TOPIC 2

SEMESTER-I (Period-2)

Introduction to



Organic Chemistry (cont'd)

LEARNING OBJECTIVE

Upon completion of this topic, learners will:

- Discuss hydrocarbon derivatives;
- Demonstrate techniques for the lab preparation and testing of hydrocarbon derivatives;
- Demonstrate practical knowledge about the production of soap;
- Distinguish between natural and synthetic organic materials;
- Discuss polymerization and polymers;
- Distinguish between plastics and resins and;
- Discuss proteins together with carbohydrates.

HYDROCARBON DERIVATIVES

2.1 ALKANOLS (ALCOHOLS)

Alcohols or alkanols are the compounds containing one or more hydroxyl groups (—OH). The alcohols contain the —OH group attached to alkyl group.

Sources of Alkanols (Alcohols)

Alcohol is not only found in sugar cane, barley, corn, wheat and potatoes but the same is also found in natural substances like petroleum and oils. These are various method to extract natural alcohol from plant oil, and other natural resourses.

Classification of Alkanols

Alkanols are classified as *mono-, di-* and *trihydric* alcohols according to the number of —OH groups contained in their molecules. Some examples of mono-, di- and trihydric alcohols are as follows:



Primary (1°), Secondary (2°) and Tertiary (3°) Alkanols

Monohydric alcohols are classified as primary, secondary or tertiary alcohols depending upon whether the hydroxyl group is attached to a primary, secondary or tertiary carbon atom, For example,



Phenols. The compounds in which —OH group is directly attached to benzene ring are known as phenols



Nomenclature

In the common system, alkanols are named as *alkyl alcohols*. In IUPAC system, the names of saturated alcohols are derived from corresponding alkanes by replacing 'e' of alkanes by 'ol'. The general IUPAC name of alcohols is **alkanol**. The IUPAC names of a few members of this class are given in Table 2.1.

Table 2.1. IUPAC names of some alkyl alcoho

Formula	Common Name	IUPAC Name
СН ₃ ОН	Methyl alcohol	Methanol
CH ₃ —CH ₂ —OH	Ethyl alcohol	Ethanol
${}^{3}_{C}H_{3}$ - ${}^{2}_{C}H_{2}$ - ${}^{1}_{C}H_{2}$ - OH	<i>n</i> -Propyl alcohol	Propan-1-ol

$^{3}_{C}H_{3} - ^{2}_{C}H - ^{1}_{C}H_{3}$	<i>iso</i> -Propyl alcohol	Propan-2-ol
OH		. 0
${}^{4}_{C}H_{3}$ - ${}^{3}_{C}H_{2}$ - ${}^{2}_{C}H_{2}$ - ${}^{1}_{C}H_{2}$ - OH	<i>n</i> -Butyl alcohol	Butan-1-ol
${}^{3}_{C}H_{3} - {}^{2}_{C}H - {}^{1}_{C}H_{2} - OH$	<i>iso</i> -Butyl alcohol	2-Methylpropan-1-ol
CH ₃		$\cdot \times \circ$
$^{1}_{H_{3}}$ $-^{2}_{CH}$ $-^{3}_{CH}$ $-^{4}_{CH_{3}}$ $-^{4}_{H_{3}}$	<i>sec</i> -Butyl alcohol	Butan-2-ol
OH		·
¹ CH ₃		
H_3C — 2C —OH	tert-Butyl alcohol	2-Methylpropan-2-ol
³ CH ₃		
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ OH	<i>n-</i> Pentyl alcohol or <i>n-</i> Amyl alcohol	Pentan-1-ol

Preparation of Alkanols

Alkanols are prepared by the following general methods:

1. BY THE HYDROLYSIS OF HALOALKANES

Haloalkanes when boiled with aqueous solution of an alkali hydroxide or moist silver oxide furnish alkanols.

 $KOH(aq) \longrightarrow ROH$ RX + KX Haloalkane Alkanol C₂H₅Br $KOH(aq) \longrightarrow C_2H_5OH$ + KBr AgOH \longrightarrow C₂H₅OH C_2H_5Br + AgBr Bromoethane Moist Ethanol silver oxide

Primary alkyl halides give good yield of alcohols. However, tertiary alkyl halides, in this reaction give, mainly alkene due to dehydrohalogenation.



2-Bromo-2-methylpropane

Secondary alkyl halides give a mixture of alkanol and alkene.

This method is not very useful for preparing alcohols because haloalkanes are themselves obtained from alcohols. However, the preparative utility of this method lies in the preparation of aromatic alcohols. For example,



2. BY HYDRATION OF ALKENES

Alkenes are obtained by cracking of petroleum. They are easily converted to alkanols by the addition of water in presence of tetraoxosulphate (VI) acid.

$$\begin{array}{c} H_2C = CH_2 + H_2O \xrightarrow{H_2SO_4} & CH_3 \xrightarrow{-} CH_2 \xrightarrow{-} OH_2 \\ \text{Ethene} & \text{Ethanol} \end{array}$$

In case of unsymmetrical alkenes, the addition takes place according to Markownikov's rule.

$$\begin{array}{c} \mathrm{CH}_{3} - \mathrm{C} = \mathrm{CH}_{2} \ + \ \mathrm{H}_{2}\mathrm{O} \ \xrightarrow{\mathrm{H}_{2}\mathrm{SO}_{4}} \ & \mathrm{CH}_{3} - \overset{\mathrm{OH}}{\underset{\mathrm{CH}_{3}}{\overset{\mathrm{I}}{\underset{1}}{\underset{\mathrm{CH}_{3}}{\underset{\mathrm{CH}_{3}}{\underset{1}}{\underset{\mathrm{CH}_{3}}{\underset{1}}{\underset{$$

Structure of Alkanols

The general formula of alkanols is R—OH, where R is some alkyl or substituted alkyl group. Since the oxygen atom of the hydroxyl group has two bond pairs and two lone pairs of electrons, therefore, the C—O—H bonds in alkanols is not linear. The C—O bond in alkanols is formed by overlap of sp^3 -hybrid orbital of carbon with sp^3 -hybrid orbital of oxygen. The C—O—H bond angle in alkanols is slightly less than the regular tetrahedral angle (109.5°). It is due to greater repulsion of lone pairs of oxygen on the bond pairs. The C—O bond length in alkanols is 142 pm.



As oxygen is more electronegative than carbon and hydrogen, therefore, C—O and O—H bonds in alkanols are polar bonds and hence alkanols possess a net dipole moment. Methanol has a dipole moment of 1.71 D.

Physical Properties of Alkanols

1. The lower members of alkanols are colourless, volatile liquids with a characteristic alcoholic smell and burning taste whereas higher alkanols are odourless and tasteless.

Higher alkanols having 12 or more carbon atoms are colourless waxy solids.

2. Solubility. The first three members are completely miscible with water. The solubility rapidly decreases with increase in molecular mass. The higher members are almost insoluble in water but are soluble in organic solvents like benzene, ether, etc.

The solubility of lower alkanols is due to the existence of hydrogen bonds between water and polar O—H group of alkanol molecules.



The solubility of alkanols in water decreases with increase in molecular mass because with increase in molecular mass, the non-polar alkyl group becomes predominant and masks the effect of polar —OH group.

In addition, *among the isomeric alkanols the solubility increases with branching of chain.*

3. Boiling Points. Boiling points of alcohols are much higher than those of alkanes, haloalkanes or ethers of comparable molecular masses. *This is because in alkanols intermolecular hydrogen bonding exists due to which a large amount of energy is required to break these bonds.*

Chemical Reactions of Alkanols

In alcohols, —OH group is the functional group. Therefore, the chemical properties of alcohols generally involve the reactions of —OH group. These can undergo **substitution** as well as **elimination** reaction. Alcohols can react both as nucleophiles and electrophiles. The bond between O–H is broken when they react as nucleophiles. The bond between C–O is broken when they react as electrophiles. Protonated alcohols react in this manner.



(protonated alcohols as electrophiles)

Some common reactions of alcohols are as follows:

ACIDIC CHARACTER

Alcohols are very weak acids (Ka = $10^{-16} - 10^{-18}$), even feeble than water (Ka = 10^{-14}). They do not turn blue litmus red but when treated with active metals like sodium, potassium and aluminium these liberate hydrogen along with the formation of alkoxides.

 $\begin{array}{cccc} 2R & \longrightarrow & 2R & \longrightarrow & 2R & \longrightarrow & H_2 \\ & & & & & \\ Sodium & alkoxide \\ 2C_2H_5OH + 2Na & \longrightarrow & 2C_2H_5 & & \\ & & & & \\ Ethanol & & & \\ & & & \\ Sodium & ethoxide \end{array}$

Alcohols behave as acids because of the presence of polar O—H group. Due to greater electronegativity of oxygen atom the shared pair between O and H is drawn.

The order of *acidic strength* among various types of alkanols is

primary > *secondary* > *tertiary*

Alkanols are weaker acids than water. This can be illustrated by the reaction of water with an alkoxide.



This reaction shows that water is a better proton donor and hence stronger acid than alkanols. Also, in the above reaction, we note that an alkoxide ion is a better proton acceptor than hydroxide ion, which shows that alkoxides are stronger bases. Thus, sodium ethoxide is a stronger base than sodium hydroxide.

Due to the presence of lone pairs of electrons on oxygen, alkanols can also act as proton acceptors and hence behave as **Bronsted bases**.

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Thus, alkanols exhibit amphoteric character.

REACTION WITH MONOCARBOXYLIC ACIDS (Esterification)

Alkanols react with monocarboxylic acids in the presence of conc. tetraoxosulphate(VI) acid to form esters. The function of conc. H_2SO_4 is to act as a protonating agent as well as a dehydrating agent. The reaction is called **esterification**.



This reaction is reversible in nature and the equilibrium can be shifted to the right by removing water as soon as it is formed. During esterification water molecule is formed by combination of —OH of carboxylic acid and H from alkanol molecule.

ACIDIC DEHYDRATION (Formation of Alkenes)

When heated with conc. H_2SO_4 or H_3PO_4 alkanols undergo dehydration to form alkenes. The reaction with conc. H_2SO_4 is carried at 443 K, whereas H_3PO_4 reacts at higher temperature.





Secondary and tertiary alkanols are dehydrated under milder conditions. For example,

$$\begin{array}{c} OH\\ CH_{3}CHCH_{3} \xrightarrow{85\% \text{ H}_{3}\text{PO}_{4}} & CH_{3} \longrightarrow CH = CH_{2} + H_{2}O\\ CH_{3} \longrightarrow CH_{3} \xrightarrow{CH_{3}} & CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} + H_{2}O\\ CH_{3} \longrightarrow CH_{3} \xrightarrow{CH_{3}} & CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} + H_{2}O \end{array}$$

The ease of dehydration of alkanols follows the order

 $3^\circ > 2^\circ > 1^\circ$

IODOFORM REACTION

Alkanols containing CH_3 —CH—structural unit on warming with

ОН

sodium hydroxide solution and iodine yield **pale yellow precipitate** of triiodomethane (iodoform).

$$CH_{3} \xrightarrow{|} C \xrightarrow{|} C \xrightarrow{|} C \xrightarrow{|} R + 4I_{2} + 6NaOH \xrightarrow{Worm} CHI_{3} \xrightarrow{\downarrow} + RCOONa + 5NaI + 5H_{2}O$$

$$OH$$

This reaction can be used as a test for detection of this particular structural unit in an alkanol.

Tests for Alkanols

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Alkanols can be identified by one of the following tests:

1. Sodium Metal Test. Alkanols can be distinguished from other organic compounds which do not contain acidic group by this test. A very small piece of sodium metal is added to the compound. *If hydrogen gas is produced with effervescence, it indicates the presence of alkanol.* It may be noted that alkanols cannot be distinguished from carboxylic acids by this test.

- **2. Ester Test.** In this test, the compound to be tested is warmed with ethanoic acid and a few drops of conc. H_2SO_4 . Formation of sweet smelling vapours of some ester indicates the presence of alkanol.
- **3. Oxidation Test.** In this test, the compound to be tested is warmed with acidified $K_2Cr_2O_7$ solution. *If the colour changes from orange to green, this indicates the presence of some alkanol.*

Similarly, the compound may be warmed with acidified potassium permanganate. *The change of colour from pink to colourless indicates the presence of some alkanol.*

Uses of Alkanols

Methanol and ethanol are the two most important alkanols. While methanol is largely manufactured from petroleum feed stock, ethanol is obtained from ethene or by fermentation of sugar and starch. Both have many uses in industry. **Methanol** is used as a solvent and in the preparation of methanol. It is also used in the preparation of ethanoic acid

 $CH_3OH + CO \longrightarrow CH_3COOH$

Ethan-1,2-diol is used in the manufacture of polymers. It is also used as an antifreeze.

Propane-1,2,3-triol is used in confectionery and cosmetics.

2.2 ALKANALS (ALDEHYDE) AND ALKANONES (KETONES)

Functional Groups of Carbonyl Compounds

Aldehydes and ketones contain the most important functional group in organic chemistry—the carbonyl group, $\sum C = O$. Hence, they are known as carbonyl compounds. The carbonyl functional group is present in many important biological molecules like testosterone, progesterone, insect pheromones etc. It also occurs in the molecules in our eyes which is responsible for vision. It is also involved in manufacture of many important industrial chemicals, from plastics to solvents. The functional groups along with general formulae is given in Table 2.2.

Table 2.2. Names, Functional Groups and General Formulae ofAlkanals and Alkanones

Name of the Family	General Structural Formula	Functional Group
1. Aldehydes or alkanals	$R \to C = O$ $H \to C = O$	eft
2. Ketones or alkanones	R > C = O >C = O	

Aldehydes and ketones are the *first oxidation* products of primary and secondary alcohols respectively. Aldehydes are obtained by replacing the two terminal hydrogen atoms of alkanes by the oxygen atom while ketones are obtained by replacing the two non-terminal hydrogen atoms by oxygen. The common feature of both aldehydes and ketones is carbonyl group (>C = O) and, therefore, they are called **carbonyl compounds**.

Structure of Carbonyl Group

Both aldehydes and ketones have carbonyl group as the functional group. The carbonyl carbon is sp^2 hybridized and, thus, it has three sp^2 hybrid orbitals and one unhybridized *p*-orbital. It uses sp^2 hybrid orbitals to form three sigma bonds, one with oxygen atom and remaining two with two other atoms or groups (**R** or **H**). All these three sigma bonds lie in same plane at the angle of 120.

The unhybridized *p*-orbital of carbonyl carbon forms π -bond with oxygen atom by sidewise overlapping with half filled *p*-orbital of oxygen atom as shown in figure.



Fig. 2.1 Orbital diagram for the formation of carbonyl group.



Ethanal, CH₃ CHO

Since carbon and oxygen have different values of electronegativity, the bond between carbon and oxygen is polar. In fact, electron density around the oxygen atom is increased which causes the development of partial positive charge (δ^+) on carbon and a partial negative charge (δ^-) on oxygen atom. It has been shown in Fig. 2.2. Thus, the carbonyl carbon is an electrophillic and carbonyl oxygen is nucleophillic centre.



Fig. 2.2 Polarised electron cloud in carbonyl group.

The polar nature of carbonyl group is confirmed by the fact that dipole moments of aldehydes and ketones (2.3 to 3.02 D) are quite high. The dipole moment of ethanal, propanone and diethyl ether are 2.72, 2.88 and 1.18 D respectively.

Names of Carbonyl Compounds

Aldehydes or Alkanals

The trivial names of aldehydes are derived from the names of the corresponding carboxylic acids (oxidation products of aldehydes) by replacing the suffix *ic acid* with *aldehyde*. Position of substituents in aldehyde chain, if any, is indicated by Greek letters α , β , γ , δ etc. The α -carbon is one which is directly attached to the *CHO* group.

$$\overset{\delta}{C} - \overset{\gamma}{C} - \overset{\beta}{C} - \overset{\alpha}{C} - CHO$$

In **IUPAC system**, aldehydes are named by replacing '*e*' from the corresponding name of alkane by suffix '*al*'. Therefore, aldehydes are called *alkanals*.

In case of higher aldehydes, the longest carbon chain is chosen and is numbered in such a way that the aldehyde group is given number one. The names of few aldehydes are given in Table 2.3.



Table 2.3. IUPAC and Trivial Names of Some Alkanals

Ketones or Alkanones

Ketones are represented by the general formula RCOR'. They are termed as *simple ketones* if both R and R' are same alkyl groups. On the other hand, they are termed as *mixed ketones* if R and R' are different. In **common system, ketones** are named by using the names of alkyl groups attached to carbonyl group followed by the word '*ketone*'.

For example,
$$CH_3COC_2H_5$$
 or \swarrow

is *ethyl methyl ketone*.

In the case of substituted ketones the positions of substituents are indicated by Greek letters, α , β , etc. (Trivial system) or numbers (IUPAC names).

According to the IUPAC system of naming compounds:

- (i) The longest carbon chain carrying the carbonyl group is considered as the parent chain.
- (*ii*) The chain is numbered from one end such that the carbonyl carbon is given the lowest possible number.
- (*iii*) The name of the ketone is obtained by replacing 'e' of the parent alkane by 'one'.
- (*iv*) The positions of the carbonyl group and substituents are indicated by numbers. The names of some ketones are given in Table 2.4.

Bond Line Formulae, Formula	Trivial Name	IUPAC Name
CH ₃ COCH ₃	Acetone	Propanone
	Ethyl methyl ketone	Butanone
	Methyl propyl ketone	Pentan-2-one
	Diethyl ketone	Pentan-3-one
CH ₃ CHCOCH ₃	Methyl isopropyl ketone	3-Methyl- butan-2-one

Table 2.4. Common and IUPAC Names of Some Ketones

2.3 ETHERS

Ethers are the compounds with general formula $C_nH_{2n+2}O$ (same as monohydric alcohols). These are represented by general structure. **R**—**O**—**R**'. They may be regarded as *dialkyl derivatives* of water or *mono alkyl* derivatives of alcohols.

 $H \longrightarrow O \longrightarrow H \xrightarrow{-2H} R \longrightarrow O \longrightarrow R \xleftarrow{-H} R \longrightarrow O \longrightarrow H$ Water Ether Alcohol

They are also considered as *anhydrides of alcohols* because they can be obtained by the elimination of water molecule from two alcohol molecules.

$$\begin{array}{ccc} R & - OH + HO & - R & - O & - R + H_2O \\ Alcohols & Ether \end{array}$$

The groups R and R' in ether may either be same or different. In case these groups are same, the compounds are known as **simple ethers** or **symmetrical ethers**. On the other hand, if R and R' groups are different, the compounds are called **mixed ether** or **unsymmetrical ethers**.

$$C_2H_5$$
—O— C_2H_5 Simple ether
 C_2H_5 —O— CH_3 Mixed ether

Nomenclature

1. Common System

According to this system, the individual members are named according to alkyl groups attached to the oxygen atom. The two alkyl or aryl groups linked to oxygen atom are named in the alphabetic order followed by the word *ether*. In case of simple ethers, the prefix *di* is attached before the name of the alkyl group. Some examples are as follows:

Simple ethers	Mixed ethers
CH ₃ —O—CH ₃	$CH_3 - O - C_2H_5$
Dimethyl ether	Ethyl methyl ether
C_2H_5 —O— C_2H_5 Diethyl ether	C_6H_5 —O— C_2H_5 Ethyl phenyl ether

2. IUPAC System

According to IUPAC system, ethers are named as *alkoxyalkanes*. The larger alkyl group forms the part of parent chain while lower alkyl group constitutes *alkoxy* radical. Some examples are:

СН ₃ —О— СН₃	Methoxymethan	
CH ₃ —O—C ₂ H ₅	Methoxyethane	

CH₃—O—
$$\overset{1}{\mathbf{C}}\mathbf{H}_{2}\overset{2}{\mathbf{C}}\mathbf{H}_{2}\overset{3}{\mathbf{C}}\mathbf{H}_{3}$$
 1-Methoxypropane
C₂H₅—O— $\overset{2}{\mathbf{C}}\mathbf{H}$ — $\overset{3}{\mathbf{C}}\mathbf{H}_{2}$ — $\overset{4}{\mathbf{C}}\mathbf{H}_{3}$ 2-Ethoxybutane
 $\overset{1}{\mathbf{C}}\mathbf{H}_{3}$

Isomerism in Ethers

Aliphatic ethers give two different type of isomers:

1. Chain Isomerism. Ethers with same formula and having different carbon chain skeletons are called chain isomers. For example,

CH ₃ CH ₂ CH ₂ CH ₂ OCH ₃	and	CH ₃ CHCH ₂ OCH ₃
1-Methoxybutane		1-Methoxy-2-methylpropane

 CH_3

2. Functional Isomers. Ethers are isomeric with alcohols. Ethers and alcohols are functional isomers.

For example, *dimethyl ether* (CH_3OCH_3) is isomeric with *ethyl alcohol* (C_2H_5OH).

Structure of Ethers

The oxygen atom in ethers assumes sp^3 hybrid state. Two of the hybrid orbitals of oxygen are used in forming σ bonds with the surrounding alkyl groups. The other two sp^3 hybrid orbitals of oxygen contain lone pairs of electrons. The electron pairs (lone pairs as well as bond pairs) surrounding oxygen atom, assume tetrahedral arrangement. However, the bond angle around oxygen atom is not exactly equal to 109 28'. The deviation in angle is caused by the repulsive interactions between the alkyl groups. Bulkier the alkyl groups, greater will be the repulsive interactions and consequently, larger will be deviation in angle. C—O—C angle in dimethyl ether is 111.7.

The C—O bond length in ethers is 141 pm which is almost same as that in alcohols.

Thus, ethers have **bent structure** and their dipole moment is greater than zero ($\mu > 0$). Hence, their molecules are **polar in nature**. For example, net dipole moment of diethyl ether is 1.18 D and that of dimethyl ether is 1.3 D.



Uses of Ethers

Ethers are used in several ways:

- 1. *Dimethyl ether* is used as refrigerant and as a solvent at low temperature.
- 2. *Diethyl ether* is used as solvent for organic reactions and also as an industrial solvent for oils, gums, resins, etc. It is also used as an extracting solvent.
- 3. Ethoxy ethane has been widely used as inhalation anaesthetic. However, because of its slow effect and unpleasant recovery period, its use as anaesthetic has been abandoned. Now-a-days substituted ethers such as ethrane and isoflurane are used as anaesthetics.



2.4 HALOCARBONS (ALKYL HALIDES)

The replacement of one or more hydrogen atoms in hydrocarbon results in the formation of a halogen derivative of the hydrocarbon. In case the hydrocarbon is alphatic, the product is haloalkane (or alkyl halide) and in case of aromatic hydrocarbons the product is haloarene (or aryl halide).

$$\begin{array}{ccc} R & \stackrel{-H}{\longrightarrow} & \stackrel{-H}{\longrightarrow} \\ Alkane & \stackrel{+X}{\longrightarrow} & \stackrel{-H}{\longrightarrow} \\ CH_{3} & \stackrel{-H}{\longrightarrow} & CH_{3} & \stackrel{-H}{\longrightarrow} \\ Ethane & \stackrel{+Cl}{\longrightarrow} & CH_{3} & \stackrel{-CH_{2}Cl}{Chloroethane} \end{array}$$

In haloalkanes, the halogen atom is bonded to sp^3 hypridized carbon atom whereas in haloarenes, the halogen atom is bonded to sp^2 -hybridized carbon atom.

Nomenclature

In the common system, aliphatic halogen derivatives are named as **alkyl halides.** The words, *n-*, *sec-*, *tert-*, *iso-*, *neo-* and *amyl* are usually used in writing the common names. In IUPAC system, they are considered as derivatives of corresponding alkanes and are named as **haloalkanes**. It may be noted that the common name of any alkyl halide is written as *two separate words* whereas the IUPAC name of the alkyl halide is written as *one word*.

The common and IUPAC names of some of the members of this class are given below:

Formula	Common or Trivial Name	IUPAC Name	
CH ₃ Cl	Methyl chloride	Chloromethane	
CH ₃ CH ₂ Cl	Ethyl chloride	Chloroethane	
CH ₃ CH ₂ CH ₂ Cl	<i>n</i> -Propyl chloride	1-Chloropropane	
¹ CH ₃ ² CHCl <i>iso</i> -Propyl chloride		2-Chloropropane	
$\overset{4}{CH_3}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{CH_2}\overset{1}{CH_2}CH_2$	<i>n</i> -Butyl chloride	1-Chlorobutane	
$\begin{vmatrix} 1\\CH_{3}-CH-CH_{2}-CH_{3}\\ \\Cl \end{vmatrix}$	<i>sec</i> -Butyl chloride	2-Chlorobutane	
$\begin{bmatrix} 3 \\ CH_3 \\ CH_2 \end{bmatrix} = \begin{bmatrix} 1 \\ CH_2 \\ CH_2 \\ CH_2 \end{bmatrix} = \begin{bmatrix} 1 \\ CH_2 \\ CH_2 \\ CH_2 \end{bmatrix} = \begin{bmatrix} 1 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \end{bmatrix} = \begin{bmatrix} 1 \\ CH_2 $	<i>iso</i> -Butyl chloride	1-Chloro-2- methylpropane	

Isomerism in Haloalkanes

Haloalkanes can exhibit the following kinds of isomerism:

1. Chain Isomerism. The haloalkanes with four or more carbon atoms exhibit this kind of isomerism. For example,

CH₃CH₂CH₂CH₂Cl 1-Chlorobutane $CH_3 \rightarrow CH \rightarrow CH_2Cl$ 1-Chloro-2-methylpropane

CH₃

2. Position Isomerism. The haloalkanes with three or more carbons show this kind of isomerism.

For example, C_3H_7Br has two position isomers.

CH₃CH₂CH₂Br 1-Bromopropane (*n*-Propyl bromide) CH₃ CHCH₃ 2-Bromopropane (*iso*-Propyl bromide)

Br

2.5 ALKANOIC (CARBOXYLIC ACID)

Carboxylic acids are organic compounds containing carboxyl group

are called **carboxylic acids**. Many common chemicals such as citric acid (lemon juice), ethanoic acid (vinegar) are carboxylic acids. The carboxyl group is made up *carbonyl*, >C = O and *hydroxyl*, —OH group, hence, its name is *carboxyl group* (*carb* from carbonyl and *oxyl* from hydroxyl). Carboxylic acids may be *aliphatic* (R—COOH) or *aromatic* (Ar—COOH) depending upon whether —COOH group is attached to aliphatic alkyl chain or aryl groups respectively.

Physical Properties of Alkanoic ACIDS

1. Physical State. The first three aliphatic acids are colourless liquids with pungent smell. The next six are oily liquids with an odour of rancid butter while the higher members are colourless, odourless waxy solids. Benzoic acid is a crystalline solid.

2. Solubility. The first four aliphatic members are soluble in water due to intermolecular hydrogen bonding with water molecules.

With increasing size of the alkyl group, the non-polar part of the molecule predominates thereby reducing the solubility in water. The higher members are practically insoluble in water.

3. Boiling Points. Carboxylic acids have quite high boiling points due to the presence of intermolecular hydrogen bonding which results in the formation of dimeric structures.



4. Melting Points. In first ten members of the homologous series, the **alternation effect** is observed. The alternation effect implies that the melting point of an acid with even number of carbon atoms is higher than the acid with odd number of carbon atoms above and below it. However, no such effect is observed in homologues with more than ten carbons.

Chemical Characteristics of Alkanoic Acids

In carboxylic acids, the functional group is carboxyl group (—C—OH). $\parallel \\ O$

1. ACIDIC NATURE

Carboxylic acids are quite strong acids because of the presence of polar O—H group. They ionize to give hydrogen ions and hence, behave as acids.

$$\begin{array}{cccc} O & O \\ \parallel & & \\ R - C - O - H & \Longrightarrow & R - C - O \\ \hline & & \\ R - C - O \\ \hline & & \\ R - C - O \\ \hline & & \\ R - C - O \\ \hline & & \\ R - C \\ \hline \\ \hline & \\ R - C \\ \hline \\ \hline \\ R - C \\ \hline \\ \\ R -$$

Carboxylic acid

Carboxylate ion

Some chemical reactions showing the acidic nature of carboxylic acids are:

(*a*) **Reaction with Metals.** Carboxylic acids react with metals such as Na, K, Zn, etc., and liberate hydrogen gas.

 $\begin{array}{ll} 2R & \longrightarrow (RCOO)_2 Zn \, + \, H_2 \\ 2CH_3 COOH \, + \, Zn \, \longrightarrow \, (CH_3 COO)_2 Zn \, + \, H_2 \\ Acetic \ acid & Zinc \ acetate \end{array}$

(*b*) **Reaction with Alkalies.** Carboxylic acids react with alkalies (NaOH, KOH) to form salt and water.

 $RCOOH + NaOH \longrightarrow RCOONa + H_2O$

 $\begin{array}{c} CH_{3}COOH + NaOH \longrightarrow CH_{3}COONa + H_{2}O \\ Acetic \ acid & Sodium \ acetate \end{array}$

(c) Reaction with Bicarbonates and Carbonates. Carboxylic acids react with bicarbonates and carbonates and produce brisk effervescence due to liberation of CO_2 .

 $\begin{array}{c} \text{RCOOH + NaHCO}_{3} \longrightarrow \text{RCOONa + CO}_{2} + \text{H}_{2}\text{O} \\ \text{CH}_{3}\text{COOH + NaHCO}_{3} \longrightarrow \text{CH}_{3}\text{COONa + CO}_{2} + \text{H}_{2}\text{O} \\ \text{Acetic acid} \qquad \text{Sodium} \\ \text{bicarbonate} \end{array}$

(*d*) **Reaction with Ammonia.** Carboxylic acid react with ammonia to form ammonium salts. Ammonium salts on heating give amides.

 $\begin{array}{c} \text{RCOOH} + \text{NH}_{3} \longrightarrow \text{RCOONH}_{4} & \stackrel{\Lambda}{\longrightarrow} \text{RCONH}_{2} + \text{H}_{2}\text{O} \\ \text{CH}_{3}\text{COOH} + \text{NH}_{3} \longrightarrow \text{CH}_{3}\text{COONH}_{4} & \stackrel{\Lambda}{\longrightarrow} \text{CH}_{3}\text{CONH}_{2} + \text{H}_{2}\text{O} \\ \text{Acetic acid} & \text{Ammonium} \\ \text{acetate} & \text{Acetamide} \end{array}$

Systematic Names and Struc-ture of Alkanoic Acids

Structure of Carboxyl Group

In carboxylic acids, The carbon of the —COOH group is sp^2 hybridised and hence the carbon along with two oxygen atoms lie in one plane and are separated by about 120. The orbital structure of —COOH is show below:



conjugation with the lone pair of electrons on the —OH group. As a result of this, the —COOH group can be represented by different electronic structures, called *canonical forms* or *mesomers*.

This phenomenon in which a compound/group can be written in two or more than two structures is known as resonance or mesomerism.

Nomenclature

The **common** or **trivial names** are derived from the source of individual acids. Formic acid, for example, was so named because it was first obtained by the distillation of ants (Latin : *fomica* meaning *ants*). Similarly, acetic acid has derived its name from vinegar (Latin : *acetum* meaning *vinegar*) Butyric acid is present in butter fat (Latin : *butyrum* meaning *butter*). The positions of substituents present is specified by Greek letters α , β , γ , etc. The carbon atom next to the carboxyl carbon is considered as α -carbon.

In **IUPAC system**, the monocarboxylic acids are named as *alkanoic acids*. The name of the acid is derived by replacing the terminal '*e*-' of the corresponding alkane with '**-oic acid**'. Carboxyl carbon is always given number one in chain of carbon atoms.

The trivial and IUPAC names of some common alkanoic acids are given in Table 2.4.

Bond Line Formulae, Formula	Common Name	IUPAC Name
о н он нсоон	Formic acid	Methanoic acid
О ОН СН ₃ СООН	Acetic acid	Ethanoic acid
OH O CH ₃ CH ₂ COOH	Propionic acid	Propanoic acid

Table 2.4. The Trivial and IUPAC Names of Some Acids



(*ii*) Functional isomerism. $C_nH_{2n}O_2$ represents saturated monocarboxylic acids, ester, hydroxy carbonyl compounds and hydroxy oxiranes. For example,

 $C_2H_4O_2$ has isomers:

CH₃COOH, HCOOCH₃, CHO ,
$$\bigcirc$$
 OH \cap OH

(*iii*) **Optical isomerism.** Carboxylic acids with one chiral atom can show optical isomerism.



Uses of Ethanoic Acid

- 1. *Solvent* for many organic chemicals especially in the textile, paint and colour making industry.
- 2. *Starting material* for the synthesis of many organic compounds, manufacture of rayon fibre.
- 3. Preservative, flavouring and tenderizer for foods, pickled foods.
- 4. Used in cooking (vinegar)

2.6 ALKYL ALKANOATE (ESTERS)

Esters are the derivatives of the carboxylic acids in which the —OH part of the carboxylic group has been replaced by —OR group where, R may be *alkyl* or *aryl* group.

Sources of Alkanoates

Alkyl alkanoates are found widely in nature. Short carbon chain simple alkyl alkanoates exist as liquids and have a characteristic pleasant odour. They occur in essential oils, many fruits and flowers and are sometimes called **fruit essences** because of their pleasant odours.

More complex alkyl alkanoates are found in fats and oils and some waxes.

Fats and oils contain one, two or three alkanoate groups which generally do not have pleasant odours. It is worth noting that there is a mixture of different alkanoate derivates of propane-1, 2, 3-triol and long-chain fatty acids in fats and oils.

Nomenclature and Structure of Alkyl AlkanOates

The esters are named by writing the name of the *alkyl* or *aryl* group of —OR' part of the molecule before the name of the parent acid and replacing the suffix *ic acid* of the (*IUPAC* or *common*) name of the acid by *ate.* some examples are:

INTRODUCTION TO ORGANIC CHEMISTRY (CONT'D)

Formula	IUPAC Name	Common Name
$\mathrm{HCOOC}_{2}\mathrm{H}_{5}$	Ethyl methanoate	Ethyl formate
CH ₃ COOC ₂ H ₅	Ethyl ethanoate	Ethyl acetate
$CH_3COOC_6H_5$	Phenyl ethanoate	Phenyl acetate
$\begin{vmatrix} \overset{\gamma}{}_{4}^{\gamma}H_{3}\overset{\beta}{}_{3}^{\beta}H_{2}-\overset{\alpha}{}_{1}\overset{\alpha}{}_{1}^{\beta}-\overset{\alpha}{}_{1}^{\gamma}OOCH_{3} \\ & \overset{2}{}_{3}\overset{\beta}{}_{1}^{2}-\overset{\alpha}{}_{1}^{\gamma}OOCH_{3} \end{vmatrix}$	Methyl-2-bromo- butanoate	Methyl, α -bromobutyrate

Structure of Alkyl Alkanoates

The alkyl alkanoates, RCOOR', contain carboxyl $-C_0$ functional

group. The carbon of -C = 0 group is sp^2 hybridised.



Uses of Alkanoates

1. Soap making. The alkyl alkanoates of higher fatty acids like palmitic, stearic or oleic acids are used in the process of soap making. The reaction is known as saponification.

The saponification process can be represented generally for fats and oils which contain one or more ester groups.

2. Flavoring and perfuming agents. Esters or alkanoates have characteristic odours and are therefore used in the manufacture of artificial flavouring and perfuming agents.

3. As plasticizers. Many esters are used as plasticizers *i.e.*, substances which are added to thermoplastics to soften them so as to be reused. Some common examples are, *di-n*-butyl pthalate, triceryl phosphate, etc.

4. As solvents. Esters are used as solvents due to their ability to dissolve various greases.

- Methyl acetate is used as solvents for many oils and resins.
- Ethyl acetate is used as extraction solvent in food processing and pharmaceutical industry.
- Butyl acetate is used as solvent for inks and as a cleaning liquid for surfaces.

2.7 NATURAL AND SYNTHETIC POLYMERS

Polymers are the chief products of modern chemical industry which form the backbone of present society. Daily life without the discovery and varied applications of polymers would not have been easier and colourful. The materials made of polymers find multifarious uses and applications in all walks of our life. They have influenced our day-today life to such an extent that it is impossible to get through the day without using a material based on polymers. Common examples of these include.

Plastic dishes, cups, non-stick, pans; automobile tyres and seat covers, plastic bags, rain coats, plastic pipes and fitting; radio, TV and computer cabinets; wide range of synthetic fibres for clothing, synthetic glues, flooring materials and materials for biomedical and surgical operations.

The word **polymers** means "many parts" (Greek: *poly* means *many* and *merors* means *parts*). A *polymer is a compound of high molecular mass formed by the combination of large number of small molecules.* The small molecules which constitute the *repeating units* in a polymer are called **monomer units**. The process by which the monomers are transformed into polymer is called **polymerisation**. For example, polyethylene is a polymer which is obtained by the polymerisation of ethylene. The ethylene molecules are referred to as monomer units.

Classification of Polymers

Polymers are classified in a number of ways depending upon one criterion or the other as described below.

On the basis of source or origin, the polymers are classified into two types:

1. Natural Polymers. *Polymers found in nature, mostly in plants* and *animal sources*, are called **natural polymers.** A few examples are:

(*a*) *Polysaccharides.* Starch and cellulose are very common examples of polysaccharides. They are the polymers of glucose.

Starch is a chief food reserve of plants while cellulose is chief structural material of plants.

- (*b*) *Proteins.* These are the polymers of α -amino acids. They are building blocks of animal cells. They constitute indispensable part of our food. Wool, natural silk, leather, etc., are proteins.
- (c) *Nucleic Acids.* These are the polymers of various *nucleotides.* RNA and DNA are common examples.
- (d) **Natural Rubber.** Substance obtained from latex is a polymer of 2-methyl buta-1, 3-diene (*isoprene*).

It may be noted that polymers like polysaccharides, nucleic acids, proteins, etc., which control various life processes in plants and animals are also called **biopolymers**.

2. Semi Synthetic Polymers. These are mostly derived from naturally occurring polymers by carrying out chemical modifications. For example,

Cellulose + $(CH_3CO)_2O \xrightarrow{H_2SO_4} Cellulose diacetate$ Acetic anhydride

Cellulose diacetate is used in making threads, films, glasses, etc.

3. Synthetic Polymers. The polymers which are prepared in the laboratory are referred to as synthetic polymers or man-made polymers. Some examples of the synthetic polymers are *polyethylene, polystyrene, PTFE synthetic rubber, nylon, PVC, bakelite, teflon, orlon,* etc.

The synthetic polymers can be further classified as these made up of monomers and comonomer units.

The polymers are also classified based on:

(*i*) Structure (*ii*) molecular forces

(iii) modes of polymerisation.

Addition and Condensation Polymerisation

1. Addition Polymers. When the monomer units are repeatedly added to form long chains without the elimination of any by-product molecules, the product formed is called *addition polymer* and the process involved is called *addition polymerisation*. The monomer units are unsaturated compounds and are usually the derivatives of alkenes. The molecular formula and hence the molecular mass of the addition polymer is an *integral multiple* of that of the monomer units. Some **examples** of addition polymerisation are:



2. Condensation Polymers. In this type of polymers, the monomers react together with the elimination of a simple molecules like H_2O , ROH or NH_3 , etc. The reaction is called condensation and the product formed is called condensation polymer.

As the process involves the elimination of by-product molecules, the molecular mass of the polymer is not the integral multiple of the monomer units. For examples, *nylon-6,6* is a condensation polymer of hexamethylene diamine and adipic acid.



Some other **examples** of condensation polymers are:

Dacron (polyester): A polymer of ethylene glycol and terepthalic acid.

Bakelite: A polymer of phenol and formaldehyde.

Properties of Polymers

On the basis of the magnitude of **inter-molecular forces** present in the polymers, we have,

1. Thermoplastics. There are the polymers in which the interparticle forces of attraction are in between those of elastomers and fibers. The polymers can be easily moulded into desired shapes by heating and subsequent cooling to room-temperature. There is no cross-linking between the polymer chains. In fact, thermoplastic polymers soften on heating and become fluids but on cooling they become hard.

They are capable of undergoing such reversible changes on heating and cooling repeatedly. Common examples of thermoplastics are *polyethene*, *polystyrene*, *polyvinyl chloride*, etc.

2. Thermosetting Polymers. These are the *polymers which become hard and infusible on heating.* They are normally made from *semi-fluid substances* with low molecular masses, by heating in a mould. Heating results in *excessive cross-linking between the chains* forming three dimensional network of bonds as a consequence of which a *non-fusible* and *insoluble* hard material is produced. Bakelite is a common example of thermosetting polymer.

In short, a **thermoplastic material** can be remelted time and again without change, while a **thermosetting material** undergoes a permanent change upon melting and thereafter sets to a solid which cannot be remelted.

Resins and Plastics

(*i*) **Resins.** Resins are amorphous organic solids or sticky organic liquids or semisolids which usually have a typical metallic lustre and are often transparent or translucent. Natural resins are secreted or flow out of plants (and some insects) when they are cut or wounded. They can harden when exposed to the air to form brittle, non-crystalline solids. Resins are insoluble in water but soluble in ether, ethanol and other organic solvents. Examples of natural resins are amber (fossil resin) and shellac.

(*ii*) **Plastics.** A plastic is a substance which is capable of being moulded whereas a resin lacks this property. Typical plastics on heating become soft but do not give mobile melts. In contrast, resins on heating give mobile melts. Plastics usually have much higher molecular mass than resins. Nevertheless, this differentiation is not very clear and the two terms are often used interchangeably.

Chemical Tests on Plastics

Some common methods are discussed as follows:

1. Heating Tests. A small amount of the material to be tested is taken in a spoon type of spatula and heated on a small bunsen flame. The ease of burning, whether the burning continues after removal from the flame, colour of flame and so on, all give an indication of the possible identity of the material. If the material explodes or burns away rapidly, it is possibly a cellulose nitrate composition. A second heating test can be conducted with the help of a **clean copper wire.** The wire is first heated in a clear bunsen flame and then touched with a small quantity of the material. It is heated again and the colour of the flame is noted. Blue and green colours indicate the presence of halogens in the composition, that is, chlorine, fluorine and rarely, bromine. Presence of poly (vinyl chloride) or its co-polymers, poly (vinylidine chloride), Poly(tetrafluoroethylene), chlorinated rubber, rubber hydrochloride or cellulose acetate containing a plasticizer like tricresyl phosphate is indicated by this test.

A third heating test is carried out by heating a small sample in a hard glass tube. The gas evolved is condensed in another tube and very carefully smelled. This can then be compared with the gas evolved from a known polymer.

2. Fusion Test. The metallic sodium fusion test, can show the presence or absence of nitrogen and halogens. Similarly, the potassium nitrate/potassium carbonate fusion test will indicate the presence or absence of phosphorus in the material under examination. Thus, one can easily distinguish between Nylon and Terylene.

Identification of Polymers

From the preliminary tests, a great deal of information can be gathered regarding the possible identity of the unknown polymer. If the polymer does not show rubber like elasticity, an elastomer is ruled out. Further, if on heating it does not melt or flow, a thermosetting polymer is indicated. If it does melt, a thermoplastic polymer is indicated.

Preparation and Uses of Polymers

1. Polythene or Polyethylene. This is addition polymer of ethene. Two types of polythenes namely; *high density polythene* and *low density polythene*, are being produced these days using different conditions for polymerisation.

$$nCH_2 = CH_2 \longrightarrow + CH_2 - CH_2 +_n$$

ethene polythene

Characterstics and uses. It is used in film wraps and bags for packaging, water pipes, coating of telephones, electric wires and cables.

2. Polypropylene. The monomer units are propylene molecules. It is generally manufactured by passing propylene through *n*-*hexane* (inert solvent) containing Ziegler-Natta catalyst (a mixture of triethyl aluminium and titanium chloride).



Characteristics and uses. It is harder, stronger and lighter than polyethene. It is used in:

packing of textile material and food, liners of bags, gramophone records, ropes, carpet fibres, etc.

3. Polystyrene or Styron. The monomer units are styrene molecules. It is prepared by free radical polymerisation of styrene in the presence of benzoyl peroxide.



Characteristics and uses. It is a white thermoplastic material which is transparent and floats on water. It is used for making toys, combs, model construction kits, ceiling tiles, packing for delicate articles and lining material for refrigerators and TV cabinets.

Polystyrene is sold under the name styrofoam or styron.

4. Teflon or Poly Tetrafluoro Ethylene (PTFE). The monomer unit is Tetrafluoro-ethylene molecules. It is prepared by heating tetrafluoroethylene under pressure in the presence of ammonium peroxo-sulphate $[(NH_4)_2S_2O_8]$.

 $nCF_{2} = CF_{2} \xrightarrow{(NH_{4})_{2} S_{2}O_{8}} \xrightarrow{(-CF_{2}-CF_{2})_{n}}$ Tetrafluoroethylene

Characteristics and uses. It is a very tough material and is resistant towards heat, action of acids or bases. It is bad conductor of electricity. It is used in:

coating utensils to make them non-sticking, making seals and gaskets which can withstand high pressures, insulations for high frequency electrical installations.

5. Buna-S. It is a copolymer of 1,3-butadiene and styrene. It is obtained by the polymerisation of butadiene and styrene in the ratio of 3: 1 in the presence of sodium. It is also known as styrene butadiene rubber (SBR).

 $nCH_{2} = CH - CH = CH_{2} + nC_{6}H_{5}CH_{5} = CH_{2}$ Butadiene Na, \downarrow Heat

$$-CH_2 - CH = CH - CH_2 - CH - CH_2 - \frac{1}{C_6}H_5$$

Buna-S

In Buna-S, *Bu* stands for butadiene; *na* for sodium which is polymerising agent and S stands for *styrene*.

Characteristics and uses. SBR has slightly less tensile strength than natural rubber. It is used in the manufacture of :

automobile tyres, rubber soles, belts, hoses, etc.

6. Nylon-6,6. It is a polymer of *adipic acid* (1, 6-hexanedioic acid) and *hexamethylene diamine* (1, 6-diaminohexane)



Characteristics and uses. Nylon-66 (read as *nylon-six-six*) can be cast into a sheet or fibers by spinning devices. Nylon fibers have high tensile strength. They are tough and resistant to abrasion. They are also somewhat elastic in nature. Nylon finds uses in:

making bristels and brushes, carpets and fabrics in textile industry, elastic hosiery in the form of crinkled nylon.

7. Nylon 6,10. It is a polymer of hexamethylene diamine (six carbon atoms) and sebacoyl chloride (ten carbon atoms)

$$\begin{array}{c} O & O \\ & O & O \\ & & H_2N(CH_2)_6 - NH_2 + nCl - C(CH_2)_8 - C - Cl \\ & & heat \downarrow \\ & H & O & O \\ & & \downarrow \\ & + O & O \\ & & - HN - (CH_2)_6 - N - C - (CH_2)_8 - C + n + 2nHCl \\ & & Nylon 610 \end{array}$$

8. Natural Rubber. Rubber is a natural polymer and possesses elastic properties. It is obtained from a rubber tree. When the bark of

the tree is cut, a sticky white liquid, *latex*, oozes out. It is a suspension of rubber particles in water.

Natural rubber is a linear polymer of 2-methyl-1, 3-butadiene (isoprene). It is also called as *cis*-1,4-poly isoprere. On an average it contains 5000 isoprene units. All the double bonds in natural rubber are Cis. Rubber is a waterproof material.



natural rubber

The *cis*-poly isoprene molecule consists of various chains held by weak van der Waals interactions and has a coiled structure. Thus it can be stretched like a spring and exhibits elastic properties. Gutta-percha (*getah* means gum and *percha* means tree) is a naturally occurring isomer of rubber in which all the double bonds are trans. Like rubber, gutta percha is exuded by certain trees. It is harder and more brittle than rubber.

2.8 INTRODUCTORY BIOCHEMISTRY

Proteins are the complex organic substances which are the basis of protoplasm and are found in all living organisms. The name protein (Greek, *proteios means first*) was introduced by Mudlar (1839) because of prime importance of such substances to animal life. In human beings, proteins constitute about 18% by mass of the body.

In general, proteins are polymers of α -amino acids. The amino acid units in proteins are held by peptide (—CONH—) linkage. Polymeric products of α -amino acids with molecular mass up to 10,000 are called *polypeptides* while those having molecular mass more than 10,000 are considered as *proteins*. However, there is no sharp demarcation between polypeptides and proteins.

Sources of Proteins

Proteins are found in the animal as well as plant foods. Animal foods such as *meat, poultry, fish, eggs, milk and cheese* contain proteins with many essential amino acids. Plant products such as *beans, groundnuts, cashew nut, cereals (maize and wheat) and pulses* are also good protein food, though they contain fewer essential amino acids.

2.9 AMINO ACIDS

These are amino substituted carboxylic acids. Of various amino acids, the α -amino acids or 2-amino acids are quite important because they are the building blocks of peptides and proteins. In α -amino acids, the amino group is present on the α -carbon atom (*i.e.*, C atom next to COOH group). Thus, they can be represented by the general formula,

R-CH-COOH

NH₂

Group R—is different for different α -amino acids.

About 20 of the α -amino acids have been identified as the constituents of most of the animal and plant proteins.

Classification of Amino Acids

The amino acids containing equal number of amino and carboxyl groups are known as **neutral amino acids**. The amino acids which contain more number of carboxyl groups than amino groups are known as **acidic amino acids** while those containing more number of amino groups are called **basic amino acids**. For example, *glutamic acid* and *aspartic acid* are acidic amino acids while *lysine* is basic amino acid. *Alanine* is a neutral amino acid.

Structure of Amino Acids

It has been found by spectroscopic means that —COOH and $-NH_2$ groups of amino acids do not exist as such but they react with each other to form *internal salt structure* which is also called **zwitter ion structure**. In the formation of zwitter ion, a proton from —COOH part of the molecule is released and attaches itself to $-NH_2$ part to constitute a dipolar ion as shown as follows:



Zwitter ion is a neutral species but carries both positive and negative charges.

Properties of Amino Acids

The amino acids are usually colourless, crystalline and high melting solids. They are moderately soluble in water. They are insoluble in organic solvents such as ether, benzene and petroleum ether. In *acidic solution* amino acids exist as *cations* and migrate towards cathode in an electric field whereas in basic solutions they exist as *anions* and migrate towards anode. At the intermediate pH, however, they exist as **zwitter ion** (a dipolar ion) and do not migrate towards either electrode. This pH is known as the **isoelectric** point of the α -amino acid.



Different amino acids have different isoelectric points. The isoelectric point of an amino acids depends upon the functional groups present in the amino acid. Neutral amino acids have isoelectric point in the pH range of 5.6–6.3.

At isoelectric point the amino acids have least solubility in water. This property of amino acids is exploited in the separation of different α -amino acids obtained by hydrolysis of proteins.

 α -Amino acids exhibit chemical reactions characteristic of primary -NH₂ group and -COOH group.

Example 2.1. Give reasons for the following:

On electrolysis in acidic solution amino acids migrate towards cathode while in alkaline solution these migrate towards anode.

Solution. In acidic medium, amino acids exist as cations (R-CH-COOH) and in basic medium they exist as anions

(R—CH—COO⁻). Therefore, on electrolysis in acidic medium they $|_{NH_2}$

migrate towards cathode while in alkaline medium they migrate towards anode.

2.10 FORMATION OF PEPTIDES AND PROTEINS

Peptides are the products formed by the condensation of two or more amino acids through their amino and carboxylic groups involving elimination of water molecules. They may be classified as *dipeptides*, *tripeptides*, *tetrapeptides*, etc., depending upon whether the number of amino acid molecules taking part in condensation is *two*, *three* or *four* respectively. When the number of such amino acids is more than ten, the product is called **polypeptide**. A polypeptide having molecular mass more than 10000 *u* is called **protein**. Thus, **polypeptides and proteins are condensation** polymers of α -amino acids. The linkage (-CO-NH-) which unites various amino acid units in a peptide molecule is called peptide linkage or peptide bond.



Hydrolysis of Proteins

Polypeptides and proteins can be hydrolysed by dilute acids or enzymes. The ultimate product of hydrolysis of proteins is a mixture of α -amino acids.

When food is digested, the proteins present in it are broken into constituent amino acid molecules. During digestion the peptide linkage that joins the amino acids in proteins gets hydrolysed. **Hydrolysis of** **proteins takes place in the stomach and small intestine** and the amino acids produced in the process are absorbed from the intestine by the blood. These amino acids are then regrouped to form specific proteins in the cells of our body.

Hydrolysis of tripeptide glycylalanylglycine (gly.ala.gly) is shown below:



Uses of Proteins

Uses of Proteins for Food

Proteins are an important component of our food. Proteins build up, maintain and replace the tissues in our body. Our muscles, our organs, and our immune systems are made up mostly of protein. Our body uses the protein we eat to make large number of specialized protein molecules that have specific functions.

The best sources of proteins are poultry, fish, eggs, nuts, dairy products, (such as milk, cheese, curd) seeds and legumes.

Proteins, in our food, supply the essential amino acids which our body is unable to synthesize. When we eat food that contains proteins, the digestive juices in the stomach and intestines break down the proteins present in food into amino acids. The amino acids then can be used to give energy that our body needs to perform various functions.

Functions of Proteins

Some of the different forms of proteins and their important functions in human body are given below:

1. Proteins are needed for **growth** and **repair** of the body growing children need proteins in large quantities for making new tissues. Proteins as muscle, skin, hair and other tissues *constitute the bulk of body's non-skeletal structure.*

- 2. Some proteins *as hormones* regulate many body functions. For example, the hormone **insulin** is a protein. It regulates sugar level in the blood.
- 3. Some proteins *as enzymes* catalyse or help in biochemical reactions. For example, **pepsin** and **trypsin**.
- 4. Some proteins act as *antibodies,* and protect the body from the effect of invading species or substances.
- 5. *Transport proteins* carry different substances in the blood to different tissues. For example, **haemoglobin** is a transport protein. It carries oxygen from lungs to the tissues and carbon dioxide from tissues to the lungs.

Tests of proteins

1. BIURET TEST

To the dispersion of the substance to be tested (say 5% solution of egg albumin) add about 2 ml of NaOH solution. Now add 4–5 drops of 1% CuSO₄ solution.

Bluish violet colouration indicates the presence of protein.

2. MILLON'S TEST

This test is given by proteins containing phenolic amino acids. *Gelatin does not give this test.*

To 1-2 ml of egg albumin dispersion add 2 drops of Millon's reagent.

White ppt. which changes to brick red on boiling, confirms the presence of proteins.

3. NINHYDRIN TEST

Take about 2 ml of egg albumin dispersion in a test-tube and add 1-2 ml of Ninhydrin solution. Boil the contents.

Intense blue or purple colouration confirms the presence of proteins.

2.11 CARBOHYDRATES

Carbohydrates constitute an important class of compounds like glucose, fructose, sucrose, starch, cellulose, etc., which play a vital role in our everyday life. They are the ultimate source of most of our food. We clothe ourselves with cellulose in the form of cotton, rayon and linen. We build furniture and houses from cellulose in the form of wood. Thus, carbohydrates provide us with basic necessities of life, food, clothing and shelter. Carbohydrates are also known as **saccharides**. Originally, the name carbohydrate was given to the compounds pertaining to general formula $C_x(H_2O)_y$, and they were considered to be hydrates of carbon. However, this definition could not hold ground for long because many compounds like *formaldehyde* (CH₂O), *acetic acid* (C₂H₄O₂), etc., conform to formula $C_x(H_2O)_y$ but they do not exhibit the characteristic properties of carbohydrates.

According to the modern definition **carbohydrates** are defined as *polyhydroxy aldehydes or polyhydroxy ketones or the compounds that yield such compounds on hydrolysis.*

Classification of Carbohydrates

Carbohydrates are classified into three major categories depending upon their behaviour towards hydrolysis:

1. MONOSACCHARIDES

These are simple carbohydrates which cannot be hydrolysed to simpler carbohydrates. About 20 monosaccharides are known to occur in nature. **Glucose** and **fructose** are common examples.

2. OLIGOSACCHARIDES

These are the carbohydrates which on hydrolysis give two to ten units of monosaccharides. Accordingly, they may be further divided into *di*, *tri* or *tetrasaccharides* depending upon the actual number of monosaccharide units formed by the hydrolysis of a particular oligosaccharide.

Disaccharides give two units of monosaccharides on hydrolysis. The two monosaccharide units obtained on hydrolysis of a disaccharide may be same or different. Common examples are **sucrose** and **maltose**. Both have molecular formula $C_{12}H_{22}O_{11}$.

Sucrose on hydrolysis gives one molecule of glucose and one molecule of fructose whereas maltose on hydrolysis gives two molecules of glucose only.

Trisaccharides give three units of monosaccharides on hydrolysis. Raffinose, $C_{18}H_{32}O_{16}$ is a common example.

Tetrasaccharides give four units of monosaccharides on hydrolysis. Stachyose, $C_{24}H_{42}O_{21}$ is a common example.

3. POLYSACCHARIDES

These are the carbohydrates which are polymeric molecules and can be hydrolysed to give large number of monosaccharide units. The commonly occurring polysaccharides have the general formula $(C_6H_{10}O_5)_n$. The common examples are **starch**, **glycogen** and **cellulose**.

It may be noted that the carbohydrates which are sweet in taste are collectively called **sugars** while those which are not sweet are called **non-sugars**. *Monosaccharides and disaccharides are* **sugars** *but polysaccharides are* **non-sugars**.

The relative degree of sweetness of various sugars is given below in tabular form:

Sugar	Lactose	Maltose	Galactose	Glucose	Sucrose	Fructose
Relative Sweetness	16	32	32	74	100	173

Reducing and Non-reducing Carbohydrates

The carbohydrates may also be classified as **reducing** and **nonreducing** sugars. The carbohydrates which can reduce Tollen's reagent or Fehling's or Benedict's solution are classified as reducing sugars, while those which do not reduce these reagents are called non-reducing sugars.

Reducing sugars contain free aldehyde or ketonic group. All monosaccharides are reducing sugars. Disaccharides may be reducing or non-reducing. If the carbonyl groups of both the monosaccharides are involved in linkage, the disaccharide is non-reducing. On the other hand, if one of the carbonyl groups is free, the disaccharide is reducing. **Sucrose is a non-reducing sugar while maltose is a reducing sugar.**

Sources of Carbohydrates

- **Glucose** occurs in *sweet fruits* such as grapes, mangoes, oranges, etc. *Honey* is also rich in glucose. In combined state it is present in maltose, sucrose, starch, cellulose, etc.
- Fructose is found in *ripe fruits* and *honey*.
- Sucrose. Major sources of sucrose are *sugarcane* and *sugarbeet*
- Lactose is present in *milk*.
- **Starch.** Major sources of starch are *wheat, rice, cassava, root tubers* such as potatoes, *legumes* and *vegetables.*
- Cellulose. Cellulose is present in *cotton*, *wood* and *jute*.

Activity

Tests for Reducing Sugars

1. FEHLING'S TEST

Take 2 cm³ of aqueous solution of carbohydrate (nearly 5%) and add 1–2 cm³ each of Fehling's solution A and Fehling's solution B. Keep the test tube in boiling water bath.

Reddish ppt. indicates the presence of a reducing sugar. Preparation of Fehling's Solution

Fehling's Solution A. Dissolve 17.5 g of $CuSO_4$ in 250 cm³ of distilled water containing few drops of H_2SO_4 .

Fehling's Solution B. Dissolve 8.65 g of sodium potassium tartarate and 35 g NaOH in 150 cm^3 of distilled water.

2. BENEDICT'S TEST

To $1-2 \text{ cm}^3$ of aqueous solution of carbohydrate in a test tube add $1-2 \text{ cm}^3$ of Benedict's reagent. Keep the test tube in a boiling water bath.

Reddish ppt. indicates the presence of reducing sugar. Preparation of Benedict's Reagent

Dissolve 17.3 g of sodium citrate and 9 g of anhydrous Na_2CO_3 in about 80 cm³ of distilled water. Heat if necessary. Dissolve 1.73 g of copper sulphate in 100 cm³ of water. Mix the two and make the volume 250 cm³ by adding water.

3. TOLLEN'S TEST

Take $2-3 \text{ cm}^3$ of aqueous solution of carbohydrate in a test tube. Add to it $2-3 \text{ cm}^3$ of Tollen's reagent. Keep the test tube in a boiling water bath for 10 minutes.

A shining silver mirror indicates the presence of reducing carbohydrate.

Preparation of Tollen's Reagent

Add NaOH solution to $AgNO_3$ solution. Then add NH_4OH solution dropwise till the ppt. just dissolved. The clear solution obtained is Tollen's reagent.

4. IODINE TEST (FOR STARCH ONLY)

To the aqueous suspension of the sample, add 1-2 drops of iodine solution.

Appearance of blue colouration indicates the presence of starch.

Uses of Carbohydrates

Some important uses of carbohydrates are discussed below:

- 1. **Glucose** is widely used in food industry in production of fruit drinks and sweets.
- 2. **Glucose** is soluble in water and is absorbed rapidly into the blood stream. Therefore, it is useful for sick people and sportsmen who need instant energy.
- 3. Fructose is the sweetest sugar. It is used as a sweetening agent.
- 4. **Sucrose** is commonly used as table sugar. It is also used as sweetening agent.
- 5. **Sucrose** is used to prepare glucose and fructose by hydrolysis. Sucrose is also used in the manufacture of ethanol by fermentation.
- 6. **Starch** can be used for the production of ethanol by hydrolysis and fermentation. It is extensively used in food.
- 7. **Starch** is used for stiffening cloth after laundering. Its suspension in water is used as an adhesive.
- 8. Cellulose is used for the production of paper.

2.12 FATS AND OILS

Fats and oils are important constituents of balanced diet for human beings. Fats are solids while oils are liquids at room temperature. A substance which behaves as an oil in a tropical country such as Ghana may behave as a fat in a country with colder climate. However, fats and oils have the same basic structure. Fats and oils are generally insoluble in water but are soluble in organic solvents.

General Structure of Fats and Oils

Fats and oils are triesters of glycerol with long chain fatty acids. Each molecule of fat is composed of one molecule of glycerol and three molecules of fatty acids. A molecule of fat may be represented by the general formula,



These triesters of glycerol and fatty acids are known as triglycerides. If the triglyceride contains all the three same acid groups, it is known as simple glyceride and if the acid groups are different, it is called a mixed glyceride. Glycerides consisting predominantly of saturated fatty acids are solid at room temperature while those with a high proportion of unsaturated acids are usually liquid at room temperature and are called **oils**.



(A saturated fat)

 $C_{17}H_{22}$ Triolein (A unsaturated fat or oil)

 $-C_{17}H_{33}$

 $C_{17}H_{33}$

Sources of Oils and Fats

Oils and fats are widely distributed both in plants and animals.

In plants oils and fats are stored in their seeds, roots and fruits. Ground nuts, cotton seeds, palm kernels, castor beans, olives are rich in fats and oils. These are rich in unsaturated fats.

Animals are also an important source of fats. Milk and milk products such as butter, cream, cheese are rich in fats. Meat and eggs also contain fat. Creamish white fat found in pig meat (pork) is called lard. Tallow, the fat from sheep and cattle is used largely for making soap.

Extraction of Fats and Oils

Fats and oils are extracted from the natural sources by the following processes:

- 1. Rendering. The animal tissues containing the fat are heated dry or with water until the fat melts and can be removed.
- 2. Pressing. Oils are obtained from seeds by crushing between steel rollers and then pressing in a *hydraulic press*.
- 3. Solvent Extraction. It is often applied to the residue after pressing or rendering for complete removal of oil or fat. The solvents used include petroleum ether and benzene.

Properties of Oils and Fats

Physical Properties

- 1. Oils and fats are liquids or solids having a greasy feel. When pure, they are colourless, odourless and tasteless.
- 2. They are insoluble in water but soluble in organic solvents such as ether, chloroform and benzene.
- 3. They have a lower density than water and consequently float on the surface when mixed with water.

Chemical Properties

Fats and oils are triesters of glycerol with saturated and unsaturated fatty acids. Their reactions are those of ester groups in triplicate and carbon-carbon double bonds.

1. Hydrolysis. They are readily hydrolysed by heating with acids or alkalies or superheated steam. When boiled with sodium or potassium hydroxide solution, the hydrolysis products are glycerol and sodium or potassium salts of long-chain fatty acids. The latter are called **soaps** and alkaline hydrolysis is known as **saponification**.



2. Hydrogenation. On catalytic hydrogenation, hydrogen adds across the carbon-carbon double bonds of the acid components of the triglycerides. This results in the formation of saturated glycerides which are solid fats at room temperature. This hydrogenation process is called **hardening of oils.** For example,



Partial hydrogenation of vegetable oils is used for the manufacture of **margarine** and other hardened oils.

Tests for Oils and Fats

SOLUBILITY TEST

This test is based on the fact that oils and fats are soluble in organic solvents such as chloroform, ethanol, etc., but are insoluble in water. Shake a small amount of the given sample with 5 cm³ each of water, ethanol and chloroform in three test tubes. Observe the solubility and draw inferences.

Test tube	Solvent	Observation		Inference	
1.	Water	(<i>i</i>) Sample is im	miscible	Oil or fat	present.
		(<i>ii</i>) Sample is mi	scible	Oil or fat a	absent.
2.	2. Alcohol (<i>i</i>) Sample forms lower layer, which <i>dissolves on heating</i>		Oil or fat j	present.	
55		(<i>ii</i>) Sample <i>does</i> even on heat	<i>not dissolve</i> ting.	Oil or fat a	absent.
3.	Chloroform	loroform (<i>i</i>) Sample is <i>miscible</i> .		Oil or fat	present.
		(<i>ii</i>) Sample is	immiscible.	Oil or fat a	absent.

TRANSLUSCENT SPOT TEST

Press a little of the substance in the folds of the filter paper. On unfolding the filter paper, the appearance of **transluscent or greasy spot** on filter paper indicates the presence of fat or oil. The spot grows larger on heating and drying the filter paper.

ACROLEIN TEST

Heat a little of the sample with some crystals of $KHSO_4$ in a test-tube. A **pungent irritating odour of acrolein** confirms the presence of fat or oil.



Soaps and Synthetic Detergents

The word 'detergent' means '*cleansing agent*' and so *the detergents are substances which remove dirt and have cleansing action in water.* According to this definition of detergents, soap is also a detergent and has been used for more than two thousand years. There are two types of detergents:

1. Soapy detergents or soaps

2. Non-soapy detergents or soapless soaps.

Soap

A soap is a sodium or potassium salt of some long chain carboxylic acids (fatty acid).

Sodium salts of fatty acids are known as **hard soaps** and potassium salts of fatty acids are known as **soft soaps**. Hard soaps are prepared from cheap oils and fats and sodium hydroxide. They contain free alkali and are used for washing purposes. Soft soaps are prepared from good oils and potassium hydroxide. They do not contain free alkali, produce more lather and are used as toilet soaps, shaving creams and shampoos.

A soap has a large non-ionic hydrocarbon group and an ionic $COO^{-}Na^{+}$ group. So for simplicity the structure of soap can be represented as



Soap Molecule

Some examples of soaps are: sodium stearate, $C_{17}H_{35}COO^{-}Na^{+}$, sodium palmitate, $C_{15}H_{31}COO^{-}Na^{+}$ and sodium oleate, $C_{17}H_{33}COO^{-}Na^{+}$.

Soaps of metals other than sodium and potassium are usually water-insoluble and do not find application as a cleansing agent. Therefore, hard water, which contains salts of magnesium and calcium, reacts with soap to form magnesium salt of fatty acid and calcium salt of fatty acid.

These calcium and magnesium salts of fatty acids are insoluble in water and separate as curdy white precipitate. Thus, a lot of soap is wasted if water is hard.

Activity

Study of Action of Soap in Hard Water

- Take two test tubes and label them as A and B.
- In test tube A, put 10 cm³ of distilled water (or rain water) and in test tube B take 10 cm³ of hard water.
- Add 5 drops of soap solution to both the tubes. Shake the test tubes vigorously for an equal period of time. *What do you observe?*

It is observed that more foam is formed in the test tube containing distilled water. In the test tube containing hard water less foam is formed and at the same time a *curdy white precipitate* is formed.

Note. If hard water is not available, it can be prepared by adding small amount of calcium chloride or magnesium sulphate to the ordinary water.

PREPARATION OF SOAP

Soap is prepared by heating oil or fat of vegetable or animal origin with calculated quantity of concentrated sodium hydroxide solution (caustic soda solution). Hydrolysis of fat takes place and a mixture of sodium salts of fatty acids and glycerol is formed.

 $\begin{array}{c} CH_2O.COH_{15}H_{31} \\ CHO.COC_{15}H_{31} + 3NaOH \longrightarrow \\ CH_2O.COC_{15}H_{31} \\ Fat or oil \\ (Tripalmitin) \end{array} \xrightarrow{\begin{array}{c} CH_2OH \\ CHOH + 3C_{15}H_{31}COONa \\ CH_2OH \\ Glycerol \\ (Sodium palmitate) \\ or Sodium \\ hexadecanoate \end{array}$

Soap which is formed as a result of alkaline hydrolysis of oil or fat is separated from the solution by the addition of sodium chloride (common salt). Salt decreases the solubility of soap which is, therefore, released soap from the solution. The process is known as **salting out**. The crude soap that separates out is called **grained soap**. Now, soap being lighter than water floats on its surface from where it is removed. The lower aqueous layer is called **lye**.

After the removal of soap the solution which is left behind contains glycerol and sodium chloride. Glycerol is then recovered from this mixture as it is an important chemical which finds use in drugs, paints, cosmetics and explosives.

Activity

Laboratory Preparation of Soap

- Take about 25 cm^3 of castor oil or vegetable oil in a beaker. To this add about 50 cm^3 of 20 per cent sodium hydroxide solution slowly with constant shaking.
- Heat the mixture slowly to boil and let it continue boiling for about ten minutes.
- Remove the beaker from the burner and add about 5 g of common salt to the beaker.
- Allow the mixture to cool.

What do you observe?

After sometime a solid crust of soap will be seen floating in the beaker.

Uses of Fats and Oils

The uses of fats and oils are as follows:

1. Oils and fats are important *constituent of food*. They are used as food mainly to provide energy.

- 2. Oils are used for the *preparation of margarine* and *soaps*.
- 3. Some oils such as cod liver oil find *medicinal* application.
- 4. Fats and oils are also used in the manufacture of *cosmetics* such as cold creams, lip-sticks, lotions, etc.
- 5. Certain drying oils such as linseed oil are used in oil-based *paints*.
- 6. Some oils are used for *lubrication of machine parts*.

Exercise

I. Multiple Choice Questions

- 1. Alcohols are the compounds containing one or more
 - (a) Carboxyl group (b) Hydoxyl group
 - (c) Carbonyl group (d) Nine of these
- 2. R—OH is the general formula of
 - (a) Alkanols (b) Aldehydes
 - (c) Ketones (d) one of these
- 3. Which of these are most important alkanols?
 - (a) Ethanol (b) Methanol
 - (c) Both (a) & (b) (d) None of these
- 4. Which of these has been used as inhalation anaesthetic?
 - (a) Dimethyl ether (b) Diethyl ether
 - (c) Ethoxy ethane (d) None of these
- 5. This polymer is also known as styrene butadiene rubber.
 - (a) Buna-S (b) Teflon
 - (c) Styron (d) None of these

II. Fill in the Blanks.

- 1. In alcohols, is the functional group.....
- 2. Alcohols behave as because of the presence of polar O—H group.
- 3. In haloalkanes, the halogen atom is bonded to carbon atom.
- 4. The molecular formula of sucrose is
- 5. In Buna-S, S stands for

6. Arrange the following sets of compounds in order of their increasing boiling points,

(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol

- (b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.
- 7. Classify the following as primary, secondary and tertiary alcohols :



- 8. Explain why is propanol has higher boiling point than butane?
- 9. Alcohols are comparatively more soluble in water than the hydrocarbons of comparable molecular masses. Explain this fact.
- 10. Give two reactions that show the acidic nature of phenol. Compare its acidity with that of ethanol.
- 11. Give IUPAC names of the following ethers :

(*i*)
$$C_2H_5OCH_2-CH-CH_3$$
 (*ii*) $CH_3OCH_2CH_2CI_2$
(*iii*) $O_2N-C_6H_4-OCH_3(p)$ (*iv*) $CH_3-CH_2-CH_2-OCH_3$



- 12. Explain the fact that in aryl ethers (*i*) the alkoxy group activates the benzene ring towards electrophilic substitution and (*ii*) it directs the incoming substituents to *ortho* and *para* position in benzene ring.
- 13. How are the following conversions carried out?
 - (*i*) Propene \longrightarrow Propan-2-ol
 - (*ii*) Benzyl chloride \longrightarrow Benzyl alcohol
 - (*iii*) Ethyl magnesium chloride \longrightarrow Propan-1-ol
 - (*iv*) Methyl magnesium bromide \longrightarrow 2-methylpropan-2-ol.