BIOMOLECULES & POLYMERS

CARBOHYDRATES

INTRODUCTION

Carbohydrates received their name because of their general formula $C_x(H_2O)_y$, according to which they appear to be hydrates of carbon.

$$xCO_2 + yH_2O \xrightarrow{\text{Sunlight, chlorophyll}} C_x(H_2O)_y + xO_2$$

Carbohydrate

A polyhydroxy compound that has an aldehyde or a ketone functional group present, either free or as hemiacetal or acetal are called carbohydrate.

Carbohydrates are substances with the general formula $C_x(H_2O)_y$, and were therefore called carbohydrates (hydrates of carbon) because they contained hydrogen and oxygen in the same proportion as in water.

However, a number of compounds have been discovered which are carbohydrates by chemical behaviour, but do not conform to the formula $C_v(H_2O)_v$, e.g., 2-deoxyribose, $C_sH_{10}O_s$.

EDUBULL KEY POINTS

It is also important to note that all compounds conforming to the formula $C_x(H_2O)_y$ are not necessarily carbohydrates, e.g., formaldehyde, CH₂O; acetic acid, $C_2H_4O_2$; etc.

Carbohydrates are often referred to as Saccharides (Latin, Saccharum = sugar) because of the sweet taste of the simpler members of the class, the sugars.

CLASSIFICATION OF CARBOHYDRATE

The carbohydrates are divided into three major classes depending on the number of simple sugar units present in their molecule.

- (i) Monosaccharide : A carbohydrate that cannot be hydrolyzed to simpler compounds is called monosaccharide. Monosaccharide which have six carbon are either aldohexoses or ketohexoses
- (ii) Oligosaccharides : Carbohydrates that yield two to ten monosaccharide units, on hydrolysis, are called oligosaccharides. They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc., depending upon the number of monosaccharides, they provide on hydrolysis. Amongst these the most common are disaccharides. The two monosaccharides units obtained on hydrolysis on a disaccharide may be same or different. For example, sucrose on hydrolysis gives one molecule each of glucose and fructose whereas maltose gives two molecules of glucose only.
- (iii) **Polysaccharide :** A carbohydrate that can be hydrolyzed to many monosaccharide molecules is called a polysaccharide. Example : Starch, Cellulose, etc.



Aldohexoses

Their structure has been elucidated as follows :

- (i) Analysis and molecular-weight determinations show that the molecular formula of the aldohexoses is $C_6 H_{12} O_6$.
- (ii) When treated with acetic anhydride, aldohexoses form the penta-acetate. This indicates the presence of five hydroxyl groups.



- (iii) Aldohexoses form an oxime when treated with hydroxylamine, or add molecule of HCN to form cyanohydrin and therefore contain a **carbonyl group**.
- (iv) When an aldohexose is oxidised with bromine-water or tollen's reagent or fehling solution a pentahydroxy-acid of formula $C_6H_{12}O_7$ is obtained. This indicates that the carbonyl group present is an aldehydic group.
- (v) When reduced with concentrated hydroiodic acid and red phosphorus at 100°C, aldohexoses give n-hexane. This indicates that the six carbon atoms in an aldohexose are in a straight chain.

The above reactions show that structure of aldohexoses is

$$\begin{array}{c|c} CH_2 - C(H) - C(H) - C(H) - C(H) - CHO \\ | & | & | & | \\ OH & OH & OH & OH \\ \end{array}$$

Due to four asymmetric carbon atoms, there are sixteen optical isomers.

or Eight pairs of enantiomers. (8D-variety & 8L-variety).

D-variety of them are as follows





Note: 1. D-aldohexoses shown above have epimeric / diastereomeric relationship with each other 2. D-aldohexoses can be either dextro (+) or laevo (-)

Aldoses : Monosaccharides containing aldehyde group are called aldoses.

Ketoses : Monosaccharides containing ketonic group are called ketoses.

Photosynthesis

 $6CO_2 + 6H_2O + 18 \text{ ATP}$ Sunlight, chlorophyll $C_6H_{12}O_6 + 6O_2$

Cellular Respiration

 $C_6H_{12}O_6 + 6O_2$ enzymes $6CO_2 + 6H_2O + 38 \text{ ATP} (36 \text{ ATP net gain})$

CLASSIFICATION AND STRUCTURE OF CARBOHYDRATES

Carbohydrates are polyhydroxy aldehydes and ketones and substances which hydrolyse to polyhydroxy aldehydes and ketones.

The simplest carbohydrates are called **sugars** or **saccharides**, (Latin: Saccharum, sugar). Carbohydrates can be classified as **monosaccharides**, **oligosaccharides** and **polysaccharides**.

GENERAL CHARACTERISTIC OF MONOSACCHARIDES

The important characteristics of monosaccharides as follows:

- (i) All monosaccharides are water soluble due to the presence of hydrogen bonding between the different OH groups and surrounding water molecules.
- (ii) Monosaccharides have sweet taste and upon heating they get charred and give the smell of burning sugar.
- (iii) Monosaccharides are optically active in nature due to the presence of chiral carbon atoms.
- (iv) The chemical characteristics of monosaccharides are due to OH groups and carbonyl group which may be either aldehydic or ketonic group.

Glyceraldehyde contains one asymmetric carbon atom (marked by an asterisk) and can thus exist in two optically active forms, called the D-form and the L-form. Clearly, the two forms are mirror images that cannot be superimposed, that is they are **enantiomers**.





All four isomers have been prepared synthetically. The D-and L-erythrose are mirror images, that is, they are enantiomers. They have exactly the same degree of rotation but in opposite directions. Equal amounts of the two would constitute a racemic mixture, that is a mixture that would allow a plane-polarised light to pass through the solution unchanged.

$$\begin{array}{c|c} C & - C &$$

Supplying hydrogen atoms to the five carbon atoms to satisfy their tetravalency, following structure (open chain) may be assigned to glucose: (* indicates asymmetric carbon atom).

GLUCOSE

Glucose is the most common monosaccharide. It is known as Dextrose because it occurs in nature principally as the optically active dextrorotatory isomers. It is act as a reducing agent (reduces both Fehling's solution and ammonical silver nitrate solution). When heated with sodium hydroxide, an aqueous solution of glucose turns brown. It is known as dextrose and found as grapes, honey, cane sugar, starch and cellulose.

Configuration of Glucose:

Since the above structure possesses four asymmetric carbon atoms (shown by asterisks), it an exist in $2^4 = 16$ optically active forms, i.e., eight pairs of enantiomers. All these are known and correspond to the D- and L-forms of glucose, mannose, galactose, allose, glucose, idose and talose.

The naturally occurring dextrorotatory glucose (+)-glucose is only one of the 16-stereoisomers.



Notations D- and L- for denoting configuration were given by Rosanoff; according to this convention any compound whose bottom asymmetric carbon atoms has the configuration similar to the configuration of dextrorotatory glyceraldehyde (drawn above, i.e. the bottom carbon atom has –OH to the left and H to the right is given L-configuration. Remember that the symbols D-and L- have no relation with the specific rotation value, i.e., with (+) or (–) value. For example, the natural (–) fructose belongs to D-series, i.e., it is D(–)-fructose)



Objections to open-chain structure of glucose:

Even through open chain structure of (+) glucose explains most of its reactions, it fails to explain the following facts about it.

- (i) Glucose does not restore Schiff's reagent colour.
- (ii) Glucose does not form a bisulphite and aldehyde-ammonia compound.
- (iii) Glucose forms two isomeric penta-acetates neither of which reacts with carbonyl reagents.
- (iv) The existence of the two isomeric glucoses and the change in specific rotation (mutarotation) is not explained by an open-chain formula.
- (v) Glucose reacts with methanol in presence of dry HCl gas to form two isomeric glucosides.

Since glucose is less soluble in ethanol, it separates out on cooling the reaction mixture. Commercially, it is obtained by the hydrolysis of starch which is available from relatively inexpensive source such as maize, potatoes and rice. **Constitution of Glucose:**

Molecular Formula: By the usual analytical methods, the molecular formula glucose is found to be $C_6 H_{12} O_6$.

Straight Chain of six carbon atoms:

(i) Reduction of glucose with conc. HI and phosphorus gives 2-iodohexane and n-hexane. This indicates that six carbon atoms in glucose are present in a straight chain

$$C_{6}H_{12}O_{6} \xrightarrow{HI/P} CH_{3} - (CH_{2})_{4} - CH_{3}$$

heating
heating
heating
heating

(ii) Glucose when oxidized with bromine water gives gluconic acid which when reduced with excess of HI gives n-hexanoic acid, CH₃(CH₂)₄. COOH confirming the presence of a straight chain of six carbon atoms in glucose.

Presence of five hydroxyl groups: When treated with acetic anhydride, glucose forms penta-acetate indicating the presence of 5 – OH groups and since glucose is a stable compound, the five –OH groups must be attached to 5 different carbon atoms.



Presence of an aldehydic groups:

(i) Glucose forms a cyanohydrin with hydrogen cyanide and a mono-oxime with hydroxylamine suggesting the presence of a carbonyl group.





- (ii) Glucose reduces Fehling solution and Tollen's reagent indicating that the carbonyl group is aldehydic in nature.
- (iii) The presence of aldehydic group in glucose is confirmed by its oxidation to gluconic acid having the same number of carbon atoms.

 $C_{5}H_{11}$. CHO + (O) $\xrightarrow{Br_{2}}$ $C_{5}H_{11}O_{5}$. COOH Glucose Gluconic acid

Now since aldehydic group is monovalent, it must be present on the end of the chain.

Open chain structure: On the basis of the above points, glucose may be assigned following part structure orientation shown in the α anomer has the –OH trans to the –CH₂OH group and the β anomer has the –OH cis to the –CH₂OH group.

FRUCTOSE

Also said to be fruit sugar

- (1) It occur both in combined as well as free state.
- (2) Fructose is named as fruit sugar because it is present in honey and most sweet fruit in free state.
- (3) It is sweetest monosaccharide and present in cane sugar and insulin in combined state.
- (4) It is also known as *a*-Laevulose i.e. natural occurring compound is laevorotatory

PREPARATION

(1) By acid hydrolysis of cane sugar :

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^{\oplus}} C_6H_{12}O_6 + C_6H_{12}O_6$$

Glucose Fructose

(2) By enzymatic action of sucrose

Sucrose $(C_{12}H_{22}O_{11})$ Invertase (Disaccharide) Invert Sugar

Note: Glucose and fructose obtained by acid hydrolysis of sucrose can be separated by treating with Ca(OH)₂ which forms calcium glucosate & calcium fructosate. Calcium fructosate being water insoluble. It is separated out easily

PROPERTIES

- (1) It is colourless crystalline solid.
- (2) It is soluble in water but insoluble in ether ketone and benzene.
- (3) It is pentahydroxy ketone and shows mutarotation like glucose.



CHEMICAL REACTION

Due to OH group at 2nd carbon :

 $(1) \, It \, forms \, fructose \, penta acetate \, with \, acetyl \, chloride:$



(2) Reaction due to keto group : It also form os zone with excess of phenyl hydrazine thus we can say that os zone formation is characteristic of α -hydroxy carbonyl compounds.





HO

α-fructose

3



Epimer : The change of configuration of one asymmetric carbon atom in a compound containing two or more asymmetric carbon atoms is known as epimerisation and compounds are known epimer.

B-fructose

D-Glucose and D-mannose are empimer (Change in configuration at IInd carbon atom only).



Such sugars are known as epimers e.g. epimerisation of glucose into mannose.





- Note: (1) Unlike other ketones, fructose can reduced Fehling sol. and Tollen's reagents it is probably due to formation of an equilibrium between glucose, mannose and fructose.
 - (2) Aldoses which produce the same osazones must have identical configuration on all their asymmetric carbon atoms except the alpha (since only the aldehyde group and α -carbon atoms are involved in osazone formation).

Conversion of Ketose into Aldose :

Z

SUCROSE

(Sucrose, cane-sugar $C_{12}H_{22}O_{11}$)

- (i) Sucrose is a white crystalline solid, soluble in water.
- (ii) When heated above its melting point, it forms a brown substance known as caramel.
- (iii) Concentrated sulphuric acid chars sucrose, the product being almost pure carbon.
- (iv) Sucrose is dextrorotatory, its specific rotation being $+ 66.5^{\circ}$.
- (v) On hydrolysis with dilute acids sucrose yields an equimolecular mixture of D(+)-glucose and D(-)-fructose:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{HCl}} C_6H_{12}O_6 + C_6H_{12}O_6$$

Glucose Fructose

Since D(-)-fructose has a greater specific rotation than D(+)-glucose, the resulting mixture is laevorotatory. Because of this, hydrolysis of cane-sugar is known as the inversion of cane-sugar this is not to be confused with the Walden inversion, and the mixture is known as invert sugar. The inversion (i.e., hydrolysis) of cane-sugar may also be effected by the enzyme invertase which is found in yeast.

(vi) Sucrose is not a reducing sugar, e.g., it will not reduce Fehling's solution ; it does not form an oxime or an osazone, and does not undergo mutarotation. This indicates that neither the aldehyde group of glucose nor the ketonic group of fructose is free in sucrose.

Structure formulas for monosaccharides:

Although many of the properties of D(+)-glucose can be explained in terms of an open-chain structure (1, 2, or 3), a considerable body of evidence indicates that the open-chain structure exists, primarily, in equilibrium with two cyclic forms. These can be represented by structures 4 and 5 or 6 and 7. The cyclic forms of D(+)-glucose are hemiacetals formed by an intramolecular reaction of the –OH group at C5 with the aldehyde group. Cyclisation creates a new stereogenic centre at C1, and this stereogenic centre explains how two cyclic forms are possible. These two cyclic forms are diastereomers that different only in the configuration of C1. In carbohydrate chemistry diastereomers of this type of called anomers, and the hemiacetal carbon atom is called the anomeric carbon atom.

Structures 4 and 5 for the glucose anomers are called Haworth formulas and, although they do not give an accurate picture of the shape of the six-membered ring, they have many practical uses. Demonstrates how the representation of each stereogenic centre of the open-chain form can be correlated with its representation in the Haworth formula.

Each glucose anomer is designated as an α anomer or a β anomer depending on the location of the –OH group of Cl. When we draw the cyclic forms of a D sugar in the

Mutarotation :

Ordinary D(+)-glucose has a melting point of 146°C. However, when D(+)-glucose is crystallized by evaporating an aqueous solution kept above 98°C, a second form of D(+)-glucose with a melting point of 150°C can be obtained. When the optical rotations of these two forms are measured, they are found to be significantly different, but when an aqueous solution of either form is allowed to stand, its rotation changes. The specific rotation of one form decreases and the rotation of the other increases, until both solutions.

Show the same value. A solution of original D-(+)glucose (mp 146°C) has an initial specific rotation of $\pm 112^{\circ}$, but, ultimately, the specific rotation of this solution falls to $\pm 52.7^{\circ}$. A solution of second form of D(+) glucose (mp 150°C)

has an initial specific rotation of $+18.7^{\circ}$, but slowly, the specific rotation of this solution rises to $+52.7^{\circ}$. This change in rotation towards an equilibrium value is called mutarotation.

The explanation for this mutarotation lies in the existence of an equilibrium between the open-chain form of D(+) glucose an the α and β forms of the cyclic hemiacetals.

Conversion to Esters:

Treating a monosaccharide with excess acetic anhydride and a weak base (such as pyridine or sodium acetate) converts all of the hydroxyl groups, including the anomeric hydroxyl, to ester groups. If the reaction is carried out at a low temperature (e.g., 0°C), the reaction occurs stereospecifically; the α anomer gives the α -acetate and the β anomer gives the β -acetate. Acetate esters are common protecting groups for carbohydrate hydroxyls.

BENEDICT'S OR TOLLENS' REAGENTS: REDUCING SUGARS

Benedict's reagent (A alkaline solution containing a cupric citrate complex ion) and Tollen's solution $[Ag^+(NH_3)_2OH]^-$ oxidize and thus give positive tests with aldoses and ketoses. The tests are positive even though aldoses and ketoses exist primarily as cyclic hemiacetals.

Sugars that give positive tests with Tollen's or Benedict's solutions are known as reducing sugars, and all carbohydrates that contain a hemiacetal group given positive tests. In aqueous solution these hemiacetals exist in equilibrium with relatively small, but not insignificant, concentration of noncyclic aldehydes or α -hydroxy ketones. It is the latter two that undergoes the oxidation until one reactant is exhausted.

Carbohydrates that contain only acetal groups do not given positive tests with Benedict's or Tollen's solutions, and they are called non-reducing sugars. Acetals do not exist in equilibrium with aldehydes or α -hydroxy ketones in the basic aqueous media of the test reagents.

Bromine Water : The synthesis of Aldonic Acid

Monosaccharides do not undergo isomerization and fragmentation reactions in mildly acids solution. Thus, a useful oxidizing reagent for preparative purposes is bromine in water (pH 6.0). Bromine water is a general reagent that selectively oxidizes the –CHO group to a – CO_2H group. It converts an aldose to an aldonic acid.

Experiments with aldopyranoses have shown that the actual course of the reaction is somewhat more complex than we have indicated above. Bromine water specifically oxidizes the β anomer, and the initial product that forms is a δ -aldonolactone. This compound may then hydrolyze to an aldonic acid, and the aldonic acid may undergo a subsequent ring closure to form a γ -aldonolactone:

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NITRICACID OXIDATION: ALDARIC ACID

Dilute nitric acid – a stronger oxidizing agent than bromine water – oxidizes the both –CHO group and the terminal –CH₂OH group of an aldose to –CO₂H groups. These dicarboxylic acids are known as aldaric acids:

This aldaric acid obtained from D-glucose is called D-glucaric acid.

PERIODATE OXIDATION: OXIDATIVE CLEAVAGE OF POLYHYDROXY COMPOUNDS

Compounds that have hydroxyl groups on adjacent atoms undergo oxidative cleavage when they are treated with aqueous periodic acid (HIO_4). The reaction breaks carbon-carbon bonds and produces carbonyl compounds (aldehydes, ketones, or acids).

Since the reaction usually takes place in quantitative yield, valuable information can often be gained by measuring the number of molar equivalents of periodic acid that is consumed in the reaction as well as by identifying the carbonyl products.

Periodate oxidations are though to take place through a cyclic intermediate:

Before we discuss the use of periodic acid in carbohydrate chemistry, we should illustrate the course of the reaction with several simple examples. Notice in these periodate oxidations that for every C - C bond broken, a C - O bond is formed at each carbon.

1. When three or more –CHOH groups are continuous, the internal ones are obtained as formic acid. Periodate oxidation of glycerol, for example, gives two molar equivalents of formaldehyde and one molar equivalent of formic acid;

2. Oxidative cleavage also take place when an – OH group is adjacent to the carbonyl group of an aldehyde or ketone (but not that of an acid or an ester). Glyceraldehyde yields two molar equivalents of formic acid and one molar equivalent of formaldehyde, while dihydroxyacetone gives two molar equivalents of formaldehyde and one molar equivalent of carbon dioxide.

Periodic acid does not cleave compound in which the hydroxyl groups are separated by an intervening $-CH_2$ group, nor those in which a hydroxyl group is adjacent to an ether or acetal.

REDUCTION OF MONOSACCHARIDES: ALDITOLS

Aldoses (and ketoses) can be reduced with sodium borohydride to compounds called alditols:

Reduction of D-glucose, for example, yields D-glucitol.

REACTIONS OF MONOSACCHARIDES WITH PHENYLHYDRAZINE: OSAZONES

The aldehyde group of an aldose reacts with such carbonyl reagents as hydroxylamine and phenylhydrazine. With hydroxylamine, the product is the expected oxime. With enough phenylhydrazine, however, three molar equivalents of phenylhydrazine are consumed and a second phenylhydrazone group is introduced at C_2 . The product is called a phenylosazone. Phenylosazones crystallize readily (unlike sugars) and are useful derivatives for identifying sugars.

A MECHANISM FOR THE REACTION

Phenylosazone Formation

Osazone formation result in a loss of the stereogenic centre at C2 but does not affect other stereogenic carbons; D-glucose and D-mannose, for example, yield the same phenylosazone:

This experiment, first done by Emil Fischer, established that D-glucose and D-mannose have the same configuration about C_3 , C_4 and C_5 . Diastereomeric aldoses that differ in configuration at only one carbon (such as D-glucose and D-mannose) are called epimers. In general, any pair of diastereomers that differ in configuration at only a single tetrahedral stereogenic carbon can be called epimers.

Epimers:

Many common sugars are closely related, differing only by the stereochemistry at a single carbon atom. For example, glucose and mannose differ only at C2, the first asymmetric carbon atom. Sugars that differs only by the stereochemistry at a single carbon are called **epimers**. and the carbon atom where they differ is generally stated. If the number of a carbon atom is not specified, it is assumed to be C2. Therefore, glucose and mannose are "C2 epimers" or simply "epimers". The C4 epimer of glucose is galactose and the C2 epimer of erythrose is threose.

Cyclic structure of Fructose:

Like glucose, fructose also has a cyclic structure. Since fructose contains a keto group, it forms an intramolecular hemiketal. In the hemiketal formation, C5–OH of the fructose combines with C2-keto group. As a result, C2 becomes chiral and thus has two possible arrangements of CH,OH and OH group around it. Thus,

D-fructose exists in two stereoisomeric forms, i.e., α -fructopyranose and β -D fructopyranose. However in the combined state (such as sucrose), fructose exists in furanose form as shown below:

Hydrolysis of Sucrose:

(Invert Sugar or Invertose). Hydrolysis of sucrose with hot dilute acid yields D-glucose and D-fructose.

$C_{12}H_{22}O_{11}$	+	H ₂ O	$\xrightarrow{H^+}$	$C_6H_{12}O_6$	+	C ₆ H ₁₂ O ₆
Sucrose				D(+)-glucose		D(-)-Fructose
$[\alpha]_{\rm D} = +66.5^{\circ}$				$[\alpha]_{D} = +53^{\circ}$		$\left[\alpha\right]_{\mathrm{D}} = -92^{\circ}$
						Invert Sugar
				$[\alpha]_{\rm D} = (+53^{\circ}) - (-9)^{\circ}$	92°)=39°	,

Sucrose is dextrorotatory, its specific rotation being +66.5%, D-glucose is also dextrorotatory, $[\alpha]_D = +53^\circ$, but D-fructose has a large negative rotation, $[\alpha]_D = -92^\circ$. Since D-fructose has a greater specific rotation than D-glucose, the resulting mixture is laevorotatory. Because of this the hydrolysis of sucrose is known as the inversion of sucrose, and the equimolecular mixture of glucose and fructose is known as invert sugar or invertose.

POLYSACCHARIDES

Polysaccharides are the polymers of monosaccharides. The natural polysaccharide generally contain about 100-3000 monosaccharide units. The three most abundant natural polysaccharides-cellulose, starch and glycogen are derived from the same monomer, i.e., glucose.

Starch: It is a polymer of glucose. Its molecular formula is $(C_6H_{10}O_5)_n$ where the value of n(200 - 1000) varies from source to source. It is the chief food reserve material or storage polysaccharide of plants and is found mainly in seeds, roots, tubers, etc. Wheat, rice, potatoes, corn, bananas etc., are rich source of starch.

Starch is not a single compound but is a mixture of two components – a water soluble component called amylose (20%) and a water insoluble component called amylopectin (80%). Both amylose and amylopectin are polymers of α -D glucose.

Amylose is a linear polymer of α -D glucose. It contains about 200 glucose units which are linked to one another through α -linkage involving C₁ of one glucose unit with C₄ of the other.

Amylopectin, on the other hand, is a highly branched polymer. It consists of a large number (several branches) of short chains each containing 20-25 glucose units which are joined together through α -linkages involving C₁ of one glucose unit with C₄ of the other. The C₁ of terminal glucose unit in each chain is further linked to C₆ of the other glucose.

Unit in the next chain through $C_1 - C_6 \alpha$ -linkage. This gives amylopectin a highly branched structure as shown below:

$$-$$
 C1 – C4 -linkage

Glucose – Glucose – Glucose

$$\leftarrow$$
 C1 – C6 α -linkage

← C1 − C6 α -linkage

Glucose – Glucose – Glucose

Hydrolysis:

Hydrolysis of starch with hot dilute acids or by enzymes give dextrins of varying complexity, maltose and finally D-glucose. Starch does not reduce Tollen's reagent and Fehling's solution.

Uses:

It is used as a food. It is encountered daily in the form of potatoes, bread, cakes, rice etc. It is used in coating and sizing paper to improve the writing qualities. Starch is used to treat textile fibres before they are woven into cloth so that they can be woven without breaking. It is used in manufacture of dextrins, glucose and ethyl alcohol. Starch is also used in manufacture of starch nitrate, which is used as an explosive.

Cellulose:

Cellulose is the chief component of wood and plane fibres; cotton, for instance, is nearly pure cellulose. It is insoluble in water and tasteless; it is a non-reducing carbohydrate. These properties, in part at least, are due to extremely high molecular weight.

Cellulose

Cellulose has the formula $(C_6H_{10}O_5)_n$. Complete hydrolysis by acid yields D(+)-glucose as the monosaccharide. Hydrolysis of completely methylated cellulose gives a high yield of 2, 3, 6-tri-O-methyl-D-glucose. Like starch, therefore, cellulose is made up of chains of D-glucose units, each unit joined by a glycoside linkage of C-4 of the next.

Cellulose differs from starch, however, in the configuration of the glycoside linkage. Upon treatment with acetic anhydride and sulfuric acid, cellulose yields octa-O- acetyl cellobiose, there is evidence that all glycoside linkages in cellulose, like the one in (+) cellobiose, are *beta* linkages.

Physical methods give molecular weights for cellulose ranging from 250000 to 1000000 or more; it seems likely that there are at least 1500 glucose units per molecule. End group analysis by both methylation and periodic acid oxidation gives a chain length of 1000 glucose units or more. X-ray analysis and electron microscopy indicate that these long chains lie side by side in bundles, undoubtedly held together by hydrogen bonds between the numerous neighbouring –OH groups. These bundles are twisted together to form.

Rope like structure which themselves are grouped to from the fibers we can see. In wood these cellulose "ropes" are embedded in lignin to give a structure that has been likened to reinforced concrete.

Properties of Cellulose:

We have seen that the glycoside linkages of cellulose are broken by the action of acid, each cellulose molecule yielding many molecules of D(+)-glucose. Now let us look briefly at reactions of cellulose in which the chain remains essentially intact. Each glucose unit in cellulose contains three free – OH groups; these are the positions at which reactions occurs.

These reactions of cellulose, carried out to modify the properties of a cheap, available ready-made polymer, are of tremendous industrial importance.

Like any alcohol, cellulose forms esters. Treatment with a mixture of nitric and sulfuric acid converts cellulose into *cellulose nitrate*. The properties and uses of the product depend upon the extent of nitration. *Guncotton*, which is used in making smokeless powder, is very nearly completely nitrated cellulose, and is often called cellulose trinitrate (three nitrate groups per glucose unit). *Pyroxylin* is less highly nitrated material containing between two and three nitrate groups per glucose unit. It is used in the manufacture of plastics like celluloid and collodion, in photographic film, and in lacquers. It has the disadvantage of being flammable, and forms highly toxic nitrogen oxides upon burning.

Industrially, cellulose is alkylated to **ethers** by the action of alkyl chlorides (cheaper than sulfates) in the presence of alkali. Considerable degradation of the long chain is unavoidable in these reactions. Methyl, ethyl, and benzyl others of cellulose are important in the production of textiles, films, and various plastic objects.

AMINO ACIDS

INTRODUCTION

Amino acids are the compounds which contain both an amino group and a carboxy group in their molecules. They constitute a particularly important class of difunctional compounds as they are the building blocks of proteins.

While several hundred different amino acids are known to occur naturally, 20 of them deserve special mention as they are present in proteins. These amino acids are listed in Table. As given in this table, for amino acids trivial names are common. The convention to use a three letter code, as an abbreviation, for each amino acid is also given in the table. These abbreviations are particularly useful in designating the sequence of amino acids in peptides and proteins which your will study.

Each living cell is made up of thousands of different proteins All proteins contain the elements like carbon, hydrogen, oxygen, nitrogen and sulphur. Some of these also contain phosphorus, iodine and traces of metals such as, Fe, Cu, Zn, & Mn. All proteins are polymers of α -amino acids and on partial hydrolysis give peptides of varying molecular masses which upon complete hydrolysis give α -amino acids.

Proteins $\xrightarrow{\text{Hydrolysis}}$ Peptides $\xrightarrow{\text{Hydrolysis}} \alpha$ -amino acids

These organic compounds contain amino as well as carboxylic acid group. On the basis of position of amino group in the chain, these are named as α , β , γ etc. amino acid.

R-CH-COOH | NH₂ α-amino acid

There are around 20 amino acids among which 10 amino acids are synthesis in our body and these are said to be **non essential amino acids** (eg. Gly, Ala, Glu, Asp, Pro and Cys) and other amino acids which are necessarily be present in our diet are called **essential amino acids** (eg. Val, Leu, I leu, Lys and Phe).

Type o	f α-amino acid	s :					
	Amino acids with non polar side chain :			Amino acids with polar and neutral side chain :			
	R –	_	R-CH-COOH NH2	R-CH ₂ OH	_	Serine	
	H –	_	Glycine	CH ₃ -CH- OH	-	Threoni	ne
	CH ₃ -	_	Alanine	HS-CH2-	-	Cystine	
	(CH ₃) ₂ CH–	_	valine				
	(CH ₃) ₂ CH–CH ₂	_	leucine				
	$C_6H_5CH_2$	-	phenylalanine				
	(3) Amino acids	with acidi	ic side chain :	(4) Amino acid	with basic	side chai	n :
	R –			R –			
	-CH ₂ -COOH	_	Aspartic acid	H ₂ N-(CH ₂) ₄ -		_	lysine
	HOOC-CH ₂ -CH	2 -	Glutamic acid		CH ₂) ₃ -	_	Arginine

Amino Acid : Building Blocks of Proteins

Amino acids are the building blocks of the molecular structure of the important and very complex class of compounds known as proteins. The proteins on hydrolysis yield mixture of the component amino acids.

Amino acids are bifunctional compounds containing both an amino and a carboxylic acid group. They are represented by the general formula :

$$\begin{array}{c|c} H & O \\ H & H \\ H_2 N & -C - C & -C \\ 1223 \\ Amine & R \\ Acid group \\ R \\ Acid group \\ R \end{array} \stackrel{Or}{} H_2 N - C H - C O O H \\ H_2 N - C H \\ H_2$$

Where, R = alkyl, aryl, or any other group.

Zwitter ion (Dipolar Nature of Amino acids) :

In a neutral amino acid solution, the -COOH loses a proton and the $-NH_2$ of the same molecule picks up one. The resulting ion is dipolar, charged but overall electrically neutral. This is called Zwitterion (German, "two ions"). Therefore amino acids are amphoteric.

Isoelectric point of α-amino acids :

When an ionised amino acid is placed in an electric field, it will actually migrate towards the opposite electrode. Depending upon the pH of the medium, three things can happen. The positive form (II) will migrate to the cathode, the neutral form (Zwitter ion) will not migrate, while the negative form (III) will migrate to the anode. The pH at which the amino acid shows no tendency to migrate when placed in an electric field is known as its isoelectric point. This is characteristic of a given amino acid. Thus glycine has its isoelectric point at pH 6.1.

Isoelectric Point :

The pH at which the amino acid shows no tendency to migrate when placed in an electric field is known as its isoelectric point.

Because of amphoteric nature in acidic solution it exist as the +ve ion. Hence it migrate towards cathode while in basic solution it exist as -ve ion and migrates towards anode.

At some intermediate pH amino acids exist as a neutral dipolar ion i.e. the concentration of the cation and anions are equal and it does not migrate towards either electrode, this pH is called iso electric point of amino acid which is different for different amino acids.

CHEMISTRY FOR JEE MAIN & ADVANCED

Nature of amino acid	E/N.E		Name	Abbreviation
Neutral amino acid	NE	H ₂ N H H	Glycine	Gly
Neutral amino acid	NE	H ₃ C OH NH ₂	Alanine	Ala
Neutral amino acid	Е	H ₃ C - CH ₃ HO - NH ₂	Valine	Val
Neutral amino acid	Е	HO CH ₃ NH ₂ CH ₃	Leucine	Leu
Neutral amino acid	Е	OH OH OH NH ₂ CH ₃	Isoleucine	Ile
Acidic amino acid	NE	HO OH NH ₂ O	Aspartic Acid	Asp
Acidic amino acid	NE	HO O O O O O O O O H	Glutamic Acid	Glu
Basic amino acid	Е	H ₂ N H ₂ N O OH	Lysine	Lys

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BIOMOLECULES & POLYMERS

Basic amino acid	NE	NH NH ₂ OH	Arginin	Arg
Basic amino acid	NE	N HN HN NH2 OH	Histidine	His
Neutral amino acid	Е	HO NH ₂ S CH ₃	Methionine	Met
Neutral amino acid	NE		Proline	Pro
Neutral amino acid	Е	С Он H ₂ N ОН	Phenylalanine	Phe
Neutral amino acid	Е	NH2 NH2	Tryptophan	Trp
Neutral amino acid	NE	он Н ₂ N ност	Serine	Ser
Neutral amino acid	Е	H ₃ C OH HO OH O	Threonine	Thr
Neutral amino acid	NE	threonine OH H ₂ N ·····	Cysteine	Cys
Neutral amino acid	NE	HO NH ₂ O H	Tyrosine	Tyr

 \mathbf{E} = essential amino acid \mathbf{NE} = Non essential amino acid

AMINOACIDAS DIPOLAR IONS:

Amino Acids contain both a basic group $(-NH_2)$ and an acidic group (-COOH). In the dry solid state, amino acids exist as dipolar ions, a form in which the carboxyl group is present as a carboxylate ion, $-CO_2^-$, and the amino group is present as an ammonium ion, $-NH_3^+$ (Dipolar ions are also called zwitterions.) In aqueous solution, an equilibrium exists between the dipolar ion and the anionic and cationic forms of an amino acids.

If alanine is dissolved in a strongly acidic solution (e.g. pH 0), it is present in mainly a net cationic form. In this state the amine group is protonated (bears a formal +1 charge) and the carboxylic acid group is neutral (has no formal charge). As is typical of α -amino acids, the pK_a for the carboxylic acid hydrogen of alanine is considerably lower (2.3) than the pK_a of an ordinary carboxylic acid (e.g., propanoic acid, pK_a 4.89):

The reason for this enhanced acidity of the carboxyl group in an α -amino acid is the inductive effect of the neighboring aminium cation, which helps to stabilize the carboxylate anion formed when it loses a proton. Loss of proton from the carboxyl group in a cationic α -amino acid leaves the molecule electrically neutral (in the form of a dipolar ion). This equilibrium is shown in the red-shaded portion of the equation below.

The protonated amine group of an α -amino acid is also acidic, but less so that the carboxylic acid group. The pK_a of the aminium group in alanine is 9.7. The equilibrium for loss of an aminium proton is shown in the blue-shaded portion of the equation below. The carboxylic acid proton is always lost before a proton from the aminium group in an α -amino acid.

 $\begin{array}{c} CH_{3}CHCO_{2}H \xrightarrow[]{H_{3}O^{+}} \\ \downarrow \\ H_{3}O^{+} \\ H_{3} \\ H_{2} \\ H_{3} \\ H_{2} \\ H_{3} \\ H_{2} \\ H_{2} \\ H_{3} \\ H_{2} \\ H_{2} \\ H_{3} \\ H_{3} \\ H_{2} \\ H_{3} \\ H_{2} \\ H_{3} \\ H_{3} \\ H_{3} \\ H_{2} \\ H_{3} \\ H_{3$

The state of an α -amino acid at any given pH is governed by a combination of two equilibrium, as shown in the above equation for alanine. The isoelectric point (pI) of an amino acid such as alanine is the average of pKa₁ and pKa₂;

 $pI = \frac{1}{2}(2.3 + 9.7) = 6.0$ (isoelectric point of alanine)

When a base is added to a solution of the net cationic form of alanine (initially at pH 0, for example), the first proton removed is the carboxylic acid proton, as we have said. In the case of alanine, when a pH of 2.3 is reached, the acid proton will have been removed from half of the molecules. This pH represents the pK_a of the alanine carboxylic acid proton, as can be demonstrated using the Henderson-Hasselbalch equation. The Henderson - Hasselbalch equation shows that for an acid (HA) and its conjugate base (A⁻),

$$pK_a = pH + log \frac{[HA]}{[A^-]}$$

When the acid is half neutralized,

b) Co-polymers are another type of polymer. These contains more than one sub-unit (or monomer).

Ex. :

In the above example styrene and maleic anhydride monomers laternate. Co-polymer can be a block co-polymer. **Ex.**:

Co-polymers can be random as well.

A and B are monomers.

• There are many polymers in nature.

Example: Cellulose, starch, pepsin, insulin, egg albumin, rubber, DNA (Deoxyribonucleic acid) etc. These are called Biopolymers.

Man made polymers are, Nylon, Terylene, Polythene, Polystyrene, PVC (Polyvinyl chloride), Bakelite, Perspex, Polysiloxane etc.

- The properties of a polymer solution are strikingly different from those of a true solution. For example, when polyvinyl alcohol is added to water, it swells.
 - a) Its shape gets distorted and after a long time it dissolves.
 - b) When more of polymer is added to a given solvent, saturation point is not reached. The mixture of polymer and solvent assumes a soft dough-like consistency.
- Addition polymers and condensation polymers are two important types of polymers.
- Polymer can be described as linear, branched and network.

POLYMERSAND POLYMERIZATION

Macromolecules, both natural and man-made, own their great size to the fact they are polymers (Greek: many parts); that is, each one is made up of a great many simpler unit - identical to each other or at least chemically similar - joined together in a regular way. They are formed by a process we touched on earlier: polymerization, the joining together of many small molecules to form very large molecules. The simple compounds from which polymers are made are called monomers.

PEPTIDES AND PROTEINS

In the last section, you studied the polymers of monosaccharides which act as structural components in plants and serve as energy storage in animals. In this section, you will study another kind of natural polymers called peptides and proteins.

Peptides are biologically important polymers in which 2-amino acids are joined by the amide linkages, formed by the reaction of the carboxy group of one amino acid with the amino group of another amino acid. These amide linkages are also called peptide bonds. The general structure of a peptide is shown below:

Peptides can be classified as dipeptides, tripeptides and tetrapeptides, depending on whether the number of amino acids, two, three or four, respectively. Peptides containing upto 50 amino acids are called polypeptides. Bradykinin is an important naturally occurring nonapeptide which is present in blood plasma and is involved in the regulation of blood pressure.

Arg—Pro — Pro — Gly — Phe — Ser — Pro — Phe — Arg Bradykinin

CONFIGURATION OF PROTEINS

- (a) Biological nature or function of protein was confirmed by its conformation.
- (b) This conformation is of 4 types

PRIMARY STRUCTURE:

- ⇒ This type of structure was given by Frederick Sanger in 1953 in Insulin (of one chain)
- \Rightarrow Primary structure is conformed by a single polypeptide chain in a linear manner.
- \Rightarrow All amino acid are attached in a straight chain by peptide bond.
- \Rightarrow No biological importance & soon changed to other forms.

SECONDARY STRUCTURE :

- \Rightarrow In it structure of straight chain from irregular changes to form coils.
- \Rightarrow H-bond + peptide bond present in secondary. structure.
- ⇒ This H bond is present between hydrogen of Amino group and oxygen atom carboxylic acid group.
- \Rightarrow This structure is of two types

(i) a-helix

- \Rightarrow Chain is spiral
- \Rightarrow 3.7 atoms in one coiling
- \Rightarrow Right handed circular.
 - **Ex.** \rightarrow Myosin, Keratin etc.

(ii) β -pleated sheet

- \Rightarrow Structure of protein is not arranged in a sequence.
- ⇒ Polypeptide chain are parallel to each other
- \Rightarrow H bond form by near chains
 - Ex. Silk fibres.

TERTIARY STRUCTURE

 \Rightarrow In this structure of protein atoms are highly coiled and form a spherical form

Ex. Albumin

- \Rightarrow This structure is formed by 4 regular hydrogen bonds which makes a regularity in it
- (i) Hydrogen bond :

$$\begin{array}{c} | \\ C = O \\ | \end{array} H - \begin{array}{c} N \\ H \\ H \end{array}$$

Hydrogen bond

- \Rightarrow They are formed between oxygen of acidic amino acid and H of basic amino acid.
- (ii) Hydrophobic bond -
- ⇒ Non polar side chains of neutral amino acid tends to be closely associated with one another in proteins.
- \Rightarrow Present in between the amino Acid.
- \Rightarrow These are not true bonds.
- (iii) lonic bond :

Ionic bond

- ⇒ These are salt bonds formed between oppositely charged groups in side chains of Amino acids Eg. Aspartic acid, Glutamic acid
- (iv) Disulphide bonds :
- \Rightarrow Relatively stable bond and thus is not broken readily under usual conditions of denaturation.
- \Rightarrow Formed between the -SH group of Amino acid Ex. Cystine and Methionine .

QUATERNARY STRUCTURE

- When 2 or more polypeptide chains united by forces other than covalent bonds (i.e. not peptide and disulphide bonds) are called Quaternary structure.
- ⇒ It is most stable structure.
 - Ex. Haemoglobin

TYPES OF PROTEINS

 \Rightarrow Classification of protein is based upon three general properties shape, Solubility and Chemical composition.

Simple proteins

 \Rightarrow It is formed of only Amino Acids

Fibrous :

- \Rightarrow It is insoluble
- \Rightarrow It is of elongated shape.
- \Rightarrow It is highly resistant to digestion by proteolytic enzymes.
- \Rightarrow Their main function Protection.
- Ex. Collagen, Keratin etc

Globular :

- \Rightarrow These are spherical and oval in shape. Chains are highly coiled
- \Rightarrow These are soluble.
- Ex. Albumin

Conjugated Proteins

- ⇒ These are complex proteins in which protein molecule is combined with characteristic non-amino acid substance.
- ⇒ Non-amino acid or Non Protein part is called as prosthetic group
- Ex. Nucleoproteins

(Protein + Nucleic acid),

Phosphoproteins (Protein + $(PO_3)^{2-}$)

Ex. \rightarrow Casein of milk., Vitelline of egg - yolk

Derived proteins :

These are obtained as a result of partial hydrolysis of natural proteins.

Eg. \rightarrow Proteose, Metaproteins, Peptones

Denaturation of Proteins

When a protein in its native form, is subjected to a physical change like change in temperature, or a chemical change like change in pH, the native conformation of the molecule is disrupted and proteins so formed are called denaturated proteins.

The denaturation may be reversible or irreversible. The coagulation of egg on boiling is an example of irreversible protein denaturation.

However, it has been shown now that in some cases, the process is actually reversible. The reverse process is called **renaturation**.

TEST OF PROTEIN :

- (a) With conc. HNO₃ on heating give yellow ppt. Which on more heating give solution On adding NH₄OH Red colour appears. It is Xanthoprotic test.
- (b) $(NH_4OH) + dil. CuSO_4$ protein give Blue violet colour. It is a biuret test.
- (c) Millon reaction. Proteins on adding Millon's reagent (a solution of mercuric and mercurous nitrates in nitric acid containing a little nitrous acid) followed by heating the solution give red precipitate or colour.
- (d) Ninhydrin reaction. Proteins, peptides and a-amino acids give a characteristic blue colour on treatment with ninhydrin.

Biological Importance of protein :

- (a) Component of plasma membrane.
- (b) All enzymes are protein.
- (c) Many hormones are protein.
- (d) Antigen and antibody are protein.
- (e) Actin and myosin protein are important in muscle contraction.
- (f) Proteins are important in growth, regeneration and repairing.
- (g) Calorific value 4.0 kcal.

LIPIDS

- (a) Lipids words is derived from greek word lipos which means fat.
- (b) Lipids are heterogeneous group of substances which have common property of being relatively insoluble in water and soluble in non-polar solvents such as ether, Chloroform etc.
- (c) Form 3-5% part of protoplasm.
- (d) $H_2O \neq 2:1$ (different from water)
- (e) Ratio of oxygen is less.
- (f) Specific gravity < 1

Th<mark>ree ty</mark>pes

Simple Compound Derived

SIMPLE LIPID

TRIGLYCERIDES

(a) These are esters of fatty acids with glycerol.

Ester bond is present

(b) Synthesis is of following type-

- (c) Fatty acids which occur in natural fats usually contain an even number of carbon atoms(4 to 30) in straight chains.
- (d) Simplest fatty acid HCOOH.
- (e) More complex fatty acid are formed by successive addition of $-CH_2$ groups.

Fatty acids are of 2 types

- (i) Saturated :
 - \Rightarrow Only single bond is present in them.
 - \Rightarrow First member is CH₃COOH.

Other examples :

 \Rightarrow Palmitic acid - C₁₅H₃₁COOH

 \rightarrow CH₃(CH₂)₁₄COOH

 \Rightarrow Stearic acid - C₁₇H₃₅COOH

 \rightarrow CH₃(CH₂)₁₆COOH

- ⇒ Palmitic and stearic acid is found in fats of animals in less amount.
- \Rightarrow These are solid and are found in fats.
- (ii) Unsaturated :
 - \Rightarrow Double bond is present in these fatty acid chain.
 - \Rightarrow These are liquids at room temperature. Found in Oils.
 - \Rightarrow These are of two types

Monounsaturated - 1 Double bond is present

Ex. Oleic acid.

 \Rightarrow Oleic acid is present in more amount in nature.

Polyunsaturated - More than two double bond

Ex. Linoleic acid with two double bonds

Linolenic acid with three double bonds

Arachidonic acid with four double bonds (Groundnut)

Wax

- These are esters of other alcohols of high \Rightarrow
 - molecular weight instead of glycerols.
- These are insoluble in water. \rightarrow
- These are monohydric alcohols.
- \Rightarrow Some examples of waxes -
 - Myricye palmitate (Honeybee wax) Cetyl palmitate (Dolphin and whale wax)
 - Cerumen (ear wax)

Compound Lipid - Are of 4 types :

(a) Phospholipids.

(b) Glycolipids.

Phospholipids :

Phosphorous is present.

Ex. cell wall

Glycolipids

- \Rightarrow Lipid + Sugar = Glycolipids
- \Rightarrow Present in brain, Adrenal glands, kidney,
 - WBC liver, thymus, Spleen, Lungs, egg yolk
- \Rightarrow Glycolipids = 2 Fatty acid + 1 sphinocine
 - +1 galactose.

Derived lipids

 \Rightarrow By hydrolysis of fats they are obtained

Derived lipids ↓ Types Sterols

Steroids

Steroids :

- These are different from other fats. \Rightarrow
- It is insoluble in water.
- **Bile acids : (i)**
 - \Rightarrow Present in secretion of liver.
- (ii) Sex hormones :
 - \Rightarrow These are androsterones.
- (iii) Adrenal hormone- Eg : Aldosterone

Sterols :

 \Rightarrow

- They have -OH groups.
- They are complex monohydroxy alcohols.

Cholesterol - It is widely distributed in all cells of body.

Biological importance of Fat :

- \Rightarrow It is source of energy.
- \Rightarrow It is important for absorption of vitamin A, D, E and K.
- \Rightarrow It is important component of plasma membrane.
- \Rightarrow It act as shock absorber of body.
- \Rightarrow Calorific value 9.3 kcal.

NUCLEICACID

- (a) These are special type of acids which are present in nucleus & cytoplasm.
- (b) Control the metabolic activities of cell.
- (c) They are also found in Mitochondria, centriole and chloroplast.

Types \rightarrow These are of 2 types

→DNA (Deoxyribonucleic acid)

- →RNA (Ribonucleic acid)
- (d) Fischer discovered Nitrogen bases in 1888

(e) Levan found sugar

Nitro	gen Base
	type
_ \	
Purine	Pyrimidine

Ribose (RNA) Decoxyribose (DNA)

DEOXYRIBONUCLEIC ACID (D.N.A.) :

STRUCTURE OF DNA (DEOXYRIBONUCLEIC ACID):

J.D. Watson and F.H.C. Crick (1953) proposed double helical structure of DNA based on the results of M.H.F. Wilkins and co-workers. All these three persons were awarded Nobel Prize in 1962 for this work.

The following are some of the characteristic features of double helical structure of DNA.

- (i) Each nucleotide consists of sugar, phosphate and a nitrogenous base. Many such nucleotides are linked by phosphodiester bonds to form a polynucleotide chain or strand.
- (ii) **Phospho diester bonds** are formed between 5'carbon of sugar of one nucleotide and 3' carbon of sugar of the next nucleotide.
- (iii) Nitrogenous base is attached to 1' carbon of sugar. At this place purine base is attached by its 5' position and pyrimidine by its 3' position.
- (iv) Polynucleotide strand is made of backbone of sugar and phosphate forming its long axis and bases at right angles to it.

BIOMOLECULES & POLYMERS

Fig. Structure of DNA- coiling in double helix of DNA

(a) It is found in Nucleus.

- (b) They on pneumococcus bacteria.
- (c) DNA made up of 3 units-

CHEMISTRY FOR JEE MAIN & ADVANCED

- (i) Thymine (i) Adenine
- (ii) Cytosine (ii) Guanine
- (d) Nucleoside

When nitrogen base combined with deoxyribose sugar it constitute a nucleoside.

S.No.	Deoxyribonucleoside
1	Adenine + Deoxyribose \rightarrow Deoxyadenosine
2	Guanine + Deoxyribose \rightarrow Deoxyguanosine
3	Cytosine + Deoxyribose \rightarrow Deoxycytidine
4	Thymine + Deoxyribose \rightarrow Deoxythymidine

Nucleotide

- (a) Nitrogen base+Sugar+Phosphate \rightarrow Nucleotide
- (b) Nucleotide is a unit of DNA.
- (c) All nucleotides combined and form a chain called polynucleotides by which RNA and DNA formed.

FUNCTION OF DNA

(i) Self - Replication or self - Duplication

DNA has the property of self - replication. It is therefore a reproducing molecule. This unique property of DNA is at the root of all reproduction. Through its replication, **DNA is acts as the key to heredity**. In the replication of DNA, the two strands of a double helix unwind and separate as a template for the formation of a new complementary strand.

(ii) Protein Synthesis

The specific sequence of base pair in DNA represents coded information for the manufacture of specific proteins. These code instructions first are transcribed into the matching nitrogen- base sequences within mRNA and the instructions in such RNA subsequently are translated into particular sequence of amino acid units within the polypeptide chains and proteins.

The major steps in the utilization of the genetic information can be represented as :

DNA Replication DNA Transcription RNA Transcription Protein

RIBONUCLEIC ACID (RNA) :

Found in cytoplasm as well as in nucleus.

Cytoplasm \rightarrow In the ribosome (higher amount)

CHEMICALNATURE

- ⇒ Ribonucleic acid is a polymer of purine and pyrimidine ribonucleotides linked by $3' \rightarrow 5'$ phosphodiester bridges. The number of nucleotides in RNA ranges from as **few as 75 to many thousands**. Although sharing many features with DNA, RNA possesses several specific difference.
- \Rightarrow As indicated by its name, sugar in RNA to which the phosphate and nitrogen- bases are attached is ribose rather than the deoxyribose of DNA.
- ⇒ Although RNA contains the ribonucleotides of adenine, guanine, and cytosine, it does not posses thymine. Instead of thymine, RNA contains the ribonucleotides of uracil. Thus the pyrimidine components of RNA differs from those of DNA.
- ⇒ RNA exists basically as a single-stranded molecule rather than as a double -stranded helical molecule, as does DNA. However the single strand of RNA is capable of folding back on itself like a hairpin and thus acquiring double-stranded characteristics. In these regions. A pairs with U and G pairs with C.

Thus a given segment of a long RNA molecule might, for example, be represented as follows.

P – R – P – R – P – R – P – R – P – R

- A U G G C
- ⇒ where R stands for ribose ; A, U, G, and C for Adenine, Uracil, Guanine and Cytosine respectively.

TYPES OF RNA AND THEIR FUNCTIONS :

There are 3 main types of RNA molecules

- (i) Messenger RNA (mRNA)
- (ii) Transfer RNA (tRNA)
- (iii) Ribosomal RNA (rRNA)
- (i) Messenger RNA (mRNA)
- ⇒ This type of RNA consists of single strand of variable length and serves as a template for protein synthesis. Codon in the chromosomes.
- mRNA forms complementary copy of DNA as it carries chemical messages in the form of nitrogen-base sequence from the nucleus to the ribosomes, i.e. from DNA to cytoplasm where proteins are synthesized. Therefore, it is called messenger RNA or mRNA
- \Rightarrow mRNA is synthesised from DNA in the nucleus.
- \Rightarrow It is called **transcription**.
- (ii) Ribosomal RNA
- ⇒ A ribosome is a cytoplasmic nucleoprotein structure which serves as the organellar machinery for protein synthesis from mRNA templates.
- > On the ribosome, the mRNA and tRNA molecules interact to translate into a specific protein molecule the information transcribed from the DNA.
- rRNA constitutes the largest part of total RNA (Highest) 80%

- (iii) Transfer RNA(RNA):
- \Rightarrow These are also called **Soluble RNA**.
- \Rightarrow Single stranded.
- \Rightarrow 10-15% of the total RNA.
- \Rightarrow Size Smallest \rightarrow 75 80 nucleotides only.
- ⇒ **Synthesis** Within **nucleus** from **DNA**.

Function- It transport amino acid from cyto plasm to the site of protein synthesis.

	Differences Between DNA and RNA				
	DNA		RNA		
1.	It usually occurs inside nucleus and some cell organelles .	1.	Very little RNA occurs inside nucleus. most of it is found in the cytoplasm.		
2.	DNA is the genetic material.	2.	RNA is not the genetic material except in certain viruses, e.g. Reovirus.		
3.	It is double stranded with the exception of itsome viruses (e.g. $\phi \times 174$).	3.	RNA is single stranded except reovirus where is double stranded.		
4.	DNA contains over a million nucleotides.	4.	Depending upon the type, RNA contains 70-1200 nucleotides.		
5.	DNA is of only two types; intra-nuclear and extra-nuclear.	5.	There are at least three types of RNAs— mRNA, rRNA and tRNA		
6.	It contains deoxyribose sugar.	6.	It contains ribose sugar.		
7.	Nitrogen base thymine occurs in DNA alongwith three others — adenine, cytosine and guanine.	7.	Thymine is replaced by uracil in RNA The other three are similar — adenine, cytosine and guanine.		
8.	It replicates to form new DNA molecules.	8.	It cannot normally replicate itself.		
9.	DNA transcribes genetic infromation to RNA.	9.	RNA translates the transcribed message for forming polypeptides.		
10.	DNA controls metabolism and genetics Including variations.	10.	It only controls metabolism under instruction from DNA.		
11.	Purine and pyrimidine bases are in equal number.	11.	There is no poroportionality between number of purines and pyrmidine bases.		

ENZYMES

Proteins which are used as a catalyst in biochemical reaction is known as biocatalysts.

SPECIFIC CHARACTERISTICS

Enzymes have following two specific character as :

(i) Specificity

(ii) Efficiency

Specificity of enzymes

- (a) Generally one enzyme can catalyze only one biochemical reaction.
- (b) It can increases rate of reaction upto 10^{20} times.
- (c) In some cases one enzyme can catalyzes more than one reaction and one reaction can be catalyzed by more than one enzyme.

Ex. Enzyme present in Yeast (Zymase) can ferment both glucose and fructose into alcohol and also cane-sugar can be hydrolyses by invertase and sucrase enzymes.

Efficiency of enzymes

(a) One molecule of enzyme can convert millions of substrate molecules into product per second.

Ex. Carbonic anhydrase enzyme present in red blood cells has a highest turn over number.

(b) With having tertiary structure it can be collected as crystals.

Enzymes are denatured at higher temperature.

(c) Enzyme can be stored at low temperature as they are inactivated.

Importance of enzymes

In the thousands of enzymes presents in body if even a single enzyme would be absent or damaged than complex disease in results.

Ex. Scarcity of Phenylalanine hydroxylase enzyme in human body is result in Phenylketonuria disease.

Factors affecting enzyme action :

(i) **Optimum temperature and pH**. Enzyme catalysed reactions have maximum rate at physiological pH of around 7.4 and human body temperature of 37°C (310 K) under one atmosphere pressure.

In fact, as the temperature or pH is increased, the rate rises to a maximum (at 37° C or pH = 7.4) and then falls off.

- (ii) Enzyme activators (co-enzymes). The activity of certain enzymes is increased in the presence of certain substances, called co-enzymes. It has been observed that if a protein contains a small amount of vitamin as the non-protein part, its activity is enhanced considerably. The activators are generally metal ions such as Na⁺, Mn²⁺, Cu²⁺, Co²⁺ etc. These metal ions are weakly bonded to the enzyme molecules and increase their catalytic activity. For example, the enzyme, amylase, in presence of NaCl, which provides Na⁺ ion, shows a very high catalytic activity.
- (iii) Enzyme inhibitors and poisons. Just as in the case of catalysts, the activity of enzyme is slowed down in the presence of certain substance. Such substances are called inhibitors or poisons. They act by combining with the active functional group thereby reducing or completely destroying the catalytic activity of the enzymes. The use of many drugs is on account of their action as enzyme inhibitors in our body.

NUTRIENTS

Sodium, Potassium and Chlorine

- (i) Na⁺ is the principal mineral cation in the extracellular fluid.
- (ii) K^+ is the principal cation inside the cell.
- (iii) Cl⁻ is the principal mineral anion in the ECF.
- (iv) Na^+ and K^+ are essential to the maintenance of water balance and acid-base balance.
- (v) Na^+ and K^+ are important in nerve impulse transmission.

Calcium and Phosphorus

- (i) Calcium and phosphorus are deposited in bones and teeth to give them strength and rigidity.
- (ii) Ca²⁺ is also essential for blood coagulation, neuromuscular function, cardiac function and actions of many enzymes and hormones.

- (iii) Phosphorus enters into many compounds such as nucleic acids and phospholipids, many coenzymes and high energy compounds like ATP.
- (iv) Calcium plays an essential role in sustaining intestinal peristalsis and growth of body tissues.

Iron

- (i) Iron is required for haemoglobin synthesis.
- (ii) Iron is essential both for transportation of oxygen to tissues and for operation of oxidative systems within the tissue cells.

Magnesium

- (i) Magnesium is required as a catalyst for many intracellular enzymatic reactions, particularly those relating to carbohydrate metabolism.
- (ii) Mg is the central metal atom in chlorophyll

Iodine

Iodine is used in the synthesis of thyroid hormones.

Zinc

- (i) Zinc is a constituent of carbonic anhydrase, present in RBCs helping in CO₂ transport.
- (ii) Zinc is a component to lactic dyhydrogenase, important for the interconversion between pyruvic acid and lactic acid
- (iii) Zinc is a component part of some peptidases and therefore is important for digestion of proteins in the alimentary canal

Cobalt

- (i) Cobalt helps in erythropoiesis and in the activities of some enzymes.
- (ii) It is present in vitamin B_{12}

Copper

- (i) Copper helps in the utilisation of iron.
- (ii) Copper deficiency may produce anaemia because of failure in iron utilisation.

Molybdenum

- (i) Molybdenum is a constituent of oxidase enzymes (xanthine oxidase)
- (ii) Molybdenum plays an important role in biological nitrogen fixation

Fluorine

- (i) Fluorine maintains normal dental enamel and prevents dental caries.
- (ii) Excessive intake of fluorine cause fluorosis characterized by mottled teeth and enlarged bones.

VITAMINS

It has been observed that certain organic compounds are required in small amounts in our diet but their deficiency causes specific diseases. These compounds are called vitamins.

CLASSIFICATION OF VITAMINS

Vitamins are classified into two groups depending upon their solubility in water or fat.

(i) Fat soluble vitamins:

Vitamins which are soluble in fat and oils. But insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.

(ii) Water soluble vitamins:

B group vitamins and vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and can not be stored (except vitamin B_{12}) in our body.

Sr. No.	Name of Vitamins	Source	Deficiency Diseases	
	Vitamin A	Fish liver oil, carrots,	Xerophthalmia	
1	(Retinol)	butter and milk	(hardening of cornea of eye)	
			Night blindness	
	Vitamin B1	Yeast, milk, Green	Beri beri (loss of appetite,	
2	(Thiamine)	Vegetables and cereals	retarded growth)	
		and grams		
	Vitamin B2	Milk, egg white,	Cheilosis (fissuring at corners of mouth	
3	(Riboflavin)	liver, Kidney	and lips), digestive disorders and	
			burning sensation of the skin	
4	Vitamin B ₆	Yeast, milk, egg yolk,	Convulsions	
т	(Pyridoxine)	cereals and grams		
5	Vitamin B12	Meat, fish,	Pernicious anaemia (RBC deficient in	
5	(Cyanocobal-amine)	egg and curd	haemoglobin)	
6	Vitamin C	Citrus fruits, amla and	scurvy (bleeding gums)	
0	(Ascorbic acid)	green leafy vegetables	1	
		Exposure to sunlight, fish	Rickets (bone deformities in children)	
7	Vitamin D	and egg yolk	and osteo-malacia (soft bones and	
	(Calciferol)		joint pain in adults)	
	Vitamin E or Jocopherolr (α , β and γ)	Eggs, Milk, Fish, Wheat	Sterility (loss of sexual power and	
8	or Antisterility factor	germ oil colton seed oil	reproduction)	
		etc.		

Some important vitamins, their sources and diseases caused by their deficiency are listed in table.

POLYMERS

The term polymer is used to describe a very large molecule that is made up of many repeating small molecular units. These small molecular units from which the polymer is formed are called monomers. The chemical reaction that joins the monomers together is called polymerisation. Starting from n molecular of a compound M, linking in a linear manner will form polymer $x-M-(M)_{n-2}-M-y$. The nature of linkages at the terminal units i.e. M-x and M-y depends upon the mode of reaction used in making the polymers.

HOMOPOLYMERS AND COPOLYMERS

Polymers which are formed by only one type of monomer are called Homopolymers. Some examples of homopolymers and their monomers are given below :

Homopolymer	Monomer
Starch	Glucose
Cellulose	Glucose
Glycogen	Glucose
Dextrin	Glucose
Inulin	Fructose

CHEMISTRY FOR JEE MAIN & ADVANCED

Polyethylene	Ethylene
Polyvinyl chloride	Vinyl chloride
Teflon	Tetraflouroethylene
Nylon–6	Caprolactam
Polystyrene	Styrene
Orlon (Acrilan)	Acrylonitrile
Plexiglas (Lucite)	Methyl methacrylate
Polyvinyl acetate	Vinyl acetate

Polymers, which are formed by more than one type of monomers are known as copolymers. Some examples are given below in the table:

Copolymer	Monomers
Saran	Vinyl chloride and vinylidene chloride
SAN	Styrene and acrylonitrile
ABS	Acrylonitrile, butadiene and styrene
Butyl rubber	Isobutylene and Isoprene
Buna–S, SBR	Styrene and Butadiene
Buna–N, NBR	Acrylonitrile and Butadiene
Nylon-66	Hexamethylen diamine and Adipic acid
Terylene	Terephthalic acid and ethylene glycol

Polymers are Two Types :

Homopolymers

Polymers in which repeating structural units are derived from only one type of monomer units are called homopolymers.

$n-CH_2 = CH_2$	Polymerization >	$-(CH_2 - CH_2)_n$
Ethylene (Monomer)		Polyethylene (Polymer)

Other examples of homopolymers are polypropylene, polyvinyl chloride (PVC), polyisoprene, neoprene (polychloroprene) polyacrylonitrile (PAN), nylon-6, polybutadiene, teflon (polytetrafluoroethylene), cellulose, starch etc.

Copolymers

Polymers in which repeating structural units are derived from two or more types of monomer units are called copolymers.

n H₂N – (CH₂)₆ – NH₂ Hexamethylenediamine (Monomer) + N HOOC – (CH₂)₄ – COOH $(CH_2)_4$ – COOH $(CH_2)_6$ NH]_n Adipic acid (Monomer)

Types of copolymers

Depending upon the distribution of monomer units, the following types of copolymers are possible.

(1) Random Copolymer

If the monomer units have random distribution throughout the chain, it is called random copolymer. For example, if the monomer A and monomer B undergo copolymerisation then the structure of the random copolymer is

$$nA + nB \longrightarrow -A-A-B-A-B-A-B-A-B-A-A-A-B-$$

segment of random copolymer

(2) Alternating Copolymer

If the two monomer units occur alternatively throughout the polymer chain, it is said to be alternating copolymer. For example,

 $nA + nB \longrightarrow -A-B-A-B-A-B$ segment of alternating copolymer

The exact distribution depends upon the proportion of the two reactant monomers and their relative reactivities. In practice neither perfectly random nor perfectly alternating copolymers are usually formed. However, most copolymers tend more towards alternating type but have many random imperfections.

(3) Block Copolymer

Polymers in which different blocks of identical monomer units alternate with each other are called block copolymers. For example,

Block copolymer can be prepared by initiating the radical polymerisation of one monomer to grow homopolymer chains, followed by addition of an excess of the second monomer.

(4) Graft Copolymer

Polymers in which homopolymer branches of one monomer unit are grafted onto a homopolymer chain of another monomer unit are called graft co-polymers. For example:

-A-A-A-	-A-A-A	A-A-A	A-A-A-
B	I B	B	I B
Ĭ	Ĭ	Ĭ	Ĭ
B	B	В	В
В	B	B	B
7		1	I

(Segment of a graft copolymer)

Graft copolymers are prepared by γ -irradiation of a homopolymer chain in the presence of a second monomer. The high energy radiation knock out H-atoms from the homopolymer chain at random points thus generating radical sites that can initiate polymerisation of the second monomer.

CLASSIFICATION OF POLYMERS

Polymers are classified in following ways:

(I) CLASSIFICATION BASED UPON SOURCE

(1) Natural polymers

Polymers which are obtained from animals and plants are known as natural polymers, Examples of natural polymers are given below.

CHEMISTRY FOR JEE MAIN & ADVANCED

Natural polymer

- 1. Polysaccharide
- 2. Proteins
- 3. Nucleic acid
- 4. Silk
- 5. Natural Rubber (cis polyisoprene)

Amino acids Isoprene (2-Methyl-1, 3-butadiene)

Monosaccharide

α-L-Amino acids

Monomers

Nucleotide

6. Gutta purcha (trans polyisoprene) Isoprene

Natural polymers which take part in metabolic processes are known as biopolymers. Examples are polysaccharides, proteins, RNA and DNA.

(2) Semisynthetic polymers

Polymers which are prepared from natural polymers are known as semisynthetic polymers. Most of the semisynthetic polymers are prepared from cellulose.

Examples are: cellulose acetate, cellulose nitrate, cellulose xanthate and Rayon.

(3) Synthetic polymers

Man-made polymers, i.e. polymers prepared in laboratory are known as synthetic polymers. Example are : PVC, polyethylene, polystyrene, nylon-6, nylon-66, nylon-610, terylene, synthetic rubbers etc.

(II) CLASSIFICATION BASED UPON SHAPE

(1) Linear polymers

Polymer whose structure is linear is known as linear polymer. The various linear polymeric chains are stacked over one another to give a well packed structure.

The chains are highly ordered with respect to one another. The structure is close packed in nature, due to which they have high densities, high melting point and high tensile (pulling) strength. Linear polymers can be converted into fibres.

Note :

(i) All fibers are linear polymers. Examples are cellulose, silk, nylon, terylene etc.

(ii) Linear polymers may be condensation as well as addition polymers. Examples are cellulose, Polypeptide, nucleic acid, nylon, terylene etc.

(2) Branched chain polymers

Branched chain polymers are those in which the monomeric units constitute a branched chain. Due to the presence of branches, these polymers do not pack well. As a result branched chain polymers have lower melting points, low densities and tensile strength as compared to linear polymers.

(3) Cross-linked or Three Dimensional network polymers

In these polymers the initially formed linear polymeric chains are joined together to form a three dimensional network structure. These polymers are hard, rigid and brittle. Cross-linked polymers are always condensation polymers. Resins are cross linked polymers.

CLASSIFICATION BASED UPON SYNTHESIS

(1) Condensation polymerisation

- (i) They are formed due to condensation reactions.
- (ii) Condensation polymerisation is also known as step growth polymerisation.
- (iii) For condensation polymerisation, monomers should have at least two functional groups. Both functional groups may be same or different.
- (iv) Monomers having only two functional group always give linear polymer. For example,

$$nNH_2-R-NH_2+nHOOC-R'-COOH \xrightarrow{Condensation} \left[\begin{array}{c} O & O \\ \parallel & \parallel \\ Reaction \end{array} \right] + (n-1)H_2O$$

Polyamide

$$nHO-R-OH+nHO-C-R'-C-OH \xrightarrow{Condensation} \left[\begin{array}{c} 0 & 0 \\ \parallel & \parallel \\ Reaction \end{array} \right] + (n-1)H_2O$$
Polyester

$$nNH_2-R-COOH \xrightarrow{Condensation} \begin{bmatrix} 0 \\ \parallel \\ -NH-R-C- \end{bmatrix}_n + (\frac{n}{2} - 1)H_2O$$

- (v) Condensation polymers do not contain all atoms initially present in the monomers. Some atoms are lost in the form of small molecules.
- (vi) Monomer having three functional groups always gives cross-linked polymer. Examples are : Urea-formaldehyde resin, phenol-formaldehyde resin.

(3) Addition polymerisation

- (i) Polymers which are formed by addition reaction are known as addition polymers.
- (ii) If monomer is ethylene or its derivative, then addition polymer is either linear polymer of branch-chain polymer. Examples are : polystyrene, polytetrafluoroethylene, polyacrylonitrile etc.

(iii) If monomer is 1, 3-butadiene or 2-substituted-1, 3-butadiene
$$\begin{pmatrix} CH_2 = C - CH = CH_2 \\ I \\ G \end{pmatrix}$$
, then

polymer is always branched chain polymer.

$$nCH_{2}=C-CH=CH_{2}\longrightarrow \begin{pmatrix} G\\ I\\ -CH_{2}-C=CH-CH_{2}\\ (Polymer) \end{pmatrix}_{n}$$

(Monomer)

(i) G = H: 1, 3-Butadiene

(ii) $G = CH_3$; 2-Methyl-1, 3-butadiene or isoprene

- (iii) G = Cl; 2-Chloro-1, 3-butadiene or chloroprene
- (iv) Addition polymers retain all the atoms of the monomer units in the polymer.
- (v) Addition polymerisation takes place in three steps: Initiation, chain propagation and chain termination.
- (vi) Addition polymers are called as chain growth polymers.

(Polymer)

- (i) Polybutadiene
- (ii) Polyisoprene
- (iii) Polychloroprene (Neoprene)

TYPES OF ADDITION POLYMERIZATION

(A) RADICAL POLYMERISATION:

(i) Radical polymerisation takes place in the presence of radical initiators. The radical initiator may be any of the following :

- (ii) Reaction intermediate of radical polymerization is a free radical.
- (iii) Radical polymerization has more chance for those monomers whose free radicals are more stable. Examples are:

```
\begin{array}{ccc} C_{6}H_{5}-CH=CH_{2}, & CH_{2}=CH-CI, & CH_{2}=CH-O-C-CH_{3} \\ \text{Styrene} & Vinyl \, \text{chloride} & Vinyl \, \text{acetate} \end{array}
\begin{array}{ccc} CH_{2}=CH-CN \\ Acrylonitrile \\ (vinyl \, cyanide) & \text{Methyl methacrylate} \end{array} \qquad \begin{array}{ccc} G \\ CH_{2}=C-CH_{3} \\ CH_{2}=C-CH_{2}(G=H, \, CH_{3} \, \text{and } CI) \\ 2-\text{substituted-1,3-butadiene} \end{array}
```

(iv) Radical polymer has linear as well as branched chain structure

Most of the commercial addition polymers are vinyl polymers obtained from alkenes and their derivatives

$$CH_2 = CH [G is H, C_6H_5, R etc.]$$

This type of polymerization is preformed by heating the monomer with only a very small amount of the initiator or by exposing the monomer to light. The general mode of radical polymerization of vinyl monomers is depicted below:

Chain initiation step :

Initiator \rightarrow In •

$$\begin{array}{c} \text{In} \bullet + \text{CH}_2 = \text{CH} \to \text{In} - \text{CH}_2 - \overset{\bullet}{\text{CH}} \\ \downarrow \\ \text{G} \\ \end{array}$$

Chain propagating step :

$$CH_2 = CH + In - CH_2 - CH \rightarrow In - CH_2 - CH - CH_2 - CH_2 \rightarrow In + CH_2 - CH_2$$

Chain terminating step :

In vinylic polymerization, various other reaction of free radicals with some other compounds present may compete with the parent addition chain reactions. One such reaction takes place with molecules that can react with the growing chain to interrupt the further growth. This leads to the lowering of the average molecular mass of the polymer. Such reagents are called as chain transfer agents and include CCl_4 , CBr_4 etc.

For example, in the presence of CCl_4 , styrene polymerises to form polystyrene of a lower average molecular mass which also contains some chlorine what happens here is that growing polystyrene radical which normally would add on a monomer reacts with the chain transfer agent to end the original chain and produces a new radical. The latter initiates a new polymerization chain and thereby forms a new polymer as depicted below.

$$\begin{array}{c} -CH_2 - \overset{\bullet}{C}H + CCI_4 \rightarrow -CH_2 - \overset{\bullet}{C}H - CI + \overset{\bullet}{C}CI_3 \\ \overset{\bullet}{C}_6H_5 & \overset{\bullet}{C}_6H_5 \end{array}$$

$$\begin{array}{c} \overset{\bullet}{C}CI_3 + CH_2 = CH \rightarrow CI_3C - CH_2 - \overset{\bullet}{C}H \xrightarrow{Styrene} + CI_3C - CH_2 - CH + (CH_2 - CH)_n \text{ etc.} \\ \overset{\bullet}{C}_6H_5 & \overset{\bullet}{C}_6H_5 & \overset{\bullet}{C}_6H_5 \end{array}$$

If the chain transfer agent a radical, which is highly unreactive, the reaction chain gets terminated such a compound thus inhibits or arrests polymerisation. Many amines, phenols, quinones etc. act as inhibitors. So, even traces of certain impurities, which can act as chain transfer agent or an inhibitor can interfere with the original polymerisation chain reaction. Hence, the monomers should be free from such inhibitors.

In case the alkene is a diene, the following kinds of polymerisation is possible:

(1) 1, 4-polymerisation

When the polymerisation takes place at C_1 and C_4 of butadiene, an unbranched polymer is formed. This product is different from that formed from an alkene having a double bond, which at each of its carbons is substituted by different groups and hence can exist either as trans-polybutadiene or cis-polybutadiene or a mixture as shown below.

$$R \bullet + CH_2 = CH - CH = CH \longrightarrow R - CH_2 - CH - CH = CH_2 - CH \iff R - CH_2 - CH = CH - CH_2$$

$$H \longrightarrow C = C \longrightarrow R - CH_2 - CH = CH_2 - CH = CH_2 - CH_2$$

(2) **1, 2-polymerisation**

Alternatively, 1, 3-butadiene can undergo polymerisation at C_1 and C_2 to yield the polymeric product, polyvinyl polythene.

The double bonds in these initial polymers can be linked by further treatment with chemicals to modify the properties of the polymers. These reactions form the basis of the formation of rubber.

(B) CATIONIC POLYMERISATION

- (i) Polymerisation which is initiated by an electrophile is known as cationic polymerisation.
- (ii) Reaction intermediate of cationic polymerisation is a carbocation.
- (iii) Carbocations can undergo rearrangement leading to the formation of a more stable carbocation.
- (iv) The electrophile commonly used for initiation is BF3.OEt2.
- (v) Monomers that are best able to undergo polymerisation by a cationic mechanism are those with electron donating substituents that can stabilise the carboncation. Some examples are:

		O II	
$CH_2 = CH - CH_3$	$CH_3 - C = CH_2$	$CH_2 = CH - O - C$	$C_6H_5-CH=CH_2$
Propene	ĊH₃	CH3	Styrene
	Isobutene	Vinyl acetate	

(v) It is terminated by a base.

Thus, when the initiator is cationic in nature, it would generate a cationic intermediate on addition to the double bond for propagating the addition chain process and is termed as cationic addition polymerisation. The process is initiated by an acid. The stages of polymerisation are depicted below.

Chain initiation step :

$$H^{\oplus} + CH_2 = CH \longrightarrow CH_2 - CH_1$$

Chain propagating step :

$$CH_3-CH + CH_2 = CH \longrightarrow CH_3-CH - CH_2-CH \longrightarrow So on$$

 $| G G G G G$

Chain terminating step :

$$\begin{array}{c} CH_{3}-CH-(CH_{2}-CH)-CH_{2}-\overset{\oplus}{C}H\xrightarrow{A^{-}} CH_{3}-CH-(CH_{2}-CH)_{n}-CH=CH + HA \\ I & I \\ G & G & G & G \\ G & G & G \\ \end{array}$$

Cationic polymerisation is facilitated in monomers containing electron - releasing groups. Thus, isobutylene undergoes cationic polymerisation easily as it has two electron releasing $-CH_3$ groups that will stabilize the intermediate carbo cation.

$$CH_{3} - CH_{3} + CH_{2} = CH_{3} + CH_{2} = CH_{3} + C$$

(C) ANIONIC POLYMERISATION:

- (i) Anionic polymerisation takes place in the presence of base or nucleophile, which is initiator in this polymerisation.
- (ii) Reaction intermediate in propagation steps are carboanion.
- (iii) the suitable initiator can be NaNH, or RLi.
- (iv) Those monomers undergo anionic polymerisation reaction whose anion is stable. Example of monomers are:

$$\begin{array}{cccc} CH_2=CH-CI & CH_2=CH-CN & CH_2=C-CH_3 & C_6H_5-CH=CN_2 \\ Vinyl \ chloride & Acrylonitrile & C-O-CH_3 & Styrene \\ & 0 & 0 & \end{array}$$

Methyl methacrylate

- (v) Anionic polymerisation always give linear polymer.
- (vi) Anionic polymerisation terminated by an acid.

The formation of polystyrene from styrene in the presence of potassium amide is an important example of this category of polymerisation. The mode of anionic polymerisation is depicted below:

Chain initiation step :

$$\begin{array}{c} (\overset{\circ}{\mathsf{N}}\overset{\circ}{\mathsf{H}} + \overset{\circ}{\mathsf{C}}\overset{\circ}{\mathsf{H}}_2 = \overset{\circ}{\mathsf{C}}\overset{\circ}{\mathsf{H}} \longrightarrow \overset{\circ}{\mathsf{N}}\overset{\circ}{\mathsf{H}}_2 = \overset{\circ}{\mathsf{C}}\overset{\circ}{\mathsf{H}}\overset{\circ}{\mathsf{H}} \xrightarrow{\mathsf{C}}\overset{\circ}{\mathsf{H}}\overset{\circ}{\mathsf{H}} \xrightarrow{\mathsf{C}}\overset{\circ}{\mathsf{H}} \overset{\circ}{\mathsf{H}} \xrightarrow{\mathsf{C}}\overset{\circ}{\mathsf{H}} \overset{\circ}{\mathsf{H}} \overset{\circ}{\mathsf$$

Chain propagating step :

$$NH_2-CH_2-CH_2+nCH_2=CH \longrightarrow NH_2-CH_2-(CH_2-CH_2)_n-CH_2 K^+$$

Chain terminating step :

$$NH_2-CH_2-(CH_2-CH_2)_n-\overset{-}{C}H\xrightarrow{H^*}H_2N-CH_2-(CH_2-CH_2)_n-CH_2$$

(D) **ZIEGLER-NATTAPOLYMERISATION:**

- (i) Addition polymerisation which takes place in the presence of Ziegler- Natta catalyst $[(C_2H_5)_3A]$ and $TiCl_4]$ is known as Ziegler- Natta polymerisation or co-ordination polymerisation.
- (ii) Ziegler- Natta polymerisation always gives linear, stereo-regular polymers.
- (iii) Ziegler- Natta catalyst revolutionised the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers (due to linear geometry) that have greater resistance to cracking and heat. High density polyethylene is prepared using a Ziegler- Natta catalyst.

CLASSIFICATION BASED ON INTERMOLECULAR FORCES (SECONDARY FORCES)

- (i) Intermolecular forces present between polymeric chains are (a) Van der waals forces (b)Hydrogen bonds and
 (c) Dipole dipole attractions.
- (ii) Mechanical properties such as tensile strength, elasticity, toughness etc. depend upon the secondary force present between the polymeric chains.
- (iii) Magnitude of secondary forces depends upon the size of the molecule and the number of functional groups along the polymeric chains.

Magnitude of secondary forces is directly proportional to the length of the polymeric chain. On the basis of magnitude of secondary forces, polymers can be divided into the following **Five categories**

(1) Elastomers

An elastomer is a plastic that stretches and then reverts back to its original shape. It is randomly oriented amorphous polymer. It must have some cross-links so that the chains do not slip over one another. Very weak Van der waal forces are present in between polymeric chains.

When elastomers are stretched, the random chains stretch out, but there are insufficient Van der Waal forces to maintain them in that configuration and position. When the stretching force is removed, they go back to their random shape. Elastomers have the ability to stretch out over ten times their normal length.

Important examples are vulcanized rubbers.

Note : Addition polymers obtained from butadiene and its derivatives are elastomers.

(2) Fibres

Fibres are linear polymers in which the individual chains of a polymer are held together by hydrogen bonds and / or dipole-dipole attraction. In the fibres, the polymeric chains are highly ordered with respect to one another.

Due to strong intermolecular forces of attraction and highly ordered geometry, fibres have high tensile strength and least elasticity. They have crystalline character and have high melting points and low solubility. Examples are cellulose, nylon, terylene, wool, silk etc.

Note: (i) Condensation polymers formed from bifunctional monomers are fibres in character.

(ii) Addition polymers of alkene derivatives having strong-I group are fibres in character.

(3) Thermoplastic Polymers

Thermoplastic polymers are polymers that have both ordered crystalline regions (the regions of the polymer in which the chains are highly ordered with respect to one another) and amorphous, non crystalline regions (the regions of the polymer in which the chains are randomly oriented).

The intermolecular forces of attraction are in between elastomers and fibres. There are no cross-links between the polymeric chains. Thermoplastic polymers are hard at room temperature, but when they are heated, the individual chains can slip past one another and the polymer become soft and viscus. This soft and viscus material become rigid on cooling. The process of heating softening and cooling can be repeated as many times as desired without any change in chemical composition and mechanical properties of the plastic. As a result, these plastics can be moulded into toys, buckets, telephone and television cases.

Some common examples are : polythene polypropylene, polystyrene, polyvinylchloride, teflon etc.

Note : Addition polymers obtained from ethylene and ethylene derivatives are thermoplastic polymers.

(4) Thermosetting Polymers

Polymers which become hard on heating are called thermosetting polymers. Thermosetting polymers can be heated only once when it permanently sets into a solid, which cannot be remelted by heating.

Thermosetting polymers are cross-linked polymers. Greater the degree of cross-linking that exist, the more rigid is the polymer. Cross-linking reduces the mobility of the polymer chains, causing them to be relatively brittle materials, the hardening on heating is due to the extensive cross-linking between different polymer chains to give a three dimensional network solid. Examples are : phenol formaldehyde resin, urea-formaldehyde resin, melamine-formaldehyde resin.

DIFFERENCE BETWEEN THERMOPLASTIC AND THERMOSETTING POLYMERS

S.No. Thermoplastic polymers

- 1. Soften and melt on heating and become hard on cooling i.e. process is reversible
- 2. Can be moulded and remoulded and reshaped.
- 3. They are addition polymers
- 4. Structure is generally linear

RUBBER

1. Natural Rubber

Natural rubber is obtained from nearly five hundred different plants but the main source is a braziliensis tree. It is obtained in the form of milky sap known as latex. This latex is coagulated with acetic acid and formic acid. The coagulated mass is then squeezed.

The raw natural rubber is a soft gummy and sticky mass. It is insoluble in water, dilute acids and alkalies but soluble in non-polar solvents. It has low elasticity and low tensile strength. Natural rubberis a polymer of 2-methyl-1, 3-butadiene (isoprene). On average, a molecule of rubber contains 5000 isoprene units held together by head to tail. All the double bonds in rubber are cis, hence natural rubber is cis-polyisoprene.

+ + Polymerisation(1,4 addition reaction)

Thermosetting polymers

Become hard on heating and process is irreversible. They can be moulded once and cannot be remoulded or reshaped. They are condensation polymers. Structure is cross - linked. Gutta - percha is a naturally occurring isomer of rubber in which all the double bonds trans. Thus, gutta-percha is trans-polyisoprene.

It is harder and more brittle than rubber. It is filling material that dentists use in root canal treatment. In order to give strength and elasticity to natural rubber, it is vulcanized. Heating of rubber with sulphur or sulphur containing compound at 150°C for few hours is known as vulcanisation. The essential feature of the vulcanisation is the formation of cross-linking between the polymeric chains. This cross-linking gives mechanical strength to the rubber. Vulcanisation process can be enhanced in the presence of certain organic compounds known as accelerator. The common accelerators are:

In addition, fillers such as carbon black and zinc oxide are usually added to the crude rubber before vulcanisation in order to improve its wearing characteristics.

Natural rubber is used for making shoes, water - proof coats and golf balls. Vulcanised rubber is used for manufacture of rubber bands, gloves tubing and car tyres.

SYNTHETIC RUBBER OR POLYMERISATION OF DIENES

Polymers of 1, 3 - butadienes are called synthetic rubbers because they have some of the properties of natural rubbers including the fact that they are water proof and elastic.

Synthetic rubbers have some improved properties. They are more flexible, tougher and more durable than natural rubber.

1. Homopolymers

Monomer of this class is 2-substituted-1, 3-butadienes.

$$G = CH_2 = C - CH = CH_2$$
 where G=H, CH, or Cl.

polymerisation is always carried out in the presence of Zieglar-natta catalyst which gives stereo regular polymers.

+ Zieglar - Natta catalyst

cis poly (1,3 butadiene)

Neoprene was the first synthetic rubber manufactured on large scale. It is also called dieprene. Its monomer, chloroprene (2-chlorobutadiene) is prepared from acetylene.

r

$$2HC \equiv CH \xrightarrow{Cu_2Cl_2} CH_2 = CH - C \equiv CH \xrightarrow{HCL} CH_2 = CH - C = CH_2$$
Acetylene Vinyl acetylene Chloroprene

Chloroprene undergoes free radical polymerisation to form neoprene (polychloroprene).

Many of the properties of neoprene are similar to natural rubber but neoprene is more resistant to action of oils, gasoline and other hydrocarbons. It is also resistant to sunlight, oxygen, ozone and heat. It is non-inflammable. It is used for making automobile and refrigerator parts, hoses for petrol and oil containers, insulation of electric wires and conveyor belts.

2. Copolymers

(a)

The following synthetic rubbers are example of copolymers.

	Synthetic rubber	Monomers
1.	Buna-S, SBR (styrene-Butadiene rubber)	$C_{6}H_{5}$ CH=-CH ₂ +CH ₂ =CHCH=-CH ₂ (25%) (75%)
2.	Buna-N, NBR (Nitrile-Butadiene rubber)	CH ₂ =CH-CN+CH ₂ =CH-CH=CH ₂ (25%) (75%)
3.	Butyl rubber	$CH_3-C=CH_2 + Butadiene$ $H_3 = 2\%$ 98%
4.	ABS; Acrylonitrile, Butadiene, Styrene	$CH_2=CH-CN+CH_2=CH-CH=CH_2$ + $C_6H_5CH=CH_2$
Thiok	ol : Thiokol is made by polymerising ethylene chlo	oride and sodium polysulphide.

$$CI-CH_{2}-CH_{$$

The repeating unit is -CH₂-S-S-CH₂-

Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

(b) Buna–S (SBR : Styrene-butadiene rubber) : Buna-S rubber is a copolymer of three moles of butadiene and one mole of styrene. In buna-S, 'Bu' stands for butadiene, 'na' for symbol of sodium (Na) which is a polymerizing agent and 'S' stands for styrene. It is an elastomer (General purpose styrene Rubber or GRS).

Buna-S is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear therefore used in the manufacture of tyres and other mechanical rubber goods. It is obtained as a result of free radical copolymerisation of its monomers.

(c) Buna-N: It is obtained by copolymerisation of butadiene and acrylonitrile (General purpose Rubber acrylonitrile or GRA).

$$nCH_2 = CH - CH = CH_2 + nCH_2 = CH \longrightarrow \begin{bmatrix} CH_2 - CH = CH - CH_2 - CH - CH_2 \end{bmatrix}_{n}$$

It is very rigid and is very resistant to action of petrol, lubricating oil and many organic solvents. It is mainly used for making fuel tanks.

(d) Cold Rubber : Cold rubber is obtained by polymerization of butadiene and styrene at -18° to 5° C temperature in the presence of redox system. Cold rubber has a greater tensile strength and greater resistance to abrasion than SBR.

NYLON

Nylon is used as a general name for all synthetic fibres forming polyamides, i.e., having a protein like structure. A number is usually suffixed with the name 'nylon' which refers to the number of carbon atoms present in the monomers.

(1) NYLON -66 (Nylon six, six)

It is obtained by the condensation polymerization of hexamethylenediamine (a diamine with six carbon atoms) and adipic acid (a dibasic acid having 6 carbon atoms).

(2) NYON-6, 10 (Nylon six, ten)

It is obtained by condensation polymerisation of hexamethylenediamine (six carbon atoms) and sebacic acid (a dibasic acid with 10 carbon atoms).

Nylon fibres are stronger than natural fibres and so are used in making cords and ropes. The fibres are elastic, light, very strong and flexible. They have drip dry property and retain creases. It is inert towards chemicals and biological agents. It can be blended with wool. Nylon fibres are used in making garments, carpets, fabrics, tyre cords, ropes etc.

(3) NYLON-6 (Perlon L)

A polyamide closely related to nylon is known as perlon L (Germany) or Nylon-6 (USA). It is prepared by prolonged heating of caprolactam at 260°-270°C. It is formed by self condensation of a large number of molecules of amino caproic acid. Since, caprolactam is more easily available, it is used for polymerization, with is carried out in the presence of H₂O that first hydrolyses the lactam to amino acid. Subsequently, the amino acid can react with the lactam and the process goes on and into form the polyamide polymer.

Carpolactam is obtained by Backmann rearrangement of cyclohexanone oxime.

(4) NYLON-2-NYLON-6

It is in alternating polyamide copolymer of glycine and amino caproic acid and is biodegradable.

POLYETHYLENE

Polyethylene is of two types:

(a) Low Density Poly Ethylene (LDPE) : It is manufactured by heating ethylene at 200°C under a pressure of 1500 atmospheres and in the presence of traces of oxygen. This polymerisation is a free radical polymerisation.

$$nCH_2 = CH_2 \xrightarrow{200^{\circ}C} \left\{ CH_2 - CH_2 \right\}_n$$

The polyethylene produced has a molecular mass of about 20,000 and has a branched structure. Due to this, polyethylene has a low density (0.92) and low melting point (110°C). That is why polyethylene prepared by free radical polymerisation is called low density polyethylene. It is a transparent polymer of moderate tensile strength and high toughness. It is widely used as a packing material and as insulation for electrical wires and cables.

High Density Poly Ethylene (HDPE): It is prepared by the use of Zieglar - Natta catalyst at 160°C under pressure of 6 to 7 atmosphere.

The polymer is linear chain, hence it has high density (0.97) and has high melting point (130°C). That is why it is called high density polyethylene. It is a translucent polymer. It has greater toughness, hardness and tensile strength than low density polyethylene. It is used in the manufacture of containers (buckets, tubes), house wares, bottles and toys.

(b)

PLASTICISER

A plasticiser is an organic compound that dissolves in the polymer and allows the polymer chains to slide past one another. This makes polymer more flexible. Dibutylphthalate is a commonly use plasticiser.

MELAMINE - FORMALDEHYDE RESIN

This resin is formed by condensation polymerisation of melamine and formaldehyde.

It is a quite hard polymer and is used widely for making plastic crockery under the name melamine. The articles made from this polymer do not break even when dropped from considerable height.

BAKELITE

Phenol-formaldehyde resins are obtained by the reaction of phenol and formaldehyde in the presence of either an acid or a basic catalyst. The reaction starts with the initial formation of ortho and para-hydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with $-CH_2$ groups. The reaction involves the formation of methylene bridges in ortho, para or both ortho and para positions. Linear or cross - linded materials are obtained depending on the conditions of the reaction.

POLYESTERS

Dacron is a common polyester, prepared using ethylene glycol and terephthalic acid. The reaction is carried out at 140° to 180° C in the presence of zinc acetate and Sb₂O₃ as catalyst.

The terylene fibre (Dacron) is crease resistant and has low moisture absorption. It has high tensile strength. It is mainly used in making wash and wear garments, in blending with wood to provide better crease and wrinkle resistance.

BIODEGRADABLE POLYMERS

By far the largest use of synthetic polymers is as plastic. A major portion of it is used as throwaway containers and packing materials. Since plastics do not disintegrate by themselves, they are not biodegradable over a period of time. Non-biodegradability is due the carbon-carbon bonds of addition polymers which are inert to enzyme catalysed reaction. These polymers create pollution problem.

Biodegradable polymers are the polymers that can be broken into small segments by enzyme catalysed reactions using enzymes produced by microorganisms. In biodegradable polymers, bonds that can be broken by the enzymes are inserted into the polymers. Therefore, when they are buried as waste, enzymes present in the ground can degrade the polymer.

One method involves inserting hydrolysable ester group into the polymer. For example, when acetal (I) is added during the polymerization of alkene, ester group is inserted into the polymeric chains.

Aliphatic polyesters are important class of biodegradable polymers. Some examples are described below:

(1) Poly - Hydroxybutyrate-CO-β-Hydroxyvalerate (PHBV)

It is a copolymer of 3-hydroxybutanoic acid and 3 hydroxypentanoic acid, in which the monomer units are connected by ester linkages.

$$\mathrm{CH_3-CH(OH)-CH_2-COOH+CH_3-CH_2-CH(OH)-CH_2-COOH} \rightarrow$$

The properties of PHBV very according to the ratio of both the acids. 3-Hydroxybutanoic acid provides stiffness and 3-hydroxypentanoic acid imparts flexibility to the co-polymer. It is used in specialty packaging, orthopaedic devices and even in controlled drug relase. When a drug is put in a capsule of PHBV. It is released only after the polymer is degraded. PHBV also undergoes bacterial degradation in the environment.

(2) POLY (GLYCOLIC ACID) AND POLY (LACTIC ACID)

They constitute commercially successful biodegradable polymers such as sutures. Dextron was the first bioadsorbable suture made for biodegradable polyesters for post - operative stitches.

MOLECULAR MASS OF POLYMER

Normally, a polymer contains chains of varying lengths and therefore, its molecular mass is always expressed as an average. In contrast, natural polymers such as protein contains chain of identical length and hence, have definite molecular mass.

The molecular mass of a polymer is expressed as

(a) Number average molecular mass (\overline{M}_{n})

$$\overline{M}_{n} = \frac{\sum N_{i}M_{i}}{\sum N_{i}}$$

Where N_i is the number of molecules of molecular mass M_i

(b) Weight average molecular mass (\overline{M}_{w})

$$\overline{M}_{w} = \frac{\sum N_{i}M_{i}^{2}}{\sum N_{i}M_{i}}$$

Where N_i is the number of molecules of molecular mass M_i. Methods such as light scattering and ultracentrifuge

depend on the mass of individual molecules and yield weight average molecular masses. \overline{M}_n is determined by employing methods which depend upon the number of molecules present in the polymer sample viz. Colligative properties like osmotic pressure.

The ratio of the weight and number average molecular masses ($\overline{M}_{w}/\overline{M}_{n}$) is called Poly Dispersity Index (PDI). Some natural polymers, which are generally monodisperesed, the PDI is unity (i.e. $\overline{M}_{w} = \overline{M}_{n}$).

In synthetic polymers, which are always polydispersed, PDI > 1 because is always higher than \overline{M}_{n} .

COM	MON POLYMERS Monomer	Repeating unit	Polymer
1.	CH ₂ =CH ₂ Ethylene	-CH ₂ -CH ₂ -	Polyethylene
2.	CH ₃ -CH=CH ₂	CH ₃ -CH ₂ -CH ₂ -	Polypropene
3.	C ₆ H ₅ -CH=CH ₂ Styrene	-CH ₂ -CH- C ₆ H ₅	Polystyrene
4.	CF ₂ =CF ₂ Tetrafluoroethylene	-CF ₂ -CF ₂ - ethylene (PTFE), Teflon	Polytetrafluoro
5.	CH ₂ =CH-Cl Vinyl chloride	CI I -CH ₂ -CH-	Polyvinyl Chloride (PVC)
6.	CH ₂ =CH-CN Vinyl cyanide or	CN I $-CH_2-CH-$ poly acrylonitrile,	Polyvinyl cyanide, Acrylonitrile Orlon.
7.	H ₃ C O $\parallel \parallel$ CH ₂ =C-C-O-CH ₃ Methyl methacrylate	СООСН ₃ -CH ₂ -C- СН ₃	Polymethyl metha acrylate,
8.	$CH_2 = CH - O - C - CH_3$	Plexiglas, Lucite OCOCH ₃ -CH ₂ -CH-	Polyvinyl Acetate
9.	$CH_2 = CH - CH = CH_2$ 1, 3-butadiene	-CH ₂ -CH-CH-CH ₂ - Buna rubber	Polybutadiene,

CHEMISTRY FOR JEE MAIN & ADVANCED

BIOMOLECULES & POLYMERS

CHEMISTRY FOR JEE MAIN & ADVANCED

PRACTICAL ORGANIC CHEMISTRY (A) FUNCTIONAL GROUPANALYSIS

1.	Unsaturation : Alkenes & alkynes :	
	(a) Bayers test : Cold dil alk. $KMnO_4$ decolourisation test	
	Purple colour Colourless + MnO ₂ (Brown ppt)	
	(b) Br_2 water decolourisation test	
	Violet colourless of $Br_2 \rightarrow Colourless$	
2.	Terminal alkynes :	
	Confirmed by ppt of Acetylide ion with $NaNH_2$ or $AgNO_2$ or $Cu_2Cl_2NH_4OH$	
3.	Alkyl halides :	
	(a) If they are capable of carbocation formation then they will give ppt with $AgNO_3$.	
	(b) Beilstein's test : A green colour is imported to the flame if small amount of organic conwire.	npound is taken on copper
4.	Alcohol :	
	(a) Cerric ammonium nitrate \rightarrow Give red colour	
	(b) Boil with acetic acid & conc. $H_2 SO_4 \rightarrow \text{fruity smell}$	
		Θ

(c) 2-alkanol & ethanol also give Iodoform test \rightarrow Yellow ppt. of CH₃I on reaction with I₂ + OH

5. Aldehyde & ketones :

2,4-Dinitrophenyl hydrazize (or) Braddy's reagent give yellow, orange or red colour with ald. & Ketones (2, 4-DNP)

6. Aldehydes:

- (a) Tollen's test \rightarrow Silver mirror
- (b) Fehling's test {except benzaldehyde} \rightarrow Red colour
- (c) Benedicts test \rightarrow Red colour
- (d) Schiff's dye colour regeneration test \rightarrow Pink colour
- (e) Gly ppt. with HgCl₂.

7. Ketones:

- (a) methyl ketones give haloform test
- (b) α -hydroxy Ketones give Tollen's & Fehling test's too.

8. Carboxylic acids :

- (a) Brisk effervescence with aq. NaHCO₃ solution.
- (b) HCOOH alone gives silver mirror test with Tollen's reagent.
- (c) Blue litmus \rightarrow red
- (d) give fruity smell of reaction with alcohols.

CHEMISTRY FOR JEE MAIN & ADVANCED

9. Phenols :

- (a) Violet colouration with neural Fecl,
- (b) Liebermann test
- (c) White ppt. with Br, water
- (d) Brisk effervescence with aq. NaHCO₃ is observed in case of Nitrophenols.

10. Primary amines :

- (a) Carbylamine reaction \rightarrow Isonitriles have very distinctive foul odors
- (b) Hoffmann mustard oil reaction \rightarrow Oily liquid with mustard like smell.
- 11. Aromatic 1° amine \rightarrow diazo test
- 12. Amide boil with NaOH \rightarrow NH₃
- 13. Nitrobenzene \rightarrow Mullikqn Baker test \rightarrow Treat it with ZnNH₄Cl then boil with Tollen's reagent \rightarrow Silver mirror will appear

14. **Proteins** :

(a) Biuret test : Also used for urea → Alkaline solution of protein treated with a drop of aq CuSO₄ when bluish violet colour is obtained

(b) Ninhydrin test: Protein treated with a puridine solution of ninhydrin give colour ranging from deep blue to violet pink.

DIFFERENTATION TEST

D1. 1°, 2° & 3° alcohols :

- (a) Luca's test : Lucas reagent is conc. HCl + ZnCl,
- (b) Victor Meyer's test (RBC test)
 - (i) 1° Alcohol \rightarrow Blood red colour
 - (ii) 2° Alcohol \rightarrow Blue
 - (iii) 3° Alcohol \rightarrow Colourless

D2. 1°, 2° & 3° amines :

- (a) Hinsberg's reagent
 - (i) 1° Amine yield a clear solution from which upon acidification an insoluble material separated.
 - (ii) 2º Amine yield an insoluble compound which is unaffected by acid
 - (iii) 3° Amine yield insoluble compound
- (b) Reaction with HNO₂.

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Lassaigne Method (Detection of Elements)

Element Sodiu	ım Extract (S.E.)	Confirmed Test	Reactions
		S.E. + FeSO ₄ + NaOH,	$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$
Nitrogen	$Na+C+N \longrightarrow NaCN(S.E.)$	boil and cool,	Fe(OH) ₂ +6NaOH → Na ₄ [Fe(CN) ₆]+2NaOH
		+ FeCl ₃ + conc. HCl Blue or green colour (i) S.E. + sodium nitro prusside (A)	$Na_{4}[Fe(CN)_{6}] + FeCl_{3} \xrightarrow{I:1} Fe_{4}[Fe(CN)_{6}]_{3} + 3NaCl$ Prussian blue (i) Na_{5}S + Na_{6}[Fe(CN)_{6}NO] \xrightarrow{F}Na_{6}[Fe(CN)_{6}NOS]
		A deep violet colour	(A) deep violet
Sulphur	$2Na + S \longrightarrow Na_2S(S.E.)$	(ii) S.E. + CH ₃ COOH + (CH ₃ COO) ₂ Pb h A black ppt. S.E. + HNO ₃ + AgNO ₃ (i) White ppt. soluble	(ii) Na ₂ S+(CH ₃ COO) ₂ Pb → PbS + 2CH ₃ COONa black ppt.
		in aq. NH ₃ confirms Cl (ii) Yellow ppt.	$NaX + AgNO_3 \xrightarrow{HNO_3} AgX$ ppt.
Halogen	Na+Cl	partially soluble in aq. NH ₃ confirm Br (iii) Yellow ppt. in soluble in aq. NH ₃ confirms I As in test for nitrogen;	AgCl+2NH ₃ (aq) [Ag(NH ₃) ₂]Cl white ppt. soluble
Nitrogen		instead of green or blue colour, blood red	$NaCNS + FeCl_3 \longrightarrow [Fe(CNS)]Cl_2 + NaCl$
and Sulphur together	Na+C+N+S → NaCNS(S.E.)	colouration confirms presence of N and S both	blood red colour