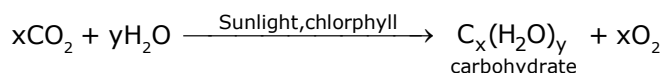


CARBOHYDRATES

1. 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.



2. Classification and structure of Carbohydrates:

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

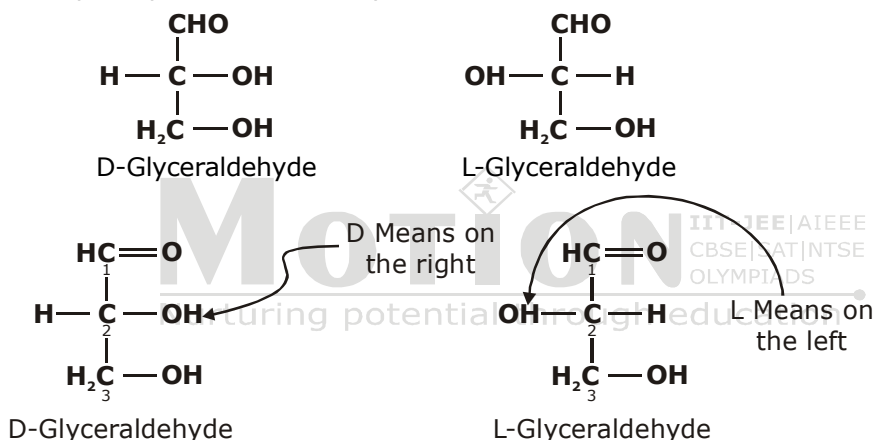
The simplest carbohydrates are called **sugars** or **saccharides**, (Latin: Saccharum, sugar). Carbohydrates can be classified as **monosaccharides**, **oligosaccharides** and **polysaccharides**.

3. General Characteristic of Monosaccharides:

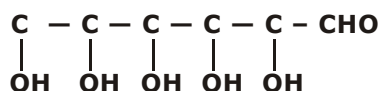
The important characteristics of monosaccharides are as follows:

- (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**.

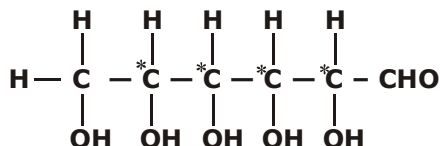


All four isomers have been prepared synthetically. The D- and L-erythrose are mirror images, that is, they are enantiomers. They have exactly the same degree of rotation but in opposite directions. Equal amounts of the two would constitute a racemic mixture, that is a mixture that would allow a plane-polarised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



Supplying hydrogen atoms to the five carbon atoms to satisfy their tetravalency, following structure

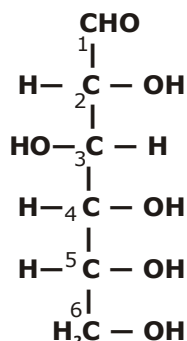
(open chain) may be assigned to glucose: (* indicates assymmetric carbon atom).



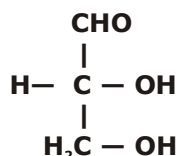
6. Configuration* of Glucose:

Since the above structure possesses four asymmetric carbon atoms (shown by asterisks), it can 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.



D(+)-Glucose



(+)-Glyceraldehyde

Notations D- and L- for denoting configuration were given by Rosanof; 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.

7. Objections to open-chain structure of glucose:

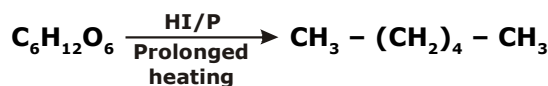
Even though open chain structure of (+) glucose explains most of its reactions, it fails to explain the following facts about it.

- Glucose does not restore Schiff's reagent colour.
- Glucose does not form a bisulphite and aldehyde-ammonia compound.
- Glucose forms two isomeric penta-acetates neither of which reacts with carbonyl reagents.
- The existence of the two isomeric glucoses and the change in specific rotation (mutarotation) is not explained by an open-chain formula.
- 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 of glucose is found to be $\text{C}_6\text{H}_{12}\text{O}_6$.
- Straight Chain of six carbon atoms:**
 - 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.

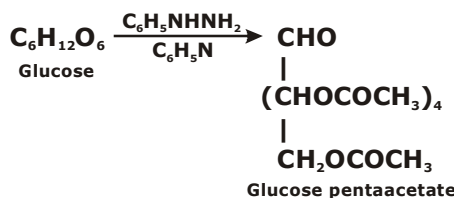


Glucose

n-hexane

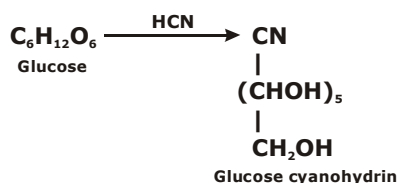
- ii) Glucose when oxidized with bromine water gives gluconic acid which when reduced with excess of HI gives n-hexanoic acid, $\text{CH}_3 \cdot (\text{CH}_2)_4 \cdot \text{COOH}$ confirming the presence of a straight chain of six carbon atoms in glucose.

3. **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.



4. 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.

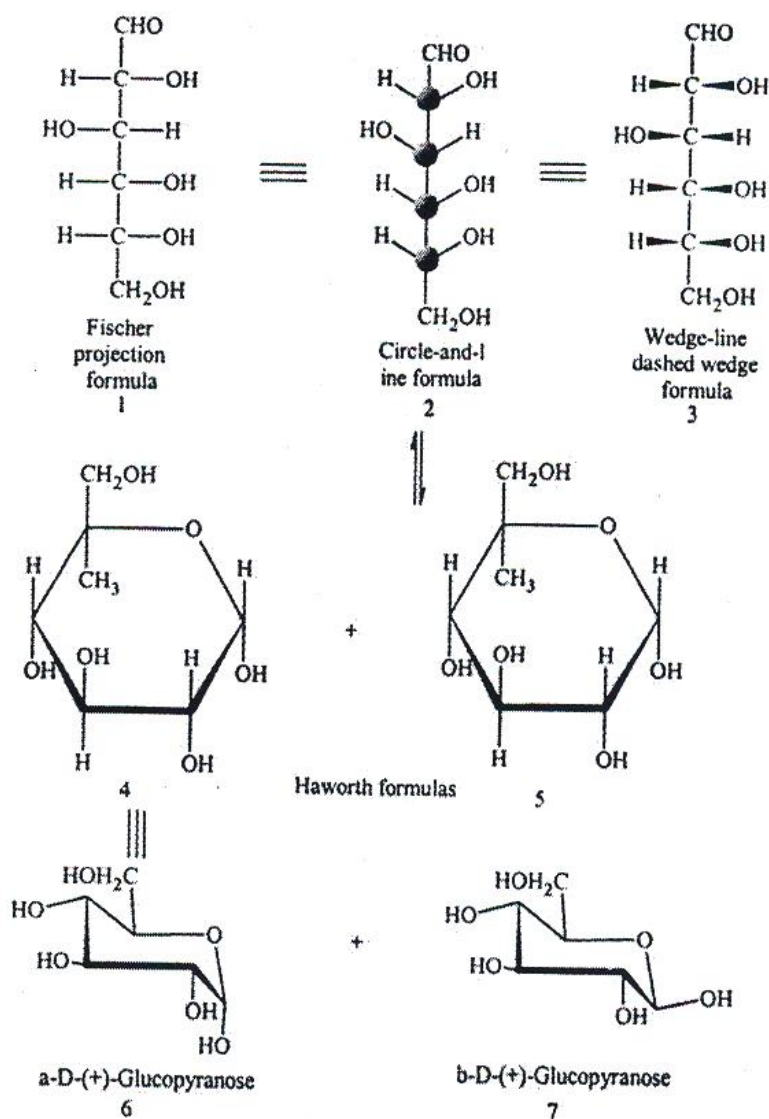


Now since aldehydic group is monovalent, it must be present on the end of the chain.

5. **Open chain structure:** On the basis of the above points, glucose may be assigned following 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.

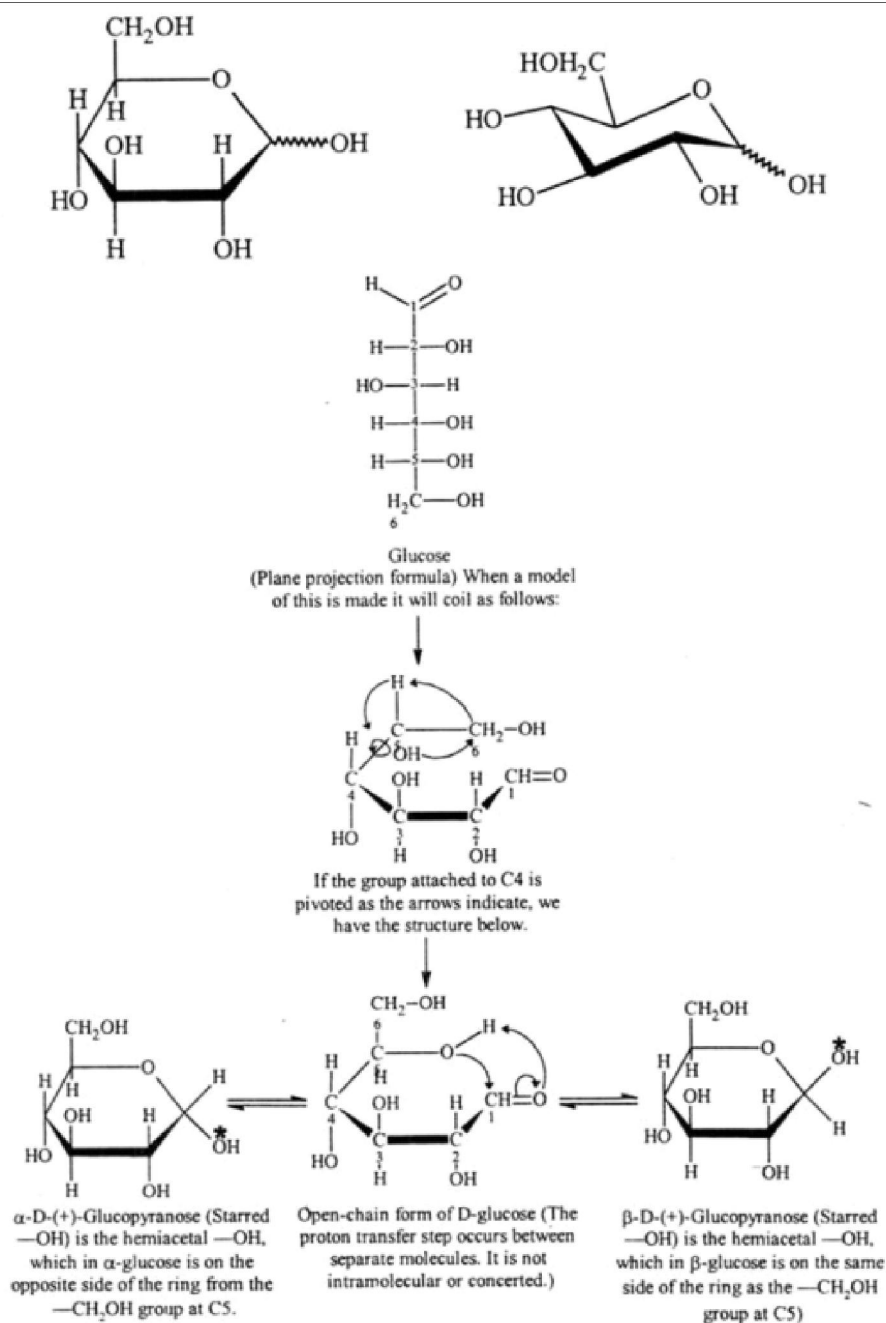
STRUCTURE FORMULAS FOR MONOSACCHARIDES:

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. Cyclization 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 differ only in the configuration of C1. In carbohydrate chemistry diastereomers of this type are 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.

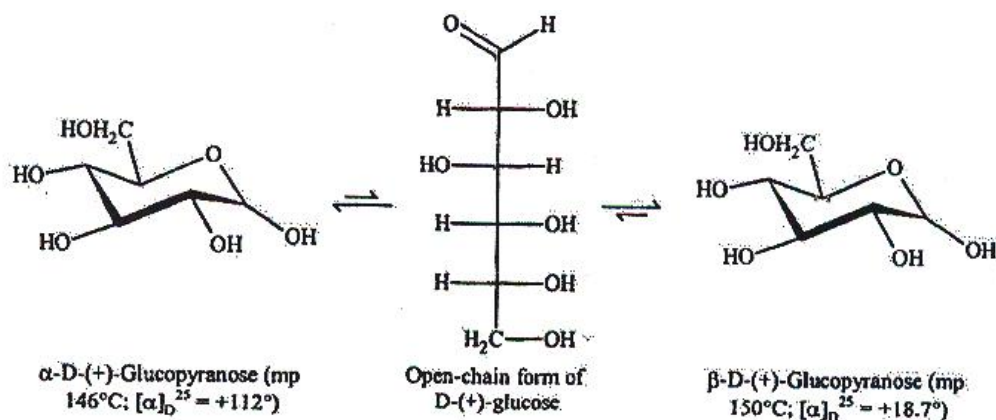
Each glucose anomer is designated as an α anomer or a β anomer depending on the location of the -OH group of C1. When we draw the cyclic forms of a D sugar in the

**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

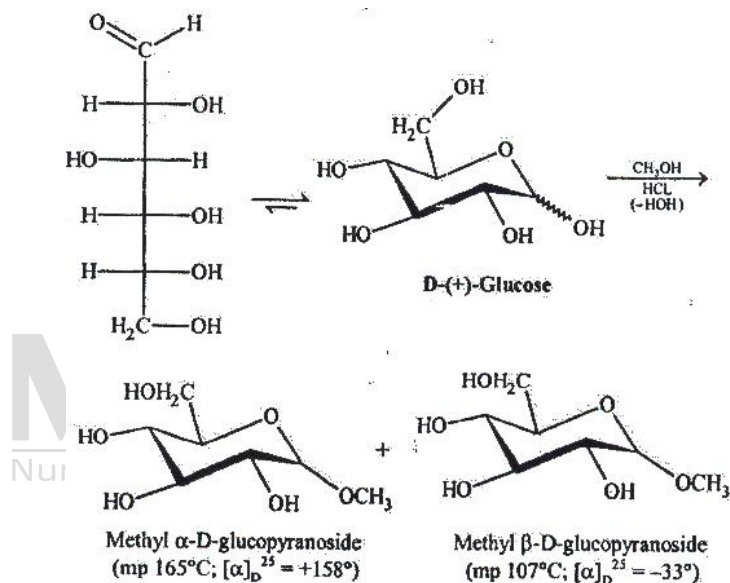
show the same value. A solution of original D-(+)-glucose (mp 146°C) has an initial specific rotation of +112°, but, ultimately, the specific rotation of this solution falls to +52.7°. A solution of second form of D(+)-glucose (mp 150°C) has an initial specific rotation of +18.7°, but slowly, the specific 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 and the α and β forms of the cyclic hemiacetals.



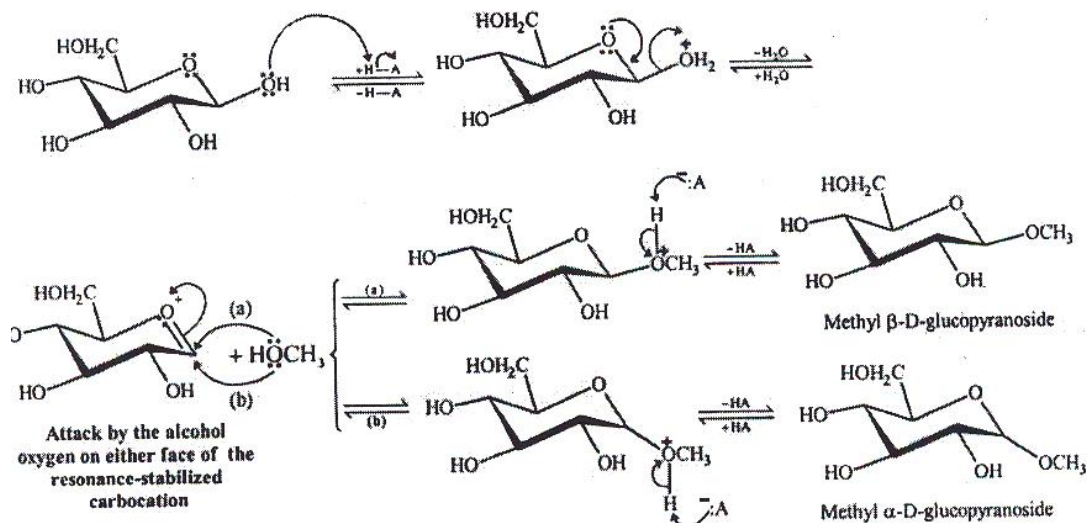
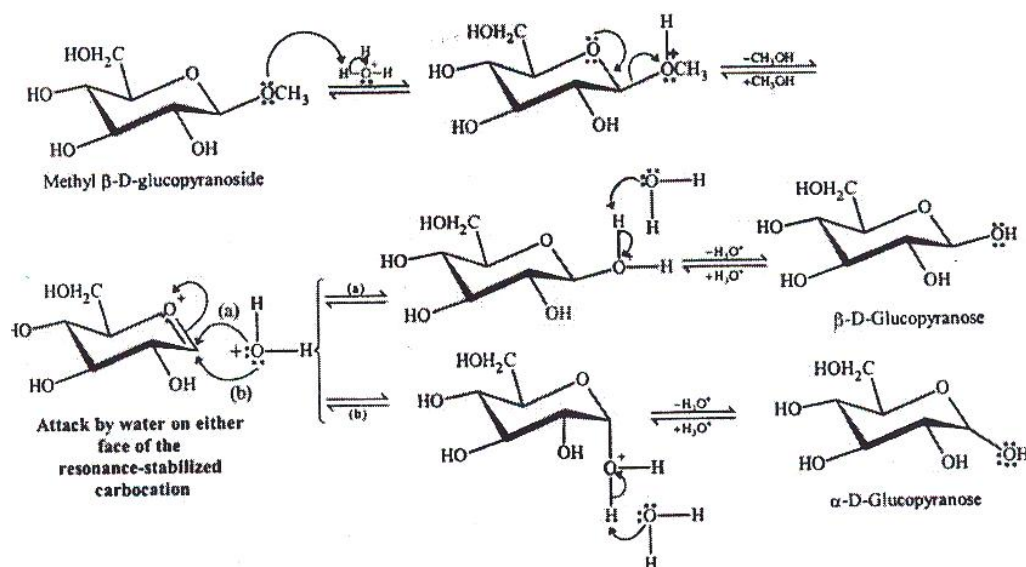
GLYCOSIDE FORMATION

When a small amount of gaseous hydrogen chloride is passed into a solution of D(+) glucose in methanol, a reaction takes place that results in the formation of anomeric methyl acetals:

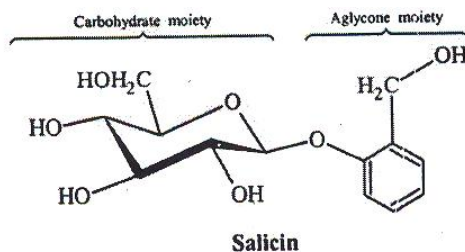


Carbohydrate acetals, generally, are called glycosides (see the following mechanism), and an acetal of glucose is called a glucoside. (Acetals of mannose are mannosides, acetals of fructose are fructosides, and so on) the methyl D-glucosides have been shown to have six-membered rings so they are properly named methyl α -D-glucopyranoside and methyl β -D-glucopyranoside.

The mechanisms for the formation of the methyl glucosides (starting arbitrarily with β -D-glucopyranose) is as follows:

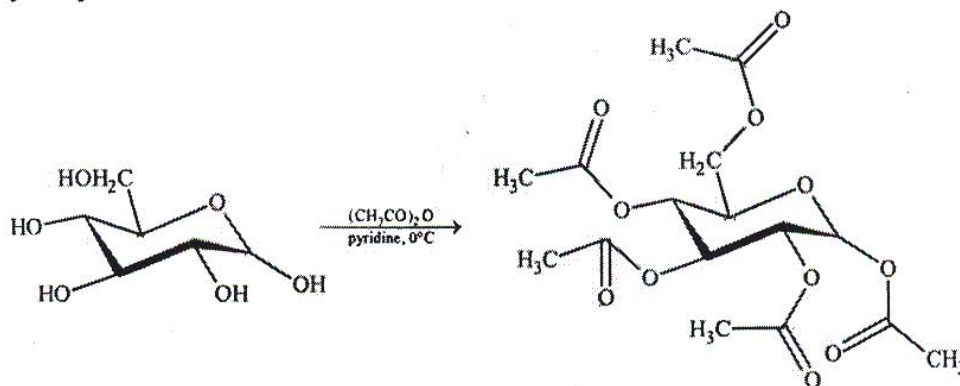
Formation of a Glycoside:**Hydrolysis of a Glycoside:**

Glycosides may be as simple as the methyl glucosides that we have just studied or they may be considerably more complex. Many naturally occurring compounds are glycosides. An example is salicin, a compound found in the bark of willow trees:

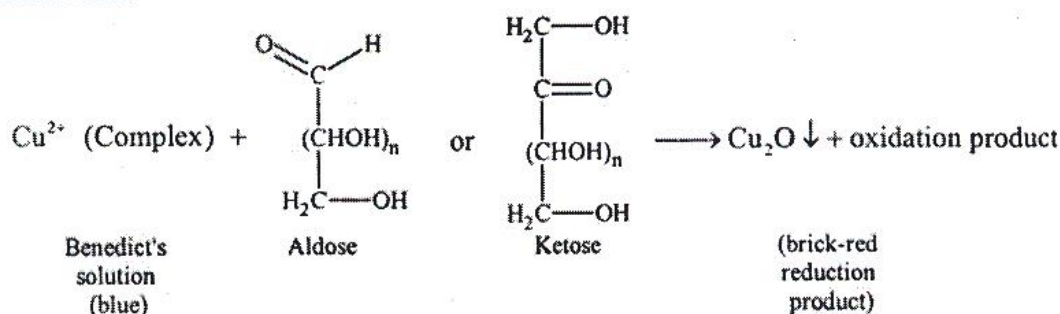


CONVERSION TO ESTERS:

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.

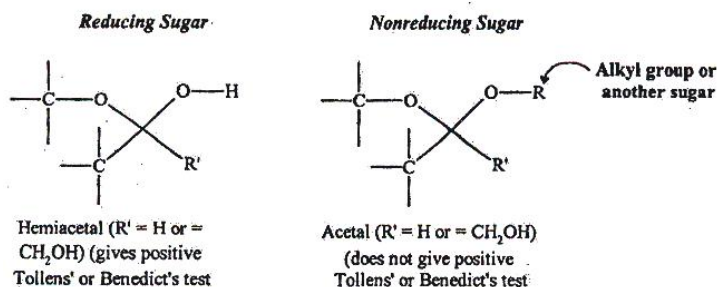
**BENEDICT'S OR TOLLENS' REAGENTS: REDUCING SUGARS**

Benedict's reagent (A alkaline solution containing a cupric citrate complex ion) and Tollen's solution [$\text{Ag}^+(\text{NH}_3)_2\text{OH}^-$] oxidize and thus give positive tests with aldoses and ketoses. The tests are positive even though aldoses and ketoses exist primarily as cyclic hemiacetals.



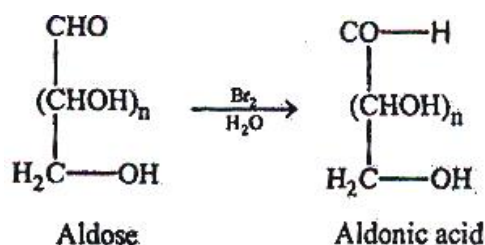
Sugars that give positive tests with Tollen's or Benedict's solutions are known as reducing sugars, and all carbohydrates that contain a hemiacetal group given positive tests. In aqueous solution these hemiacetals exist in equilibrium with relatively small, but not insignificant, concentrations of noncyclic 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 give 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.

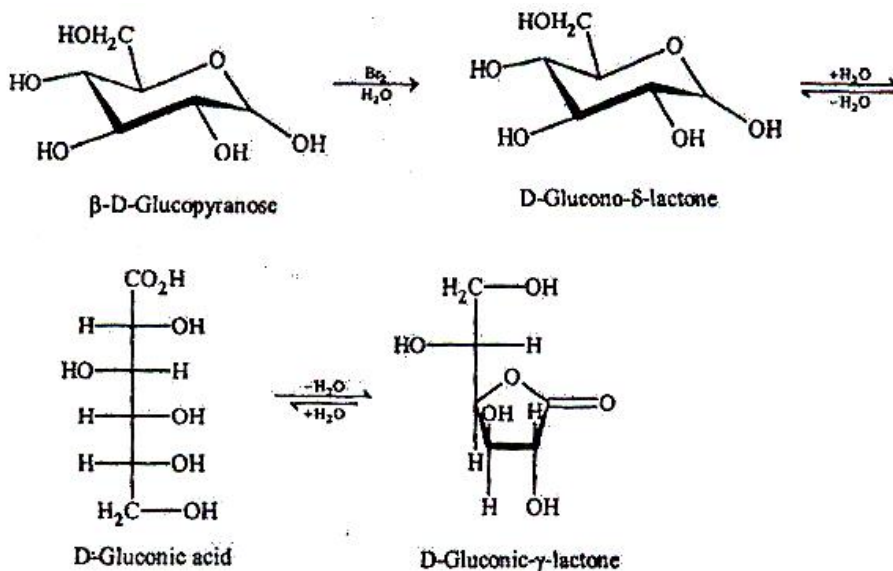


BROMINE WATER : THE SYNTHESIS OF ALDONIC ACID

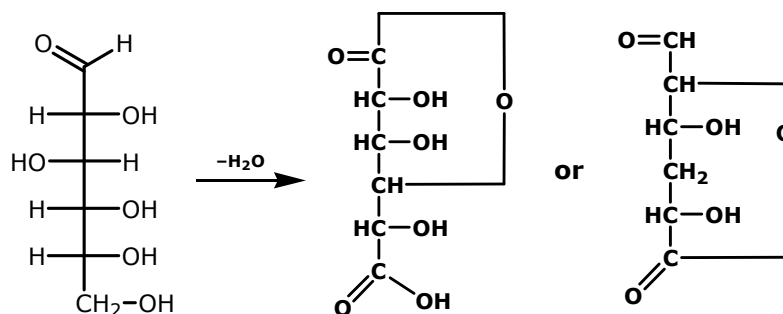
Monosaccharides do not undergo isomerization and fragmentation reactions in mildly acidic solution. Thus, a useful oxidizing reagent for preparative purposes is bromine in water (pH 6.0). Bromine water is a general reagent that selectively oxidizes the $-\text{CHO}$ group to a $-\text{CO}_2\text{H}$ 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:

**NITRIC ACID OXIDATION: ALDARIC ACID**

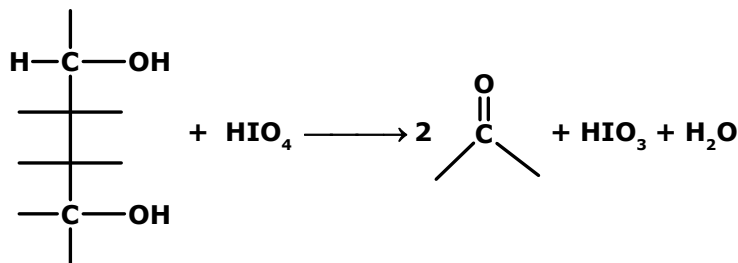
Dilute nitric acid – a stronger oxidizing agent than bromine water – oxidizes both the $-\text{CHO}$ group and the terminal $-\text{CH}_2\text{OH}$ group of an aldose to $-\text{CO}_2\text{H}$ groups. These dicarboxylic acids are known as aldaric acids:



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

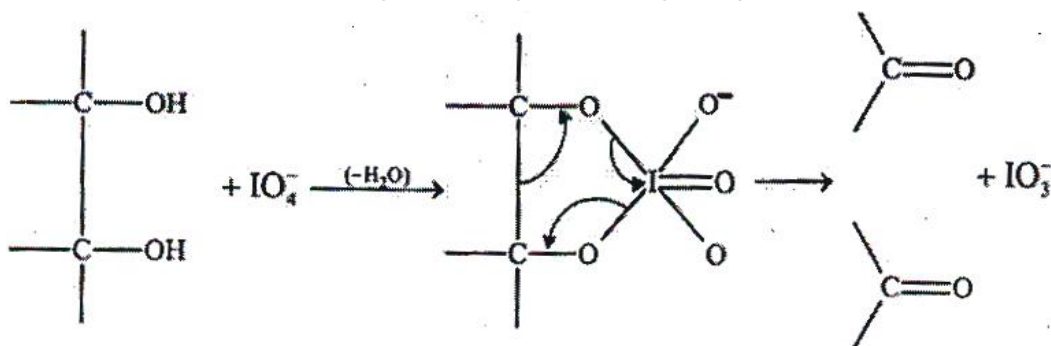
PERIODATE OXIDATION: OXIDATIVE CLEAVAGE OF POLYHYDROXY COMPOUNDS

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).



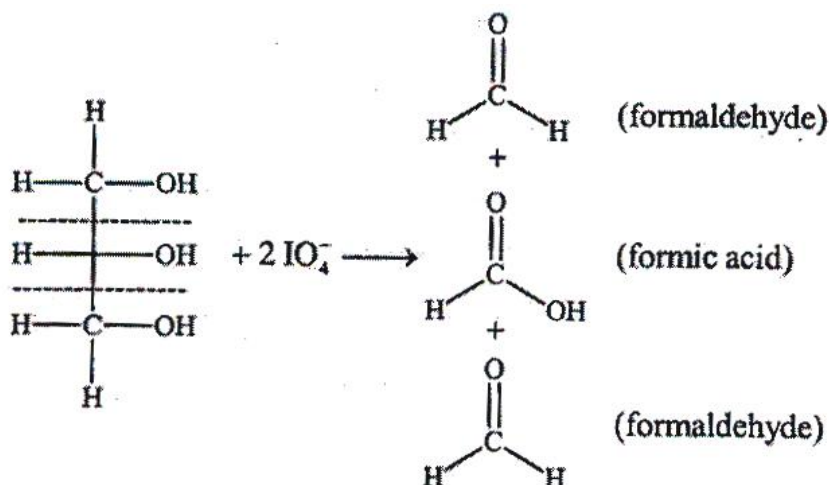
Since the reaction usually takes place in quantitative yield, valuable information can often be gained by measuring the number of molar equivalents of periodic acid that is consumed in the reaction as well as by identifying the carbonyl products.

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

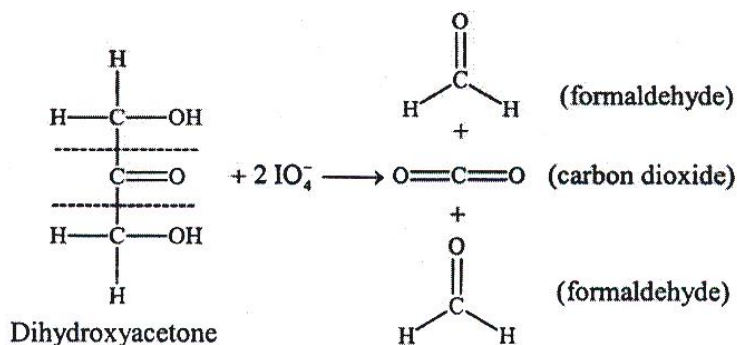
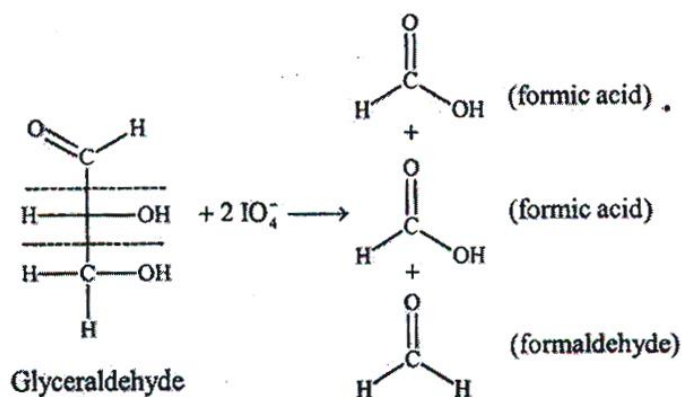


Before we discuss the use of periodic acid in carbohydrate chemistry, we should illustrate the course of the reaction with several simple examples. Notice in these periodate oxidations that for every C - C bond broken, a C - O bond is formed at each carbon.

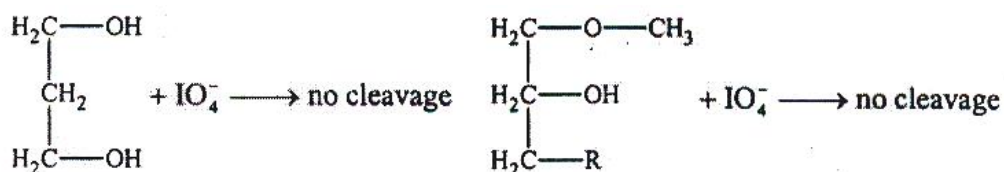
- When three or more $-\text{CHOH}$ groups are continuous, the internal ones are obtained as formic acid. Periodate oxidation of glycerol, for example, gives two molar equivalents of formaldehyde and one molar equivalent of formic acid;



- Oxidative cleavage also takes place when an $-\text{OH}$ group is adjacent to the carbonyl group of an aldehyde or ketone (but not that of an acid or an ester). Glyceradehyde 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.

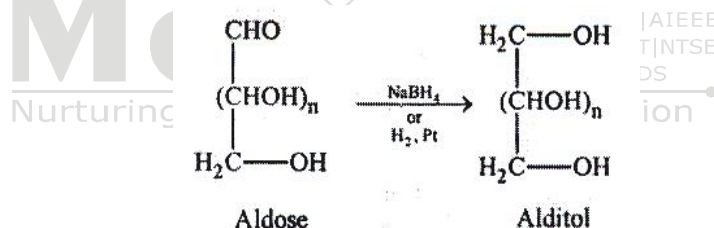


Periodic acid does not cleave compound in which the hydroxyl groups are separated by an intervening CH_2 group, nor those in which a hydroxyl group is adjacent to an ether or acetal.



REDUCTION OF MONOSACCHARIDES: ALDITOLS

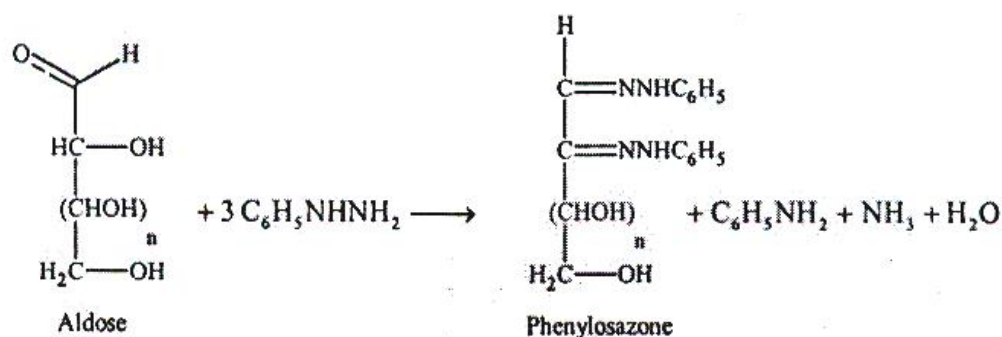
Aldoses (and ketoses) can be reduced with sodium borohydride to compounds called alditols:



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

REACTIONS OF MONOSACCHARIDES WITH PHENYLHYDRAZINE: OSAZONES

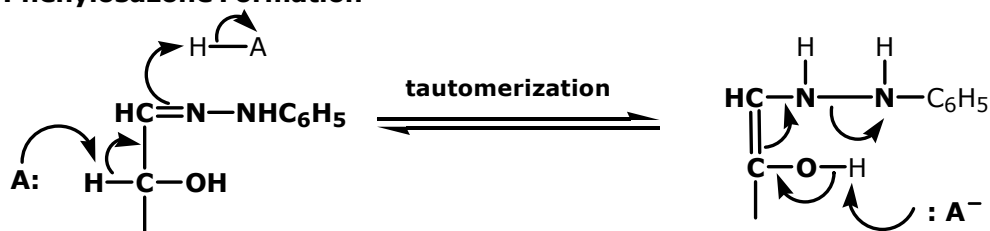
The aldehyde group of an aldose reacts with such carbonyl reagents as hydroxylamine and phenylhydrazine. With hydroxylamine, the product is the expected oxime. With enough phenylhydrazine, however, three molar equivalents of phenylhydrazine are consumed and a second phenylhydrazone group is introduced at C2. The product is called a phenylosazone. Phenylosazones crystallize readily (unlike sugars) and are useful derivatives for identifying sugars.



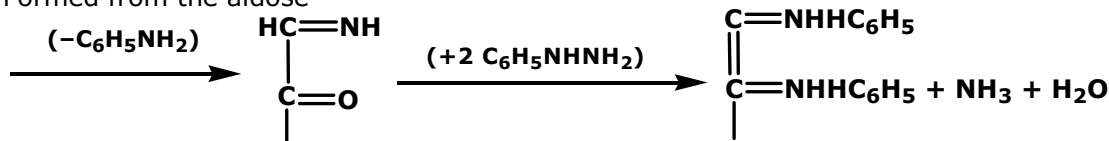
The mechanism for osazone formation probably depends on a series of reaction in which

behaves very much like $\text{C}=\text{O}$ in giving a nitrogen version of an enol.

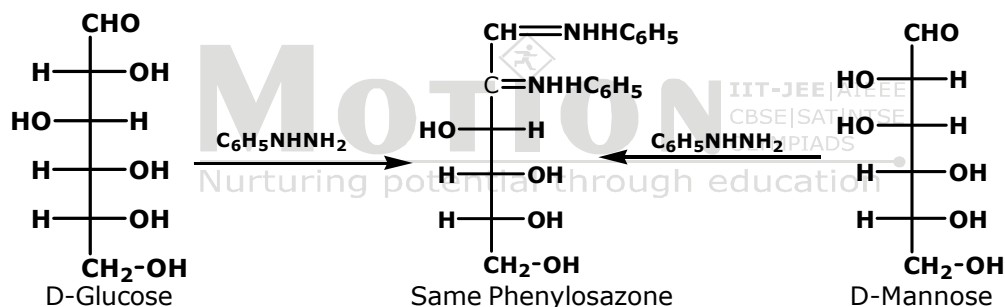
A Mechanism for the Reaction Phenylosazone Formation



Formed from the aldose



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 C3, C4 and C5. 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.

SYNTHESIS AND DEGRADATION OF MONOSACCHARIDES

Kiliani-Fischer Synthesis:

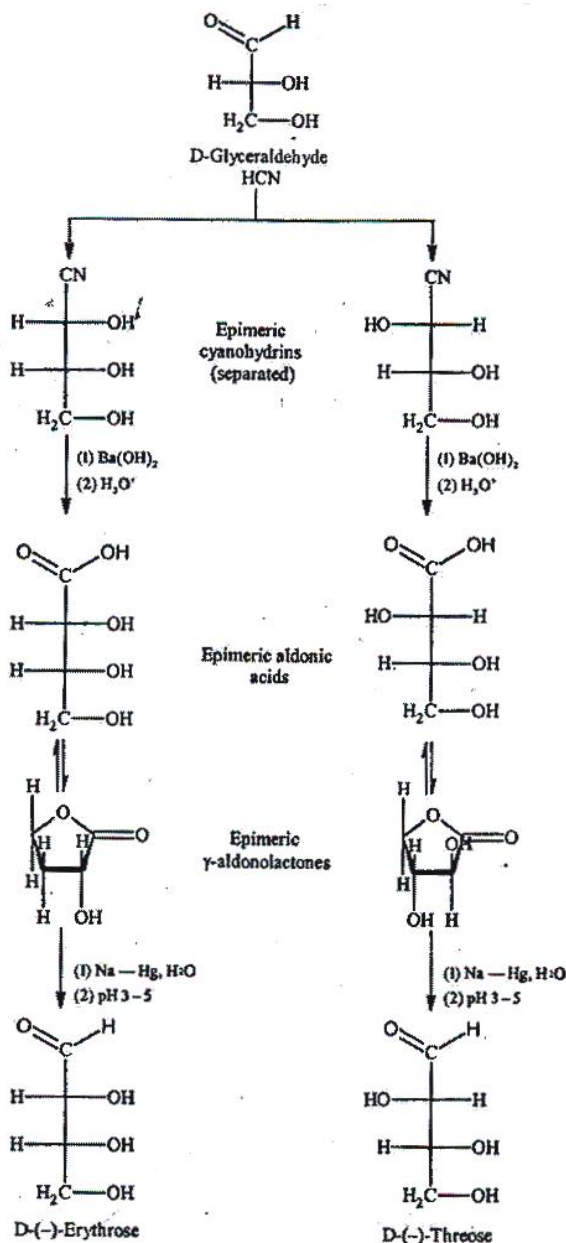
In 1885, Heinrich Kiliani (Freiburg, Germany) discovered that an aldose can be converted to the epimeric aldonic acids having one additional carbon through the addition of hydrogen cyanide and subsequent hydrolysis of the epimeric cyanohydrins. Fischer later extended this method by showing that aldonolactones obtained from the aldonic acids can be reduced to aldoses. Today, this method for

lengthening the carbon chain of an aldose is called the Kiliani - Fischer synthesis.

We can illustrate the Kiliani - Fischer synthesis with the synthesis of D-threose and D-erythrose (aldotetroses) from D-glyceraldehyde (an aldotriose).

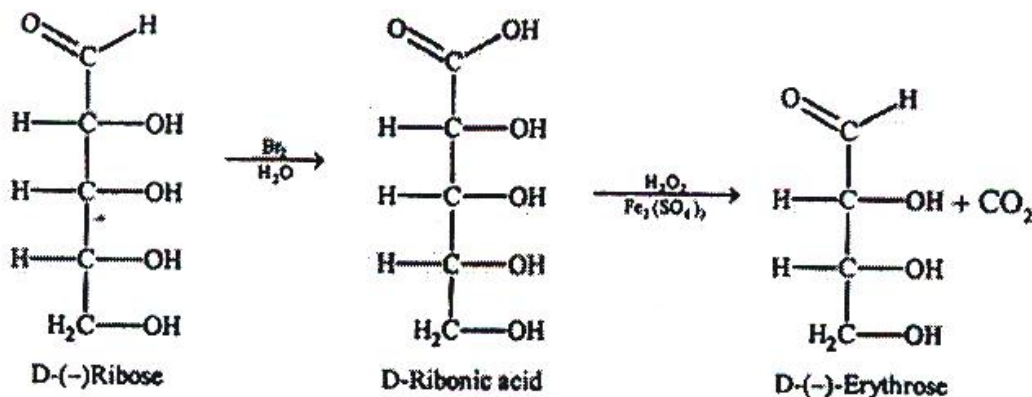
Addition of hydrogen cyanide to glyceraldehyde produces two epimeric cyanohydrins because the reaction creates a new stereogenic centre, the cyanohydrins can be separated easily (since they are diastereomers), and each can be converted to an aldose through hydrolysis, acidification, lactonization, and reduction with Na-Hg at pH 3-5. One cyanohydrine ultimately yields D(-) erythrose and the other yields D(-) threose.

We can be sure that the aldotetroses that we obtain from this Kiliani - Fischer synthesis are both D sugars because the starting compound is D-glyceraldehyde and its stereogenic carbon is unaffected by the synthesis. On the basis of the Kiliani - Fischer synthesis, we cannot know just which aldotetrose has both -OH groups on the right and which has the top -OH on the left in the Fischer projection. However, if we oxidize both aldotetroses to aldaric acids, one (D(-) erythrose) will yield an optically inactive (meso) product while the other [D(-)threose] will yield a product that is optically inactive (meso) product while the other [D(-)erythrose] will yield a product that is optically active.

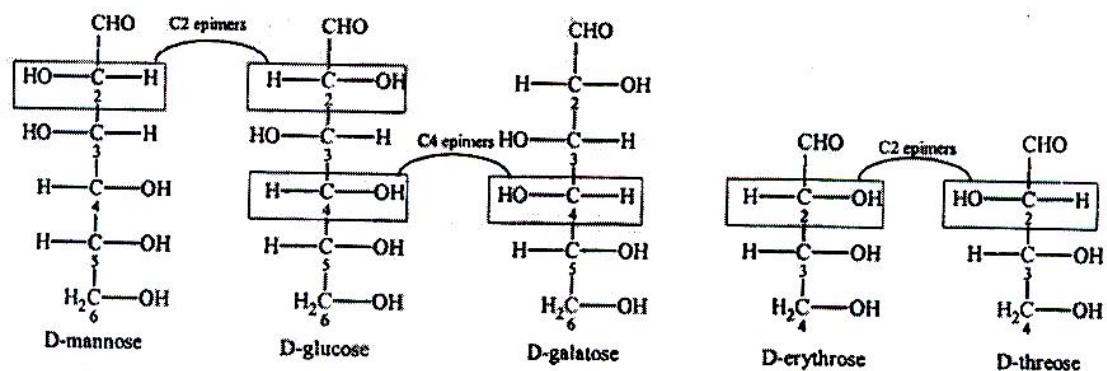


THE RUFF DEGRADATION

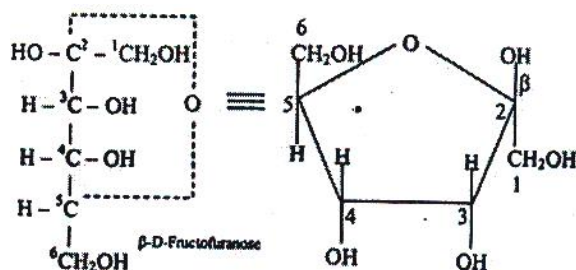
Just as the Kiliani - Fischer synthesis can be used to lengthen the chain of an aldose by one carbon atom, the Ruff degradation can be used to shorten the chain by a similar unit. The Ruff degradation involves (1) oxidation of the aldose to an aldonic acid using bromine water and (2) oxidative decarboxylation of the aldonic acid to the next lower aldose using hydrogen peroxide and ferric sulfate. D(-) Ribose, for example, can be degraded to D(-)erythrose:

**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 differ 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.

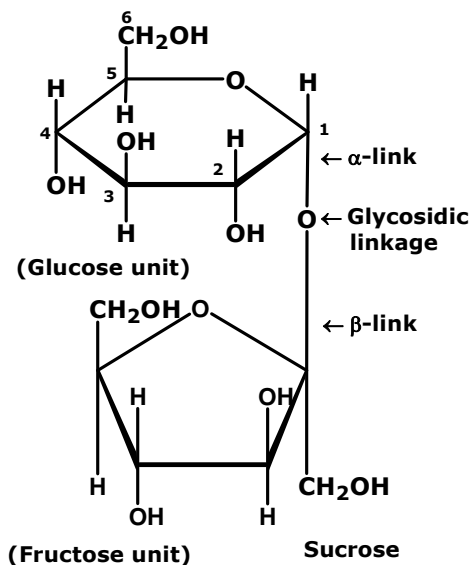
**Cyclic structure of Fructose:**

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 CH₂OH and OH group around it. Thus,

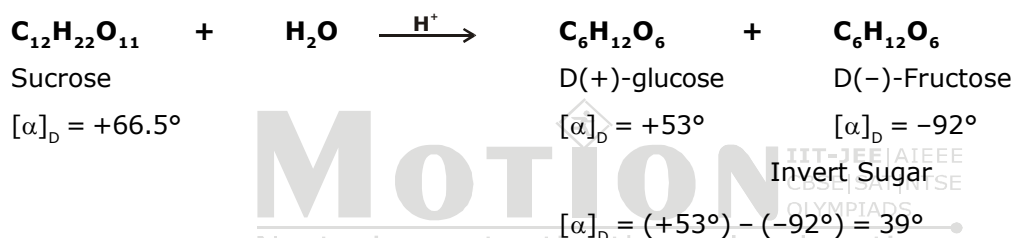


D-fructose exists in two stereoisomeric forms, i.e., α -fructopyranose and β -D fructopyranose. However in the combined state (such as sucrose), fructose exists in furanose form as shown below:

Hydrolysis of Sucrose:



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



Sucrose is dextrorotatory, its specific rotation being $+66.5^\circ$, 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 polysaccharides 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 $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ where the value of n (200 –

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-acetylcellobiose, 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 form 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 occur.

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.

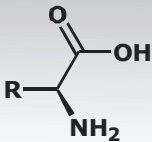
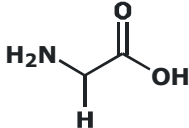
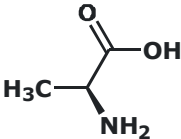
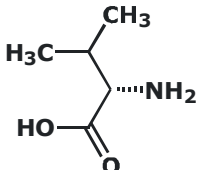
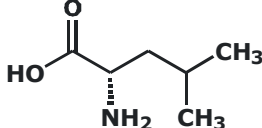
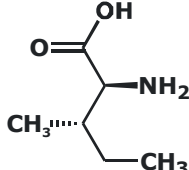
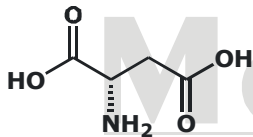
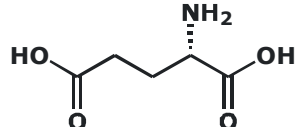
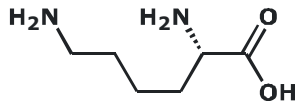
Industrially, cellulose is alkylated to **ethers** by the action of alkyl chlorides (cheaper than sulfates) in the presence of alkali. Considerable degradation of the long chain is unavoidable in these reactions. Methyl, ethyl, and benzyl ethers of cellulose are important in the production of textiles,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

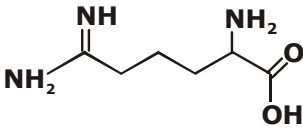
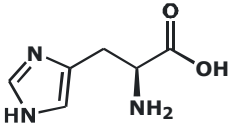
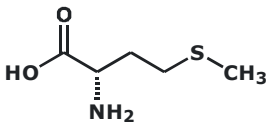
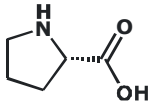
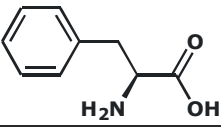
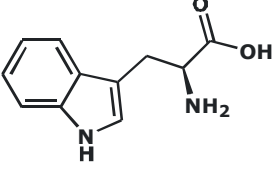
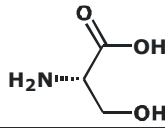
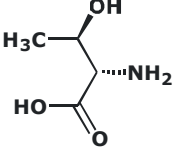
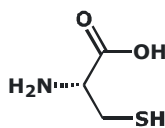
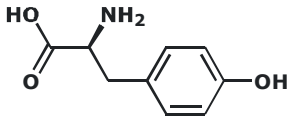
Nurturing potential through education

1. 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.

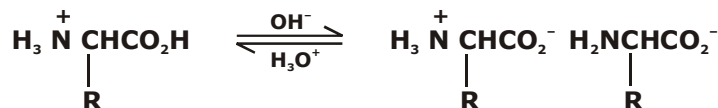
While several hundred different amino acids are known to occur naturally, 20 of them deserve special mention as they are present in proteins. These amino acids are listed in Table. As given in this table, for amino acids trivial names are common. The convention to use a three letter code, as an abbreviation, 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 you will study.

	Name	Abbreviation
	Glycine	Gly
	Alanine	Ala
	Valine	Val
	Leucine	Leu
	Isoleucine	Ile
	Aspartic Acid	Asp
	Glutamic Acid	Glu
	Lysine	Lys

	Arginin	Arg
	Histidine	His
	Methionine	Met
	Proline	Pro
	Phenylalanine	Phe
	Tryptophan	Trp
	Serine	Ser
	Threonine	Thr
threonine 	Cysteine	Cys
	Tyrosine	Tyr

AMINO ACID AS DIPOLAR IONS:

Amino Acids contain both a basic group ($-\text{NH}_2$) and an acidic group ($-\text{COOH}$). In the dry solid state, amino acids exist as dipolar ions, a form in which the carboxyl group is present as a carboxylate ion, $-\text{CO}_2^-$, and the amino group is present as an aminium ion, $-\text{NH}_3^+$ (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.

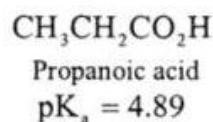
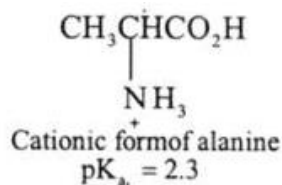


Cationic form (Predominant in strongly acidic solutions, e.g., At pH 0)

Dipolar ion

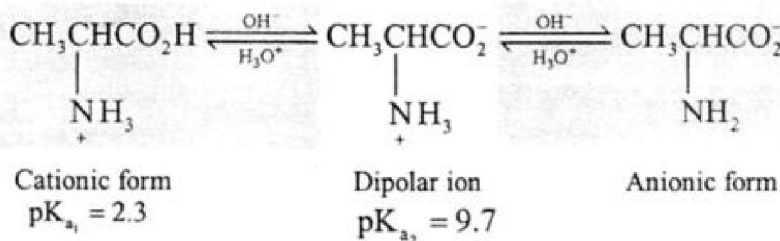
Anionic form (Predominant in strongly basic solutions, e.g., At pH 14)

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 than 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.



The state of an α -amino acid at any given pH is governed by a combination of two equilibria, as shown in the above equation for alanine. The isoelectric point (pI) of an amino acid such as alanine is the average of pK_{a_1} and pK_{a_2} ;

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

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,

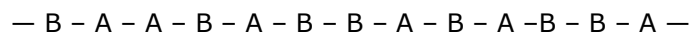
b) Co-polymers are another type of polymer. These contain more than one sub-unit (or monomer).

Example:

In the above example styrene and maleic anhydride monomers alternate. Co-polymer can be a block co-polymer.

Example:

Co-polymers can be random as well.



A and B are monomers.

6. 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.

7. 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.

8. Addition polymers and condensation polymers are two important types of polymers.

9. Polymer can be described as linear, branched and network.

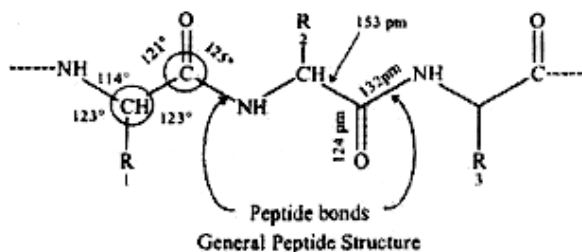
POLYMERS AND POLYMERIZATION:

Macromolecules, both natural and man-made, owe 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.

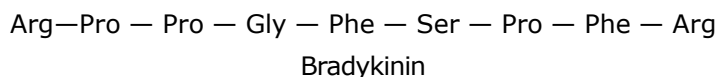
PETIDES AND PROTEINS:

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:



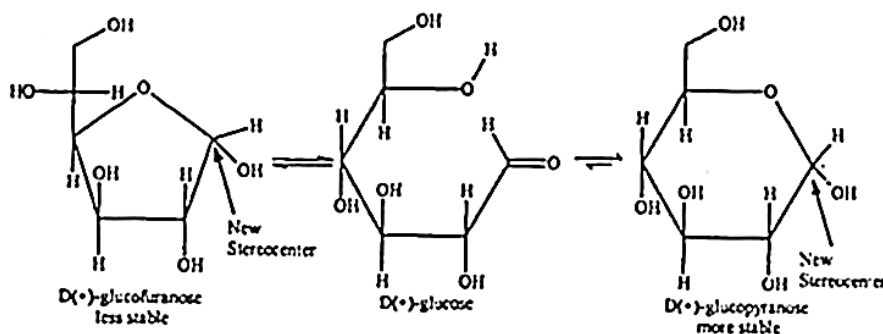
Peptides can be classified as dipeptides, tripeptides and tetrapeptides, depending on whether the number of amino acids, two, three or four, respectively. Peptides containing upto 50 amino acids are called polypeptides. Bradykinin is an important naturally occurring nonapeptide which is present in blood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



SOLVED SUBJECTIVE PROBLEMS

Problem 1: Write the hemiacetal formation for glucose.

Solution:

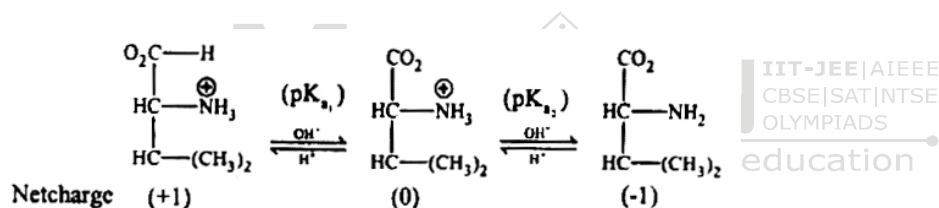


Problem 2: The pK_a of the carboxyl group in an amino acid valine, $(\text{CH}_3)_2\text{CHCH}(\text{NH}_2)(\text{COOH})$ is 2.31 and the pK_a for the amino group of the same amino acid is 9.69. compute the Isoelectric point (pI) for valine and draw the structure of this amino acid when the pH of the solution equals pI . Also draw the structures of valine that predominate at $pH = 2$ and $pOH = 2$.

Solution: The isoelectric point (pI) is the pH at which the amino acid exists only as a dipolar ion with net charge zero.

At isoelectric point, for a neutral amino acid, $pI = \frac{(pK_{a_1} + pK_{a_2})}{2}$

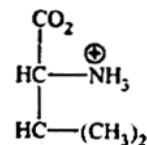
The dissociation of cationic form of valine can be represented as



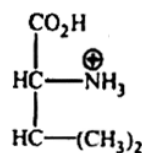
The species with zero net charge exists between species with (+1) and (-1) net charges.

$$pI = \frac{(pK_{a_1} + pK_{a_2})}{2} = \frac{9.69 + 2.31}{2} = 6$$

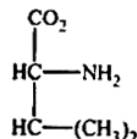
When the pI of the solution equals to pI , the structure of valine is



When the pH of the solution is two, the structure of valine is



When the pH of the solution is 12, the structure of valine is



Problem 3: Sucrose on hydrolysis yields a mixture which is

- (a) Optically inactive (b) Dextrorotatory (c) Laevorotatory (d) Racemic

Solution: (c) Sucrose on hydrolysis yields equimolar mixture of D-(–)-fructose and D-(+)glucose. Since specific rotation of (–)-fructose is greater than (+)-glucose the mixture is laevorotatory.

Problem 4: A high molecular weight molecule which does not contain repeating structural units is called a

- (a) Polymer (b) Macromolecule (c) Both (a) and (b) (d) None of these

Solution: (b) A polymer has always repeating structural units derived from monomer. For example proteins and nucleic acid are regarded as macromolecules, but not polymers because their molecules do not contain repeating structural units. All polymers are macromolecules, but all macromolecules are not polymers.

Problem 5: The force of attraction between the neighbouring peptide chains is

- (a) van der Waal's force (b) Covalent bond
(c) Hydrogen bond (d) Peptide linkage

Solution: (c) Neighbouring peptide chains are held by hydrogen bonds between –CO– and –NH–.

Problem 6: Peptides on hydrolysis give

- (a) Ammonia (b) Amines (c) Amino acids (d) Hydroxy acids

Solution: (c) Peptides are formed by condensation of α-amino acids. Therefore, on hydrolysis they yield α-amino acids.

Problem 7: An example of a condensation polymer is

- (a) PVC (b) terylene
(c) polypropylene (d) polystyrene

Solution: (b) In condensation polymerization, a series of condensation reactions between the (generally two) monomers containing atleast two functional groups each occur with the loss of a small molecule such as H₂O, CH₃OH or HX (X = halogen). Terylene is a condensation polymer of ethylene glycol and terephthalic acid.

Problem 8: Suggest a mechanism for the process. Is polymerisation of the chain reaction or step reaction type ?

Problem 9: Although both polymers are prepared by free radical processes, poly (vinyl chloride) is amorphous and poly (vinylidene chloride) (saran) is highly crystalline. How do you account for the different ? (vinylidene chloride is 1,1-dichloroethene).

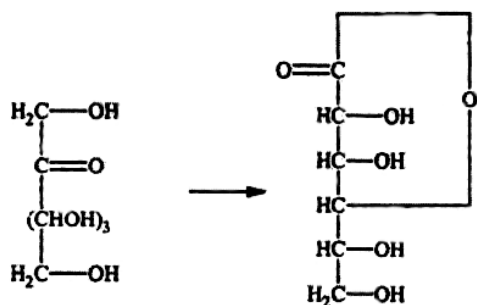
Solution: As poly (vinyl chloride) is able to show stereoisomerism and further it is formed by a free radical process, it is atactic (chlorine atoms (distributed randomly), the molecules fit together poorly.

Poly (vinylidene chloride) has two identical substituents on each carbon and the chains fit together well.

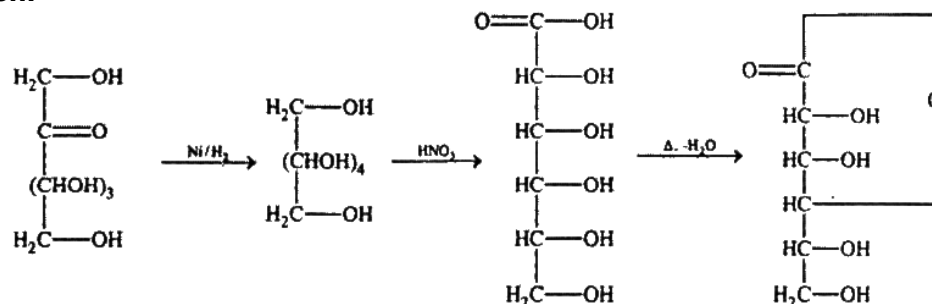
Problem 10: Compound A $C_5H_{10}O_4$ is oxidized by $Br_2 - H_2O$ to the acid, $C_5H_{10}O_5$. (A) Forms a triacetate (Ac_2O) and is reduced by HI to n-pentane. Oxidation of (A) with HIO_4 gives, among other product, 1 molecule of CH_2O and 1 molecule of HCO_2H . What are the possible structures of (A) and how could you distinguish between them?

Solution: (A) is an aldehyde, contains three hydroxyl groups and the carbon skeleton consists of five carbon atoms in a straight chain. Also, the formula $C_5H_{10}O_4$ therefore suggests that (A) is a deoxy-sugar. If we now try to work out the possibilities based directly on the periodic oxidation of (A), we shall find it.

Problem 11: Convert



Solution:



Problem 12: i) Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acid.

ii) Sulphanilic acid is not soluble in organic solvents.

Solution: i) Sulphanilic acid exist as Zwitterion

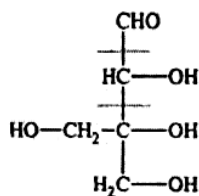


The weakly acidic $-NH_3^+$ transfers H^+ to OH^- to form a soluble salt, $P-NH_2-C_6H_4-SO_3^-Na^+$ on the other hand $-SO_3^-$ is too weakly basic to accept H^+ from strong acids.

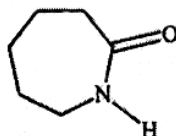
iii) Due to its ionic character it is insoluble in organic solvents.

Problem 13: Compound (A) $C_5H_{10}O_7$, give a tetra-acetate with Ac_2O and oxidation of (A) with $Br_2 - H_2O$ gives an acid, $C_5H_{10}O_6$. Reduction of (A) with HI and red phosphorous gives 3-methylbutane. What is structure of (A) ?

Solution: The formation of tetracetate indicates of 4OH group and oxidation with bromine water indicates presence of CHO group. Reduction with red phosphorous and HI indicates presence of one carbon in the side chain. Thus, the structure of (A) would be

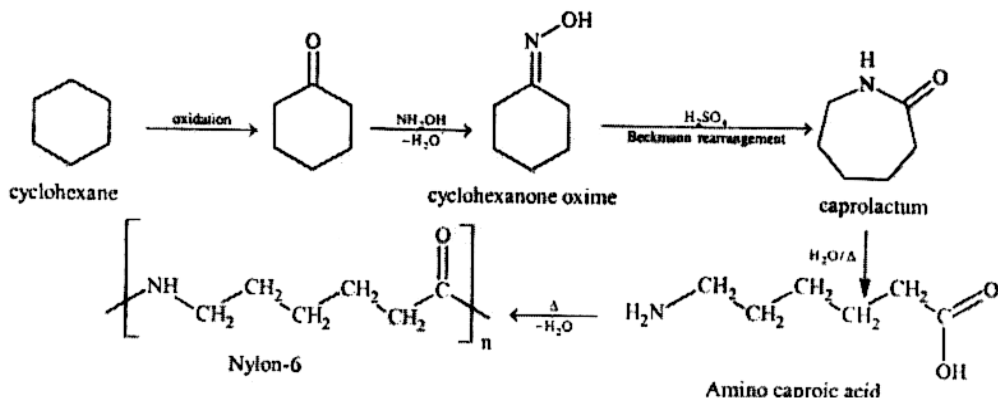


Problem 14: What is the structure of nylon-6, made by alkaline polymerisation of caprolactum ?



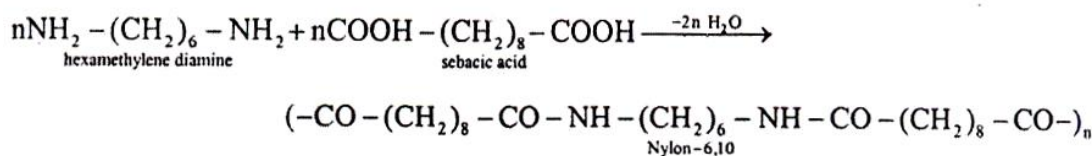
Solution: The configuration of these carbons which are unchanged in the reactions, must be identical in order to get the same osazone.

a) **Nylon-6:** Another polymer of this class is nylon-6. It is a monomer of caprolactum which is obtained from cyclohexane.



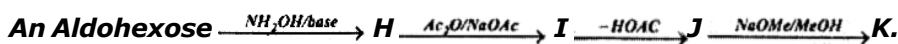
It used for making tyre cords, fabrics and ropes.

b) **Nylon-6, 10:** A polymer of hexamethylene diamine (six carbon atoms) and sebacic acid (ten carbon atoms).



These polymers are formed by the condensation of two or more monomers with the elimination of simple molecules like H_2O , NH_3 , ROH etc.

Problem 15: Supply structures for H through K. Given :



(b) Explain the last step (c). What is net structural change (d) Name this overall method. (c) Discuss the possibility of epimer formation.

Solution: a) H is an oxime $\text{HOCH}_2(\text{CHOH})_4\text{CH}=\text{NOH}$; I is the completely acetylated oxime, $\text{AcOCH}_2(\text{CHOH})_4\text{CH}=\text{NOAc}$ that loses 1 mole of HOAc to form J, $\text{AcOCH}_2(\text{CHOAc})_4\text{CH}=\text{N}$; K is an aldopentose, $\text{HOCH}_2(\text{CHOH})_3\text{CHO}$.

b) The acetates undergo transesterification to give methyl acetate freeing all the sugar OH's. This is followed by reversal of HCN addition.

c) There is loss of one C from the carbon chain.

d) Wohl Degradation

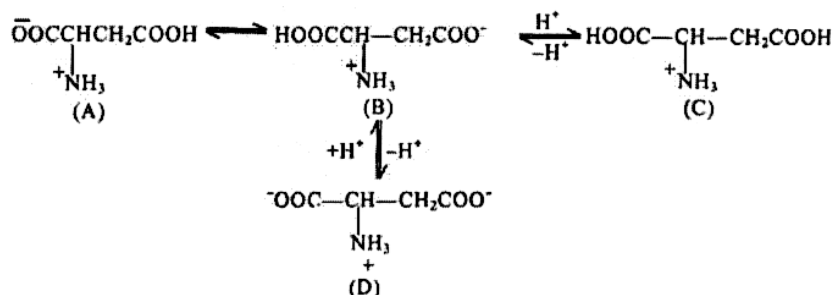
e) The $\alpha\text{-CHOH}$ becomes the $-\text{CH}=\text{O}$ without any configurational changes of the other chiral carbons. Thus no epimers are formed.

Problem 16: Glycine exists as $(\text{H}_3\text{N}^+ + \text{CH}_2\text{COO}^-)$ while anthranilic acid ($\text{P} - \text{NH}_2 - \text{C}_6\text{H}_4 - \text{COOH}$) does not exist as dipolar ion.

Solution: $-\text{COOH}$ is too weakly acidic to transfer H^+ to the weakly basic $-\text{NH}_2$ attached to the electron withdrawing benzene ring. When attached to an aliphatic carbon, the $-\text{NH}_2$ is sufficiently basic to accept H^+ from $-\text{COOH}$ group.

Problem 17: Why should isoelectric point for Aspartic acid (2.98) be so much lower than that of leucine ?

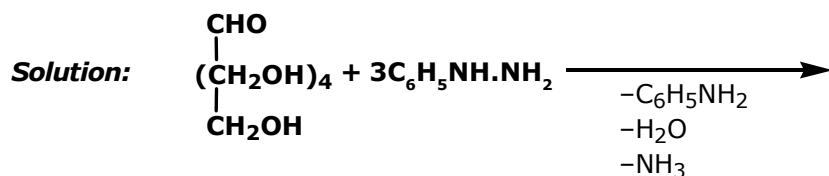
Solution: This may be explained by considering following ion equilibrium



It is apparent that ions (A) and (B) are neutral, while (C) is a cation and (D) is dianion. In species (D), the anion is derived from the second $-\text{COOH}$ group present in aspartic acid and is not possible in leucine. At neutral pH a significant concentration of (D), will be present in aqueous solution. It will therefore, be necessary to decrease the pH of such a solution if the formation of (D) is to be suppressed to a stage where anions and cations are present in equal concentration (the isoelectric point).

Problem 18: (a) Show how an aldohexose can be used to synthesize 2-ketohexose.

(b) Since glucose is converted to fructose by this method, what can you say about the configuration of C_3 , C_4 and C_5 in the sugars.



Here aldohexose reacts with one molecule of phenylhydrazine which condenses with the aldehyde

group to give phenylhydrazone. When warmed with excess of phenyl hydrazine, the secondary alcoholic group adjacent to the aldehyde group is oxidised by another molecule of phenylhydrazine, to a ketonic group. With this ketonic group, the third molecule of phenylhydrazine condenses to given osazone. The phenylhydrazinyl group is transferred from osazone to C_6H_5CHO giving $C_6H_5CH=N.NHC_6H_5$ and a dicarbonyl compound called an osone. The more reactive aldehyde group of the osone is reduced, not the less reactive keto group and it give the 2-ketohexose.

Problem 19: Starch is polymer of

- (a) Fructose (b) Glucose (c) Lactose (d) None

Solution: (b) Starch is homopolysaccharide of glucose having 24 — 30 glucose units.

Problem 20: The commonest disaccharide has the molecular formula

- (a) $C_{10}H_{18}O_9$ (b) $C_{10}H_{20}O_{10}$ (c) $C_{11}H_{22}O_{11}$ (d) $C_{12}H_{22}O_{11}$

Solution: (d) The most common disaccharide is sucrose, whose molecular formula is $C_{11}H_{22}O_{11}$.

Problem 21: The structure of glycine (amino acid) is $H_3N^+CH_2COO^-$ (Zwitter Ion.)

Select the correct statement of the following.

- (a) Glycine, as well as other amino acids are amphoteric.
 (b) The acidic functional group in amino acids is $-NH_3^+$
 (c) The basic functional group in amino acids is $-CO_2^-$
 (d) All the statements are correct

Solution: (d) Glycine and all other amino acids are amphoteric because of the presence of NH_2 and CO_2H group both. The amino acid exists as Zwitter ion and acidic group is $-NH_3^+$ while basic group is $-CO_2^-$.

Problem 22: Sugars are characterised by the preparation of osazone derivatives. Which sugar have identical osazones.

- (a) Glucose and lactose (b) Glucose and fructose
 (c) Glucose and arabinose (d) Glucose and maltose

Solution: (b) The reaction with phenyl hydrazone gives same osazone because glucose and fructose differ only on carbon atoms 1 and 2 which are involved in osazone formation.

Problem 23: Cane sugar on hydrolysis yields

- (a) Glucose and maltose (b) Glucose and lactose
 (c) Glucose and fructose (d) Only glucose

Solution : (c) $C_{12}H_{22}O_{11} \xrightarrow[H^+]{HOH} C_6H_{12}O_6 + C_6H_{12}O_6$

Glucose Fructose

The process is known as inversion of cane sugar.

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 molecule 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	Fuctose
Polyethylene	Ethylene
Polyvinyl chloride	Vinyl chloride
Teflon	Tetrafluoro ethylene
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:

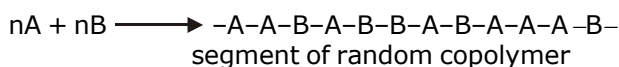
Copolymer	Monomers
Saran	Vinyl chloride and vinylidene chloride
SAN	Styrene and acrylonitrile
ABS	Acrylonitrile, butadiene and styrene
Butyl rubber	Isobutylene and Isoprene
Buna-S, SBR	Styrene and Butadiene
Buna-N, NBR	Acrylonitrile and Butadiene
Nylon-66	Hexamethylen diamine and Adipic acid
Terylene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

Types of copolymers

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

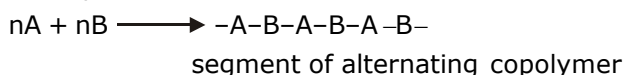
(1) Random Copolymer

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



(2) Alternating Copolymer

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

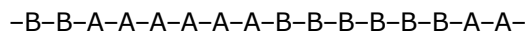


The exact distribution depends upon the proportion of the two reactant monomers and their relative reactivities. In practice neither perfectly random nor perfectly alternating copolymers are usually formed. However, most copolymers tend more towards alternating type but have many random imperfections.

(3) Block Copolymer

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

For example,

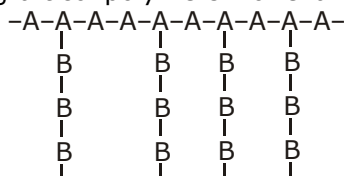


segment of block copolymer

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:



(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.

Natural polymer

- | | |
|--------------------------------------|-------------------------|
| 1. Polysaccharide | Monomers |
| 2. Proteins | Monosaccharide |
| 3. Nucleic acid | α -L-Amino acids |
| 4. Silk | Nucleotide |
| 5. Natural Rubber (cis polyisoprene) | Amino acids |
| 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

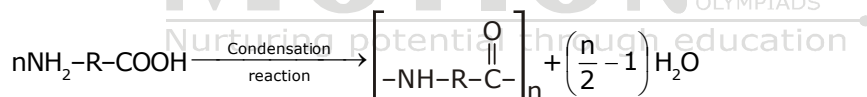
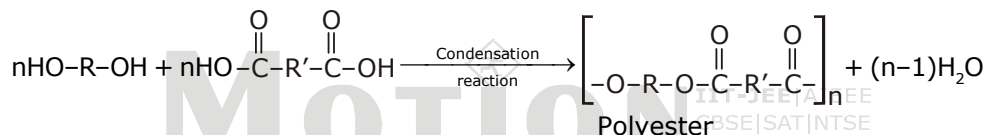
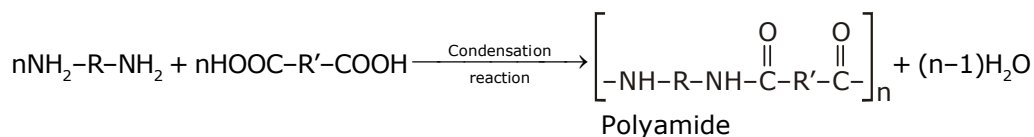
Branched chain polymers are those in which the monomeric units constitute a branched chain. Due to the presence of branches, these polymers do not pack well. As a result branched chain polymers have lower melting points, low densities and tensile strength as compared to linear polymers.

**(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,

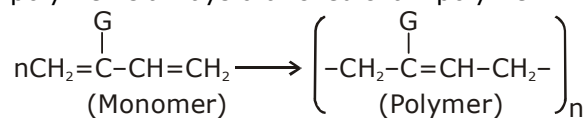


- (v) Condensation polymers do not contain all atoms initially present in the monomers. Some atoms are lost in the form of small molecules.
- (vi) Monomer having three functional groups always gives cross-linked polymer.
Examples are : Urea-formaldehyde resin, phenol-formaldehyde resin.

(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 or branch-chain polymer.
Examples are : polystyrene, polytetrafluoroethylene, polyacrylonitrile etc.

- (iii) If monomer is 1, 3-butadiene or 2-substituted-1, 3-butadiene $\left(\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ | \\ \text{G} \end{array} \right)$, then polymer is always branched chain polymer.



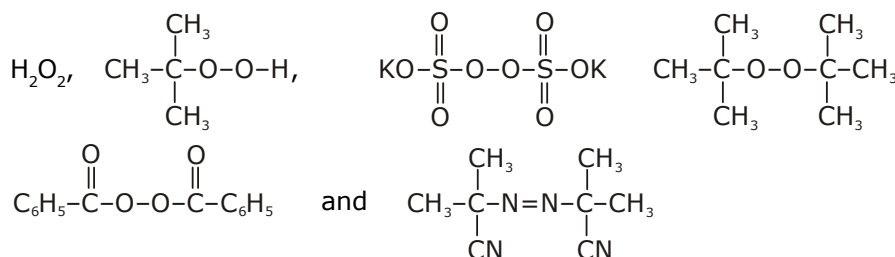
- | (Monomer) | (Polymer) |
|--|----------------------------------|
| (i) G = H: 1, 3-Butadiene | (i) Polybutadiene |
| (ii) G = CH ₃ : 2-Methyl-1, 3-butadiene or isoprene | (ii) Polyisoprene |
| (iii) G = Cl: 2-Chloro-1, 3-butadiene or chloroprene | (iii) Polychloroprene (Neoprene) |

- (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.

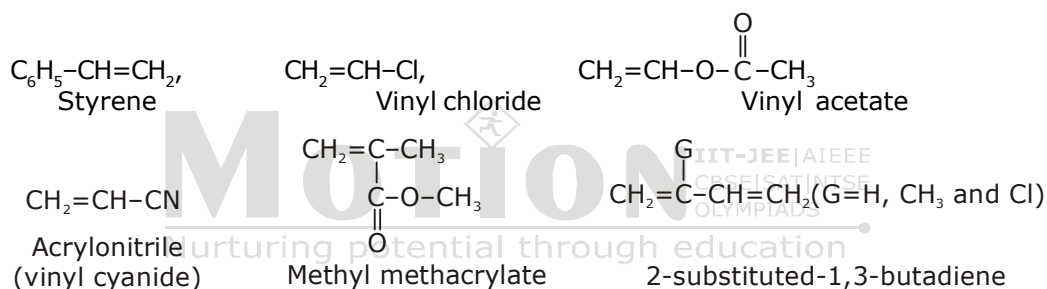
Types of Addition Polymerization

(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:

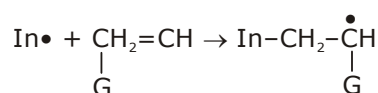


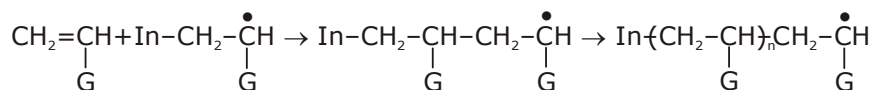
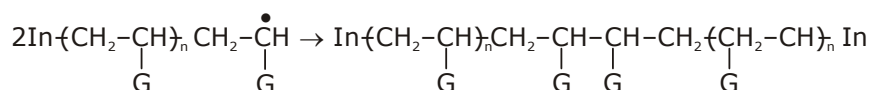
- (iv) Radical polymer has linear as well as branched chain structure
 Most of the commercial addition polymers are vinyl polymers obtained from alkenes and their derivatives $\text{CH}_2=\underset{\text{G}}{\text{CH}}$ [G is H, C₆H₅, R etc.]

This type of polymerization is performed 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 $\rightarrow \text{In} \bullet$

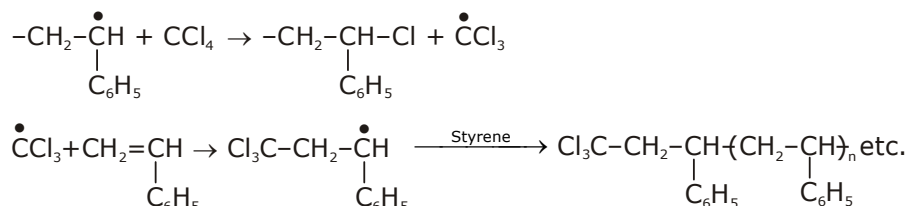


Chain propagating step :**Chain terminating step :**

Polymer

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.

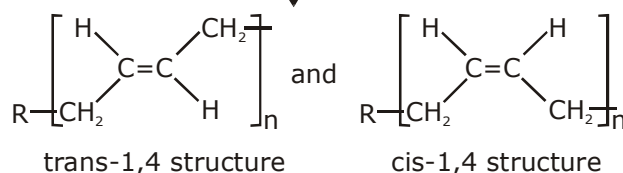


If the chain transfer agent a radical, which is highly unreactive, the reaction chain gets terminated such a compound thus inhibits or arrests polymerisation. Many amines, phenols, quinones etc. act as inhibitors. So, even traces of certain impurities, which can act as chain transfer agent or an inhibitor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

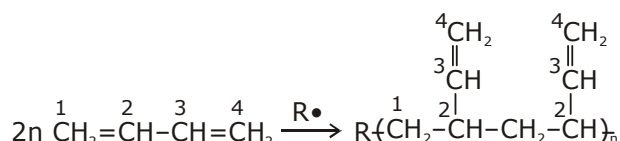
In case the alkene is a diene, the following kinds of polymerisation is possible:

(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.

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

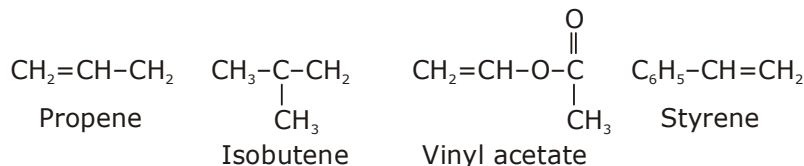
Alternatively, 1, 3-butadiene can undergo polymerisation at C_1 and C_2 to yield the polymeric product, polyvinyl polythene.



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 :

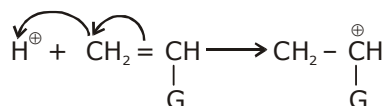
- (i) Polymerisation which is initiated by an electrophile is known as cationic polymerisation.
- (ii) Reaction intermediate of cationic polymerisation is a carbocation.
- (iii) Carbocations can undergo rearrangement leading to the formation of a more stable carbocation.
- (iv) The electrophile commonly used for initiation is $\text{BF}_3 \cdot \text{OEt}_2$.
- (v) Monomers that are best able to undergo polymerisation by a cationic mechanism are those with electron - donating substituents that can stabilise the carbocation. Some examples are:



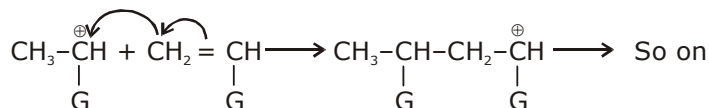
- (v) It is terminated by a base.

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.

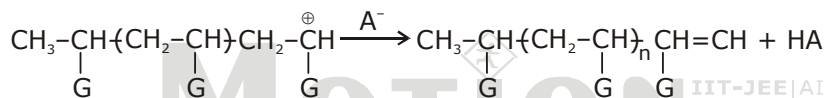
Chain initiation step :



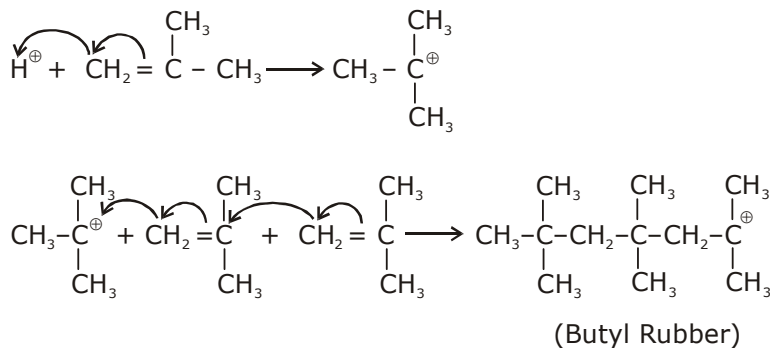
Chain propagating step :



Chain terminating step :

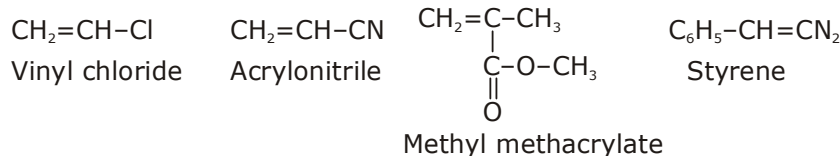


Cationic polymerisation is facilitated in monomers containing electron - releasing groups. Thus, isobutylene undergoes cationic polymerisation easily as it has two electron releasing $-\text{CH}_3$ groups that will stabilize the intermediate carbo cation.

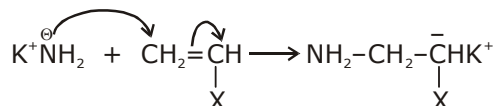
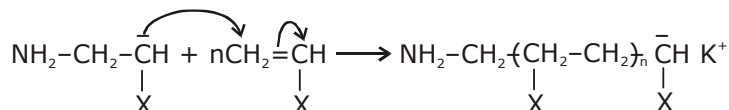
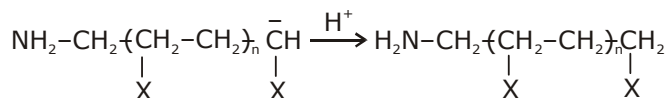


(C) Anionic Polymerisation:

- (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_2 or RLi .
- (iv) Those monomers undergo anionic polymerisation reaction whose anion is stable.
Example of monomers are:



- (v) Anionic polymerisation always give linear polymer.
- (iv) 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 :**Chain propagating step :****Chain terminating step :****(D) Ziegler- Natta polymerisation :**

- (i) Addition polymerisation which takes place in the presence of Ziegler- Natta catalyst $[(\text{C}_2\text{H}_5)_3\text{Al}$ and $\text{TiCl}_4]$ 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) Elastomes**

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 viscous. This soft and viscous 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 : polyethene 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	Thermosetting polymers
1.	Soften and melt on heating and become hard on cooling i.e. process is reversible	Become hard on heating and process is irreversible.
2.	Can be moulded and remoulded and reshaped.	They can be moulded once and cannot be remoulded or reshaped.
3.	They are addition polymers	They are condensation polymers.
4.	Structure is generally linear	Structure is cross - linked.

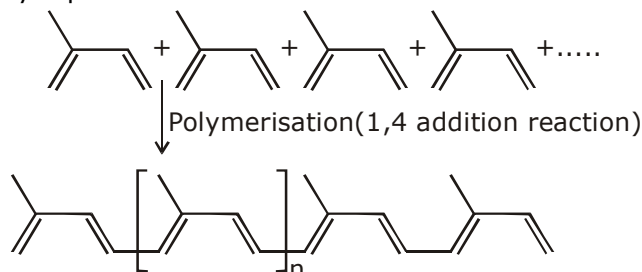
RUBBER

1. Natural Rubber

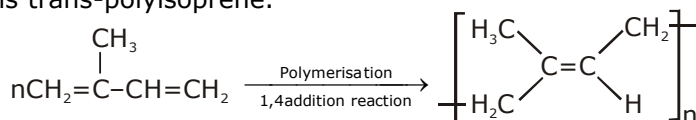
Natural rubber is obtained from nearly five hundred different plants but the main source is a brazilian tree. It is obtained in the form of milky sap known as latex. This latex is coagulated with acetic acid and formic acid. The coagulated mass is then squeezed.

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 rubber is a polymer of 2-methyl-1, 3-butadiene (isoprene). On average, a molecule of rubber contains 5000

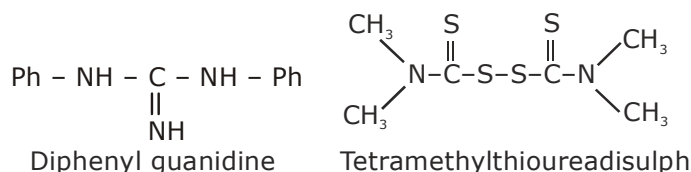
isoprene units held together by head to tail. All the double bonds in rubber are cis, hence natural rubber is cis-polyisoprene.



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.

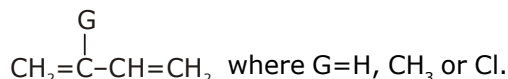
Natural rubber is used for making shoes, water - proof coats and golf balls. Vulcanised rubber is used for manufacture of rubber bands, gloves tubing and car tyres.

SYNTHETIC RUBBER OR POLYMERISATION OF DIENES

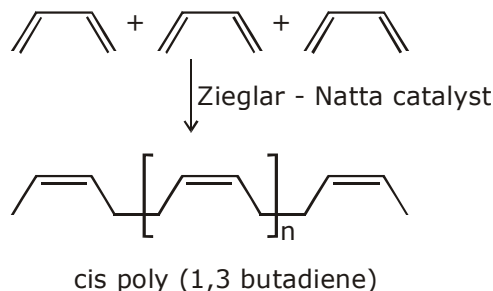
Polymers of 1, 3 - butadienes are called synthetic rubbers because they have some of the properties of natural rubbers including the fact that they are water proof and elastic. Synthetic rubbers have some improved properties. They are more flexible, tougher and more durable than natural rubber.

1. Homopolymers

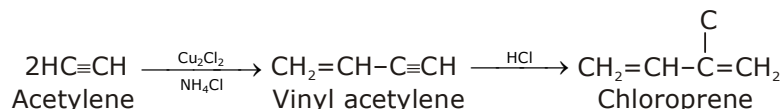
Monomer of this class is 2-substituted-1, 3-butadienes.



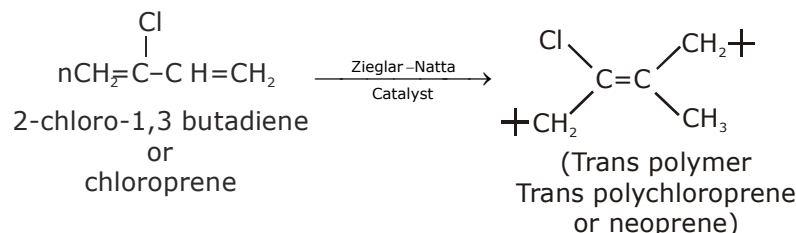
polymerisation is always carried out in the presence of Ziegler-natta catalyst which gives stereo regular polymers.



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



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.

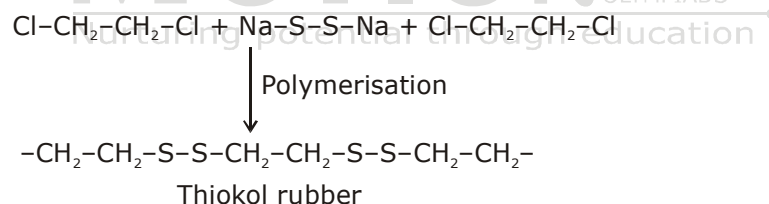
It is used for making automobile and refrigerator parts, hoses for petrol and oil containers, insulation of electric wires and conveyor belts.

2. Copolymers

The following synthetic rubbers are example of copolymers.

	Synthetic rubber	Monomers
1.	Buna-S, SBR (styrene-Butadiene rubber)	$\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ (25%) (75%)
2.	Buna-N, NBR (Nitrile-Butadiene rubber)	$\text{CH}_2=\text{CH}-\text{CN} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ (25%) (75%)
3.	Butyl rubber	$\text{CH}_3-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2 + \text{Butadiene}$ 98% 2%
4.	ABS; Acrylonitrile, Butadiene, Styrene	$\text{CH}_2=\text{CH}-\text{CN} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + \text{C}_6\text{H}_5\text{CH}=\text{CH}_2$

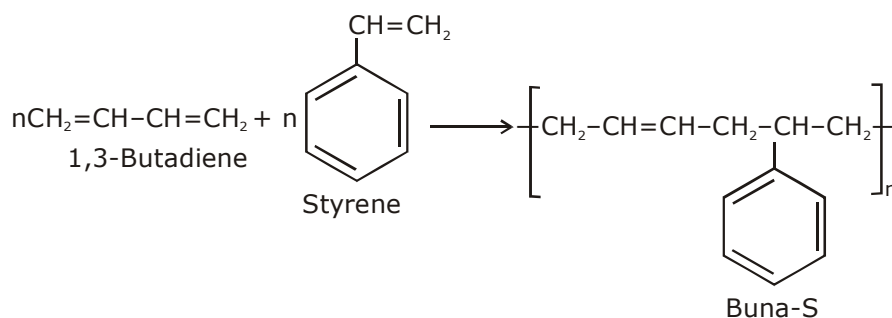
(a) **Thiokol** : Thiokol is made by polymerising ethylene chloride and sodium polysulphide.



The repeating unit is $-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-$

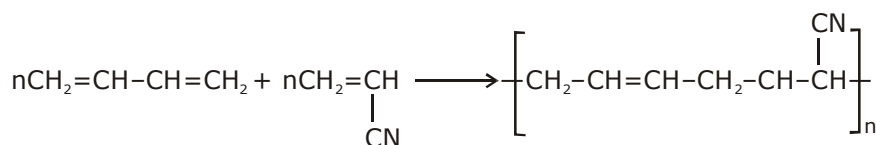
Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

(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).



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.

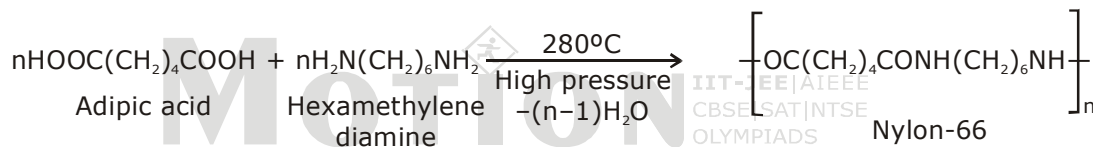
- (d) **Cold Rubber** : Cold rubber is obtained by polymerization of butadiene and styrene at -18° to 5°C temperature in the presence of redox system. Cold rubber has a greater tensile strength and greater resistance to abrasion than SBR.

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) **NYLON-6, 10** (Nylon six, ten)

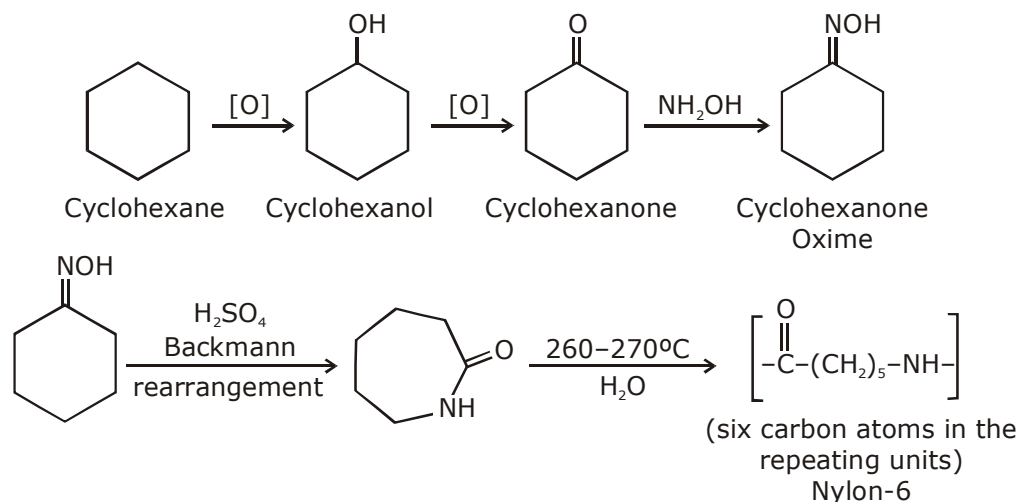
It is obtained by condensation polymerisation of hexamethylenediamine (six carbon atoms) and sebacic acid (a dibasic acid with 10 carbon atoms).

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 H_2O 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.



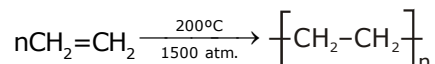
(4) NYON-2 – NYLON-6

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 $200^\circ C$ under a pressure of 1500 atmospheres and in the presence of traces of oxygen. This polymerisation is a free radical polymerisation.



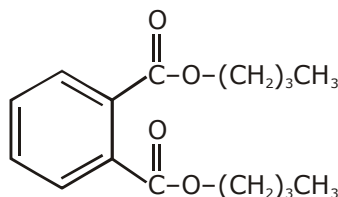
The polyethylene produced has a molecular mass of about 20,000 and has a branched structure. Due to this, polyethylene has a low density (0.92) and low melting point ($110^\circ C$). That is why polyethylene prepared by free radical polymerisation is called low density polyethylene. It is a transparent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

- (b) **High Density Poly Ethylene (HDPE)** : It is prepared by the use of Ziegler - Natta catalyst at $160^\circ C$ under pressure of 6 to 7 atmosphere.

The polymer is linear chain, hence it has high density (0.97) and has high melting point ($130^\circ C$). 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.

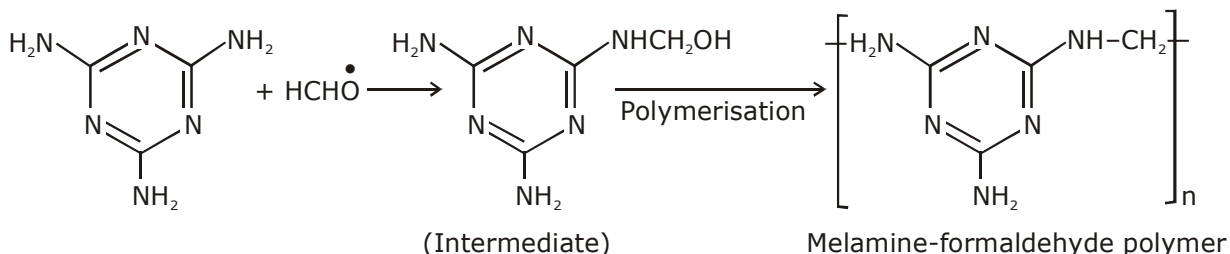
PLASTICISER

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 used plasticiser.



MELAMINE - FORMALDEHYDE RESIN

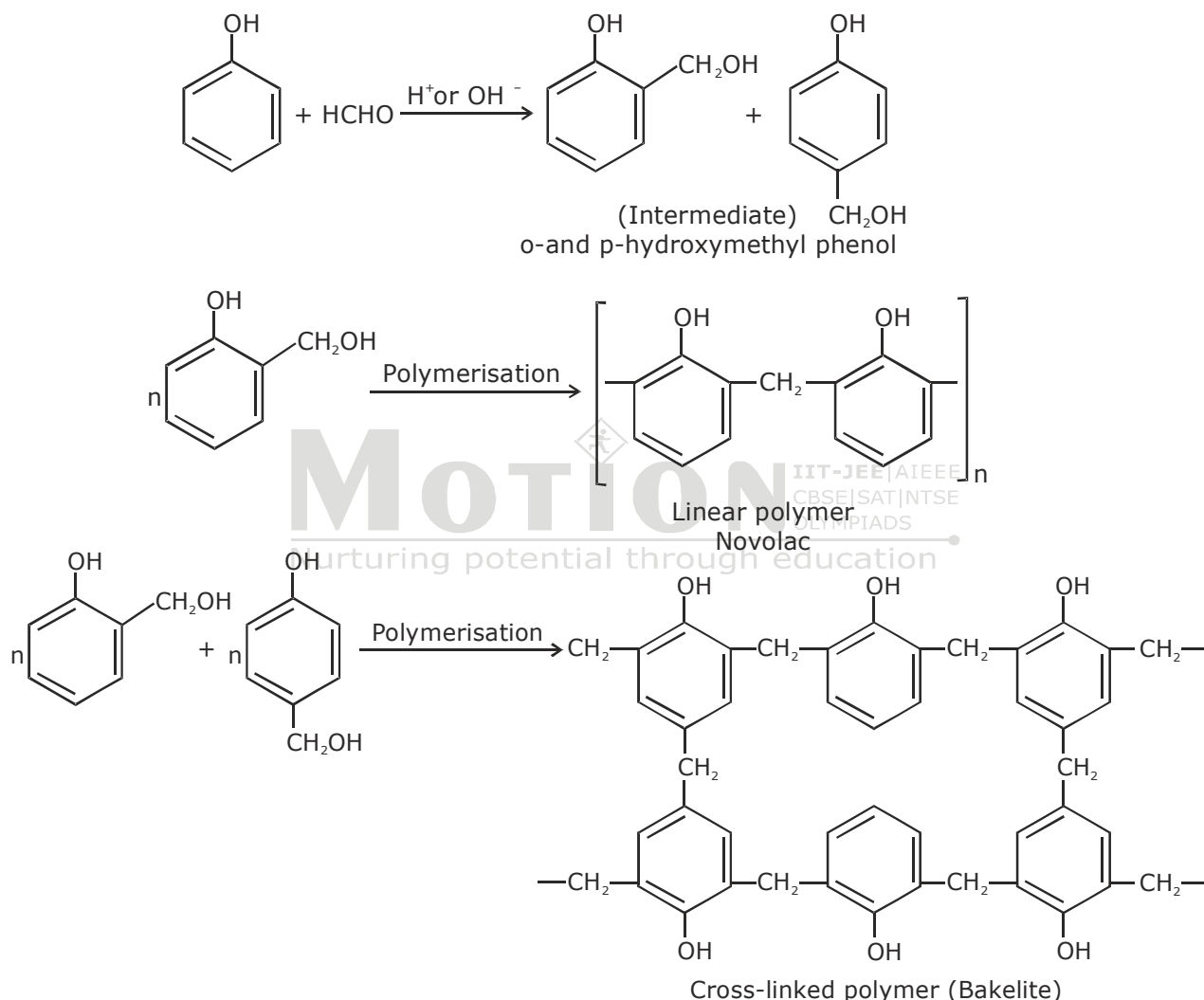
This resin is formed by condensation polymerisation of melamine and formaldehyde.



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.

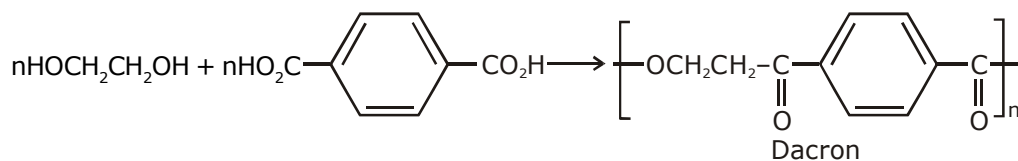
BAKELITE

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 $-\text{CH}_2-$ groups. The reaction involves the formation of methylene bridges in ortho, para or both ortho and para positions. Linear or cross-linked 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 Sb_2O_3 as catalyst.



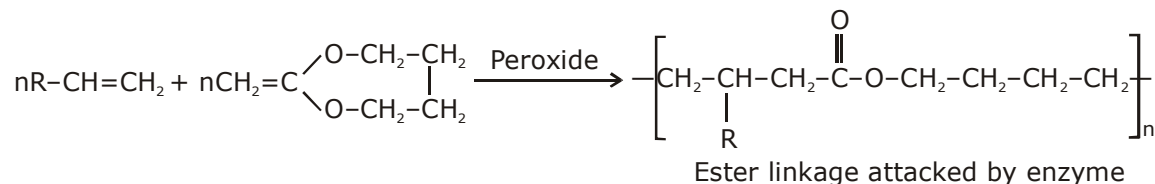
The terylene fibre (Dacron) is crease resistant and has low moisture absorption. It has high tensile strength. It is mainly used in making wash and wear garments, in blending with wool to provide better crease and wrinkle resistance.

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 to 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.

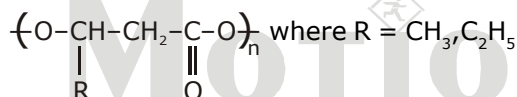
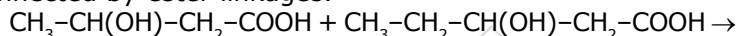
One method involves inserting hydrolysable ester group into the polymer. For example, when acetal (I) is added during the polymerization of alkene, ester group is inserted into the polymeric chains.



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.



The properties of PHBV vary 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 release. 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 contain chain of identical length and hence, have definite molecular mass.

The molecular mass of a polymer is expressed as

- (a) Number average molecular mass (
- \bar{M}_n
-)

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

Where N_i is the number of molecules of molecular mass M_i

- (b) Weight average molecular mass (
- \bar{M}_w
-)

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

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.

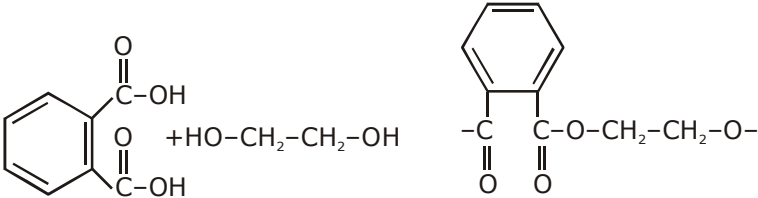
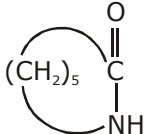
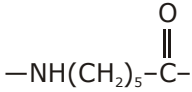
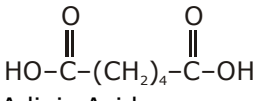
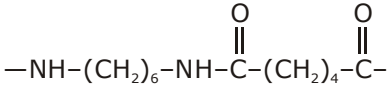

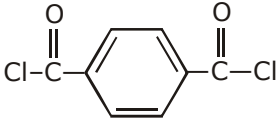
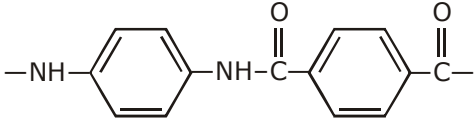
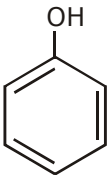
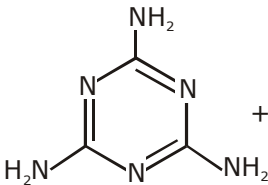
\bar{M}_n is determined by employing methods which depend upon the number of molecules present in the polymer sample viz. Colligative properties like osmotic pressure.

The ratio of the weight and number average molecular masses (\bar{M}_w/\bar{M}_n) is called Poly Dispersity Index (PDI). Some natural polymers, which are generally monodispersed, the PDI is unity (i.e. $\bar{M}_w = \bar{M}_n$). In synthetic polymers, which are always polydispersed, PDI > 1 because is always higher than \bar{M}_n .

COMMON POLYMERS

Monomer	Repeating unit	Polymer
1. $\text{CH}_2=\text{CH}_2$ Ethylene	$-\text{CH}_2-\text{CH}_2-$	Polyethylene
2. $\text{CH}_3-\text{CH}=\text{CH}_2$ Propene	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{CH}_2- \end{array}$	Polypropene
3. $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$ Styrene	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{C}_6\text{H}_5 \end{array}$	Polystyrene
4. $\text{CF}_2=\text{CF}_2$ Tetrafluoroethylene	$-\text{CF}_2-\text{CF}_2-$	Polytetrafluoroethylene (PTFE), Teflon
5. $\text{CH}_2=\text{CH}-\text{Cl}$ Vinyl chloride	$\begin{array}{c} \text{Cl} \\ \\ -\text{CH}_2-\text{CH}- \end{array}$	Polyvinyl Chloride (PVC)
6. $\text{CH}_2=\text{CH}-\text{CN}$ Vinyl cyanide or Acrylonitrile	$\begin{array}{c} \text{CN} \\ \\ -\text{CH}_2-\text{CH}- \end{array}$	Polyvinyl cyanide, poly acrylonitrile, Orlon.
7. $\begin{array}{c} \text{H}_3\text{C} \quad \text{O} \\ \quad \\ \text{CH}_2=\text{C}-\text{C}-\text{O}-\text{CH}_3 \end{array}$ Methyl methacrylate	$\begin{array}{c} \text{COOCH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{CH}_3 \end{array}$	Polymethyl methacrylate,

			Plexiglas, Lucite
8.	$\text{CH}_2=\text{CH}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$ Vinyl acetate	$\begin{array}{c} \text{OCOCH}_3 \\ \\ -\text{CH}_2-\text{CH}- \end{array}$	Polyvinyl Acetate
9.	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ 1, 3-butadiene	$-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-$	Polybutadiene, Buna rubber
10.	$\text{CH}_2=\text{CH}-\text{Cl} \text{ (vinyl chloride)}$ $+$ $\text{CH}_2=\text{CCl}_2 \text{ (Vinylidene chloride)}$	$\begin{array}{c} \text{Cl} \\ \\ -\text{CH}_2-\text{CH}-\text{CCl}_2-\text{CH}_2- \end{array}$	Saran
11.	$\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 \text{ (Styrene)}$ $+$ $\text{CH}_2=\text{CH}-\text{CN} \text{ (acrylonitrile)}$	$\begin{array}{c} \text{C}_6\text{H}_5 \quad \text{CN} \\ \quad \\ -\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2- \end{array}$	SAN
12.	$\text{CH}_2=\text{CH}-\text{CN} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ $+$ $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$	-	ABS
13.	$\text{CH}_2=\underset{\text{CH}_3}{\underset{ }{\text{C}}}-\text{CH}_2 + \text{CH}_2=\overset{\text{CH}_3}{\overset{ }{\text{C}}}-\text{CH}=\text{CH}_2$	-	Butyl rubber
14.	$\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	-	Buna-S, SBR
15.	$\text{CH}_2=\text{CH}-\text{CN} + \text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$	-	Buna-N, NBR
16.	$\begin{array}{c} \text{Cl} \\ \\ \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \end{array}$ Chloroprene	$\begin{array}{c} \text{Cl} \\ \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \end{array}$	Neoprene
17.			Poly(ethylene terephthalate, Terylene, Dacron or Mylar)
18.			Kodel Polyester

19.  Polyethylene
phthalate alkyd resin (Glyptal)
20.  Caprolactam
 Nylon-6
21. $\text{NH}_2(\text{CH}_2)_6\text{NH}_2$ Hexamethylenediamine
+
 Adipic Acid
 Nylon-66
22.  1, 4-Diaminobenzene
+
 Terephthaloyl chloride
 Kelvar
23.  + HCHO
Bakelite or resol
24. $\text{NH}_2\text{-C(=O)-NH}_2$ + HCHO
Urea-formaldehyde resin
25.  + HCHO
Melamine-formaldehyde resin

PRACICAL ORGANIC CHEMISTRY**(A) FUNCTIONAL GROUP ANALYSIS****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 $\text{Br}_2 \rightarrow$ Colourless

2. Terminal alkynes :

Confirmed by ppt of Acetylide ion with NaNH_2 or AgNO_2 or $\text{Cu}_2\text{Cl}_2\text{NH}_4\text{OH}$

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 compound is taken on copper wire.

4. Alcohol :

- (a) Ceric ammonium nitrate \rightarrow Give red colour
- (b) Boil with acetic acid & conc. $\text{H}_2\text{SO}_4 \rightarrow$ fruity smell
- (c) 2-alkanol & ethanol also give Iodoform test \rightarrow Yellow ppt. of CH_3I on reaction with $\text{I}_2 + \text{OH}^-$

5. Aldehyde & ketones :

2,4-Dinitrophenyl hydrazide (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 HgCl_2 .

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. NaHCO_3 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.

9. Phenols :

- (a) Violet colouration with neutral FeCl_3
- (b) Liebermann test
- (c) White ppt. with Br_2 water
- (d) Brisk effervescence with aq. NaHCO_3 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 $\text{NaOH} \rightarrow \text{NH}_3$** **13. Nitrobenzene \rightarrow Mulliken Baker test \rightarrow Treat it with ZnNH_4Cl then boil with Tollen's reagent \rightarrow Silver mirror will appear****14. Proteins :**

- (a) Biuret test : Also used for urea \rightarrow Alkaline solution of protein treated with a drop of aq CuSO_4 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.

DIFFERENTIATION TEST**D1. 1° , 2° & 3° alcohols :**

- (a) Luca's test : Lucas reagent is conc. $\text{HCl} + \text{ZnCl}_2$
- (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) 2° Amine yield an insoluble compound which is unaffected by acid
 - (iii) 3° Amine yield insoluble compound
- (b) Reaction with HNO_2 .

(A) ELEMENTAL ANALYSIS**Lassaigne Method (Detection of Elements)**

Element	Sodium Extract (S.E.)	Confirmed Test	Reactions
Nitrogen	Na + C + N $\xrightarrow{\text{NaCN(S.E.)}}$ boil and cool,	S.E. + FeSO_4 + NaOH, + FeCl_3 + conc. HCl Blue or green colour (i) S.E. + sodium nitro prusside (A) A deep violet colour	$\text{FeSO}_4 + 2\text{NaOH} \rightarrow \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4$ $\text{Fe(OH)}_2 + 6\text{NaOH} \rightarrow \text{Na}_4[\text{Fe(CN)}_6] + 2\text{NaOH}$ $\text{Na}_4[\text{Fe(CN)}_6] + \text{FeCl}_3 \xrightarrow{\text{HCl}} \text{Fe}_4[\text{Fe(CN)}_6]_3 + 3\text{NaCl}$ Prussian blue (i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe(CN)}_5\text{NO}] \rightarrow \text{Na}_4[\text{Fe(CN)}_5\text{NOS}]$ (A) deep violet (ii) $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}} \text{PbS} \downarrow + 2\text{CH}_3\text{COONa}$ black ppt.
Sulphur	$2\text{Na} + \text{S} \xrightarrow{\text{Na}_2\text{S(S.E.)}}$ (ii) S.E. + CH_3COOH + $(\text{CH}_3\text{COO})_2\text{Pb}$ A black ppt. S.E. + HNO_3 + AgNO_3 (i) White ppt. soluble in aq. NH_3 confirms Cl (ii) Yellow ppt. partially soluble in aq. NH_3 confirm Br (iii) Yellow ppt. in soluble in aq. NH_3 confirms I As in test for nitrogen; instead of green or blue colour, blood red		$\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow$ ppt.
Halogen	$\text{Na} + \text{Cl} \xrightarrow{\text{NaCl(S.E.)}}$		$\text{AgCl} + 2\text{NH}_3(\text{aq}) \rightarrow [\text{Ag(NH}_3)_2]\text{Cl}$ white ppt. soluble $\text{NaCNS} + \text{FeCl}_3 \rightarrow [\text{Fe(CNS)}]\text{Cl}_2 + \text{NaCl}$ blood red colour
Nitrogen and Sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\text{NaCNS(S.E.)}}$ colouration confirms presence of N and S both		