Periodic Classification – I.....222
5. S-block Elements-1.....
6. S-block Elements-2.....
7. p-Block elements.....

Physical Chemistry:-

8. Solid state
9. Gaseous state
10. Chemical Bonding
11. Colligative Properties
12. Thermodynamics
13. Chemical Equilibrium
14. Chemical Kinetics

Organic Chemistry:-

15. Basic Concepts of Organic Chemistry
16. Purification of Organic compounds
17. Detection and Estimation of Elements
18. Hydrocarbons
19. Aromatic Hydrocarbons
20. Organic Halogen Compounds

15. BASIC CONCEPTS OF ORGANIC CHEMISTRY

OBJECTIVES

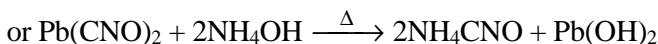
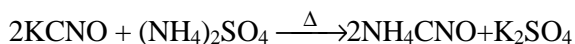
This topic explains the nature of organic compounds and explores the possibilities of all basic concepts of organic chemistry.

- *Catenation and the reason for innumerable number of organic compounds.*
- *Classification of organic compounds based on functional groups.*
- *IUPAC method of naming all types of organic compounds.*
- *Details about isomerism.*
- *Fission of bonds and types of organic reactions.*
- *Nature of reagents, electrophiles and Nucleophiles.*
- *Knowledge about carboniumion and carbanion and free radicals.*
- *Different types of electron displacements in organic chemistry.*

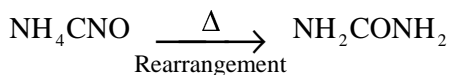
Introduction

Initially (before 1828), the name organic chemistry was given for the chemistry of compounds obtained from plants and animals (i.e, from living organisms). The word organic signifies life. Lavoisier (who is considered as the father of chemistry) showed that the compounds obtained from plants are often made of C, H and O and the compounds obtained from animals contain C, H, O, N, S, P. etc.

Berzelius proposed vital force theory (a theory of life process) to deal with organic compounds. The vital force theory suffered blow in 1828 when Wohler synthesized the first organic compound urea in the laboratory from an inorganic compound, i.e, from ammonium cyanate ($\text{NH}_4 \text{CNO}$).



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Later on, a further blow to vital force theory was given by Kolbe (1845) who prepared acetic acid, the first organic compound, in laboratory from its elements.

Now a days organic chemistry is defined as **the chemistry of carbon compounds or the chemistry of hydrocarbons and their derivatives**. Organic compounds obey the same fundamental laws of chemistry as the inorganic compounds. However they are studied as a separate branch of chemistry because of two reasons:

- i. The total number of organic compounds known so far exceeds several times the total number of inorganic compounds known.
- ii. There are marked differences between the structure, composition and behaviour of organic and inorganic compounds. The phenomenon of **isomerism** and tendency of **catenation** are unique properties of organic compounds.

15.1 Catenation

1. The tendency of atoms of an element to unite with each other forming a chain of covalent bond is known as **catenation**.
2. Catenation may give rise to open chain or closed chain compounds.
3. Carbon possesses maximum tendency for catenation i.e. **Bond energy (kcal mol⁻¹) for catenation of C is maximum.**

C-C,	Si-Si,	N-N,	P-P,	O-O,	S-S
85	54	39	50	35	54

4. Carbon also forms double as well as triple bonds.
5. A large number of compounds of carbon are known due to catenation.
6. The stability or strength of bond decreases as the bond energy decreases. Hence the catenation order among the following is $\text{C} > \text{Si} \approx \text{S} > \text{P} > \text{N} > \text{O}$.

15.2 Classification into open chain and cyclic compounds

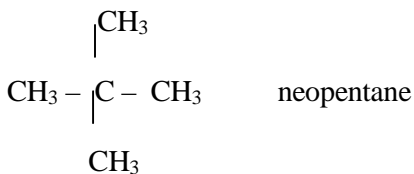
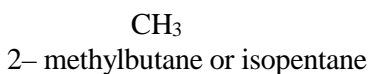
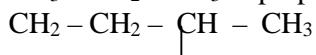
The organic compounds are classified into two main types, namely.

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(1) Open - chain or acyclic compounds or aliphatic compounds

The open chain or acyclic compounds are those in which carbon atoms are linked to each other either in linear or branched fashion such that the molecule is having open chain structure. These compounds are also called aliphatic compounds (Greek word : aliphar meaning fat).

Examples

**(2) Closed chain or cyclic compounds**

Organic compounds with closed chain of atoms are called closed chain compounds or ring compounds.

These compounds are further classified into

- (a) Homocyclic or carbocyclic compounds
- (b) Heterocyclic compounds

(a) Homocyclic compounds : In these compounds the ring structure is made up of only carbon atoms.

These compounds are further classified into

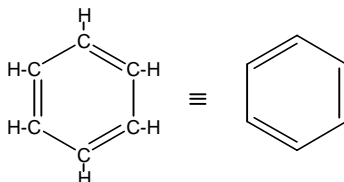
- (i) Aromatic compounds and
- (ii) Alicyclic compounds

(i) Aromatic compounds (Benzenoid) : Compounds containing one or more benzene rings in their structure are classified as aromatic benzenoid compounds. Most of these compounds have pleasant odour (Greek : Aroma - sweet smell).

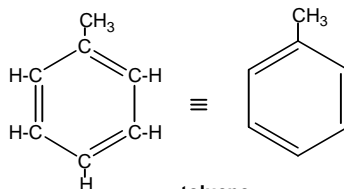
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Examples

Monocyclic

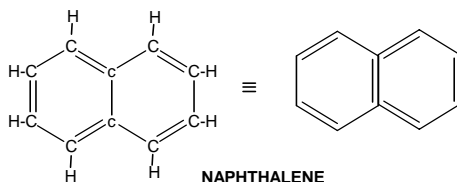


benzene

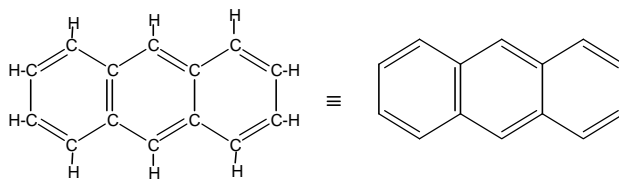


toluene

Polycyclic



NAPHTHALENE

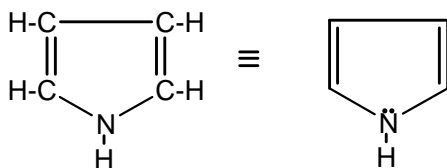


ANTHRACENE

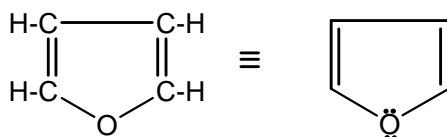
Heterocyclic compounds (Non - benzenoid aromatic) : Cyclic compounds in which the ring atoms are made up of hetero atoms like nitrogen, oxygen and sulphur in addition to carbon atoms are called heterocyclic compounds.

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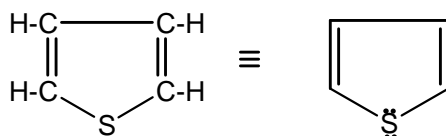
Examples



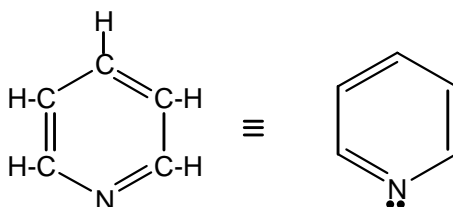
pyrrole



furan



thiophene



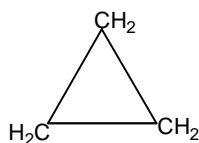
pyridine

The above compounds are aromatic non-benzenoid compounds.

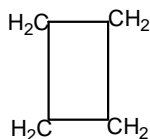
- (ii) **Alicyclic compounds** : Cyclic compounds with ring structure containing only carbon atoms are called alicyclic or carbocyclic compounds. Though these compounds possess a ring structure, they behave more like aliphatic compounds.

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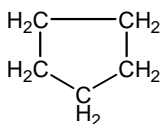
Examples



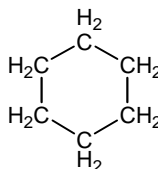
cyclopropane



cyclobutane

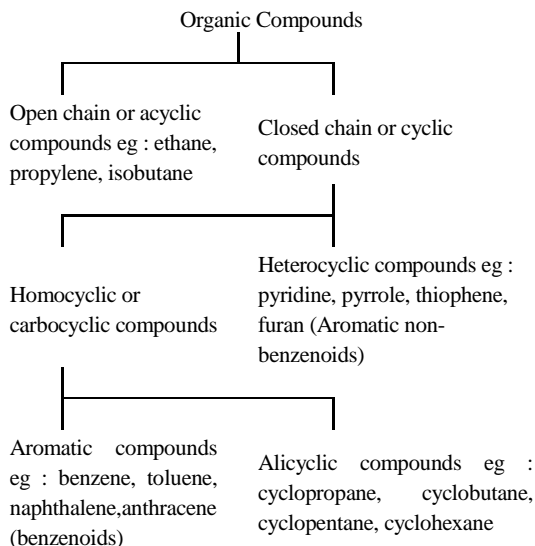


cyclopentane



cyclohexane

The above classification can be schematically represented as follows :

**Characteristics of organic compounds**

All organic compounds have the following characteristic properties

- (1) Many organic compounds are inflammable
- (2) They are mostly covalent compounds

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- (3) They are generally soluble in non - polar solvents like carbon tetrachloride, benzene etc.
- (4) They have generally low boiling point and melting point.
- (5) They exhibit isomerism

Homologous series

A group or class of organic compounds related to each other by a general molecular formula constitutes homologous series.

Characteristics of homologous series

Homologous series have the following characteristics :

- (1) All members of a series contain same elements and the same functional groups.
- (2) All the members of a homologous series can be represented by a general formula

Examples

Alkanes	C_nH_{2n+2}
Alkenes	C_nH_{2n}
Alkynes	C_nH_{2n-2}

- (3) All the members of a homologous series can be prepared by similar methods.
- (4) All members of a homologous series usually undergo similar chemical reactions.
- (5) Successive members in a series differ by a $-CH_2$ group
- (6) The physical properties of the members of a homologous series vary in a regular way down the series. For example, boiling point, melting point and density of the alkane series vary in a regular way with increasing number of carbon atoms.

15.3 Functional groups

The chemical properties of all the members of a homologous series are characterised by a group called the functional group. It is characteristic of a particular series.

The following table gives a list of functional groups and names.

Halide	- X
Alcohol	- OH
Ether	- O -

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Aldehyde	$-\text{CHO}$
Ketone	$\begin{array}{c} \text{---C---} \\ \\ \text{O} \end{array}$
Carboxylic acid	$-\text{COOH}$
Ester	$-\text{COOR}$
Amide	$\begin{array}{c} \text{---C---NH}_2 \\ \\ \text{O} \end{array}$
Acid halide	$\begin{array}{c} \text{---C---X} \\ \\ \text{O} \end{array} \quad (\text{X} = -\text{Cl}, -\text{Br}, -\text{I})$
Acid anhydride	$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \qquad \text{---O---} \quad \\ \text{---C} \qquad \qquad \text{C---} \end{array}$
Amine	$-\text{NH}_2$
Nitro compounds	$-\text{NO}_2$

15.4 IUPAC system of nomenclature (1993)

The international union of pure and applied chemistry (abbreviated as IUPAC) has done a commendable job in framing set rules for naming organic compounds. Two commonly used systems of nomenclature are described below.

- (1) Common or Trivial system (2) IUPAC system

IUPAC Nomenclature of Aliphatic Compounds

The IUPAC name of a compound essentially consists of three parts.

- (a) Root word (b) Suffix (c) Prefix

Root words for alkanes

The root words for the first four members are taken from their trivial or common names.

e.g.

Meth	-	for Methane
Eth	-	for Ethane
Prop	-	for Propane
But	-	for Butane

For the higher homologue, root words are derived from the Greek/Latin number indicating the total number of carbon atoms.

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- e.g. Pent - is derived from penta for five
 Hex - is derived from hexa for six
 Hept - is derived from hepta for seven
 Oct - is derived from octa for eight

Suffix

There are two types of suffixes **Primary suffix** and secondary suffix.

Primary suffix

A primary suffix is added to the **Root word** to indicate whether the parent chain is saturated or unsaturated. Some primary suffixes are given below.

Sl. No.	Nature of carbon chain (parent chain)	Primary suffix
1.	Saturated	ane
2.	Unsaturated with One double bond Two double bond Three double bond	ene diene triene
3.	Unsaturated with One triple bond Two triple bond	yne diyne

Sl. No.	Structural formula	No. of C atoms	Root word	Primary suffix	IUPAC name
1.	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$	4	But	ane	Butane
2.	$\text{CH}_3\text{-CH=CH}_2$	3	Prop	ene	Propene
3.	$\text{CH}\equiv\text{CH}$	2	Eth	yne	Ethyne
4.	$\text{CH}_2\text{=CH-CH=CH}_2$	4	Buta [*]	diene	Butadiene
5.	$\text{HC}\equiv\text{C-C}\equiv\text{CH}$	4	Buta [*]	diyne	Butadiyne

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* extra 'a' has been added to the root word since the primary suffix, ie diene or diyne begins with a consonant (d).

Secondary suffix

Secondary suffix is used to indicate the functional group in the organic compound secondary suffixes for various functional groups are given below.

Sl. No.	Class	Functional group	Secondary suffix	IUPAC name
1.	Alcohols (R-OH)	-OH	-ol	Alkanols
2.	Aldehyde (R-CHO)	-CHO	-al	Alkanals
3.	Ketones (RCOR')	$>C=O$	-one	Alkanones
4.	Carboxylic acids (R-COOH)	-COOH	-oic acid	Alkanoic acid
5.	Ester (RCOOR')	-COOR	-alkanoate	alkyl alkanoates

Secondary suffix is added to the primary suffix; ie written after the primary suffix. While adding the secondary suffix to the primary suffix following rules should be followed.

- If the secondary suffix begins with a vowel, then the terminal **e** of the primary suffix is dropped before adding the secondary suffix.
- If the secondary suffix begins with a consonant, then the last (terminal) **e** is retained and the secondary suffix is added after e.
- If the secondary suffix has some **numerical prefix**, such as, **di, tri etc.**, before it then the terminal **e** of the primary suffix is retained.

The addition of the secondary suffix to the primary suffix is illustrated below

Sl. No.	Structu-ral formula	No. of C atoms	Root word	Primar y suffix	Secondar y suffix	IUPAC name	Remarks
1.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2\text{-OH} \end{array}$	2	Eth	ane	ol	Ethanol	'e' of prim suffix dropped

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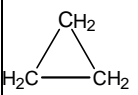
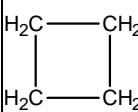
2.	$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{CH}_2\text{-OH} \end{array}$	2	Eth	ane	diol	Ethane diol	'e' of prim suffix not dropped
3.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CHO} \end{array}$	3	Prop	ane	al	Propanal	'e' of the prim suffix dropped
4.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{COOH} \end{array}$	4	But	ane	oic acid	Butanoic acid	'e' of prim suffix dropped

Prefix

Prefix is a part of the name which appears before the root word. There are two types of prefixes - primary prefix and secondary prefix.

Primary prefix

A primary prefix is used to distinguish alicyclic (aliphatic cyclic compounds) from acyclic (open chain) compounds. If the given compound is an alicyclic compound, then a prefix cyclo is used just before the root word. For example.

Structural formula	No. of C atoms	Root word	Primary suffix	Primary prefix	IUPAC name
	3	Prop	ane	Cyclo	Cyclo propane
	4	But	ane	Cyclo	Cyclo butane

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Secondary prefix

In the IUPAC system of nomenclature, certain characteristic groups are not considered as functional groups. Such characteristic groups are considered as the **substituents**. Each such group or substituent is denoted by a secondary prefix. Some typical secondary prefixes are listed below.

Substituent group	Secondary prefix
- F	Fluoro
- Cl	Chloro
- Br	Bromo
- I	Iodo
- CH ₃	Methyl
- C ₂ H ₅	Ethyl
CH ₃ - CH ₂ - CH ₂ -	n-propyl
(CH ₃) ₂ CH -	Iso propyl
(CH ₃) ₃ C -	t - Butyl
- NO ₂	Nitro
- NH ₂	Amino
- NO	Nitroso
N \equiv N	Diazo
- OCH ₃	Methoxy
- OC ₂ H ₅	Ethoxy

In the case of open chain compounds, the secondary prefix is added just before the root word in the **alphabetical** order. This is illustrated below.

Sl. No.	Structural formula	No. of C atoms	Root word	Suffix		Prefix		IUPAC Name
				Primary	Sec	Pri	Sec	
1.	CH ₃ -CH ₂ -Cl	2	Eth	ane	-	-	Chloro	Chloro ethane
2.	CH ₃ -NO ₂	1	Meth	ane	-	-	Nitro	Nitro methane

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Saturated Hydrocarbons : Alkanes

General formula : C_nH_{2n+2} Suffix : ane

Sl. No.	Structural formula	Common Name	IUPAC name
1.	CH ₄	Methane	Methane
2.	H ₃ C - CH ₃	Ethane	Ethane
3.	H ₃ C - CH ₂ - CH ₃	Propane	Propane
4.	H ₃ C - CH ₂ - CH ₂ - CH ₃	n-butane	Butane

Alkyl groups

The univalent hydrocarbon unit derived from an alkane by the loss of one hydrogen atom is termed as alkyl group.

The alkyl groups are named after their parent alkanes by replacing the suffix **-ane** by **-yl**.

Continuous straight chain alkyl groups (or, normal alkyl (n-) groups)

Sl. No.	Alkane		Alkyl group	
	Formula	Name	Formula	Name
1.	CH ₄	Methane	CH ₃ -	Methyl
2.	CH ₃ - CH ₃	Ethane	CH ₃ - CH ₂ -	Ethyl
3.	CH ₃ -CH ₂ -CH ₃	Propane	CH ₃ -CH ₂ -CH ₂ -	Propyl

Branched chain alkyl groups

When a hydrogen atom from a secondary or tertiary carbon atom in any carbon chain is removed, a branched chain alkyl group is obtained. The common prefixes used are,

a) iso - b) sec - c) tert - d) neo –

a) **iso** – The alkyl group in which a - CH₃ branch is present at the end of the chain is designated as isoalkyl group. In other words, the alkyl group in which the second last carbon atom in the chain is branched to one - CH₃ group is called on isoalkyl group.

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Sl.No.	Structure	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \\ \\ \text{CH}_3 \end{array}$	1-methyl ethyl (iso-propyl)
2.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \\ \\ \text{CH}_3 \end{array}$	2-methyl propyl (iso-butyl)
3.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \\ \\ \text{CH}_3 \end{array}$	3-methyl butyl (iso-pentyl)

b) Sec - The prefix sec - before the name of the alkyl group indicates that the H-atom was removed from a secondary carbon atom.

Sl.No.	Structure	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \end{array}$	1 - Methyl ethyl (Sec - propyl)
2.	$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} - \\ \\ \text{CH}_3 \end{array}$	1 - methyl propyl (Sec - butyl)
3.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH} - \end{array}$	1 - methyl butyl (Sec - pentyl)

c) Tert - (or) t -

The prefix tert - before the name of the alkyl group indicates that the H - atom has been removed from a tertiary carbon atom.

Sl. No.	Structure	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \\ \\ \text{CH}_3 \end{array}$	1,1 - dimethyl ethyl (tert - butyl)
2.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \\ \\ \text{CH}_3 \end{array}$	1,1 - dimethyl propyl (tert - pentyl)

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Alkenes

General formula : C_nH_{2n} **Suffix :** ene

The common name of alkene is obtained by replacing the ending - **ane** from the name of its parent alkane with - **ylene**.

The IUPAC name of an alkene is obtained by replacing - **ane** of the alkane by - **ene**.

Structural formula	Common Name	IUPAC name
$CH_2 = CH_2$	Ethylene	Ethene
$CH_3 - CH = CH_2$	Propylene	Propene
$CH_3-CH_2-CH=CH_2$ (double bond starts at C_1)	1- Butylene	But-1-ene
$CH_3-CH=CH-CH_3$ (double bond starts at C_2)	2- Butylene	But-2-ene

Alkenyl group

The group obtained by removing a hydrogen atom from an alkene molecule, are called **alkenyl** group.

The IUPAC name of alkenyl group is obtained by replacing - **e** of the alkene by the suffix - **yl**.

Sl. No.	Structure	Common name	IUPAC name
1.	$CH_2 = CH_2$	vinyl	ethenyl
2.	$CH_2=CH-CH_2-$	allyl	Prop - 2 - enyl

Alkynes

General formula : C_nH_{2n-2} **Suffix :** - yne

The IUPAC name of an alkyne is obtained by replacing the ending - **ane** from the name of the parent alkane with - **yne**.

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Sl. No.	Structural formula	Common Name	IUPAC name
1.	$\text{HC} \equiv \text{CH}$	Acetylene	Ethyne
2.	$\text{CH}_3 - \text{C} \equiv \text{CH}$	Methyl acetylene	Propyne
3.	$\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$	Dimethyl acetylene	But-2-yne

Alkyl halides

The general formula of alkyl halides is R-X where R stands for alkyl group and "X" stands for halogen (F, Cl, Br, I). They are named by introducing the prefix halo (chloro, bromo, iodo, fluoro) to the name of the parent alkane.

Formula	Common name	IUPAC name
$\text{CH}_3\text{-Cl}$	Methyl chloride	Chloromethane
$\text{CH}_3\text{-CH}_2\text{-Br}$	Ethyl bromide	Bromoethane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br}$	n-propyl bromide	1-bromopropane
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{I} \end{array}$	Iso-propyl iodide	2-iodopropane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Cl}$	n-butyl chloride	1-chlorobutane
$\begin{array}{c} \text{CH}_3\text{-CH}_2\text{-CH-CH}_3 \\ \\ \text{Br} \end{array}$	Sec-butyl bromide	2-bromobutane
$\begin{array}{c} \text{CH}_3\text{-CH-CH}_2\text{-Cl} \\ \\ \text{CH}_3 \end{array}$	Isobutyl chloride	1-chloro-2-methyl propane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{I} \\ \\ \text{CH}_3 \end{array}$	ter-butyl iodide	2-iodo-2-methyl propane
$\text{CH}_2=\text{CH-Cl}$	Vinyl chloride	Chloroethene
$\text{CH}_2=\text{CH-CH}_2\text{-Cl}$	Allyl chloride	3-Chloro-1-propene

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Alcohols

The term alcohol is applied to all organic compounds obtained by replacing one or more hydrogen atoms of an open-chain hydrocarbon by hydroxyl groups. The alcohols are further classified into **mono-, di-, tri-**hydric alcohols according to the number of hydroxyl groups which they may contain.

In IUPAC nomenclature, the terminal "e" of the alkane is replaced by "ol".

Monohydric alcohols

Alcohols which contain only one hydroxyl group per molecule are called monohydric alcohols.

Formula	Common name	IUPAC name
$\text{CH}_3\text{-OH}$	Methyl alcohol	methanol
$\text{CH}_3\text{-CH}_2\text{-OH}$	Ethyl alcohol	ethanol
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}$	n-propyl alcohol	1-propanol
$\begin{array}{c} \text{CH}_3\text{-CH-CH}_3 \\ \\ \text{OH} \end{array}$	Isopropyl alcohol	2-propanol
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$	n-butyl alcohol	1-butanol
$\begin{array}{c} \text{CH}_3\text{-CH}_2\text{-CH-CH}_3 \\ \\ \text{OH} \end{array}$	sec-butyl alcohol	2-butanol
$\begin{array}{c} \text{CH}_3\text{-CH-CH}_2\text{-OH} \\ \\ \text{CH}_3 \end{array}$	Isobutyl alcohol	2-methyl-1-propanol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \\ \\ \text{CH}_3\text{-C-OH} \\ \\ \text{CH}_3 \end{array}$	tert-butyl alcohol	2-methyl-2-propanol
$\text{CH}_2\text{=CH-CH}_2\text{-OH}$	Allyl alcohol	2-propene-1-ol

Dihydric alcohols

Alcohols which contain two -OH groups per molecule are called dihydric alcohols.

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Structural formula	Common name	IUPAC name
$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{CH}_2\text{-OH} \end{array}$	Ethylene glycol	1,2-Ethanediol

Trihydric alcohols

Alcohols which contain three -OH groups per molecule are called trihydric alcohols.

Structural formula	Common name	IUPAC name
$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{CH-OH} \\ \\ \text{CH}_2\text{-OH} \end{array}$	Glycerol	1,2,3-propanetriol

Ethers

An ether is a substance that has two organic groups bonded to the same oxygen atom, **R-O-R'**. The organic group may be alkyl or aryl. When the groups attached to the oxygen atom are the same, they are termed as simple ethers. When the groups attached to the oxygen atom are different, they are termed as mixed ethers.

In IUPAC system, ethers are considered to be alkoxy derivatives of hydrocarbons.

Structural formula	Common name	IUPAC name
Simple ethers		
$\text{CH}_3\text{-O-CH}_3$	Dimethyl ether	Methoxymethane
$\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$	Diethyl ether	Ethoxyethane
Mixed ethers		
$\text{CH}_3\text{-O-CH}_2\text{-CH}_3$	Ethyl methyl ether	Methoxyethane
$\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-CH}_3$	Methyl n-propyl ether	1-methoxypropane
$\begin{array}{c} \text{CH}_3\text{-O-CH-CH}_3 \\ \\ \text{CH}_3 \end{array}$	Isopropyl methyl ether	2-methoxypropane

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Aldehydes

Aldehydes and ketones are two important classes of compounds containing the carbonyl group $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$. In aldehydes the $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$ group is

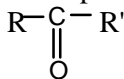
linked to an alkyl group and a hydrogen or two hydrogens. Aldehydes are represented by the general formula R-CHO .

IUPAC names of aldehydes are obtained by replacing the terminal "e" of alkane with "al".

Structural formula	Common name	IUPAC name
H-CHO	Formaldehyde	Methanal
$\text{CH}_3\text{-CHO}$	Acetaldehyde	Ethanal
$\text{CH}_3\text{-CH}_2\text{-CHO}$	Propionaldehyde	Propanal
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CHO}$	Butyraldehyde	1-Butanal
$\begin{array}{c} \text{CH}_3\text{-CH-CHO} \\ \\ \text{CH}_3 \end{array}$	Isobutyraldehyde	2-Methylpropanal

Ketones

In ketones $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$ group is united with 2 alkyl groups. These compounds are represented by the general formula.



Ketones are named by replacing the terminal "e" of the corresponding alkane name with "one".

Structural formula	Common name	IUPAC name
$\begin{array}{c} \text{CH}_3-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_3 \end{array}$	Acetone (Dimethyl ketone)	Propanone
$\text{CH}_3\text{-CH}_2\text{-}\overset{\text{O}}{\underset{\text{ }}{\text{C}}}\text{-CH}_3$	Ethylmethyl ketone	Butanone
$\text{CH}_3\text{-CH}_2\text{-}\overset{\text{O}}{\underset{\text{ }}{\text{C}}}\text{-CH}_2\text{-CH}_3$	Diethyl ketone	3-pentanone

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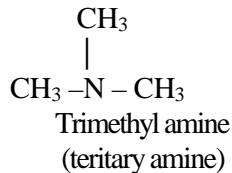
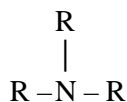
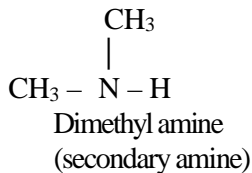
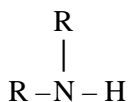
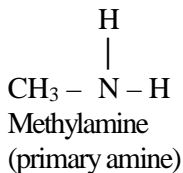
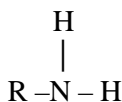
Carboxylic acids

These are represented by the general formula $R-COOH$. IUPAC name is derived by replacing the terminal "e" of the alkane name with "**oic acid**". These compounds are further classified into **mono**- and **di**-carboxylic acids.

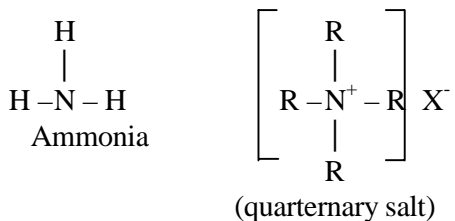
Structural formula	Common name	IUPAC name
Monocarboxylic acids		
$H-COOH$	Formic acid	Methanoic acid
CH_3-COOH	Acetic acid	Ethanoic acid
CH_3-CH_2-COOH	Propionic acid	Propanoic acid
$CH_3-CH_2-CH_2-COOH$	Butyric acid	Butanoic acid
Dicarboxylic acids		
$\begin{array}{c} COOH \\ \\ COOH \end{array}$	Oxalic acid	Ethanedioic acid
$\begin{array}{c} COOH \\ / \quad \backslash \\ CH_2 \\ \backslash \quad / \\ COOH \end{array}$	Malonic acid	Propanedioic acid
$\begin{array}{c} CH_2 - COOH \\ \\ CH_2 - COOH \end{array}$	Succinic acid	Butanedioic acid

Amines

Amines are the derivatives of ammonia in which one or more H-atoms have been replaced by alkyl groups. They are designated as primary, secondary and tertiary amines according as one, two or three hydrogen atoms in ammonia molecule have been replaced by alkyl groups.



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When one alkyl group is attached to N-atom, it is called primary amine, when two alkyl groups are attached to nitrogen atom, then it is called secondary amine. When three alkyl groups are attached to nitrogen atom it is called tertiary amine. When four alkyl groups are attached to nitrogen atom it is called quarternary salt.

Structural formula	Common	IUPAC name
Primary Amines		
$\text{CH}_3\text{-NH}_2$	Methyl amine	aminomethane
$\text{CH}_3\text{-CH}_2\text{-NH}_2$	Ethyl amine	aminoethane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH}_2$	n-propyl amine	1-aminopropane
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{NH}_2 \end{array}$	Isopropyl amine	2-aminopropane
Secondary Amines		
$\text{CH}_3\text{-NH-CH}_3$	Dimethyl amine	(N-methylamino) methane
$\text{CH}_3\text{-CH}_2\text{-NH-CH}_2\text{-CH}_3$	Diethyl amine	(N-ethylamino) ethane
$\text{CH}_3\text{-NH-CH}_2\text{-CH}_3$	Ethylmethyl amine	(N-methylamino) ethane

Structural formula	Common name	IUPAC name
Tertiary Amines		
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N} \\ \\ \text{CH}_3 \end{array}$	Trimethyl amine	(N,N - dimethyl amino) methane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_2\text{H}_5 - \text{N} \\ \\ \text{CH}_3 \end{array}$	Ethyldimethyl amine	(N,N - dimethyl amino) ethane

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Nitro compounds

These compounds are represented by the general formula RNO_2 . IUPAC names are obtained by adding the prefix "**nitro**" to the alkane.

Structural formula Common/IUPAC name

- | | |
|---|----------------|
| 1. $\text{CH}_3 - \text{NO}_2$ | Nitromethane |
| 2. $\text{CH}_3 - \text{CH}_2 - \text{NO}_2$ | Nitroethane |
| 3. $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{NO}_2$ | 1-Nitropropane |
| 4. $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{NO}_2 \end{array}$ | 2-Nitropropane |

15.5 Isomerism

The molecular formula of an organic compound represents only the number of different atoms present in a molecule. But the molecular formula does not tell about the arrangement of atoms. A given molecular formula may lead to more than one arrangement of atoms such that there are many compounds which may have same molecular formula but with different physical and chemical properties. This phenomenon in which the same molecular formula may exhibit different structural arrangement is called isomerism.

Compounds that have the same molecular formula but different structural formulae are called isomers (from the Greek word isos + meros, "made of the same parts").

There are two types of isomerism, namely,

1. Structural isomerism 2. Stereoisomerism

Structural isomerism

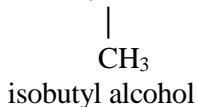
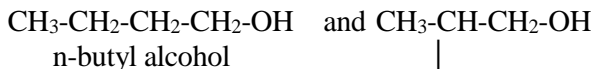
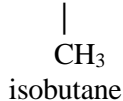
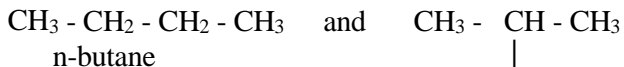
When two or more compounds possess the same molecular formula but different structural formulae, they are said to exhibit structural isomerism. Structural isomerism is divided into.

1. Chain isomerism or Nuclear isomerism

Chain isomers are compounds that have the same molecular formula but have different carbon skeletons.

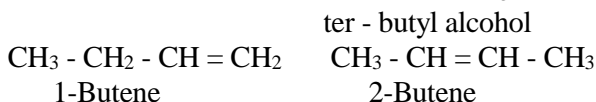
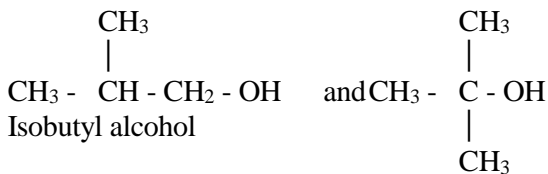
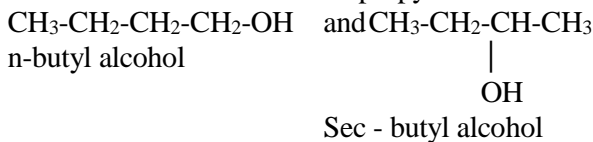
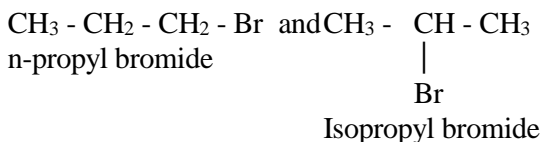
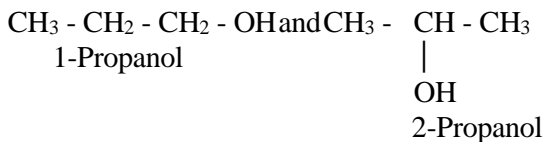
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Examples



2. Position Isomerism

Position isomers are compounds that have the same formula, carbon skeleton and functional groups but have the functional groups located at different positions along the carbon skeleton.



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Functional isomerism

Functional isomers are compounds that have the same molecular formula but have different functional groups.

Examples

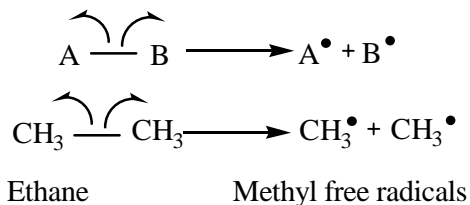
- $\text{CH}_3 - \text{CH}_2 - \text{OH}$ and $\text{CH}_3 - \text{O} - \text{CH}_3$
 Ethyl alcohol Dimethyl ether
- $\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3$ and $\text{CH}_3 - \text{CH}_2 - \text{CHO}$
 Acetone Propionaldehyde
- $\text{CH}_3 - \text{CH}_2 - \text{COOH}$ and $\text{CH}_3 - \text{COO} - \text{CH}_3$
 Propionic acid Methyl acetate

15.6 Fission of bonds**How bond fission occurs?**

A covalent bond (σ bond) joining two atoms exist because of the shared pair of electrons. When two atoms are separated from each other, bond fission is said to have taken place. The fission process can take place in two ways.

Homolytic fission

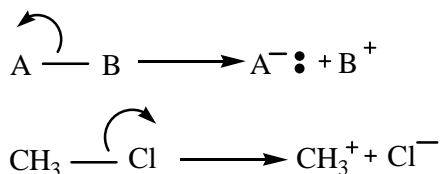
A covalent bond between two atoms A and B may be shown as $\text{A} \cdot \cdot \text{B}$ or $\text{A}-\text{B}$. This bond may undergo fission in such a way that each atom retains the electrons of the shared pair. Such species are known as **free radicals** or odd electron molecules.

**Heterolytic fission**

A covalent bond breaks in such a way that the shared pair of electron

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stay on any one of the atoms. Breaking of the bond in this manner is known as heterolytic fission or heterolysis.



The atom or group which carries the unshared pair of electrons are represented with a negative sign as A^- : is known as anions. The carbonium ion carries the positive charge which lacks a pair of electrons. Heterolysis occurs only when the initially bonded atoms are of different in electronegativities and in that the electron pair becomes attached to the more electronegative atom.

An organic reaction may be represented as :

Reactants + attacking agent \rightarrow [intermediate] \rightarrow product

Depending upon the nature of the reaction which the intermediate species undergo, the reactions of the organic compounds are classified as substitution reactions, addition reactions, elimination reactions, polymerisation reactions, condensation reaction, hydrolysis, oxidation and reduction reactions.

15.7 Types of Reactions

Substitution or Displacement reactions

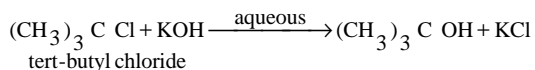
Displacement reaction is one in which an atom or group linked to a carbon atom is removed and in its place another atom or group is attached.

The substitution reactions are classified into three types.

a) Nucleophilic substitution reaction (S_N)

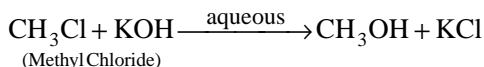
When a substitution reaction is brought about by a nucleophile, the reaction is termed as S_N (S stands for substitution and N for nucleophile). These reactions are divided into two classes :

(1) S_N^1 (substitution, nucleophilic, unimolecular)



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(2) S_N^2 (Substitution, nucleophilic, bimolecular)

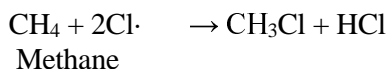
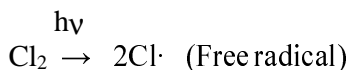


b) Electrophilic substitution reaction (S_E)

When a substitution reaction involves an attack by an electrophile, the reaction is referred to as S_E (S - stands for substitution and E for electrophile).

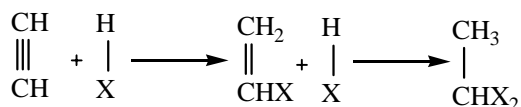
c) Free radicals substitution reaction

These reactions are initiated by free radicals.



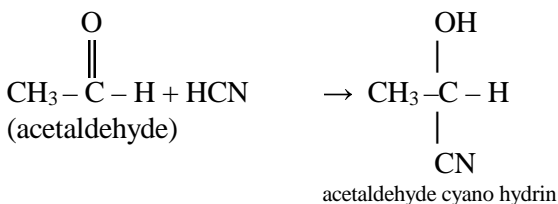
Addition Reactions

All organic compounds having double or triple bond adopt addition reactions in which two substances unite to form a single compound.

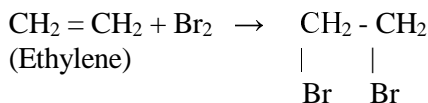


Depending on the type of reagent initiating these reactions, addition reactions are classified into three types.

(a) Nucleophilic addition

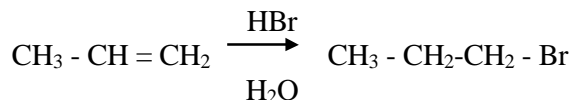


(b) Electrophilic addition



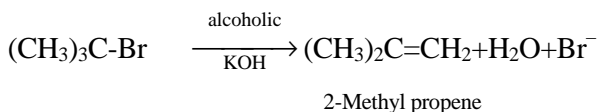
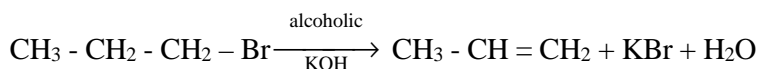
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(c) Free radical addition



Elimination reactions

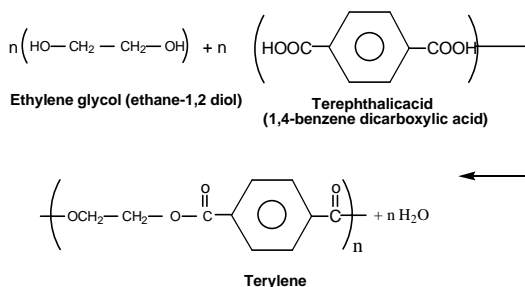
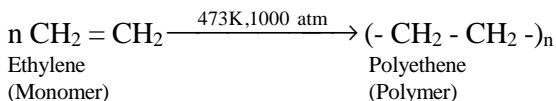
In these reactions, two atoms or groups are removed from a molecule without being substituted by other atoms (or) groups. The reverse of addition reactions are eliminations. These reactions are classified into two types.

(a) Unimolecular elimination (E_1)(b) Bimolecular elimination (E_2)

Polymerisation

The union of two or more molecules to form a large single molecule is called **polymerisation** and the product is a polymer.

Examples

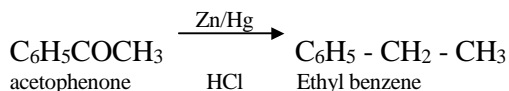


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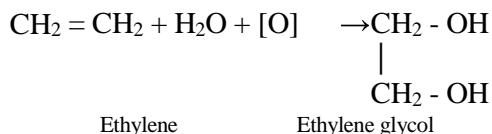
Reduction and the one that involves the addition of oxygen is called **Oxidation**. For example,

1) **Clemmensen Reduction**

Ketones can be reduced to their corresponding hydrocarbons by the mixture of Zn/Hg and conc. HCl.



2) Very mild oxidising agent such as KMnO_4 , causes a splitting of the molecule at the double bond.



15.7.1 Types of Reagents

Electrophilic reagents

These reagents are electron deficient. This deficiency accounts for their affinity for electrons (electro = electron, philic = loving). They are also called cationic reagents and may carry positive charge or have incomplete valence shells. These reagents can therefore, be of two types.

- (i) Positive electrophiles (or) Ionic electrophiles
- (ii) Neutral electrophiles

Some common electrophiles are given in the table

S. No.	Ionic electrophiles	Neutral electrophiles (Lewis acids)
1.	H^+ (proton)	AlCl_3
2.	Cl^+ (chloronium)	BF_3
3.	Br^+ (bromonium)	ZnCl_2
4.	NO_2^+ (Nitronium)	FeCl_3
5.	$>\text{C}^+$ carbonium	SO_3

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Nucleophilic reagents

Nucleophiles or nucleophilic reagents are electron rich substances containing atoms which have at least an unshared pair of electron. These reagents are nucleus loving (nucleo = nucleus, philic = loving). Nucleophiles can be (i) negatively charged (or) Ionic (ii) neutral species (Lewis bases). Some of the common nucleophiles are reported in table

S. No.	Neutral nucleophiles (Lewis bases)	Ionic nucleophiles
1.	NH ₃	X ⁻ (halide ions)
2.	H ₂ O	OH ⁻ (hydroxide)
3.	R-OH	RO ⁻ (alkoxide)
4.	R-NH ₂	CN ⁻ (cyanide)
5.	R ₃ -N	<C ⁻ (carbanion)

The differences between these reagents are summarised in the following table.

S. No.	Electrophiles	Nucleophiles
1.	are electron deficient	are electron rich
2.	are cations	are often anions
3.	are Lewis acids	are Lewis bases
4.	accept an electron pair	donate an electron pair
5.	attack on electron rich sites	attack on electron deficient sites
6.	possess an empty orbital to house the lone pair from the nucleophiles	possess a minimum of one lone pair of electron.

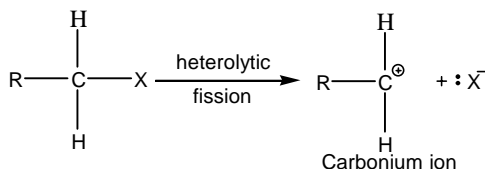
15.7.2 Carbonium ions

Let us consider the heterolytic fission of the bond C – X present in an organic molecule. If the atom X has greater electronegativity than the carbon atom, the former takes away the bonding electron pair and becomes negatively charged while the carbon will lose its electron and thus acquire a positive charge. Such cationic species carrying a positive charge on carbon

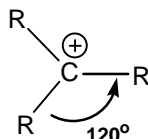
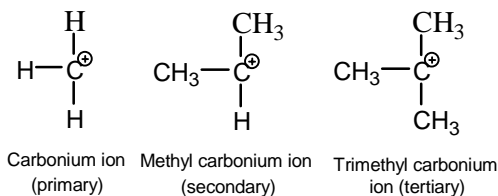
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are known as carbonium ions.

For illustration



These carbonium ions are called primary, secondary and tertiary depending up on the nature of the carbon atom bearing the charge.



The geometry of alkyl carbonium ion

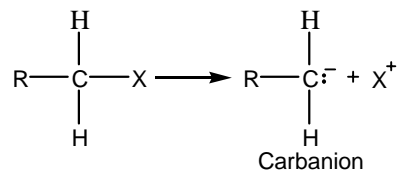
Since the carbon of the carbonium ion is in sp^2 hybridised state, the ion is planar with a vacant p orbital perpendicular to the plane of the three covalent bonds to carbon.

Carbanion

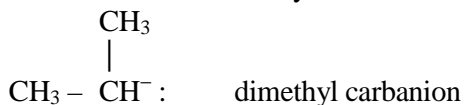
Let us consider the heterolytic fission of the bond C - X present in an organic molecule. If the carbon atom has greater electronegativity than the atom X, the former takes away the bonding electron pair and acquires a negative charge. The resulting carbon anion is known as carbanion.

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For illustration



Examples



15.8 Free Radicals

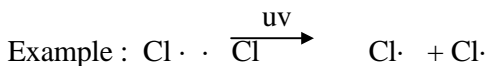
Free radicals are species with one or more unpaired electrons obtained by the homolytic fission of covalent bond. The free radicals themselves are electrically neutral. The free radicals are denoted by putting a dot against the atom or group of atoms.

Few examples : $\text{Cl}\cdot$, $\text{CH}_3\cdot$, $\text{C}_6\text{H}_5\cdot$

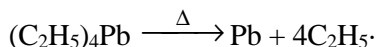
They are classified as short lived free radicals and long lived free radicals on the basis of their life time.

Formation of free radicals

(a) Photochemical fission : When an organic compound is exposed to ultraviolet region it under goes bond fission.



(b) Thermal fission : All organic compounds on heating yield free radicals.



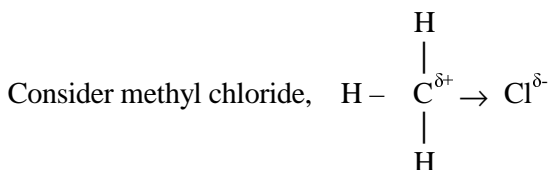
Polar Effects

Inductive Effect

If a covalent bond is formed by two atoms differing much in electronegativity then the bond is said to be polarised. The electron pair

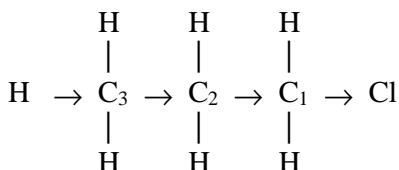
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shifts towards the more electronegative atom resulting in the origin of fractional charges on the atoms.



In this molecule, chlorine atom is more electronegative than the carbon atom. Due to this, chlorine pulls the electron pair and acquires a small negative charge.

Let us consider, 1 - chloropropane



As C_1 is positively charged, it attracts towards itself the electron pair shared between C_1 and C_2 . This causes C_2 to acquire a small positive charge but the charge is smaller than the charge on C_1 . This type of electron displacement occurring in saturated compounds along a carbon chain is termed, inductive effect.

It is a permanent effect and decreases rapidly as the distance from the electronegative atom increases. It is represented by \rightarrow the arrow head pointing towards the more electronegative atom. This effect operates in the case of σ - electrons only.

For measurements of relative inductive effect, atoms or groups having greater electron affinity than hydrogen are said to have - I effect. Similarly, atoms or groups having lesser electron affinity than hydrogen are said to have + I effect. Some of the atoms and groups arranged in the increasing order of inductive effect are given as

Groups having - I effect [electron - attracting].

- C_6H_5 , OH , I , Br , Cl , F

Groups having + I effect [electron pumping]

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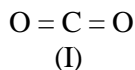
CH₃ -, CH₃ - CH₂ -, (CH₃)₂CH-, (CH₃)₃C -

(Methyl) (Ethyl) Isopropyl tertiarybutyl

Resonance (Mesomeric) Effect

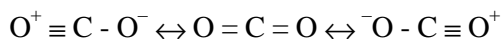
When several structures may be assumed to contribute to the true structure of a molecule but none of them can be said to represent it uniquely, then the molecule is referred to as a resonance hybrid and the phenomenon is termed as resonance.

It is somewhat abstract, but it can be better understood if we consider the structure of a simple molecule carbon dioxide.



The above structure does not account for all observed properties although it can explain many. The C-O bond length in CO₂ molecule is 1.15 Å where as it is expected to be 1.22 Å on the basis of the above structure.

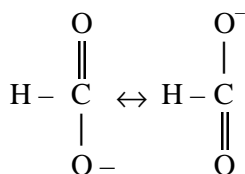
Again, the heat of formation of carbon dioxide is 1592 kJ.mol⁻¹ where as on the basis of the above structure it is expected to be approximately 1466 kJ.mol⁻¹. These discrepancies can be explained only if we assume the following resonance hybrid for carbon dioxide.



The difference in energy i.e. 126 KJ.mol⁻¹ is regarded as resonance energy.

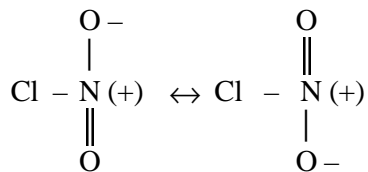
Few other examples

1. Formate ion, HCOO⁻

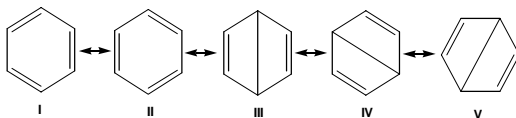


2. Nitryl chloride, NO₂Cl

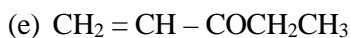
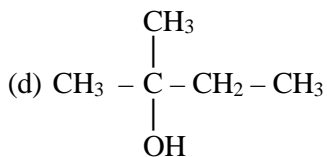
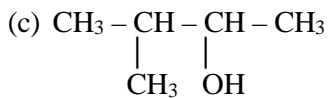
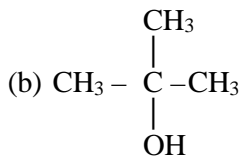
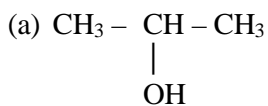
ADVANCED LEVEL CHEMISTRY NOTES BK 1



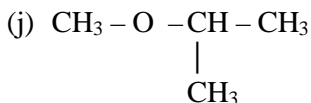
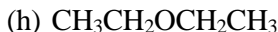
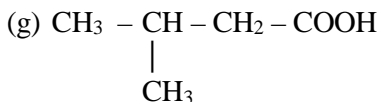
3.



Benzene

Questions**A. Write IUPAC name of the following**

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**B. Explain briefly on the following**

1. Homolytic and heterolytic fission.
2. Substitution reaction.
3. Addition reaction.
4. Elimination reaction.
5. Polymerisation reaction.
6. Condensation reaction.
7. Hydrolysis.
8. Reduction and oxidation reactions.
9. Electrophilic and Nucleophilic reagents.
10. Carbonium ions and carbanions.
11. Free radicals.
12. Inductive effect.
13. Resonance effect.

SUMMARY

- This chapter explains the ability of carbon atoms to form long chains held together by strong carbon-carbon bonds, catenation.
- Characteristics of homologous series and structural isomers are explained.

15. BASIC CONCEPTS OF ORGANIC CHEMISTRY

OBJECTIVES

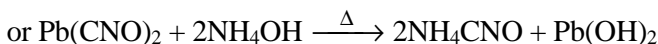
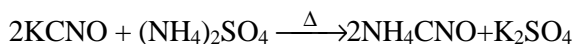
This topic explains the nature of organic compounds and explores the possibilities of all basic concepts of organic chemistry.

- *Catenation and the reason for innumerable number of organic compounds.*
- *Classification of organic compounds based on functional groups.*
- *IUPAC method of naming all types of organic compounds.*
- *Details about isomerism.*
- *Fission of bonds and types of organic reactions.*
- *Nature of reagents, electrophiles and Nucleophiles.*
- *Knowledge about carboniumion and carbanion and free radicals.*
- *Different types of electron displacements in organic chemistry.*

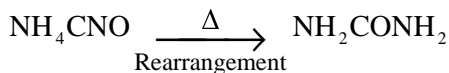
Introduction

Initially (before 1828), the name organic chemistry was given for the chemistry of compounds obtained from plants and animals (i.e, from living organisms). The word organic signifies life. Lavoisier (who is considered as the father of chemistry) showed that the compounds obtained from plants are often made of C, H and O and the compounds obtained from animals contain C, H, O, N, S, P. etc.

Berzelius proposed vital force theory (a theory of life process) to deal with organic compounds. The vital force theory suffered blow in 1828 when Wohler synthesized the first organic compound urea in the laboratory from an inorganic compound, i.e, from ammonium cyanate ($\text{NH}_4 \text{CNO}$).



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Later on, a further blow to vital force theory was given by Kolbe (1845) who prepared acetic acid, the first organic compound, in laboratory from its elements.

Now a days organic chemistry is defined as **the chemistry of carbon compounds or the chemistry of hydrocarbons and their derivatives**. Organic compounds obey the same fundamental laws of chemistry as the inorganic compounds. However they are studied as a separate branch of chemistry because of two reasons:

- i. The total number of organic compounds known so far exceeds several times the total number of inorganic compounds known.
- ii. There are marked differences between the structure, composition and behaviour of organic and inorganic compounds. The phenomenon of **isomerism** and tendency of **catenation** are unique properties of organic compounds.

15.1 Catenation

1. The tendency of atoms of an element to unite with each other forming a chain of covalent bond is known as **catenation**.
2. Catenation may give rise to open chain or closed chain compounds.
3. Carbon possesses maximum tendency for catenation i.e. **Bond energy (kcal mol⁻¹) for catenation of C is maximum.**

C-C,	Si-Si,	N-N,	P-P,	O-O,	S-S
85	54	39	50	35	54

4. Carbon also forms double as well as triple bonds.
5. A large number of compounds of carbon are known due to catenation.
6. The stability or strength of bond decreases as the bond energy decreases. Hence the catenation order among the following is $\text{C} > \text{Si} \approx \text{S} > \text{P} > \text{N} > \text{O}$.

15.2 Classification into open chain and cyclic compounds

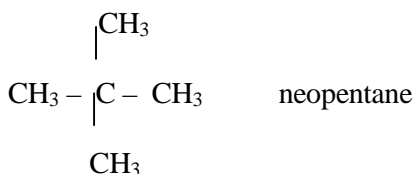
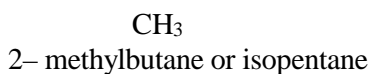
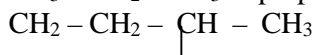
The organic compounds are classified into two main types, namely.

ADVANCED LEVEL CHEMISTRY NOTES BK 1

(1) Open - chain or acyclic compounds or aliphatic compounds

The open chain or acyclic compounds are those in which carbon atoms are linked to each other either in linear or branched fashion such that the molecule is having open chain structure. These compounds are also called aliphatic compounds (Greek word : aliphar meaning fat).

Examples

**(2) Closed chain or cyclic compounds**

Organic compounds with closed chain of atoms are called closed chain compounds or ring compounds.

These compounds are further classified into

- (a) Homocyclic or carbocyclic compounds
- (b) Heterocyclic compounds

(a) Homocyclic compounds : In these compounds the ring structure is made up of only carbon atoms.

These compounds are further classified into

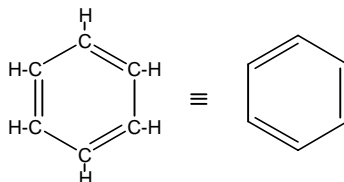
- (i) Aromatic compounds and
- (ii) Alicyclic compounds

(i) Aromatic compounds (Benzenoid) : Compounds containing one or more benzene rings in their structure are classified as aromatic benzenoid compounds. Most of these compounds have pleasant odour (Greek : Aroma - sweet smell).

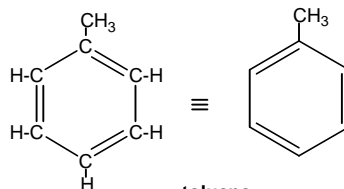
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Examples

Monocyclic

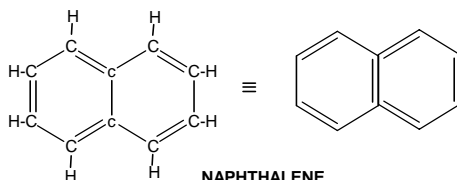


benzene

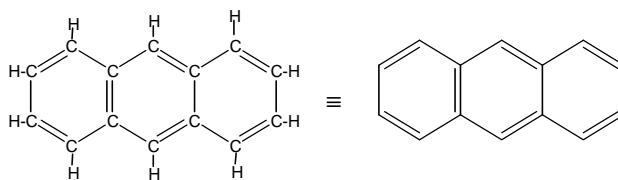


toluene

Polycyclic



NAPHTHALENE

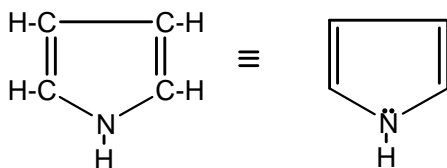


ANTHRACENE

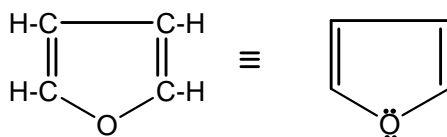
Heterocyclic compounds (Non - benzenoid aromatic) : Cyclic compounds in which the ring atoms are made up of hetero atoms like nitrogen, oxygen and sulphur in addition to carbon atoms are called heterocyclic compounds.

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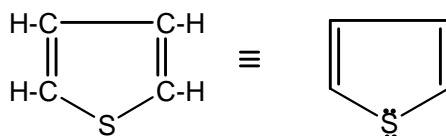
Examples



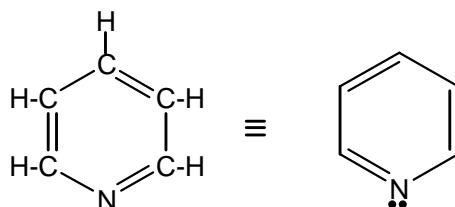
pyrrole



furan



thiophene



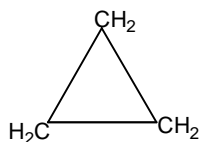
pyridine

The above compounds are aromatic non-benzenoid compounds.

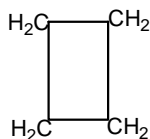
- (ii) **Alicyclic compounds** : Cyclic compounds with ring structure containing only carbon atoms are called alicyclic or carbocyclic compounds. Though these compounds possess a ring structure, they behave more like aliphatic compounds.

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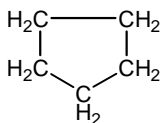
Examples



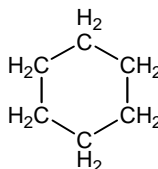
cyclopropane



cyclobutane

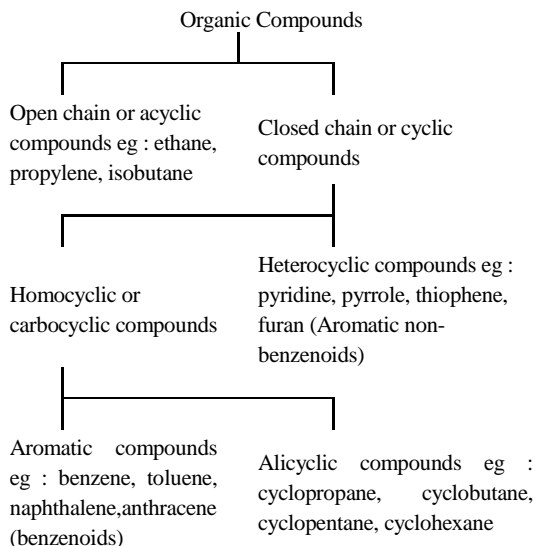


cyclopentane



cyclohexane

The above classification can be schematically represented as follows :

**Characteristics of organic compounds**

All organic compounds have the following characteristic properties

- (1) Many organic compounds are inflammable
- (2) They are mostly covalent compounds

ADVANCED LEVEL CHEMISTRY NOTES BK 1

- (3) They are generally soluble in non - polar solvents like carbon tetrachloride, benzene etc.
- (4) They have generally low boiling point and melting point.
- (5) They exhibit isomerism

Homologous series

A group or class of organic compounds related to each other by a general molecular formula constitutes homologous series.

Characteristics of homologous series

Homologous series have the following characteristics :

- (1) All members of a series contain same elements and the same functional groups.
- (2) All the members of a homologous series can be represented by a general formula

Examples

Alkanes	C_nH_{2n+2}
Alkenes	C_nH_{2n}
Alkynes	C_nH_{2n-2}

- (3) All the members of a homologous series can be prepared by similar methods.
- (4) All members of a homologous series usually undergo similar chemical reactions.
- (5) Successive members in a series differ by a $-CH_2$ group
- (6) The physical properties of the members of a homologous series vary in a regular way down the series. For example, boiling point, melting point and density of the alkane series vary in a regular way with increasing number of carbon atoms.

15.3 Functional groups

The chemical properties of all the members of a homologous series are characterised by a group called the functional group. It is characteristic of a particular series.

The following table gives a list of functional groups and names.

Halide	$-X$
Alcohol	$-OH$
Ether	$-O-$

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Aldehyde	$-\text{CHO}$
Ketone	$\begin{array}{c} \text{---C---} \\ \\ \text{O} \end{array}$
Carboxylic acid	$-\text{COOH}$
Ester	$-\text{COOR}$
Amide	$\begin{array}{c} \text{---C---NH}_2 \\ \\ \text{O} \end{array}$
Acid halide	$\begin{array}{c} \text{---C---X} \\ \\ \text{O} \end{array} \quad (\text{X} = -\text{Cl}, -\text{Br}, -\text{I})$
Acid anhydride	$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \qquad \text{---O---} \quad \\ \text{---C} \qquad \qquad \text{C---} \end{array}$
Amine	$-\text{NH}_2$
Nitro compounds	$-\text{NO}_2$

15.4 IUPAC system of nomenclature (1993)

The international union of pure and applied chemistry (abbreviated as IUPAC) has done a commendable job in framing set rules for naming organic compounds. Two commonly used systems of nomenclature are described below.

- (1) Common or Trivial system (2) IUPAC system

IUPAC Nomenclature of Aliphatic Compounds

The IUPAC name of a compound essentially consists of three parts.

- (a) Root word (b) Suffix (c) Prefix

Root words for alkanes

The root words for the first four members are taken from their trivial or common names.

e.g.

Meth	-	for Methane
Eth	-	for Ethane
Prop	-	for Propane
But	-	for Butane

For the higher homologue, root words are derived from the Greek/Latin number indicating the total number of carbon atoms.

ADVANCED LEVEL CHEMISTRY NOTES BK 1

- e.g. Pent - is derived from penta for five
 Hex - is derived from hexa for six
 Hept - is derived from hepta for seven
 Oct - is derived from octa for eight

Suffix

There are two types of suffixes **Primary suffix** and secondary suffix.

Primary suffix

A primary suffix is added to the **Root word** to indicate whether the parent chain is saturated or unsaturated. Some primary suffixes are given below.

Sl. No.	Nature of carbon chain (parent chain)	Primary suffix
1.	Saturated	ane
2.	Unsaturated with One double bond Two double bond Three double bond	ene diene triene
3.	Unsaturated with One triple bond Two triple bond	yne diyne

Sl. No.	Structural formula	No. of C atoms	Root word	Primary suffix	IUPAC name
1.	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_3$	4	But	ane	Butane
2.	$\text{CH}_3\text{-CH=CH}_2$	3	Prop	ene	Propene
3.	$\text{CH}\equiv\text{CH}$	2	Eth	yne	Ethyne
4.	$\text{CH}_2\text{=CH-CH=CH}_2$	4	Buta [*]	diene	Butadiene
5.	$\text{HC}\equiv\text{C-C}\equiv\text{CH}$	4	Buta [*]	diyne	Butadiyne

ADVANCED LEVEL CHEMISTRY NOTES BK 1

* extra 'a' has been added to the root word since the primary suffix, ie diene or diyne begins with a consonant (d).

Secondary suffix

Secondary suffix is used to indicate the functional group in the organic compound secondary suffixes for various functional groups are given below.

Sl. No.	Class	Functional group	Secondary suffix	IUPAC name
1.	Alcohols (R-OH)	-OH	-ol	Alkanols
2.	Aldehyde (R-CHO)	-CHO	-al	Alkanals
3.	Ketones (RCOR')	$>C=O$	-one	Alkanones
4.	Carboxylic acids (R-COOH)	-COOH	-oic acid	Alkanoic acid
5.	Ester (RCOOR')	-COOR	-alkanoate	alkyl alkanoates

Secondary suffix is added to the primary suffix; ie written after the primary suffix. While adding the secondary suffix to the primary suffix following rules should be followed.

- If the secondary suffix begins with a vowel, then the terminal **e** of the primary suffix is dropped before adding the secondary suffix.
- If the secondary suffix begins with a consonant, then the last (terminal) **e** is retained and the secondary suffix is added after e.
- If the secondary suffix has some **numerical prefix**, such as, **di, tri etc.**, before it then the terminal **e** of the primary suffix is retained.

The addition of the secondary suffix to the primary suffix is illustrated below

Sl. No.	Structu-ral formula	No. of C atoms	Root word	Primar y suffix	Secondar y suffix	IUPAC name	Remarks
1.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2\text{-OH} \end{array}$	2	Eth	ane	ol	Ethanol	'e' of prim suffix dropped

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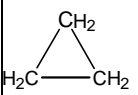
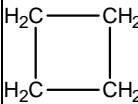
2.	$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{CH}_2\text{-OH} \end{array}$	2	Eth	ane	diol	Ethane diol	'e' of prim suffix not dropped
3.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CHO} \end{array}$	3	Prop	ane	al	Propanal	'e' of the prim suffix dropped
4.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{COOH} \end{array}$	4	But	ane	oic acid	Butanoic acid	'e' of prim suffix dropped

Prefix

Prefix is a part of the name which appears before the root word. There are two types of prefixes - primary prefix and secondary prefix.

Primary prefix

A primary prefix is used to distinguish alicyclic (aliphatic cyclic compounds) from acyclic (open chain) compounds. If the given compound is an alicyclic compound, then a prefix cyclo is used just before the root word. For example.

Structural formula	No. of C atoms	Root word	Primary suffix	Primary prefix	IUPAC name
	3	Prop	ane	Cyclo	Cyclo propane
	4	But	ane	Cyclo	Cyclo butane

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Secondary prefix

In the IUPAC system of nomenclature, certain characteristic groups are not considered as functional groups. Such characteristic groups are considered as the **substituents**. Each such group or substituent is denoted by a secondary prefix. Some typical secondary prefixes are listed below.

Substituent group	Secondary prefix
- F	Fluoro
- Cl	Chloro
- Br	Bromo
- I	Iodo
- CH ₃	Methyl
- C ₂ H ₅	Ethyl
CH ₃ - CH ₂ - CH ₂ -	n-propyl
(CH ₃) ₂ CH -	Iso propyl
(CH ₃) ₃ C -	t - Butyl
- NO ₂	Nitro
- NH ₂	Amino
- NO	Nitroso
N \equiv N	Diazo
- OCH ₃	Methoxy
- OC ₂ H ₅	Ethoxy

In the case of open chain compounds, the secondary prefix is added just before the root word in the **alphabetical** order. This is illustrated below.

Sl. No.	Structural formula	No. of C atoms	Root word	Suffix		Prefix		IUPAC Name
				Primary	Sec	Pri	Sec	
1.	CH ₃ -CH ₂ -Cl	2	Eth	ane	-	-	Chloro	Chloro ethane
2.	CH ₃ -NO ₂	1	Meth	ane	-	-	Nitro	Nitro methane

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Saturated Hydrocarbons : Alkanes

General formula : C_nH_{2n+2} Suffix : ane

Sl. No.	Structural formula	Common Name	IUPAC name
1.	CH ₄	Methane	Methane
2.	H ₃ C - CH ₃	Ethane	Ethane
3.	H ₃ C - CH ₂ - CH ₃	Propane	Propane
4.	H ₃ C - CH ₂ - CH ₂ - CH ₃	n-butane	Butane

Alkyl groups

The univalent hydrocarbon unit derived from an alkane by the loss of one hydrogen atom is termed as alkyl group.

The alkyl groups are named after their parent alkanes by replacing the suffix-**ane** by- **yl**.

Continuous straight chain alkyl groups (or, normal alkyl (n-) groups)

Sl. No.	Alkane		Alkyl group	
	Formula	Name	Formula	Name
1.	CH ₄	Methane	CH ₃ -	Methyl
2.	CH ₃ - CH ₃	Ethane	CH ₃ - CH ₂ -	Ethyl
3.	CH ₃ -CH ₂ -CH ₃	Propane	CH ₃ -CH ₂ -CH ₂ -	Propyl

Branched chain alkyl groups

When a hydrogen atom from a secondary or tertiary carbon atom in any carbon chain is removed, a branched chain alkyl group is obtained. The common prefixes used are,

a) iso - b) sec - c) tert - d) neo –

a) **iso** – The alkyl group in which a - CH₃ branch is present at the end of the chain is designated as isoalkyl group. In other words, the alkyl group in which the second last carbon atom in the chain is branched to one - CH₃ group is called on isoalkyl group.

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Sl.No.	Structure	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \\ \\ \text{CH}_3 \end{array}$	1-methyl ethyl (iso-propyl)
2.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \\ \\ \text{CH}_3 \end{array}$	2-methyl propyl (iso-butyl)
3.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \\ \\ \text{CH}_3 \end{array}$	3-methyl butyl (iso-pentyl)

b) Sec - The prefix sec - before the name of the alkyl group indicates that the H-atom was removed from a secondary carbon atom.

Sl.No.	Structure	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \end{array}$	1 - Methyl ethyl (Sec - propyl)
2.	$\begin{array}{c} \text{CH}_3 - \text{CH}_2 - \text{CH} - \\ \\ \text{CH}_3 \end{array}$	1 - methyl propyl (Sec - butyl)
3.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH} - \end{array}$	1 - methyl butyl (Sec - pentyl)

c) Tert - (or) t -

The prefix tert - before the name of the alkyl group indicates that the H - atom has been removed from a tertiary carbon atom.

Sl. No.	Structure	IUPAC name
1.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \\ \\ \text{CH}_3 \end{array}$	1,1 - dimethyl ethyl (tert - butyl)
2.	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{CH}_2 - \text{C} - \\ \\ \text{CH}_3 \end{array}$	1,1 - dimethyl propyl (tert - pentyl)

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Alkenes

General formula : C_nH_{2n} **Suffix :** ene

The common name of alkene is obtained by replacing the ending - **ane** from the name of its parent alkane with - **ylene**.

The IUPAC name of an alkene is obtained by replacing - **ane** of the alkane by - **ene**.

Structural formula	Common Name	IUPAC name
$CH_2 = CH_2$	Ethylene	Ethene
$CH_3 - CH = CH_2$	Propylene	Propene
$CH_3-CH_2-CH=CH_2$ (double bond starts at C_1)	1- Butylene	But-1-ene
$CH_3-CH=CH-CH_3$ (double bond starts at C_2)	2- Butylene	But-2-ene

Alkenyl group

The group obtained by removing a hydrogen atom from an alkene molecule, are called **alkenyl** group.

The IUPAC name of alkenyl group is obtained by replacing - **e** of the alkene by the suffix - **yl**.

Sl. No.	Structure	Common name	IUPAC name
1.	$CH_2 = CH_2$	vinyl	ethenyl
2.	$CH_2=CH-CH_2-$	allyl	Prop - 2 - enyl

Alkynes

General formula : C_nH_{2n-2} **Suffix :** - yne

The IUPAC name of an alkyne is obtained by replacing the ending - **ane** from the name of the parent alkane with - **yne**.

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Sl. No.	Structural formula	Common Name	IUPAC name
1.	$\text{HC} \equiv \text{CH}$	Acetylene	Ethyne
2.	$\text{CH}_3 - \text{C} \equiv \text{CH}$	Methyl acetylene	Propyne
3.	$\text{CH}_3 - \text{C} \equiv \text{C} - \text{CH}_3$	Dimethyl acetylene	But-2-yne

Alkyl halides

The general formula of alkyl halides is R-X where R stands for alkyl group and "X" stands for halogen (F, Cl, Br, I). They are named by introducing the prefix halo (chloro, bromo, iodo, fluoro) to the name of the parent alkane.

Formula	Common name	IUPAC name
$\text{CH}_3\text{-Cl}$	Methyl chloride	Chloromethane
$\text{CH}_3\text{-CH}_2\text{-Br}$	Ethyl bromide	Bromoethane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-Br}$	n-propyl bromide	1-bromopropane
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{I} \end{array}$	Iso-propyl iodide	2-iodopropane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Cl}$	n-butyl chloride	1-chlorobutane
$\begin{array}{c} \text{CH}_3\text{-CH}_2\text{-CH-CH}_3 \\ \\ \text{Br} \end{array}$	Sec-butyl bromide	2-bromobutane
$\begin{array}{c} \text{CH}_3\text{-CH-CH}_2\text{-Cl} \\ \\ \text{CH}_3 \end{array}$	Isobutyl chloride	1-chloro-2-methyl propane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{I} \\ \\ \text{CH}_3 \end{array}$	ter-butyl iodide	2-iodo-2-methyl propane
$\text{CH}_2=\text{CH-Cl}$	Vinyl chloride	Chloroethene
$\text{CH}_2=\text{CH-CH}_2\text{-Cl}$	Allyl chloride	3-Chloro-1-propene

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Alcohols

The term alcohol is applied to all organic compounds obtained by replacing one or more hydrogen atoms of an open-chain hydrocarbon by hydroxyl groups. The alcohols are further classified into **mono-, di-, tri-**hydric alcohols according to the number of hydroxyl groups which they may contain.

In IUPAC nomenclature, the terminal "e" of the alkane is replaced by "ol".

Monohydric alcohols

Alcohols which contain only one hydroxyl group per molecule are called monohydric alcohols.

Formula	Common name	IUPAC name
$\text{CH}_3\text{-OH}$	Methyl alcohol	methanol
$\text{CH}_3\text{-CH}_2\text{-OH}$	Ethyl alcohol	ethanol
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}$	n-propyl alcohol	1-propanol
$\begin{array}{c} \text{CH}_3\text{-CH-CH}_3 \\ \\ \text{OH} \end{array}$	Isopropyl alcohol	2-propanol
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$	n-butyl alcohol	1-butanol
$\begin{array}{c} \text{CH}_3\text{-CH}_2\text{-CH-CH}_3 \\ \\ \text{OH} \end{array}$	sec-butyl alcohol	2-butanol
$\begin{array}{c} \text{CH}_3\text{-CH-CH}_2\text{-OH} \\ \\ \text{CH}_3 \end{array}$	Isobutyl alcohol	2-methyl-1-propanol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \\ \\ \text{CH}_3\text{-C-OH} \\ \\ \text{CH}_3 \end{array}$	tert-butyl alcohol	2-methyl-2-propanol
$\text{CH}_2\text{=CH-CH}_2\text{-OH}$	Allyl alcohol	2-propene-1-ol

Dihydric alcohols

Alcohols which contain two -OH groups per molecule are called dihydric alcohols.

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Structural formula	Common name	IUPAC name
$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{CH}_2\text{-OH} \end{array}$	Ethylene glycol	1,2-Ethanediol

Trihydric alcohols

Alcohols which contain three -OH groups per molecule are called trihydric alcohols.

Structural formula	Common name	IUPAC name
$\begin{array}{c} \text{CH}_2\text{-OH} \\ \\ \text{CH-OH} \\ \\ \text{CH}_2\text{-OH} \end{array}$	Glycerol	1,2,3-propanetriol

Ethers

An ether is a substance that has two organic groups bonded to the same oxygen atom, **R-O-R'**. The organic group may be alkyl or aryl. When the groups attached to the oxygen atom are the same, they are termed as simple ethers. When the groups attached to the oxygen atom are different, they are termed as mixed ethers.

In IUPAC system, ethers are considered to be alkoxy derivatives of hydrocarbons.

Structural formula	Common name	IUPAC name
Simple ethers		
$\text{CH}_3\text{-O-CH}_3$	Dimethyl ether	Methoxymethane
$\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$	Diethyl ether	Ethoxyethane
Mixed ethers		
$\text{CH}_3\text{-O-CH}_2\text{-CH}_3$	Ethyl methyl ether	Methoxyethane
$\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-CH}_3$	Methyl n-propyl ether	1-methoxypropane
$\begin{array}{c} \text{CH}_3\text{-O-CH-CH}_3 \\ \\ \text{CH}_3 \end{array}$	Isopropyl methyl ether	2-methoxypropane

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Aldehydes

Aldehydes and ketones are two important classes of compounds containing the carbonyl group $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$. In aldehydes the $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$ group is

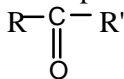
linked to an alkyl group and a hydrogen or two hydrogens. Aldehydes are represented by the general formula R-CHO .

IUPAC names of aldehydes are obtained by replacing the terminal "e" of alkane with "al".

Structural formula	Common name	IUPAC name
H-CHO	Formaldehyde	Methanal
$\text{CH}_3\text{-CHO}$	Acetaldehyde	Ethanal
$\text{CH}_3\text{-CH}_2\text{-CHO}$	Propionaldehyde	Propanal
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CHO}$	Butyraldehyde	1-Butanal
$\begin{array}{c} \text{CH}_3\text{-CH-CHO} \\ \\ \text{CH}_3 \end{array}$	Isobutyraldehyde	2-Methylpropanal

Ketones

In ketones $\text{—}\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{—}$ group is united with 2 alkyl groups. These compounds are represented by the general formula.



Ketones are named by replacing the terminal "e" of the corresponding alkane name with "one".

Structural formula	Common name	IUPAC name
$\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_3 \\ \\ \text{O} \end{array}$	Acetone (Dimethyl ketone)	Propanone
$\text{CH}_3\text{-CH}_2-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_3$	Ethylmethyl ketone	Butanone
$\text{CH}_3\text{-CH}_2-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_2\text{-CH}_3$	Diethyl ketone	3-pentanone

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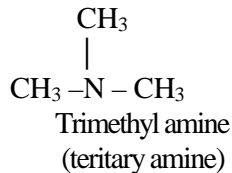
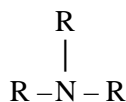
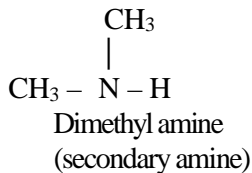
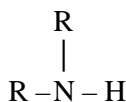
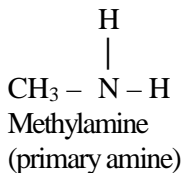
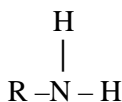
Carboxylic acids

These are represented by the general formula $R-COOH$. IUPAC name is derived by replacing the terminal "e" of the alkane name with "**oic acid**". These compounds are further classified into **mono-** and **di-**carboxylic acids.

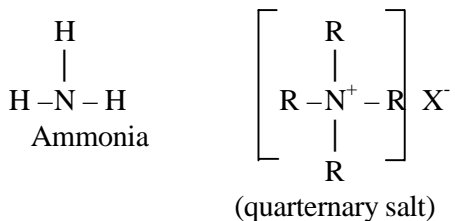
Structural formula	Common name	IUPAC name
Monocarboxylic acids		
$H-COOH$	Formic acid	Methanoic acid
CH_3-COOH	Acetic acid	Ethanoic acid
CH_3-CH_2-COOH	Propionic acid	Propanoic acid
$CH_3-CH_2-CH_2-COOH$	Butyric acid	Butanoic acid
Dicarboxylic acids		
$\begin{array}{c} COOH \\ \\ COOH \end{array}$	Oxalic acid	Ethanedioic acid
$\begin{array}{c} COOH \\ / \quad \backslash \\ CH_2 \\ \backslash \quad / \\ COOH \end{array}$	Malonic acid	Propanedioic acid
$\begin{array}{c} CH_2 - COOH \\ \\ CH_2 - COOH \end{array}$	Succinic acid	Butanedioic acid

Amines

Amines are the derivatives of ammonia in which one or more H-atoms have been replaced by alkyl groups. They are designated as primary, secondary and tertiary amines according as one, two or three hydrogen atoms in ammonia molecule have been replaced by alkyl groups.



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When one alkyl group is attached to N-atom, it is called primary amine, when two alkyl groups are attached to nitrogen atom, then it is called secondary amine. When three alkyl groups are attached to nitrogen atom it is called tertiary amine. When four alkyl groups are attached to nitrogen atom it is called quarternary salt.

Structural formula	Common	IUPAC name
Primary Amines		
$\text{CH}_3\text{-NH}_2$	Methyl amine	aminomethane
$\text{CH}_3\text{-CH}_2\text{-NH}_2$	Ethyl amine	aminoethane
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NH}_2$	n-propyl amine	1-aminopropane
$\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{NH}_2 \end{array}$	Isopropyl amine	2-aminopropane
Secondary Amines		
$\text{CH}_3\text{-NH-CH}_3$	Dimethyl amine	(N-methylamino) methane
$\text{CH}_3\text{-CH}_2\text{-NH-CH}_2\text{-CH}_3$	Diethyl amine	(N-ethylamino) ethane
$\text{CH}_3\text{-NH-CH}_2\text{-CH}_3$	Ethylmethyl amine	(N-methylamino) ethane

Structural formula	Common name	IUPAC name
Tertiary Amines		
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{N} \\ \\ \text{CH}_3 \end{array}$	Trimethyl amine	(N,N - dimethyl amino) methane
$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_2\text{H}_5 - \text{N} \\ \\ \text{CH}_3 \end{array}$	Ethyldimethyl amine	(N,N - dimethyl amino) ethane

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Nitro compounds

These compounds are represented by the general formula RNO_2 . IUPAC names are obtained by adding the prefix "nitro" to the alkane.

Structural formula Common/IUPAC name

- | | |
|---|----------------|
| 1. $\text{CH}_3 - \text{NO}_2$ | Nitromethane |
| 2. $\text{CH}_3 - \text{CH}_2 - \text{NO}_2$ | Nitroethane |
| 3. $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{NO}_2$ | 1-Nitropropane |
| 4. $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_3 \\ \\ \text{NO}_2 \end{array}$ | 2-Nitropropane |

15.5 Isomerism

The molecular formula of an organic compound represents only the number of different atoms present in a molecule. But the molecular formula does not tell about the arrangement of atoms. A given molecular formula may lead to more than one arrangement of atoms such that there are many compounds which may have same molecular formula but with different physical and chemical properties. This phenomenon in which the same molecular formula may exhibit different structural arrangement is called isomerism.

Compounds that have the same molecular formula but different structural formulae are called isomers (from the Greek word isos + meros, "made of the same parts").

There are two types of isomerism, namely,

1. Structural isomerism 2. Stereoisomerism

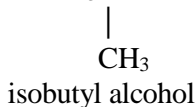
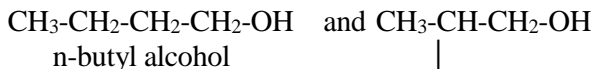
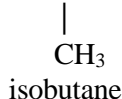
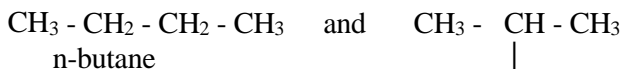
Structural isomerism

When two or more compounds possess the same molecular formula but different structural formulae, they are said to exhibit structural isomerism. Structural isomerism is divided into.

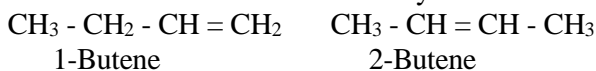
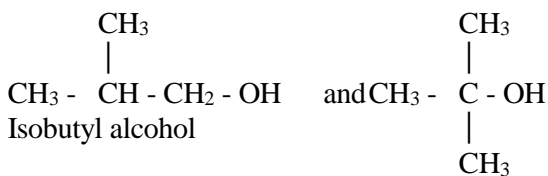
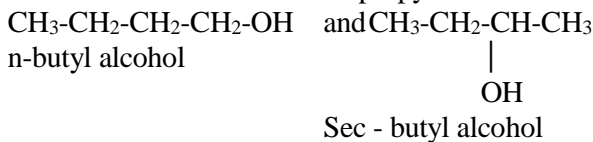
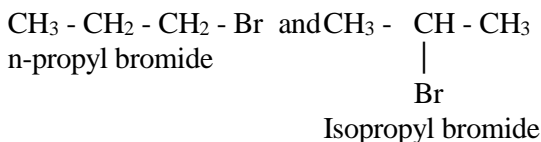
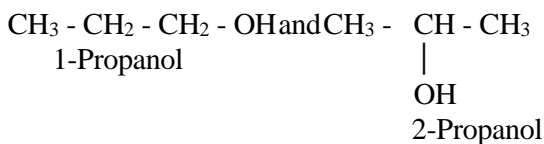
1. Chain isomerism or Nuclear isomerism

Chain isomers are compounds that have the same molecular formula but have different carbon skeletons.

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Examples**2. Position Isomerism**

Position isomers are compounds that have the same formula, carbon skeleton and functional groups but have the functional groups located at different positions along the carbon skeleton.



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Functional isomerism

Functional isomers are compounds that have the same molecular formula but have different functional groups.

Examples

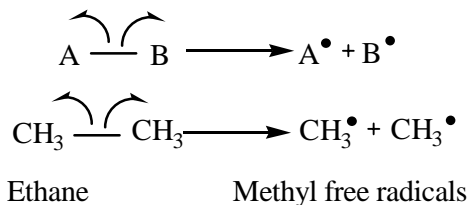
- $\text{CH}_3 - \text{CH}_2 - \text{OH}$ and $\text{CH}_3 - \text{O} - \text{CH}_3$
 Ethyl alcohol Dimethyl ether
- $\text{CH}_3 - \underset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{CH}_3$ and $\text{CH}_3 - \text{CH}_2 - \text{CHO}$
 Acetone Propionaldehyde
- $\text{CH}_3 - \text{CH}_2 - \text{COOH}$ and $\text{CH}_3 - \text{COO} - \text{CH}_3$
 Propionic acid Methyl acetate

15.6 Fission of bonds**How bond fission occurs?**

A covalent bond (σ bond) joining two atoms exist because of the shared pair of electrons. When two atoms are separated from each other, bond fission is said to have taken place. The fission process can take place in two ways.

Homolytic fission

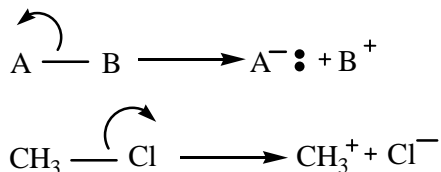
A covalent bond between two atoms A and B may be shown as $\text{A} \cdot \cdot \text{B}$ or $\text{A}-\text{B}$. This bond may undergo fission in such a way that each atom retains the electrons of the shared pair. Such species are known as **free radicals** or odd electron molecules.

**Heterolytic fission**

A covalent bond breaks in such a way that the shared pair of electron

ADVANCED LEVEL CHEMISTRY NOTES BK 1

stay on any one of the atoms. Breaking of the bond in this manner is known as heterolytic fission or heterolysis.



The atom or group which carries the unshared pair of electrons are represented with a negative sign as A^- : is known as anions. The carbonium ion carries the positive charge which lacks a pair of electrons. Heterolysis occurs only when the initially bonded atoms are of different in electronegativities and in that the electron pair becomes attached to the more electronegative atom.

An organic reaction may be represented as :

Reactants + attacking agent \rightarrow [intermediate] \rightarrow product

Depending upon the nature of the reaction which the intermediate species undergo, the reactions of the organic compounds are classified as substitution reactions, addition reactions, elimination reactions, polymerisation reactions, condensation reaction, hydrolysis, oxidation and reduction reactions.

15.7 Types of Reactions

Substitution or Displacement reactions

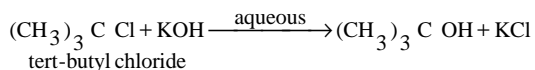
Displacement reaction is one in which an atom or group linked to a carbon atom is removed and in its place another atom or group is attached.

The substitution reactions are classified into three types.

a) Nucleophilic substitution reaction (S_N)

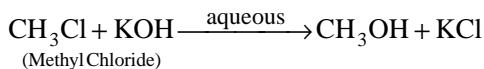
When a substitution reaction is brought about by a nucleophile, the reaction is termed as S_N (S stands for substitution and N for nucleophile). These reactions are divided into two classes :

(1) S_N^1 (substitution, nucleophilic, unimolecular)



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(2) S_N^2 (Substitution, nucleophilic, bimolecular)

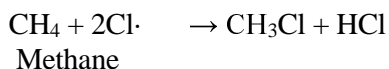
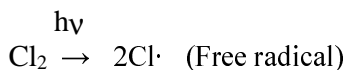


b) Electrophilic substitution reaction (S_E)

When a substitution reaction involves an attack by an electrophile, the reaction is referred to as S_E (S - stands for substitution and E for electrophile).

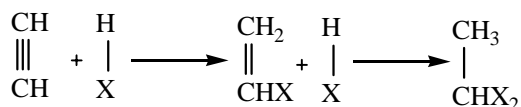
c) Free radicals substitution reaction

These reactions are initiated by free radicals.



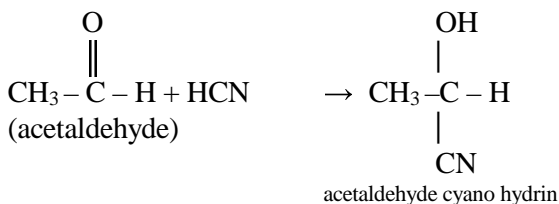
Addition Reactions

All organic compounds having double or triple bond adopt addition reactions in which two substances unite to form a single compound.

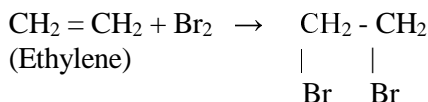


Depending on the type of reagent initiating these reactions, addition reactions are classified into three types.

(a) Nucleophilic addition

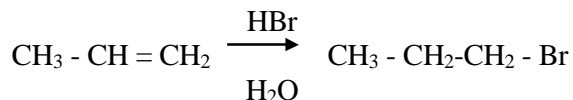


(b) Electrophilic addition



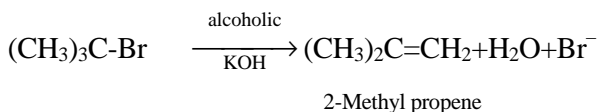
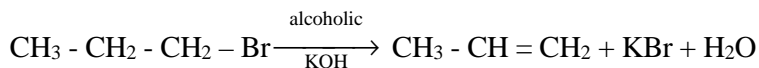
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(c) Free radical addition



Elimination reactions

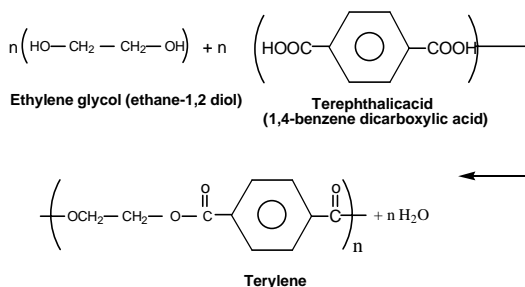
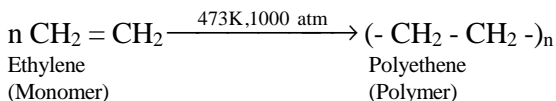
In these reactions, two atoms or groups are removed from a molecule without being substituted by other atoms (or) groups. The reverse of addition reactions are eliminations. These reactions are classified into two types.

(a) Unimolecular elimination (E_1)(b) Bimolecular elimination (E_2)

Polymerisation

The union of two or more molecules to form a large single molecule is called **polymerisation** and the product is a polymer.

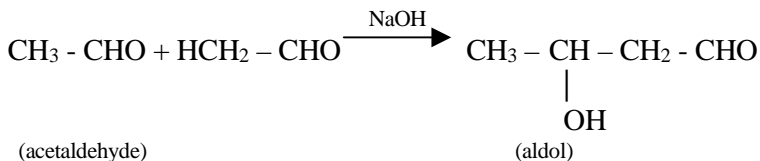
Examples



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Condensation reactions

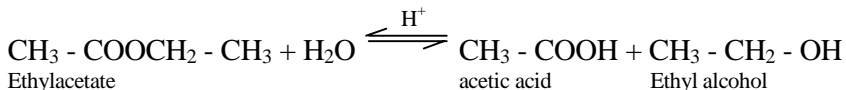
When two molecules (similar or different) combine to form a single molecule with or without the elimination of simple molecules like H_2O , NH_3 , HCl , CO_2 , it is called a **condensation** reaction.

Example**Aldol condensation reaction****Hydrolysis**

Esters are hydrolysed by boiling with mineral acids or alkalis.

a) Acid hydrolysis

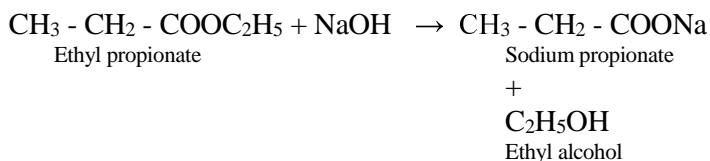
An ester can be hydrolysed to give the parent carboxylic acid and alcohol by using mineral acid (H_2SO_4 or HCl) as catalyst.



The above reaction is reversible and is exactly opposite of esterification. In order to hydrolyse most of the ester, the equilibrium must be pushed to the right by using large excess of water.

b) Basic hydrolysis

When an ester is treated with an alkali (NaOH or KOH) as catalyst, the hydrolysis yields the parent alcohol and sodium salt of the carboxylic acid.

**Reduction and oxidation reactions**

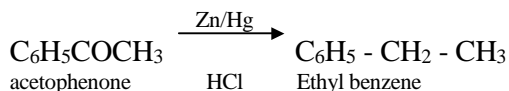
A reaction which proceeds by the addition of hydrogen is termed

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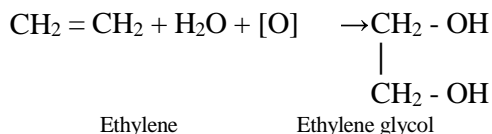
Reduction and the one that involves the addition of oxygen is called **Oxidation**. For example,

1) **Clemmensen Reduction**

Ketones can be reduced to their corresponding hydrocarbons by the mixture of Zn/Hg and conc. HCl.



2) Very mild oxidising agent such as KMnO_4 , causes a splitting of the molecule at the double bond.



15.7.1 Types of Reagents

Electrophilic reagents

These reagents are electron deficient. This deficiency accounts for their affinity for electrons (electro = electron, philic = loving). They are also called cationic reagents and may carry positive charge or have incomplete valence shells. These reagents can therefore, be of two types.

- (i) Positive electrophiles (or) Ionic electrophiles
- (ii) Neutral electrophiles

Some common electrophiles are given in the table

S. No.	Ionic electrophiles	Neutral electrophiles (Lewis acids)
1.	H^+ (proton)	AlCl_3
2.	Cl^+ (chloronium)	BF_3
3.	Br^+ (bromonium)	ZnCl_2
4.	NO_2^+ (Nitronium)	FeCl_3
5.	$>\text{C}^+$ carbonium	SO_3

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Nucleophilic reagents

Nucleophiles or nucleophilic reagents are electron rich substances containing atoms which have at least an unshared pair of electron. These reagents are nucleus loving (nucleo = nucleus, philic = loving). Nucleophiles can be (i) negatively charged (or) Ionic (ii) neutral species (Lewis bases). Some of the common nucleophiles are reported in table

S. No.	Neutral nucleophiles (Lewis bases)	Ionic nucleophiles
1.	NH ₃	X ⁻ (halide ions)
2.	H ₂ O	OH ⁻ (hydroxide)
3.	R-OH	RO ⁻ (alkoxide)
4.	R-NH ₂	CN ⁻ (cyanide)
5.	R ₃ -N	<C ⁻ (carbanion)

The differences between these reagents are summarised in the following table.

S. No.	Electrophiles	Nucleophiles
1.	are electron deficient	are electron rich
2.	are cations	are often anions
3.	are Lewis acids	are Lewis bases
4.	accept an electron pair	donate an electron pair
5.	attack on electron rich sites	attack on electron deficient sites
6.	possess an empty orbital to house the lone pair from the nucleophiles	possess a minimum of one lone pair of electron.

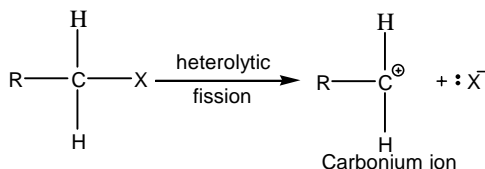
15.7.2 Carbonium ions

Let us consider the heterolytic fission of the bond C – X present in an organic molecule. If the atom X has greater electronegativity than the carbon atom, the former takes away the bonding electron pair and becomes negatively charged while the carbon will lose its electron and thus acquire a positive charge. Such cationic species carrying a positive charge on carbon

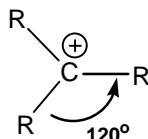
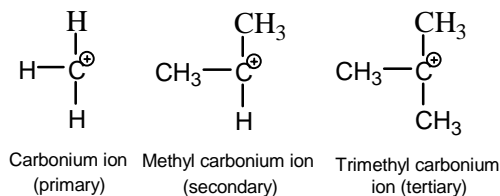
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are known as carbonium ions.

For illustration



These carbonium ions are called primary, secondary and tertiary depending up on the nature of the carbon atom bearing the charge.



The geometry of alkyl carbonium ion

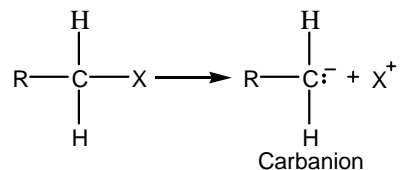
Since the carbon of the carbonium ion is in sp^2 hybridised state, the ion is planar with a vacant p orbital perpendicular to the plane of the three covalent bonds to carbon.

Carbanion

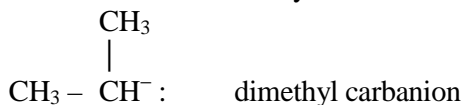
Let us consider the heterolytic fission of the bond C - X present in an organic molecule. If the carbon atom has greater electronegativity than the atom X, the former takes away the bonding electron pair and acquires a negative charge. The resulting carbon anion is known as carbanion.

ADVANCED LEVEL CHEMISTRY NOTES BK 1

For illustration



Examples



15.8 Free Radicals

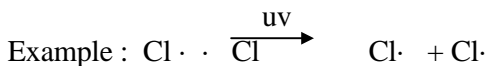
Free radicals are species with one or more unpaired electrons obtained by the homolytic fission of covalent bond. The free radicals themselves are electrically neutral. The free radicals are denoted by putting a dot against the atom or group of atoms.

Few examples : $\text{Cl}\cdot$, $\text{CH}_3\cdot$, $\text{C}_6\text{H}_5\cdot$

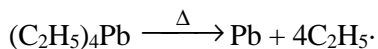
They are classified as short lived free radicals and long lived free radicals on the basis of their life time.

Formation of free radicals

(a) Photochemical fission : When an organic compound is exposed to ultraviolet region it under goes bond fission.



(b) Thermal fission : All organic compounds on heating yield free radicals.



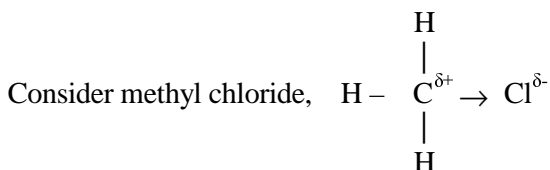
Polar Effects

Inductive Effect

If a covalent bond is formed by two atoms differing much in electronegativity then the bond is said to be polarised. The electron pair

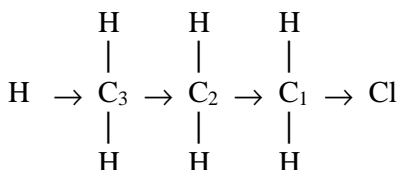
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shifts towards the more electronegative atom resulting in the origin of fractional charges on the atoms.



In this molecule, chlorine atom is more electronegative than the carbon atom. Due to this, chlorine pulls the electron pair and acquires a small negative charge.

Let us consider, 1 - chloropropane



As C_1 is positively charged, it attracts towards itself the electron pair shared between C_1 and C_2 . This causes C_2 to acquire a small positive charge but the charge is smaller than the charge on C_1 . This type of electron displacement occurring in saturated compounds along a carbon chain is termed, inductive effect.

It is a permanent effect and decreases rapidly as the distance from the electronegative atom increases. It is represented by \rightarrow the arrow head pointing towards the more electronegative atom. This effect operates in the case of σ - electrons only.

For measurements of relative inductive effect, atoms or groups having greater electron affinity than hydrogen are said to have - I effect. Similarly, atoms or groups having lesser electron affinity than hydrogen are said to have + I effect. Some of the atoms and groups arranged in the increasing order of inductive effect are given as

Groups having - I effect [electron - attracting].

- C_6H_5 , OH , I , Br , Cl , F

Groups having + I effect [electron pumping]

ADVANCED LEVEL CHEMISTRY NOTES BK 1

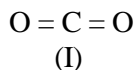
CH₃ -, CH₃ - CH₂ -, (CH₃)₂CH-, (CH₃)₃C -

(Methyl) (Ethyl) Isopropyl tertiarybutyl

Resonance (Mesomeric) Effect

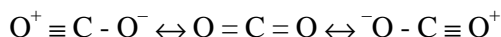
When several structures may be assumed to contribute to the true structure of a molecule but none of them can be said to represent it uniquely, then the molecule is referred to as a resonance hybrid and the phenomenon is termed as resonance.

It is somewhat abstract, but it can be better understood if we consider the structure of a simple molecule carbon dioxide.



The above structure does not account for all observed properties although it can explain many. The C-O bond length in CO₂ molecule is 1.15 Å where as it is expected to be 1.22 Å on the basis of the above structure.

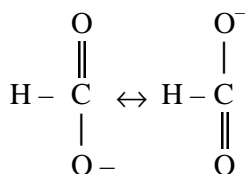
Again, the heat of formation of carbon dioxide is 1592 kJ.mol⁻¹ where as on the basis of the above structure it is expected to be approximately 1466 kJ.mol⁻¹. These discrepancies can be explained only if we assume the following resonance hybrid for carbon dioxide.



The difference in energy i.e. 126 KJ.mol⁻¹ is regarded as resonance energy.

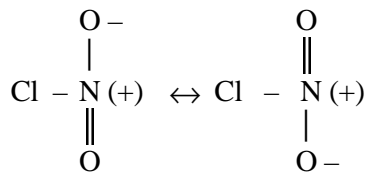
Few other examples

1. Formate ion, HCOO⁻

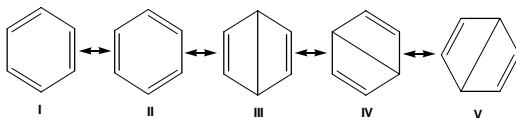


2. Nitryl chloride, NO₂Cl

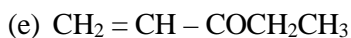
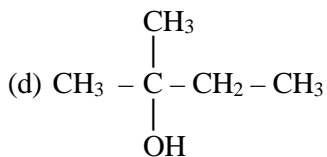
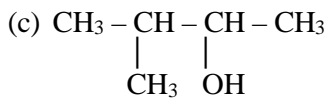
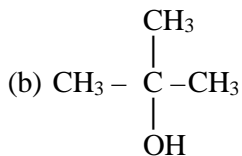
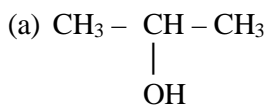
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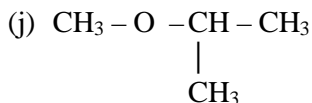
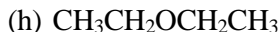
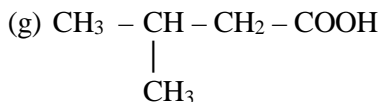
3.



Benzene

Questions**A. Write IUPAC name of the following**

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**B. Explain briefly on the following**

1. Homolytic and heterolytic fission.
2. Substitution reaction.
3. Addition reaction.
4. Elimination reaction.
5. Polymerisation reaction.
6. Condensation reaction.
7. Hydrolysis.
8. Reduction and oxidation reactions.
9. Electrophilic and Nucleophilic reagents.
10. Carbonium ions and carbanions.
11. Free radicals.
12. Inductive effect.
13. Resonance effect.

SUMMARY

- This chapter explains the ability of carbon atoms to form long chains held together by strong carbon-carbon bonds, catenation.
- Characteristics of homologous series and structural isomers are explained.

ADVANCED LEVEL CHEMISTRY NOTES BK 1

- Method of writing IUPAC names of different organic compounds are explained with suitable examples.
- All types of organic reactions, like substitution, addition, elimination, condensation, polymerisation, hydrolysis, oxidation and reduction reactions are explained with suitable examples.
- Different types of isomerism and the representations are explained.
- Nature of fission of bonds, reagents, carbonium ions carbanions and free radicals are structurally explained with suitable examples.
- Notable electron displacements in organic chemistry like inductive and mesomeric effect in covalent bond are explained.

REFERENCES

1. Advanced Organic Chemistry by I.L.Finar.
2. Organic Chemistry by Bahl and Arun Bahl.

16. PURIFICATION OF ORGANIC COMPOUNDS

OBJECTIVES

The main objectives of this chapter are to provide

- * *Characteristics of organic compounds*
- * *Need for purification*
- * *Methods of purifying organic substances like crystallisation, distillation, fractional distillation, steam distillation, distillation under reduced pressure and various methods of chromatography.*

16.1 Characteristics of organic compounds

Organic compounds have the following general characteristics.

- i) Organic compounds are generally covalent and hence they do not dissolve in water (polar solvents) but dissolve in organic solvents (non-polar solvents) such as ether, alcohol, benzene etc.
- ii) Due to maximum catenation and tetravalency of carbon, they have tendency to form long open and closed chain compounds.
- iii) They are volatile, inflammable and possess low boiling points and melting points.
- iv) Some organic compounds exhibit the phenomenon of polymerisation. For example, ethylene polymerises to poly ethylene.
- v) They exhibit isomerism.
- vi) They contribute homologous series.
- vii) They are non-conductors of electricity.

Need for purification of organic compounds

The organic compounds obtained from natural sources are not pure. They contain a number of other compounds which occur with them. Similarly, the organic compounds prepared in the laboratory are also not pure. They are found to contain other products formed during the reaction. In order to investigate the structure and properties of an organic compound, it should be in the purest form. Hence purification of organic compounds become essential.

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Various methods used for purification and separation of organic compounds are:

- i) Crystallisation
- ii) Fractional Crystallisation
- iii) Sublimation
- iv) Distillation
- v) Extraction with solvents
- vi) Chromatography

16.2 Crystallisation

Crystallisation is carried out in four stages (a) preparation of the solution of the substance in a suitable solvent (b) filtration of the hot solution (c) crystallisation by cooling the hot filtrate (d) isolation and drying of the purified substance.

a) Preparation of the solution : The powdered organic substance is taken in a semi-micro round bottom flask and the solvent is added little by little with constant stirring and heating till the amount added is just sufficient to dissolve the solute, when the solution is just boiled. If the solvent is non-inflammable, heating may be done on the wire gauze, while in the case of inflammable solvents, heating should be done on a water bath.

b) Filtration of the Solution : The hot saturated solution obtained is filtrated through a fluted filter paper placed in a hot water funnel.

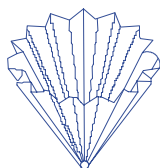


Fig. 16.1 Fluted Filter paper

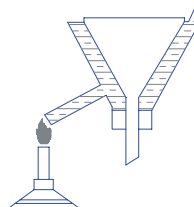


Fig. 16.2 Water funnel

ADVANCED LEVEL CHEMISTRY NOTES BK 1

c) Crystallisation : When the filtration is over, the beaker containing the solution is allowed to cool when pure crystals separate. Sometimes the crystals do not separate due to super cooling of the solution. Crystallisation can be started in such cases by scratching the sides of the vessel containing the solution with a glass rod or seeding with a tiny crystal of the substances.

d) Isolation and drying of the purified crystals : The purified crystals are separated from the mother liquor by filtration using Buchner funnel and a suction pump.

When the whole of the mother liquor has been drained off, the crystals are washed with small amounts of cold solvent thrice. The crystals are then transferred to a porous plate, pressed by using filter paper and then dried by using infra-red light or by keeping in sunlight. If the crystals are coloured, decolourisation is effected by using animal charcoal.

Fractional Crystallisation

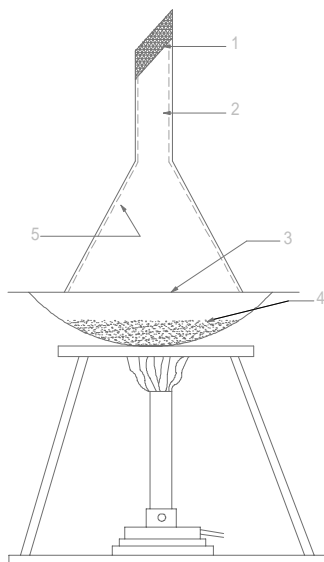
When the solubility of two substances in any solvent is not much different from one another, then the two compounds can be separated by fractional crystallisation, involving a series of repeated crystallisations. For example, when a solution containing two substances A and B is subjected to crystallisation, the slightly less soluble substances (say A) containing a small amount of the other substance (B) crystallises out. The mother liquor when subjected to crystallisation gives crystals of B containing a small amount of A.

Now, if these crystals are subjected to recrystallisation separately and the process is repeated number of times to get pure A and pure B.

16.3 Sublimation

Certain solid substances like Naphthalene or camphor when heated pass directly from solid to the vapour state without melting. The vapours when cooled give back the solid substance. This process is known as sublimation.

ADVANCED LEVEL CHEMISTRY NOTES BK 1



- | | |
|------------------------------|--------------------|
| 1. Cotton | 2. Inverted funnel |
| 3. Perforated asbestos sheet | 4. Mixture |
| | 5. Sublimate |

Fig. 16.3

This process is very helpful in separating a volatile solid from a non-volatile solid. The powdered substance is taken in a China dish and covered with a perforated filter paper and an inverted funnel. The dish is carefully heated on a sand bath.

The vapours passing through the holes in the paper condense on the inner sides of the funnel. The non-volatile impurities remain in the dish.

16.4 Methods for the purification of liquids Distillation

Distillation is used for separating the constituents of a liquid mixture which differ in their boiling points. Depending upon the difference in the boiling points of the constituents, different types of distillation are employed. These are described below.

i) Simple Distillation

Liquids with boiling points widely apart (about 40K and above) can be purified by simple distillation if they do not decompose under ordinary pressure. Simple distillation involves conversion of a liquid into its vapour

ADVANCED LEVEL CHEMISTRY NOTES BK 1

by heating in a distilling flask and then condensation of the vapour into a liquid in the receiver.

Mixtures like the following can be separated by this simple distillation.

- a Nitro benzene (b.p 484K) and benzene (b.p.354K)
- b. Diethyl ether (b.p.308K) and ethyl alcohol (b.p.351K)

Note : Simple distillation is also helpful in separating non-volatile impurities from liquids.

16.4.1 Fractional Distillation

This method is applicable for the separation and purification of a mixture of two or more miscible liquids whose boiling points lie very close to each other.

This is similar to the ordinary distillation method with the only exception that a fractionating column is introduced in-between the distillation flask and the condenser.

The process of separation of the components in a liquid mixture at their respective boiling points in the form of vapours and the subsequent condensation of those vapours is called fractional distillation.

The fractionating columns used for the purpose are of different shapes.

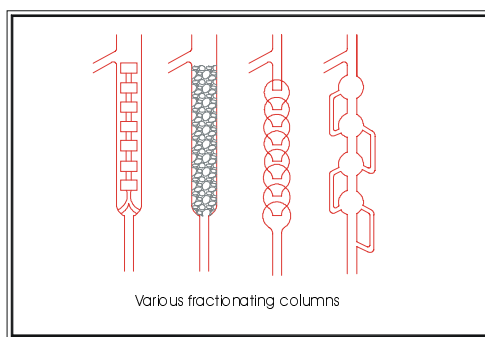


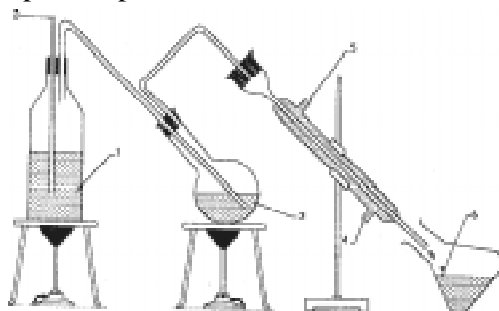
Fig. 16.4

16.4.2 Steam Distillation

In steam distillation impure compounds are distilled in a current of steam. This method is applicable to solids as well as liquids. For purification by steam distillation, an impure compound must satisfy the following conditions:

ADVANCED LEVEL CHEMISTRY NOTES BK 1

- i) It should not decompose at the steam temperature.
- ii) It should have a fairly high vapour pressure at 373 K.
- iii) It should be insoluble in water.
- iv) The impurities present should be non-volatile

**Fig. 16.5**

- | | | | |
|---------------------|--------------------|----------|--------------------|
| 1. Water | 2. Protective tube | 3. Flask | 4. Inlet for water |
| 5. Outlet for water | 6. Pure liquid | | |

The apparatus used for steam distillation is shown in the figure (16.5). The impure compound is taken in the round bottomed flask and a small quantity of water is added. The flask is then heated gently. Now steam is bubbled through the contents in the flask. The vapours of the compound mix up with steam and escape into the condenser. The condensate thus obtained is a mixture of water and the organic compound which can be separated.

Theory of steam distillation

Let p_1 represent the vapour pressure of water and p_2 the vapour pressure of the organic liquid. In steam distillation the liquid boils at a temperature at which

$$p_1 + p_2 = \text{Atmospheric Pressure}$$

This temperature must be lower than the normal boiling point of water or the organic liquid. The reason that $p_1 + p_2$ becomes equal to the atmospheric pressure must earlier than p_1 or p_2 alone. Thus in steam distillation, the impure liquid boils at a temperature which is lower than its normal boiling point. Hence, steam distillation serves the same purpose as

ADVANCED LEVEL CHEMISTRY NOTES BK 1

distillation under reduced pressure. However, the former is cheaper but less useful than the latter.

16.4.3 Distillation under reduced pressure

This technique is used for purifying or separating thermally unstable liquid compounds which decompose at their normal boiling points.

Principle : Lowering of pressure on the surface of a liquid lowers its boiling point. As a result, a liquid can be boiled and distilled at a temperature much below the normal boiling point without any decomposition.

Procedure : Distillation under reduced pressure or vacuum is carried out in a specially designed glass apparatus as shown in (Fig.17.6).

The receiver is attached to a vacuum pump to reduce pressure. The pressure is measured with the help of a manometer.

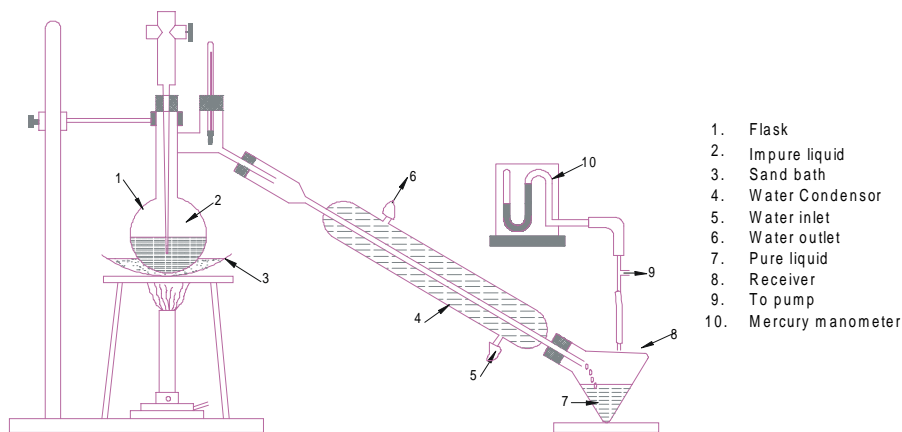


Fig.16.6 Distillation under reduced pressure

Advantages of distillation under reduced pressure

Distillation under reduced pressure has the following advantages:

ADVANCED LEVEL CHEMISTRY NOTES BK 1

- i) The compounds which decompose on heating to their boiling points under normal pressure can be purified by distillation under reduced pressure. This is because at a reduced pressure, a liquid would boil at temperature much below its normal boiling point.
- ii) In distillation under reduced pressure, a liquid boils at temperature well below the normal boiling point. So, the distillation under reduced pressure is more fuel-economical.

16.4.4 Extraction with solvents

This method is based on the fact that organic substances are more soluble in organic solvents than in water.

The organic substance is extracted from its aqueous solution adopting the following procedure.

- a. The aqueous solution containing organic substance is shaken with a suitable organic solvent which dissolves the substance but is immiscible with water. Two layers are formed; the organic layer and aqueous layer.
- b. The solvent layer containing the organic substance (organic layer) is separated using a 'separating funnel'. The impurities remain in the aqueous layer removed by distillation to obtain the organic substance.
- c. The organic solvent is removed by distillation to obtain the organic substance.

16.5 Chromatography

This technique was introduced by M.S.Tswett, a Russian botanist in 1906 when he reported the separation of different coloured constituents of chlorophyll. He achieved it by passing a petroleum ether solution of the chlorophyll present in leaves through a column of calcium carbonate firmly packed into a narrow glass tube. Different components of the pigment got separated into band or zones of different colours.

Chromatography is based on the general principle of distributing the components of a mixture of organic compounds between two phases - a stationary phase and a moving phase. The stationary phase can be a solid or liquid supported on a solid, while the moving phase is a liquid or a gas. When the stationary phase is a solid, the basis of separation is adsorption; when it is a liquid, the basis is partition.

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Hence, chromatography can be defined as the technique for the separation of a mixture of compounds where the separation is brought about by the differential movement of the individual compounds through a porous medium under the influence of a moving solvent. The technique has now a days undergone tremendous modification and is widely used for the separation and purification of different types of organic compounds.

The different chromatographic techniques used are : column chromatography (CC), thin-layer chromatography (TLC), paper chromatography (PC), gas-liquid chromatography (GLC) and ion-exchange chromatography.

a) Column Chromatography

The simplest chromatographic method is column chromatography. It is carried out in a long glass column having a stop-cock near the bottom. To start the operation, a plug of cotton or glass wool is placed at the bottom of the column to support the adsorbent powder. The tube is packed uniformly with suitable adsorbent. This constitutes what is known as the stationary phase. The commonly employed adsorbents are activated aluminium oxide (alumina), magnesium oxide, silica gel and starch. A loose plug of cotton or glass wool is then placed at the top of the adsorbent column.

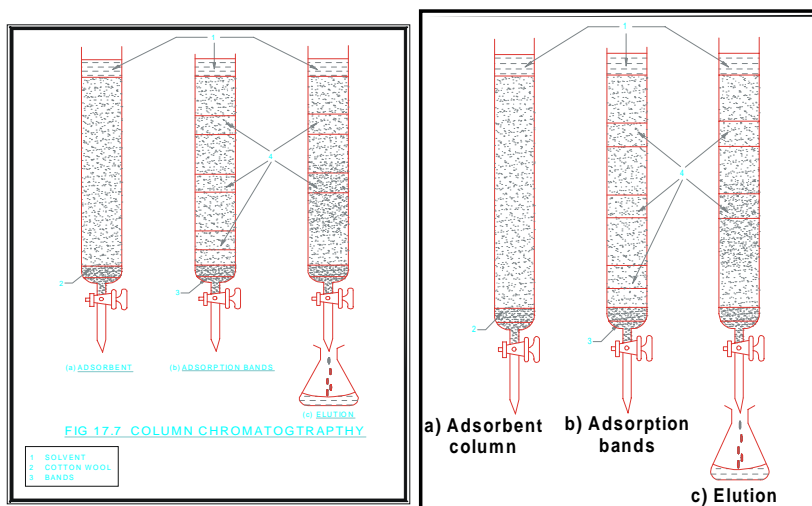


Fig. 16.7 Column chromatography

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The substance to be purified is added, as such if it is a liquid or in the form of its solution in some suitable solvent if it is a solid, at the top of the column and allowed to pass slowly through it. As it passes through the column, the different components of a mixture (Say A, B and C) got adsorbed to different extent and are thus retained by the adsorbent at different levels of the column. The components which are adsorbed very strongly are retained at the top while others are retained at lower levels. In this way different zones or bands are formed in the column which contain different components of a mixture. As soon as the last portion of the substances enter the column, a selected solvent, known as eluent, is added to the column. This acts as moving phase. The elements dissolve out the different components from the various zones selectively and thus 'take out' the different bands in the form of fractions which are collected separately.

b) Thin Layer Chromatography (TLC)

Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of the substances of a mixture over a thin layer of an adsorbent. 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. 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 solvent (Below 2cm height). As the solvent jar moves up the plate, the components of mixture move up along the plate to different distances depending on this degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its retention factor ie., R_f Value.

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

c) Paper Chromatography

It is an important and useful class of partition chromatography. In this technique, the stationary phase is considered to be made up of water molecules bound to the cellulose network (inert support) of the paper. The mobile phase, known as the developing solvent consists of either one solvent or a mixture of different solvents. Separation of the mixture into pure compounds takes place by the partitioning of different compounds

ADVANCED LEVEL CHEMISTRY NOTES BK 1

between these two liquid phases. The mobile phase travels by capillary action through the paper. Depending upon the way the solvent travels on the paper, there are three types of paper chromatography.

- i) Ascending Paper Chromatography : The mobile phase moves upwards on the paper strip in this case.
- ii) Descending Paper Chromatography : The mobile phase in this case moves downward on the paper strip.
- iii) Circular or radial paper chromatography: The mobile phase moves horizontally along a circular sheet of paper in this case.

In the ascending paper chromatography, the mixture of compounds is applied on the paper as a spot little above the lower end and then this end is dipped in the solvent. When the solvent has risen more than two third length of the paper, then it is removed from the solvent. The paper is dried and is known as chromatogram.

Now the spots for different compounds can be visualised using some suitable chemicals. The ratio of the distance travelled by the compound in a particular solvent to that the distance travelled by the solvent is a constant and is known as retention factor (R_f). This value is used in identifying the compounds.

$$R_f = \frac{\text{Distance travelled by the compound}}{\text{Distance travelled by the solvent}}$$

Type of Chromatography	Stationary Phase	Mobile Phase
1. Column Chromatography	Solid	Liquid
2. Thin Layer Chromatography (TLC)	Solid	Liquid
3. Paper Chromatography	Liquid	Liquid
4. Gas Liquid Phase Chromatography	Liquid	Gas

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Difference between paper chromatography and thin layer chromatography

Paper Chromatography	Thin Layer Chromatography
(i) Separation based on partition	Separation is based on partition, adsorption and ion exchange.
(ii) Stationary phase is the water molecules bound on the paper.	Stationary phase is a layer of silica gel or alumina on glass plate.

Questions

A. Choose the best answer

- Organic compounds are soluble in
 - Non-polar Solvents
 - Polar solvents
 - Water
 - HCl
- Decolourisation of coloured compounds can be effected by using
 - Animal charcoal
 - Carbon
 - Coke
 - Infra-red rays
- Compounds having boiling points widely apart 40 K and above can be purified by
 - Crystallisation
 - Simple distillation
 - Fractional distillation
 - Sublimation
- Nitrobenzene and benzene can be separated by the method of
 - Steam distillation
 - Crystallisation
 - Fractional crystallisation
 - Chromatography
- Purification of two miscible liquids possessing very close boiling points can be separated using
 - Fractional distillation
 - Sublimation
 - Simple distillation
 - Steam distillation
- Purification of mixture of compounds can be done by steam distillation only if the impurities are
 - Non-volatile
 - Volatile
 - Insoluble in Water
 - both a & c
- When the stationary phase is solid, then the compounds can be separated on the basis of
 - Adsorption
 - Partition
 - Both partition and adsorption
 - Either
- Column Chromatography is based on the principle of
 - Adsorption
 - Partition
 - Absorption
 - Distribution
- In Ascending paper Chromatography, the solvent moves
 - Upwards
 - Downwards
 - Horizontally
 - None
- The existence of wide range of organic compounds is due to their, property of
 - Extensive catenation
 - Lower boiling points
 - Polymerisation
 - Isomerism

ADVANCED LEVEL CHEMISTRY NOTES BK 1**B. Fill in the blanks**

1. The Compounds separated and purified by crystallisation can be dried over _____.
2. Camphor can be purified by the process of _____.
3. In simple distillation the compounds should not decompose at _____.
4. Water insoluble compounds can be purified by _____.
5. In T.L.C the stationary phase is a _____.
6. Chromatographic technique was first introduced by _____.
7. In paper chromatography, the mobile phase travels by _____ action through the paper.
8. The adsorbent used in column Chromatography method is _____.
9. In Chromatographic technique, the separation of compounds are brought about by _____ movement of the compounds.
10. Paper Chromatography is _____ Chromatography.

C. Write in one or two sentence

1. What are the different stages followed during Crystallisation?
2. Define steam distillation.
3. What are different types of distillation?
4. Give the advantages of distillation under reduced pressure.
5. What are the types of paper chromatography?

D. Explain briefly on the following

1. Explain the method of purifying a solid organic compound.
2. Write short notes on
a) Fractional crystallisation b) Solvent extraction
3. Explain the purification of compounds by using thin layer chromatography.
4. What are the various principles used in chromatographic separation?
5. Write down the general characteristics of organic compounds.

SUMMARY

All organic compounds must be purified before study. There are various purification methods adopted. Depending on the physical and chemical properties of the organic compounds, purification methods are done. Methods like crystallization, sublimation, distillation, solvent extraction and chromatographic techniques are dealt in detail in this chapter.

REFERENCES

1. Organic Chemistry by Bahl and Arun Bahl.
2. Organic Quantitative Analysis by Arthur I Vogel, ELBS edition.

17. DETECTION AND ESTIMATION OF ELEMENTS

OBJECTIVES

The main objectives of the chart are to provide

- * *Detection and estimation of carbon, hydrogen, nitrogen, sulphur and halogens.*
- * *The various methods for the detection and estimations are discussed in detail.*

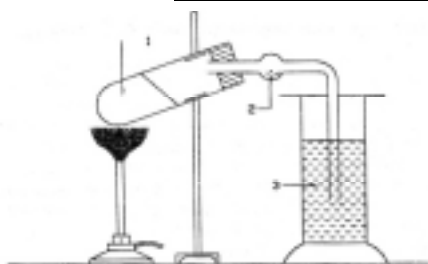
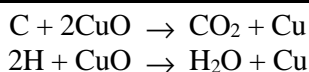
17.1 Qualitative Analysis

Qualitative analysis of an organic compound involves the detection of various elements present in it. The elements commonly present in organic compounds are carbon, hydrogen, oxygen, nitrogen, halogens and sulphur and sometimes phosphorous. The carbon and hydrogen are present in almost all the organic compounds.

A) Detection of carbon and hydrogen

The detection of carbon and hydrogen in an organic compound is done by a single experiment.

A small quantity of pure and dry compound is mixed with about ten times its weight of copper oxide (CuO). The mixture is taken in a hard glass test tube fitted with a delivery tube having a small bulb. The other end of the tube is immersed in freshly prepared lime water. In the bulb of delivery tube, a small amount of anhydrous copper sulphate (white) is placed. The mixture is heated strongly when carbon and hydrogen present are oxidised to carbon dioxide and water respectively.

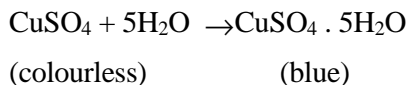
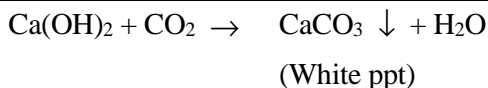


1. Organic Compound + Copper (II) oxide
2. Anhydrous copper sulphate
3. Lime water

Fig. 17.1

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Carbon dioxide turns **lime water milky** and the water vapour turns colourless copper sulphate, blue.



Turning of lime water milky and of colourless copper sulphate blue shows the **presence of carbon and hydrogen** respectively.

B. Detection of Oxygen

There is no direct method for the detection of oxygen in organic compounds. It is detected indirectly. For example,

- If any organic compound on heating in a dry test tube, gives out water vapour, then the presence of oxygen in the organic compound is indicated.
- If any organic compound is found to contain any oxygen containing functional groups such as - OH, -CHO, -COOH, -NO₂ etc., then the compound contains oxygen.
- If the sum of the percentages of various elements present in the compound is less than 100, then the compound contains oxygen.

C) Detection of nitrogen, sulphur and halogens

All these can be detected by **Lassaigne's Test**.

Lassaigne's Test : The organic compound is taken in an ignition tube. A pea-size sodium metal is added to it and heated to red hot. The hot tube is crushed to powder under a few ml of water in a mortar. The solution is filtered and the filtrate is known as 'sodium extract' or '**lassaigne's filtrate**'. The filtrate is used for the detection of the elements.

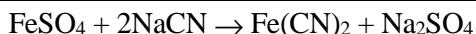
Nitrogen : During fusion, the carbon and nitrogen of the organic compound combine with sodium metal forming sodium cyanide.



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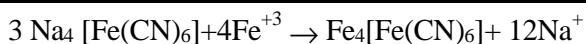
The unreacted sodium combines with water forming caustic soda, so the solution becomes alkaline.

Test : To the extract, ferrous sulphate solution is added and warmed. Sodium ferrocyanide is formed.



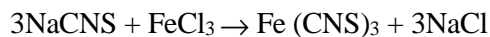
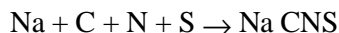
sodiumferrocyanide

A few drops of **ferric chloride** are added to it and the solution is **acidified with dilute sulphuric acid**. The ferric ions react with sodium ferrocyanide giving a bright blue (prussion blue) coloration



ferric ferrocyanide
(prussion blue)

Test : If an organic compound contains nitrogen along with sulphur, a blood red colour will be obtained in the above test.

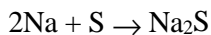


(Ferric sulphocyanide)

(blood red colour)

Sulphur

Organic compounds containing sulphur give sulphide on fusion with sodium.



Test : To the Lassaigne's filtrate, sodium nitroprusside is added. **Purple colour** is developed.



sodium nitroprusside

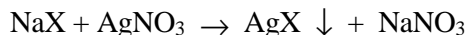
purple

ADVANCED LEVEL CHEMISTRY NOTES BK 1

Halogens : In sodium extract, the halogen is present as sodium halide.



Test : The extract is acidified with dilute nitric acid and silver nitrate solution is added. Formation of precipitate indicates the presence of halogen.



The halogen is identified from the **colour** and the **solubility** of the precipitate in ammonium hydroxide.

Sl. No.	Colour of the precipitate	Halogen present	Solubility in ammonium hydroxide
1.	White	chlorine	Easily soluble
2.	Pale yellow	bromine	Sparingly soluble
3.	Yellow	iodine	Insoluble

17.2 Quantitative analysis of organic compounds

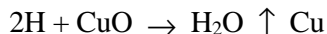
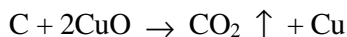
Once we have known the various elements present in any organic compound, the next point of interest is to know how much of each element is present in the compound. Determination of the relative proportions (generally as percentages) of various elements present in an organic compound is called **quantitative analysis of that compound**. For quantitative analysis, the percentages of the various elements present in any compound are estimated by suitable chemical methods.

(a) Estimation of carbon and hydrogen (liebig's combustion method)

The estimation of carbon and hydrogen is carried out in one experiment.

A known weight of the organic compound is strongly heated with excess of dry copper oxide in an atmosphere of dry and pure oxygen or air. Carbon of the compound is oxidised to carbon dioxide and hydrogen to water.

ADVANCED LEVEL CHEMISTRY NOTES BK 1



The CO_2 and H_2O are absorbed by a strong solution of **caustic potash** and **anhydrous calcium chloride** respectively. The percentage of carbon and hydrogen is calculated from the weights of CO_2 and H_2O obtained. These weights are obtained by finding the weights of caustic potash and calcium chloride tubes before and after the experiment.

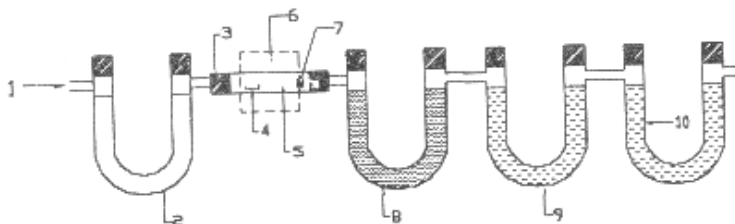


Fig.17.2

- | | | |
|--|---|--|
| 1. Oxygen supply | 2. Drying tube | 3. Glass joints |
| 4. Platinum boat with organic compound | 5. CuO | |
| 6. Combustion tube | 7. Copper coil to remove nitrogen oxide | |
| 8. CaCl_2 guard tube | 9. KOH tube | 10. To prevent the incoming CO_2 and H_2O |

Calculation

Let, weight of organic compound = wg

Increase in weight of CaCl_2 tube
(weight of water formed) = $w_1\text{g}$

Increase in weight of potash bulbs
(weight of carbon dioxide formed) = $w_2\text{g}$

Percentage of carbon

Molecular weight of $\text{CO}_2 = (12 + 32) = 44$

44 g of carbon dioxide contains, carbon = 12 g

$w_2\text{g}$ of carbon dioxide contains,

$$= \frac{12}{44} \times w_2\text{g carbon}$$

wg of compound contains

ADVANCED LEVEL CHEMISTRY NOTES BK 1

$$= \frac{12}{44} \times w_2 \text{ g of carbon}$$

∴ 100 g of compound contains

$$= \frac{12}{44} \times \frac{w_2}{w} \times 100 \text{ g of carbon}$$

$$\text{Percentage of carbon in the compound} = \frac{12}{44} \times \frac{w_2}{w} \times 100$$

Percentage of hydrogen

$$\text{Molecular weight of H}_2\text{O} = (2 + 16) = 18$$

$$18 \text{ g of water contains, hydrogen} = 2 \text{ g}$$

$$w_1 \text{ g of water contains, hydrogen} = \frac{2}{18} \times w_1 \text{ g}$$

wg of compound contains

$$= \frac{2}{18} \times w_1 \text{ g of hydrogen.}$$

∴ 100 g of compound contains

$$= \frac{2}{18} \times \frac{w_1}{w} \times 100$$

Example 1

0.30 g of a substance gives 0.88 g of carbon dioxide and 0.54 g water. Calculate the percentage of carbon and hydrogen in it.

Solution

$$\text{Weight of organic compound} = 0.30 \text{ g}$$

$$\text{Weight of carbon dioxide} = 0.88 \text{ g}$$

$$\text{Weight of water} = 0.54 \text{ g}$$

Percentage of carbon

$$44 \text{ g of carbondioxide contains, carbon} = 12 \text{ g}$$

ADVANCED LEVEL CHEMISTRY NOTES BK 1

$$0.88 \text{ g of carbon dioxide contains, carbon} = \frac{12 \times 0.88}{44} \text{ g}$$

$$0.30 \text{ g substance contains, carbon} = \frac{12 \times 0.88}{44} \text{ g}$$

100 g substance contains

$$= \frac{12 \times 0.88}{44} \times \frac{100}{0.30} = 80 \text{ g of carbon}$$

Percentage of carbon = 80

Percentage of hydrogen

$$18 \text{ g of water contains, hydrogen} = 2 \text{ g}$$

$$0.54 \text{ g of water contains, hydrogen} = \frac{2 \times 0.54}{18} \text{ g}$$

$$0.30 \text{ g of substance contains hydrogen} = \frac{2 \times 0.54}{18 \times 0.30} \text{ g}$$

$$100 \text{ g of substance contains} = \frac{2 \times 0.54}{18 \times 0.30} \times 100 \text{ g}$$

$$= 20 \text{ g of hydrogen}$$

$$\text{Percentage of hydrogen} = 20$$

(b) Estimation of oxygen

Oxygen is commonly estimated by the method of difference. The percentage of all other elements are added together and then subtracted from 100. The balance is the percentage of oxygen.

Example 2

0.2004 g of glucose gave on combustion 0.2940 g of CO_2 and 0.1202 g of H_2O . Find the percentage composition.

Solution

$$\text{Weight of organic compound} = 0.2004 \text{ g}$$

$$\text{Weight of carbon dioxide} = 0.2940 \text{ g}$$

$$\text{Weight of water} = 0.1202 \text{ g}$$

Percentage of carbon

$$44 \text{ g of } \text{CO}_2 \text{ contains, carbon} = 12 \text{ g}$$

ADVANCED LEVEL CHEMISTRY NOTES BK 1

$$0.2940 \text{ g of CO}_2 \text{ contains, carbon} = \frac{12 \times 0.2940}{44} \text{ g}$$

$$\text{Percentage of carbon} = \frac{12 \times 0.2940}{44} \times \frac{100}{0.2004} = 40.01$$

Percentage of hydrogen

$$18 \text{ g of H}_2\text{O contains, hydrogen} = 2 \text{ g}$$

$$0.1202 \text{ of H}_2\text{O contains, hydrogen} = \frac{2 \times 0.1202}{18}$$

$$\text{Percentage of hydrogen} = \frac{2 \times 0.1202}{18} \times \frac{100}{0.2004} = 6.66$$

Percentage of oxygen is therefore by difference,
 $= [100 - (40.01 + 6.66)] = 53.33$

Estimation of nitrogen**c) Kjeldahl Method**

This method is based on the fact that many nitrogenous organic compounds when heated with con. H_2SO_4 , are quantitatively converted into ammonium sulphate. The ammonium sulphate so obtained is heated with excess NaOH and the ammonia liberated is absorbed in a known volume of standard acid.

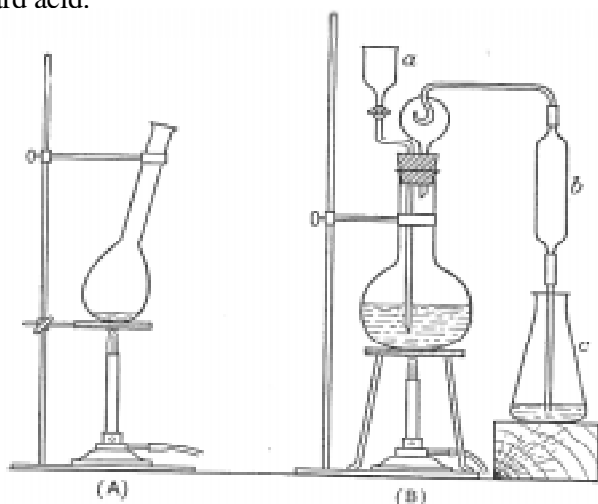
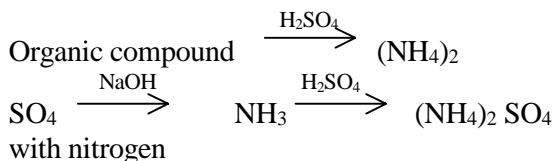


Fig. 17.3 Kjeldahl's method

ADVANCED LEVEL CHEMISTRY NOTES BK 1

From the volume of standard acid used by ammonia and the mass of organic compound taken for the experiment, we can calculate the mass of nitrogen in the compound.



Note : 1000 ml 1N acid \equiv 17 g $\text{NH}_3 \equiv$ 14 g nitrogen.

Calculation

Mass of the nitrogenous substance = W g

Volume of acid used up by NH_3 = V_1 ml

Normality of acid = N_1

Volume of 1 N acid = V_1 N

$$\text{Mass of nitrogen} = \frac{14 \times V_1 \times N_1}{1000}$$

$$\% \text{ of nitrogen} = \frac{14 \times V_1 \times N_1 \times 100}{1000 \times w}$$

Example 1

The ammonia evolved from 0.21 g of an organic compound by Kjeldahl method neutralised 15 ml of N/20 sulphuric acid solution. Calculate the percentage of nitrogen.

Weight of organic compound = 0.21 g

$$\text{Normality of acid} = \frac{N}{20}$$

Volume of standard acid neutralised by ammonia = 15 ml

ADVANCED LEVEL CHEMISTRY NOTES BK 1

1000 ml of 1N ammonia contains = 14 g of nitrogen

15 ml of ammonia of normality

$$\frac{N}{20} \text{ contains nitrogen} = \frac{14 \times 15 \times 1}{1000 \times 20}$$

0.21 g of compound contains nitrogen

$$= \frac{14 \times 15}{1000 \times 20}$$

100 g of compound contains nitrogen

$$= \frac{14 \times 15 \times 100}{1000 \times 20 \times 0.21} = 5\text{g}$$

$$\therefore \text{Percentage of nitrogen} = 5$$

Example 2

0.35 g of an organic substance was Kjeldahlised and the ammonia obtained was passed into 100 ml of N/5 H₂SO₄. The excess acid required 154 ml of N/10 NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.

Solution

Volume of N/5 H₂SO₄ solution taken = 100 mL

The volume of N/5 H₂SO₄ neutralised by N/10

NaOH can be obtained as follows :

$$\begin{array}{rcl} N_{\text{acid}} \times V_{\text{acid}} & = & N_{\text{alkali}} \times V_{\text{alkali}} \\ \frac{N}{5} \times V_{\text{acid}} & = & \frac{N}{10} \times 154 \text{ mL} \\ & & \frac{154}{10} \\ V_{\text{acid}} & = & \text{ x 5 mL} \end{array}$$

ADVANCED LEVEL CHEMISTRY NOTES BK 1

$$= 77 \text{ mL}$$

Therefore,

Volume of $N/5 \text{ H}_2\text{SO}_4$ used for

$$\begin{aligned} \text{neutralising ammonia} &= (100 - 77) \text{ mL} \\ &= 23 \text{ mL} \end{aligned}$$

Then,

Percentage of nitrogen in the sample

$$= \frac{1.4 \times \text{Normality volume of acid used for neutralising } \text{NH}_3}{\text{Mass of the compound taken}}$$

Percentage of nitrogen in the sample

$$= \frac{1.4 \times 1/5 \times 23}{0.35} = 18.4$$

d) Estimation of sulphur

Carius method

A known mass of the organic compound is heated in a sealed tube with fuming nitric acid. The sulphur present in the organic compound will be oxidised to sulphuric acid. The tube is cooled and broken in dilute hydrochloric acid. Then excess of barium chloride solution is added. The precipitate of barium sulphate obtained is filtered, washed, dried and weighed accurately.

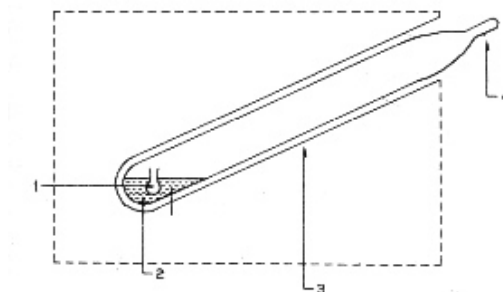


Fig.17.4

1. Organic compound 2. Nitric acid 3. Iron tube 4. Carius tube

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Calculations

Mass of the organic compound = w g

Mass of barium sulphate = w_1 g

233.4 g BaSO_4 contains 32 g sulphur

$\therefore w_1$ g BaSO_4 will contain $\frac{32 \times w_1}{233.4}$ g sulphur

Percentage of sulphur

$$= \frac{32 \times w_1}{233.4 \times w} \times 100$$

Example

0.316 g of an organic compound, after heating with fuming nitric acid and barium nitrate crystals in a sealed tube gave 0.466 g of the precipitate of barium sulphate. Determine the percentage of sulphur in the compound.

(Atomic masses : Ba = 137, S = 32, O = 16, C = 12, H = 1).

Solution

Mass of the substance taken = 0.316 g

Mass of BaSO_4 formed = 0.466 g

Molecular mass of BaSO_4 = $137 + 32 + 64 = 233$

Then, mass of S in 0.466 g of BaSO_4

$$= \frac{0.466 \times 32}{233} \text{ g}$$

Percentage of S in compound

$$= \frac{0.466 \times 32 \times 100}{233 \times 0.316}$$

$$= 20.25$$

ADVANCED LEVEL CHEMISTRY NOTES BK 1

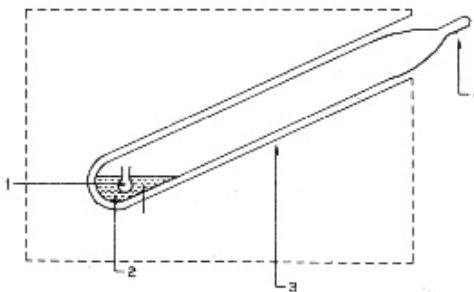
e) Estimation of halogens

Carius Method

Principle : The organic compound is heated with silver nitrate and fuming nitric acid. The halogen in the organic compound becomes the halide ion and this reacts with silver ion of the silver nitrate solution. The silver halide is precipitated. The precipitate is filtered, washed, dried and then weighed accurately.

Procedure

About 0.2 g of the organic compound is weighed accurately in a small glass tube. The tube is introduced into the Carius tube containing fuming nitric acid and silver nitrate crystals. The upper end of the tube is sealed. The tube is then heated in a furnace for 5 to 6 hours. The organic compound breaks up and the halogen present gives a precipitate of silver halide. The Carius tube is cooled and then broken. The precipitate of silver halide is washed, dried and weighed accurately.

**Fig.17.5**

- | | |
|---------------------|---------------------------------|
| 1. Organic compound | 2. Nitric acid + Silver nitrate |
| 3. Iron tube | 4. Carius tube |

Calculation

Mass of organic compound = w g

Let the mass of silver halide be w_1 g

143.5 g of silver chloride contains

35.5 g Cl_2

w_1 g of AgCl contains $\frac{35.5 \times w_1}{143.5}$ g of Cl_2

ADVANCED LEVEL CHEMISTRY NOTES BK 1

$$\text{Percentage of chlorine} = \frac{35.5 \times w_1 \times 100}{143.5 \times w}$$

similarly,

$$\begin{aligned} \text{Percentage of bromine} \\ = \frac{80}{188} \times \frac{w_1}{w} \times 100 \end{aligned}$$

$$\begin{aligned} \text{Percentage of iodine} \\ = \frac{127}{235} \times \frac{w_1}{w} \times 100 \end{aligned}$$

Example

0.15 g of iodoform gave 0.2682 g of AgI. Calculate the percentage of iodine.

$$\text{Weight of compound} = 0.15 \text{ g}$$

$$\text{Weight of silver iodide} = 0.2682 \text{ g}$$

$$\text{Molecular weight of silver iodide} = 108 + 127 = 235$$

235 g of silver iodide contains 127 g of iodine

$$\begin{aligned} 0.2682 \text{ g of AgI contains} &= \frac{127 \times 0.2682}{235} \\ &= 0.144 \text{ g iodine} \end{aligned}$$

0.15 g of compound contains 0.144 g of iodine

$$100 \text{ g of compound contains} = \frac{100 \times 0.144}{0.15} = 96.6 \text{ g}$$

$$\therefore \text{Percentage of iodine} = 96.6$$

Problems**Estimation of carbon and hydrogen**

- 0.12 g of an organic compound gave on combustion 0.18 g of water and 0.11 g of CO₂. Calculate the percentage of C and H in the organic compound. [Ans : C = 25%, H = 16.66%]
- An organic compound contains C, H and O. 0.2475 g of the organic compound yielded on combustion 0.4950 g of CO₂ and 0.2025 g of H₂O. Find the percentage composition of the organic compound. [Ans : C = 54.54%, H = 9.09%, O = 36.37%]

ADVANCED LEVEL CHEMISTRY NOTES BK 1

- 0.2004 g of glucose gave on combustion 0.2940 g of CO_2 and 0.1202 g of H_2O . Find the percentage composition.
[Ans : C = 40.01%, H = 6.66%, O = 53.33%]
- 0.2056 g of an organic compound gave on combustion 0.114 g of H_2O and 0.880 g of CO_2 . Find the percentage of hydrogen and carbon in the organic compound. [Ans : C = 93.76%, H = 6.128]
- On complete combustion, 0.246 g of an organic compound gave 0.198 g of CO_2 and 0.1014 of H_2O . Find the percentage composition of the organic compound. [Ans : C = 21.95%, H = 4.58%]

Estimation of nitrogen

- 1.15 g of an organic compound was analysed by Kjeldahl's method and the ammonia produced was collected in 30 mL of normal HCl solution. The excess of acid consumed 18.4 mL of normal sodium hydroxide solution for back titration. Calculate the percentage of nitrogen in the substance. [Ans : N = 14.12%]
- 0.80 g of a substance was digested with sulphuric acid and then distilled with an excess of caustic soda. The ammonia gas evolved was passed through 100 ml of 1N H_2SO_4 . The excess of the acid required 80 ml of 1N caustic soda solution for its complete neutralisation. Calculate the percentage of nitrogen in the organic compound.
[Ans : N = 35%]
- 0.36 g of a nitrogenous organic compound was Kjeldahlised and the ammonia liberated was exactly neutralised by 20 ml of 0.3 N H_2SO_4 . Calculate the percentage of nitrogen in the compound.
- 0.257 g of an organic substance was Kjeldahlised and ammonia evolved was absorbed in 50 mL of N/10 HCl which required 23.2 ml of N/10 NaOH for neutralization. Determine the percentage of nitrogen in the compound. [Ans : N = 14.6%]
- During nitrogen estimation present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen neutralised 10 ml of 1 M H_2SO_4 . Find the percentage of nitrogen in the compound. [Ans : N = 56%]

Estimation of sulphur

- 0.4037 g of an organic substance containing sulphur was heated with conc. nitric acid in a carius tube. On precipitation with BaCl_2 , 0.1963 g of BaSO_4 was produced. Determine the percentage of sulphur in the compound. [Ans : S = 7.66%]

ADVANCED LEVEL CHEMISTRY NOTES BK 1

2. 0.316 g of an organic compound gives 0.466 g of barium sulphate by carius method. Calculate the percentage of sulphur?
[Ans : S = 20.25%]
3. 0.530 g of an organic compound gave 0.90 g of BaSO_4 in carius determination of sulphur. Calculate the percentage of sulphur.
[Ans : S = 23.32%]

Estimation of halogens

1. 0.24 g of an organic compound gave 0.287 g of AgCl in the carius method. Calculate the percentage of chlorine in the compound.
[Ans : Cl = 25%]
2. In carius method of estimation of halogen 0.15 g of an organic compound gave 0.12 g of AgBr . Find the percentage of bromine in the compound. [Ans : Br = 34.04%]
3. 0.301 g of an organic compound gave 0.282 g of silver bromide by carius method. Find the percentage of bromine. [Ans : Br = 39.83%]
4. 0.196 g of an organic compound gave 0.22 g of CO_2 and 0.0675 g of H_2O . In carius determination, 0.3925 g of the substance gave 0.717 g of dry AgCl . Find the percentage composition of the substance.
[Ans : C = 30.6%, H = 3.8%, Cl = 45.2%, O = 20.4%]
5. 0.25 g of an organic compound was found to produce 0.35 g of AgCl after heating with fuming HNO_3 and AgNO_3 in a sealed carius method. Determine the percentage of chlorine in the compound.
[Ans : Cl = 34.75%]

SUMMARY

This chapter explains various methods of detection and estimation.

The principles behind various methods of detection and estimation are explained.

REFERENCES

1. I.L. Finar organic chemistry Vol.1, ELBS edition.
2. Vogel's Organic quantitative analysis ELBS.

18. HYDROCARBONS

OBJECTIVES

The main objectives of this chapter is to give

- * knowledge on sources, classification and nomenclature of hydrocarbons.*
- * general methods of preparation of alkanes, alkenes and alkynes and their chemical properties.*

18.1 Classification of Hydrocarbons

Hydrocarbons are made of only carbon and hydrogen. They are obtained mainly from petroleum, natural gas and coal. They are divided into two main categories :

- * aliphatic hydrocarbons
- * aromatic hydrocarbons

The aliphatic hydrocarbons are further classified into saturated (alkanes), unsaturated (alkenes and alkynes) and alicyclic (cycloalkanes) hydrocarbons.

Aliphatic Saturated Hydrocarbons

These are otherwise called alkanes. Alkanes are often referred to as paraffins. Alkanes show little chemical affinity towards other compounds and are chemically inert to most reagents.

18.2 IUPAC nomenclature

With the exception of the first four compounds (methane, ethane, propane and butane) whose names have historical roots, other alkanes are named from Greek number according to the number of carbon atoms present.

Table 18.1

Number of Carbon atoms	Name	Molecular formula C_nH_{2n+2}
1	Methane	CH_4
2	Ethane	C_2H_6
3	Propane	C_3H_8
4	Butane	C_4H_{10}
5	Pentane	C_5H_{12}
6	Hexane	C_6H_{14}