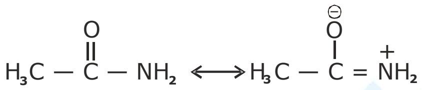
ALIPHATIC AMINE

Basic nature of amines

1. Aniline is less basic than ammonia. The phenyl group –R i.e. resonance effect that pla major role for less basicity that emmonia exerts- I (inductive effect, i.e., it withdraw electrons. This results to the lower availability of electrons on nitrogen for protonation.
2. Ethylamine and acetamide both contain an amino group but acetamide does not show basic nature. This is because lone pair of electrons on nitrogen is delocalized by resonance with the carbonyl group which makes it less available for protonation.



$$H_3C-\overset{\overset{O}{\|}}{C}-NH_2 \longleftrightarrow H_3C-\overset{\overset{\ominus}{O}}{\overset{|}{C}}=\overset{+}{N}H_2$$

3. The compound with least 's' character (sp^3 hybridized) is most basic and with more 's' character (sp-hybridized) is least basic. Examples in decreasing order of basicity are :

(i) $\underset{(sp^3)}{CH_3\ddot{N}H_2} > \underset{(sp^2)}{CH_3-\ddot{N}=CHCH_3} > \underset{(sp)}{CH_3-C\equiv\ddot{N}}$

(ii) $CH_3CH_2CH_2NH_2 > H_2C=CHCH_2NH_2 > HC\equiv CCH_2NH_2$

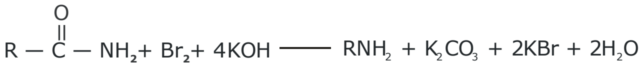
(iii) $(CH_3)_2NH > CH_3NH_2 > NH_3 > C_6H_5NH_2$

Electron withdrawing (C_6H_5—) groups cause decrease in electron density on nitrogen atom and there by decreasing basicity.

(iv) $CH_3CH_2NH_2 > C_6H_5CONH_2 > CH_3CONH_2$

Methods of preparation

1. **Hoffmann's bromamide reaction :** Amines (only primary) can also be prepared by Hoffmann degradation. In this method the amine will have one carbon atom less than the amide. The reaction proceeds via formation of nitrene.

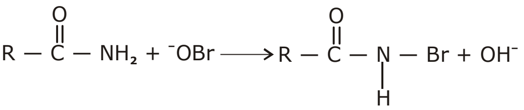


$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$$

Mechanism of above reaction has been proposed as given below :

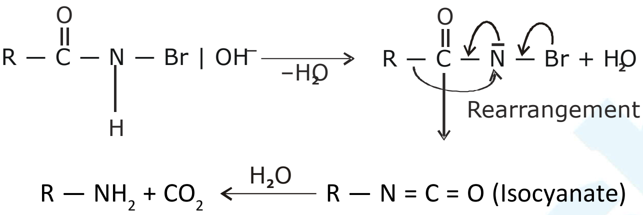
$Br_2 + KOH \longrightarrow K^+O^-Br + HBr$

$2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O$

(a) 

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + {}^-OBr \longrightarrow R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-Br + OH^-$$

N-bromoacetone

(b) 

$$R-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-Br \mid OH^- \xrightarrow[-H_2O]{} R-\overset{\overset{O}{\|}}{C}-\ddot{\bar{N}}-Br + H_2O$$

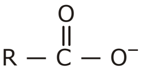
Rearrangement

$$R-NH_2 + CO_2 \xleftarrow{H_2O} R-N=C=O \text{ (Isocyanate)}$$

2. **Curtius, Schmidt and Lossen Rearrangement :** These reaction are basically rearrangement reaction in which carbon migrates from carbon to nitrogen with the formation of an isocyanate. In these migration i.e., 1, 2 shift, migrating group is an alkyl or aryl group and leaving group may be

— Br in Hoffmann rearrangement

— N_2 in curtius and Schmidt rearrangement

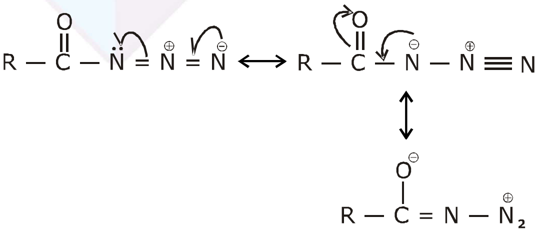


$R-\overset{\overset{O}{\|}}{C}-O^-$ Lossen rearrangement

The isocyanate formed on hydrolysis gives amine.

(a) Curtius Reaction : Acid chloride on treatment with sodium azide give acid azides which on pyrolysis gives isocyanates on hydrolysis gives corresponding amines.

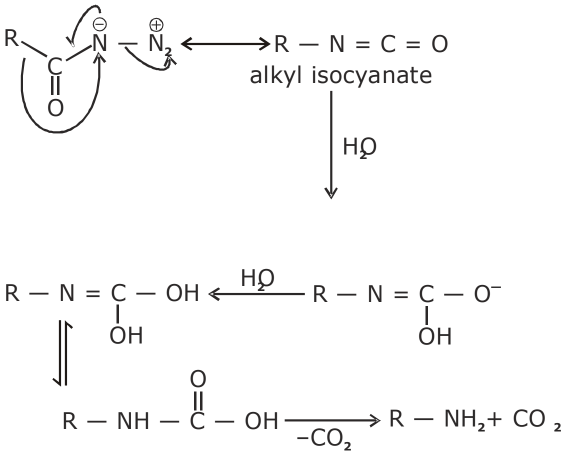
$RCOCl + NaN_3 \longleftrightarrow RCON_3 + NaCl$



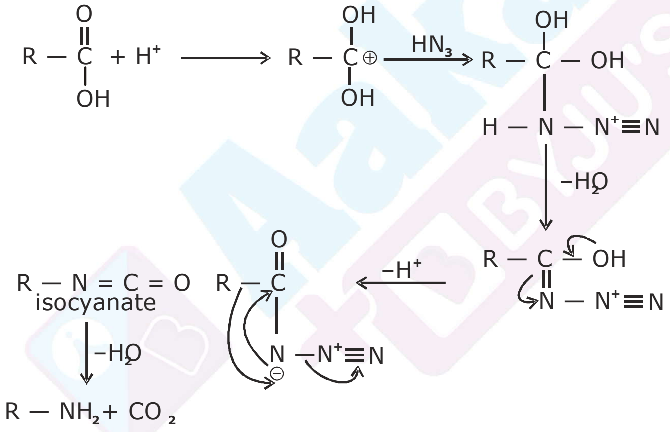
$$R-\overset{\overset{O}{\|}}{C}-\ddot{N}=\overset{\oplus}{N}=\overset{\ominus}{N} \longleftrightarrow R-\overset{\overset{O}{\|}}{C}-\overset{\ominus}{N}-\overset{\oplus}{N}\equiv N$$

$$\updownarrow$$

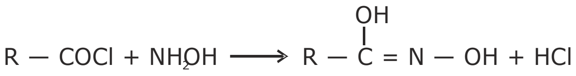
$$R-\overset{\overset{O^{\ominus}}{|}}{C}=N-\overset{\oplus}{N_2}$$



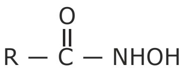
(b) Schmidt Reaction : Carboxylic acid reacts with hydraozoic acid in presence of concentrated H_2SO_4 to give isocyanates.



(c) Lossen Reaction : Hydroxylamine on treatment with acid chloride gives acyl derivatives of hydroxyl amine the acyl derivatives exist in two tautomeric form keto form called hydroxamic form and enol form called hydroximic acid.

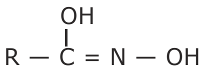


$$R - COCl + NH_2OH \longrightarrow R - \overset{OH}{\overset{|}{C}} = N - OH + HCl$$



$R-\overset{\overset{O}{\parallel}}{C}-NHOH$

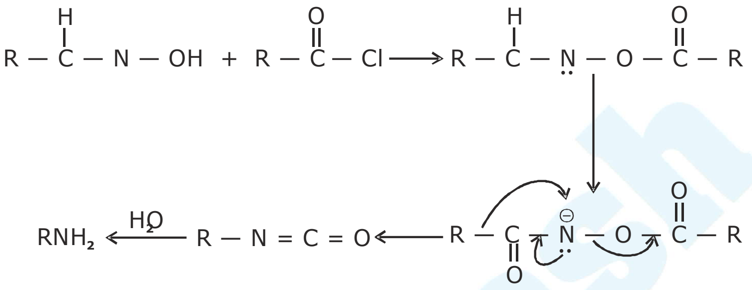
Keto form the
hydroxamic from



$R-\overset{\overset{OH}{|}}{C}=N-OH$

The hydroximic
form (enol form)

The hydroxamic form (keto form) forms o-acyl derivatives of hydroxamic form which on heating with bases forms isocyanates and finally amines upon hydrolysis.



3. **By reduction of nitroethane :**

$$C_2H_5NO_2 + 6[H] \xrightarrow{Sn\ +\ HCl} C_2H_5NH_2 + 2H_2O$$

Nitroethane Ethylamine

4. **By reduction of methyl cyanide :**

$$CH_3CN + 4[H] \xrightarrow{Na\ +\ C_2H_5OH} CH_3CH_2NH_2$$

Methyl cyanide Ethylamine

5. **By reduction of acetamide :** Ethylamine is obtained by reduction of acetamide with sodium and absolute alcohol or $LiAlH_4$ in ether or hydrogen in presence of nickel catalyst.

$$CH_3CONH_2+4[H] \xrightarrow{Na\ +\ C_2H_5OH} CH_3CH_2NH_2+H_2O$$

Acetamide Ethylamine

6. **By reduction of aldoxime :** Aldoxime on reduction with hydrogen and nickel catalyst or sodium and absolute alcohol or $LiAlH_4$ in ether yields ethylamine.

$$CH_3CH = NOH + 4[H] \longrightarrow CH_3CH_2NH_2 + H_2O$$

Acetaloxime Ethylamine

7. **By the hydrolysis of ethyl isocyanate :** Ethyl isocyanate on heating with caustic potash solution undergoes hydrolysis forming ethylamine.

$C_2H_5NCO + 2KOH \longrightarrow C_2H_5NH_2 + K_2CO_3$

Ethyl isocyanate — Ethylamine

8. **By the acid hydrolysis of ethyl isocyanide :** Ethyl isocyanide undergoes hydrolysis with a mineral acid and forms ethylamine.

$C_2H_5NC + 2H_2O \longrightarrow C_2H_5NH_2 + HCOOH$

Ethyl isocyanide — Ethylamine — Formic acid

9. **By Schmidt reaction :**

$C_2H_5COOH + N_3H \longrightarrow C_2H_5NH_2 + N_2 + CO_2$

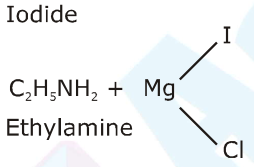
Hydrazoic acid — Ethylamine

In this reaction the acyl azide $(RCON)_3$ and alkyl isocyanate (R —NCO) are formed as an intermediate.

10. **By the action of chloramine on Grignard reagent :** When chloramine reacts with ethyl magnesium iodide, the formation of ethylmine occurs.

$C_2H_5MgI + ClNH_2 \longrightarrow$

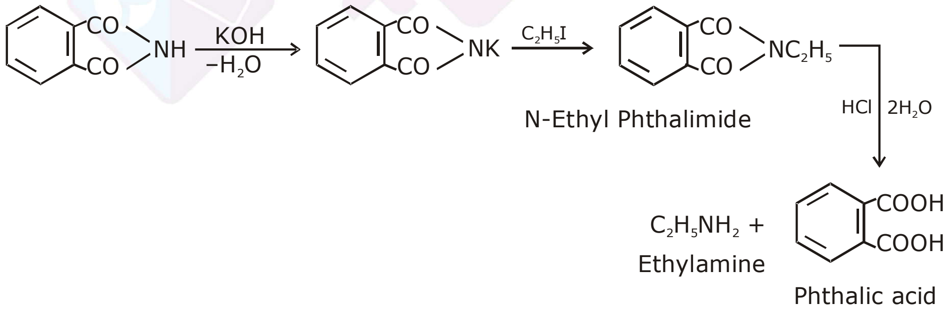
Ethyl magnesium Iodide — Chloramine



$C_2H_5NH_2 + Mg\begin{matrix} I \\ Cl \end{matrix}$

Ethylamine

11. **By Gabriel's phthalimide reaction :**



12. **Laboratory preparation of ethylamine :** Ethylamine is prepared in the laboratory by Hofmann's bromide reaction. Proprionamides is heated with bromine and pottassium hydroxide solution.

$C_2H_5CONH_2 + Br_2 + 4KOH \longrightarrow C_2H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O$

Propionamide Ethylamine

Physical properties

(a) It is a colourless inflammable liquid. It's boiling point is 19ºC.

(b) It has fishy ammonical odour.

(c) It is highly soluble in water. Its aqueous solution is basic in nature and turns red limus blue.

The solubility in water is due to hydrogen bonding with water moelcules.

Chemical properties

(i) Basic nature : It is more basic than ammonia. Following reactions prove its basic nature

(a) It forms ethyl ammonium hydroxide when dissolved in water.

$C_2H_5NH_2 + H_2O \longrightarrow C_2H_5NH_3OH$

Ethyl ammonium hydroxide

Ethyl ammonium hydroxide ionises to give OH^- ions

$C_2H_5NH_3OH \rightleftharpoons C_2H_5\overset{+}{N}H_3 + OH^-$

(b) It reacts with acids to form salts.

$C_2H_5NH_2 + HCl \longrightarrow C_2H_5NH_3Cl$ or $C_2H_5NH_2.HCl$

Ethyl ammonium chloride

or

Ethylamine hydrochloride

$C_2H_5NH_2 + H_2SO_4 \longrightarrow (C_2H_5NH_3)_2\ SO_4$

Ethyl ammonium sulphate

(ii) Reaction with alkyl halides (Alkylation) :

Ethylamine reacts with alkyl halides and form secondary, tertiary amines and quaternary ammonium salt.

$C_2H_5NH_2 + C_2H_5I \longrightarrow (C_2H_5)_2NH\ .\ HI$

Diethyl ammonium iodide

$(C_2H_2)_2\ NH + C_2H_5I \longrightarrow (C_2H_5)_3NHI$

Triethyl ammonium iodide

$(C_2H_5)_3N + C_2H_5I \longrightarrow (C_2H_5)_4NI$

Tetraethyl ammonium iodide

(iii) Reaction with acetyl chloride or acetic anhydride : Acetylation takes place when ethylamine combines with acetyl chloride or acetic anhydride.

$$C_2H_5NH_2 + ClOCCH_3 \longrightarrow C_2H_5NHCOCH_3 + HCl$$

Acetyl chloride

Acetyl ethylamine or N-Ethyl acetamide

$$C_2H_5NH_2 + (CH_3CO)_2O \longrightarrow C_2H_5NHCOCH_3 + CH_3COOH$$

Ethylamine; Acetic anhydride; N-Ethyl acetamide

(iv) Carbylamine Reaction

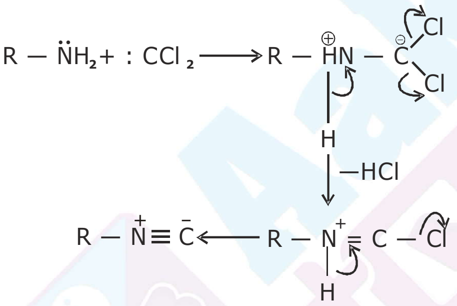
$$RNH_2 + CHCl_3 + 3KOH \longrightarrow R - N^+ \equiv C^- + 3KCl + 3H_2O$$

an isocyanide (foul smelling)

Nucleophilic RNH_2 attacks electrophilic intermediate $[:CCl_2]$ dichlorocarbene.

This reaction is used for the detection of primary amines.

Mechanism :



(v) Reaction with sodium : Hydrogen is evolved when ethylmine is heated with sodium.

$$2C_2H_5NH_2 + 2Na \longrightarrow 2C_2H_5NHNa + H_2$$

Sodium derivative of ethylamine

(vi) Reaction with Grignard reagents : Ethylamine reacts with Grignard reagents to form alkanes.

$$C_2H_5NH_2 + RMgX \longrightarrow R - H + C_2H_5NHMgX$$

Grignard reagent; Alkane

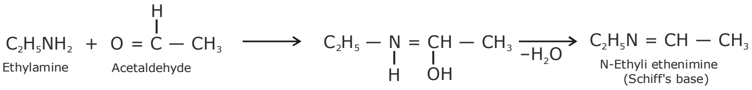
$$C_2H_5NH_2 + CH_3MgI \longrightarrow CH_4 + C_2H_5NHMgI$$

Methyl Magnesium iodide; Methane

(vii) Hofmann's mustard oil reaction : Carbon disulphide reacts with ethylamine in presence $HgCl_2$ to form ethyl isothiocyanate which has a mustard oil like smell.

$$C_2H_5NH_2 + CS_2 + HgCl_2 \longrightarrow \underset{\text{Ethyl isothiocyanate}}{C_2H_5N = C = S} + 2HCl + HgS$$

(viii) Reaction with aldehydes : Ethylamine reacts additively with aldehydes to form α-hydroxyl amines which are changed to Schiff bases with the elimination of water molecule.



$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + \underset{\text{Acetaldehyde}}{O = \overset{\overset{\displaystyle H}{|}}{C} - CH_3} \longrightarrow C_2H_5 - \underset{\underset{\displaystyle H}{|}}{N} = \underset{\underset{\displaystyle OH}{|}}{CH} - CH_3 \xrightarrow[-H_2O]{} \underset{\substack{\text{N-Ethyli ethenimine}\\ \text{(Schiff's base)}}}{C_2H_5N = CH - CH_3}$$

DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY AMINES

Test	Primary amine	Secondary amine	Tertiary amine
1. Action Test $CHCl_3$ and alcoholic KOH.	Bad smelling carbyl-amine (Isocyanide is formed)	No action.	No action.
2. Action of CS_2 and $HgCl_2$ (Mustard Oil test	Alkyl isothiocyanate is formed which has pungest smell like mustard oil.	No action.	No action.
3. Action of Nitrous acid.	Alcohol is formed with evolution of nitrogen.	Forms nitrosoamine which gives green colour with phenol and conc. H_2SO_4 (Liebermann's test.)	Forms nitrite in cold which on heating gives nitrosoamine which responds to Liebermann's test.
4. Action of acetyl chloride.	Acetyl derivative is formed	Acetyl derivative is formed	No action.
5. Action of Hinsberg's reagent	Monoalkyl sulphon-amide is formed which is soluble in KOH.	Dialkyl sulphonamide is formed which is insoluble in KOH.	No action.
6. Action of methyl iodide.	3 molecules (moles) of CH_3I to form quaternary salt with one mole of of primary amine.	2 moles of CH_3I to form quaternary salt with one mole of secondary amine.	One mole of CH_3I to form quaternary salt with one mole of tertiary amine.

General chemical properties of aromatic amines

Reaction with nitrous acid

1. **Primary Amines :** Primary amines react with nitrous acid to produce diazonium ion as follows.

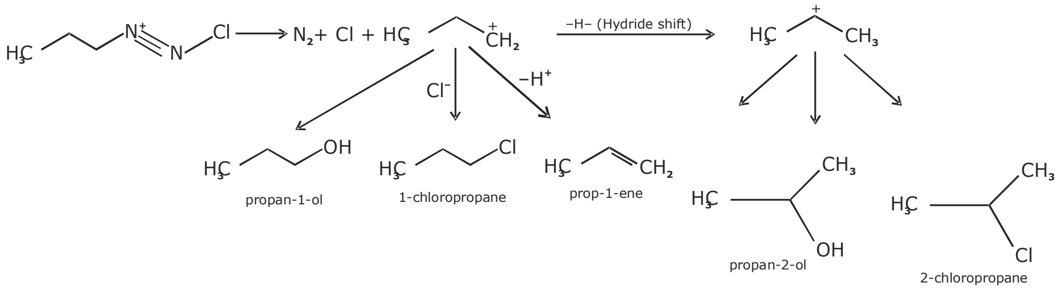
$$ArNH_2 + HNO_2 \longrightarrow Ar - N^{\oplus} \equiv N:$$

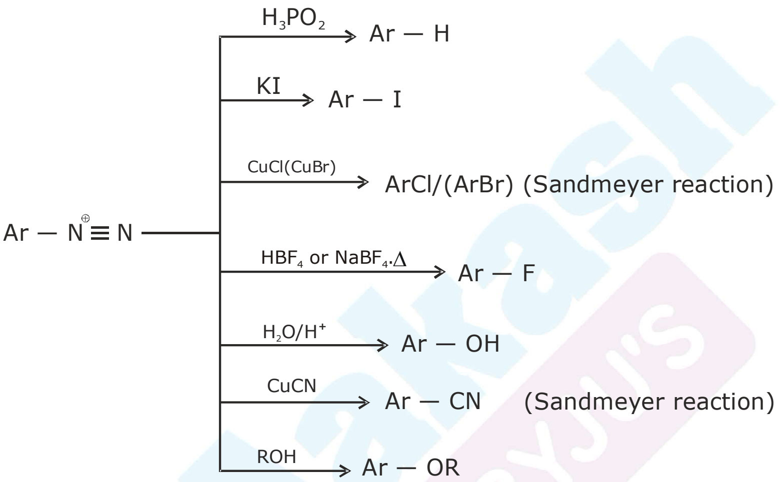
$$R - NH_2 + HNO_2 \longrightarrow R - N^{\oplus} \equiv N$$

But the diazonium ions of aliphatic amines are very unstable and produces carbocation immediately, which can produce different products.

$$R - N^{\oplus} \equiv N \xrightarrow{-N_2} R^+ \text{ (Carbocation)}$$

ALIPHATIC AMINE





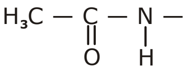
AROMATIC AMINE

Introduction

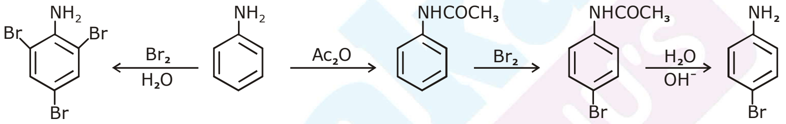
Aromatic amines are organic compounds that consist of an amine substituent (e.g., NH_2) attached to an aromatic structure. NH_2 — NHR and —NR_2 strongly activate the benzene ring towards electrophilic substitution.

Ring reactions of aromatic amines

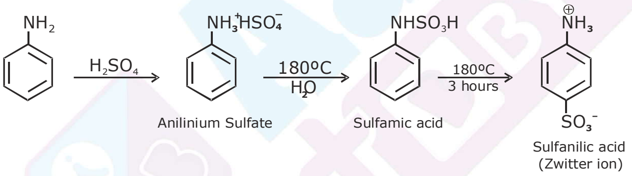
1. **Halogenation :** For monohalogenation, —NH_2 is first acetylated, because



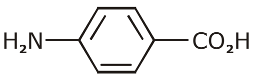
$H_3C - \underset{\underset{O}{\|}}{C} - \underset{\underset{H}{|}}{N} -$ is only moderately activating and is o and p-director in nature



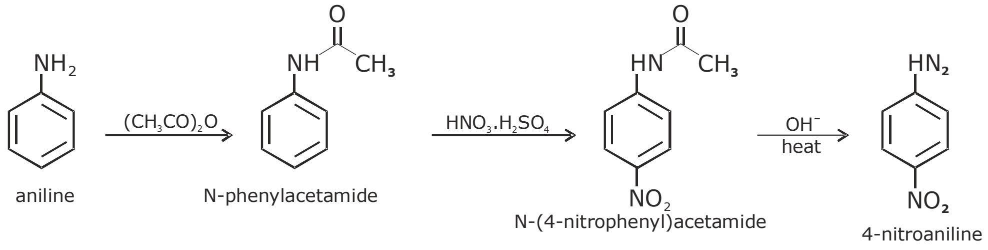
2. **Sulfonation :**

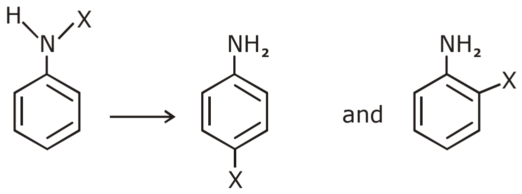


The dipolar ion structure of sulfanilic acid account for its (a) high melting point, (b) insolubility in H_2O and organic solvents, (c) solubility in aqueous NaOH, (d) insolubility in aqeous HCl.



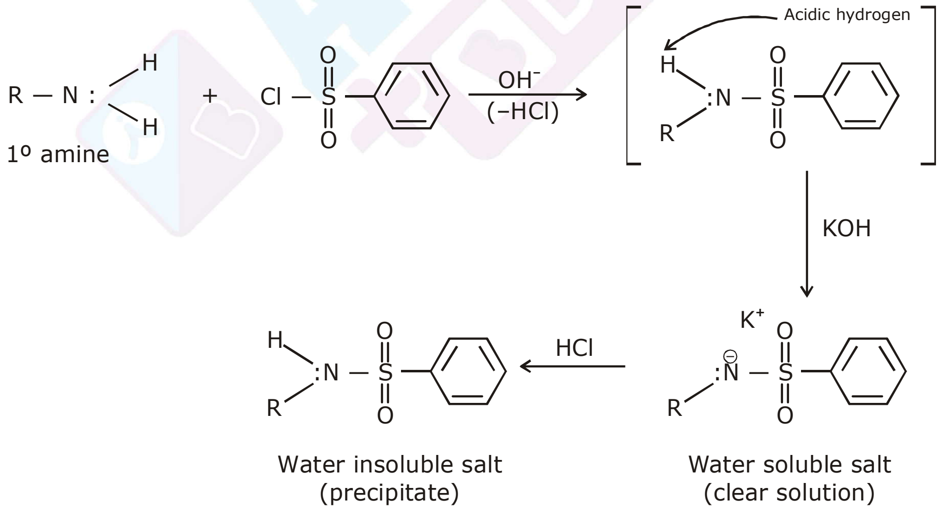
will not exists as a dipolar ino since, –COOH is too weakly acidic to transfer an H^+ to the weakly basic –NH_2 attached to the electron withdrawing benzene ring. When attached to an aliphatic C, the NH_2 is sufficiently basic to accept H^+ from COOH.





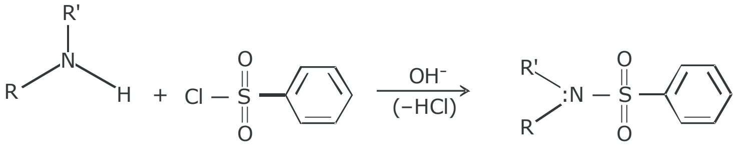
(i) The Hinsberg Test

The test can be used to demonstrate whether an amine is primary, secondary or tertiary. Primary amines react with benzenesulfonyl chloride to form N-substituted benzenesulfonamides. These, in turn, undergo acid-base reactions with the excess potassium hydroxide to form water - soluble potassium salt. Acidification of this solution will, cause the water-insoluble N-substituted sulfonamide to precipitate.



Secondary amines react with benzenesulfonyl chloride in aqueous potassium hydryoxide to form insoluble, N_1 - N-disubstituted sulfonamides that precipitate after the first stage. N_1N–

Disubstituted sulfonamides do not dissolved in aqueous potassium hydroxide.



Water insoluble salt
(precipitate)

If the amine is a tertiary amine and if it is water insoluble, no apprated change will take place in the mixture as we shake it with benzenesulfonyl choride and aqueous KOH. When we acidify the mixture, the tertiary amine dissolves because it forms a water soluble salt.

BIOMOLECULE AND POLYMER

SECTION-A

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.

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

- **Photosynthesis :**

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

- **Cellular Respiration :**

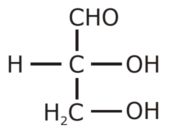
$$C_6H_{12}O_6 + 6O_2 \xrightarrow{\text{Enzymes}} 6CO_2 + 6H_2O + 38\ ATP$$

(36 ATP net gain)

2. Classification and structure of Carbohydrates:

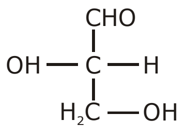
Carbohydrates are polyhydroxy aldehydes and ketones and substances which hydrolyse to polyhydroxy aldehydes and ketones.

The simplest carbohydrates are called ***sugars*** or ***saccharides***, (Latin: Saccharum, sugar). Carbohydrates can be classified as ***monosaccharides, oligosaccharides*** and ***polysaccharides.*** Glyceraldehyde contains one asymmetric carbon atom (marked by an astrisk) 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, which means they are **enantiomers**.



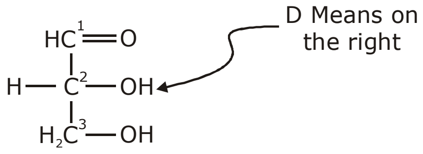
$$\begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ H_2C-OH \end{array}$$

D-Glyceraldehyde

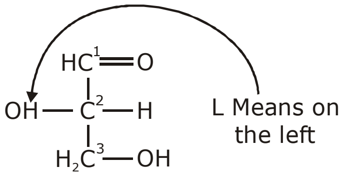


$$\begin{array}{c} CHO \\ | \\ OH-C-H \\ | \\ H_2C-OH \end{array}$$

L-Glyceraldehyde

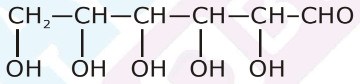


D-Glyceraldehyde



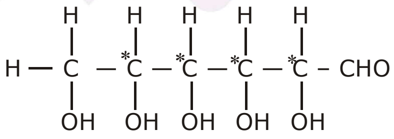
L-Glyceraldehyde

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, i.e. a mixture that would allow a plane-polarised light to pass through the solution unchanged.



$$\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH}-\underset{OH}{CH}-\underset{OH}{CH}-CHO$$

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

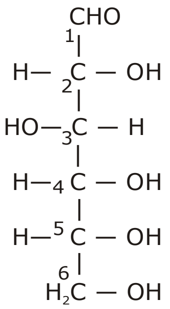


$$H-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{{}^{*}C}}-\underset{OH}{\overset{H}{{}^{*}C}}-\underset{OH}{\overset{H}{{}^{*}C}}-\underset{OH}{\overset{H}{{}^{*}C}}-CHO$$

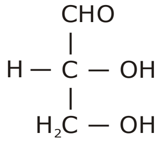
3. **Configuration* of Glucose:**

   Since the above structure possesses four asymmetric carbon atoms (shown by asterisks), it 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, fructose, idose and talose.

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



D(+)Glucose



(+)-Glyceraldehyde

Notations D- and L- for denoting configuration which was given by Rosanoff; According to his 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.

Constitution of Glucose :

1. **Molecular Formula:** By the usual analytical methods, the molecular formula of glucose is found to be $C_6H_{12}O_6$.

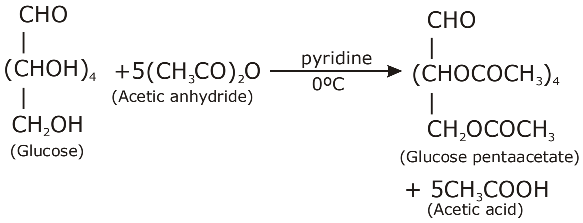
2. **Straight chain of six carbon atoms:**

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

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow[\text{Prolonged heating}]{\text{HI/P}} \underset{\text{n-Hexane}}{CH_3-(CH_2)_4-CH_3}$$

(ii) Glucose when oxidized with bromine water gives gluconic acid which when reduced with excess of HI gives n-hexanoic acid, $CH_3.(CH_2)_4.COOH$ confirming the presence of a straight chain of six carbon atoms in glucose.

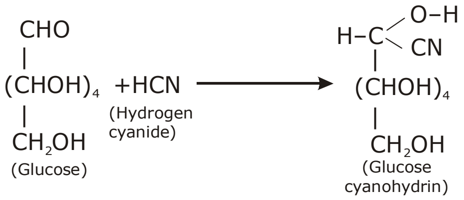
3. **Presence of five hydroxyl groups:** When treating with acetic anhydride, glucose forms penta-acetate indicating the presence of 5 – OH groups and since glucose is a stable compound, the five –OH groups must be attached to 5 different carbon atoms.



$$\underset{\text{(Glucose)}}{\begin{array}{c}CHO\\|\\(CHOH)_4\\|\\CH_2OH\end{array}} + \underset{\text{(Acetic anhydride)}}{5(CH_3CO)_2O} \xrightarrow[0^{o}C]{\text{pyridine}} \underset{\text{(Glucose pentaacetate)}}{\begin{array}{c}CHO\\|\\(CHOCOCH_3)_4\\|\\CH_2OCOCH_3\end{array}} + \underset{\text{(Acetic acid)}}{5CH_3COOH}$$

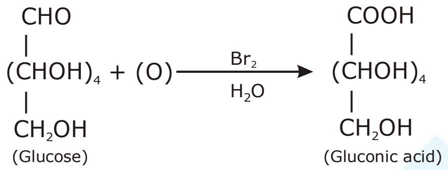
4. Presence of an aldehydic groups:

(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.

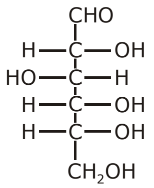


$$\underset{\text{(Glucose)}}{\begin{matrix}\text{CHO}\\|\\(\text{CHOH})_4\\|\\\text{CH}_2\text{OH}\end{matrix}} + (\text{O}) \xrightarrow[\text{H}_2\text{O}]{\text{Br}_2} \underset{\text{(Gluconic acid)}}{\begin{matrix}\text{COOH}\\|\\(\text{CHOH})_4\\|\\\text{CH}_2\text{OH}\end{matrix}}$$

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

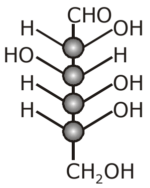
Structure formulas for monosaccharides:

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



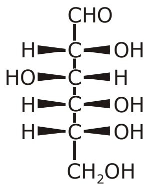
Fischer projection formula
1

≡



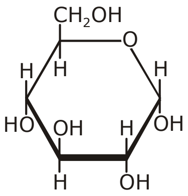
Circle - and - line formula
2

≡



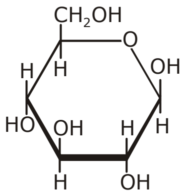
Wedge-line dashed wedge formula
3

⇌



4

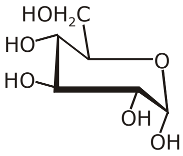
+



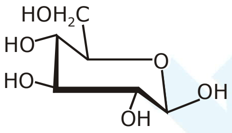
5

Haworth formulas

≡



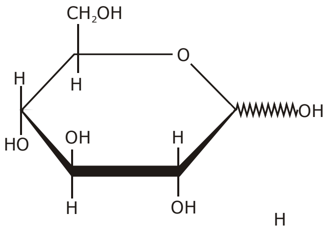
α-D-(+)-Glucopyranose
6

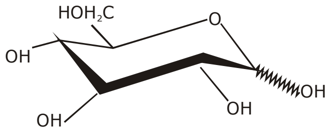


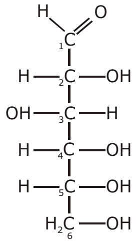
β-D-(+)-Glucopyranose
7

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. Its demonstrates how the representation of each stereogenic centre of the open-chain form can be correlated with its representation in the Haworth formula.

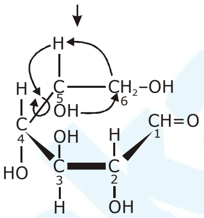
Each glucose anomer is designated as an α anomer or a β anomer depending on the location of the –OH group of C1.



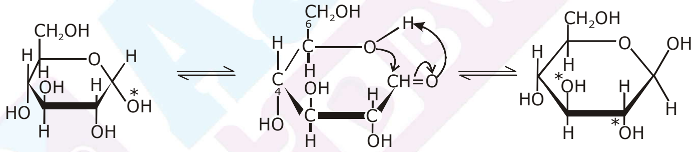




Glucose
(Plane projection formula) When a model
of this is made it will coil as follows:



If the group to C4 is
pivoted as the arrows indicate,
we have the structure below



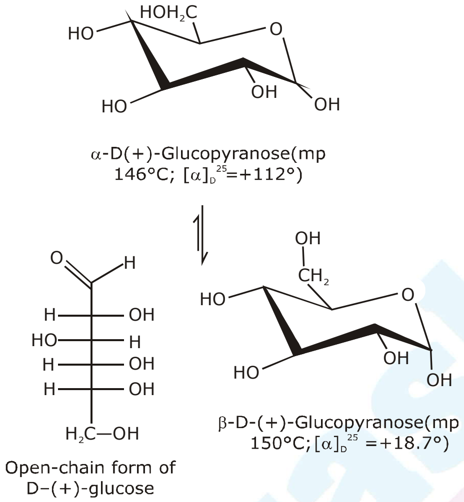
α- D - (+)-Glucopyranose
(starred – OH) is the
hemiacetal – OH, which is
α-glucose is on the opposite
side of the ring from the
– CH$_2$OH group at C5.

β-D-(+)-Glucopyranose
(starred – OH) is the
hemiacetal – OH, which in
β -glucose is on the same
side of the ring as the
– CH$_2$OH group at C5.

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 (melting point) 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°. This change in rotation towards an equilibrium value is called mutarotation.

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



α-D(+)-Glucopyranose(mp 146°C; $[\alpha]_D^{25}$=+112°)

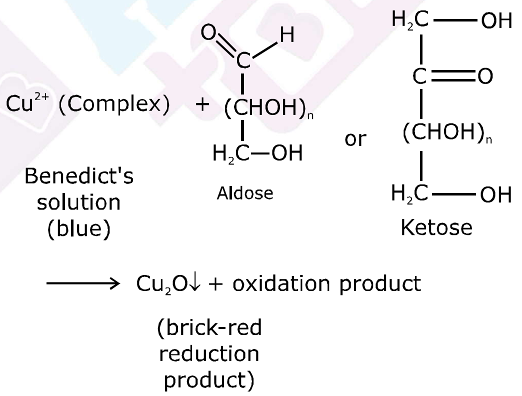
Open-chain form of D–(+)-glucose

β-D-(+)-Glucopyranose(mp 150°C; $[\alpha]_D^{25}$ =+18.7°)

Benedict’s or tollen’s reagents

Reducing Sugars

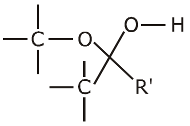
Benedict’s reagent (An alkaline solution containing a cupric citrate complex ion) and Tollen’s solution $[Ag(NH_3)_2]OH$ oxidize and thus give positive tests with aldoses and ketoses. The tests are positive even though aldoses and ketoses exist primarily as cyclic hemiacetals.



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, concentration of noncyclic aldehydes or α-hydroxy ketones. It is the latter two that undergoes the oxidation until one reactant is exhausted.

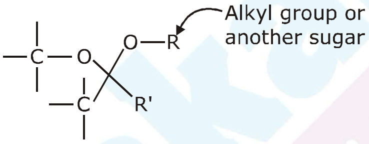
Carbohydrates that contain only acetal groups do not give positive tests with Benedict's or Tollen's solutions, and they are called non-reducing sugars. Acetals do not exist in equilibrium with aldehydes or α-hydroxy ketones in the basic aqueous media of the test reagents.

Reducing Sugar



Hemiacetal(R'=H or = CH_2OH) (gives positive Tollen's or Benedict's test)

Nonreducing Sugar

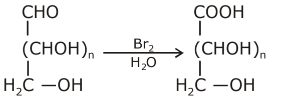


Acetal (R' = H or=CH_2OH) (does not give positive Tollens' or Benedict's test)

Bromine Water :

The synthesis of Aldonic Acid

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

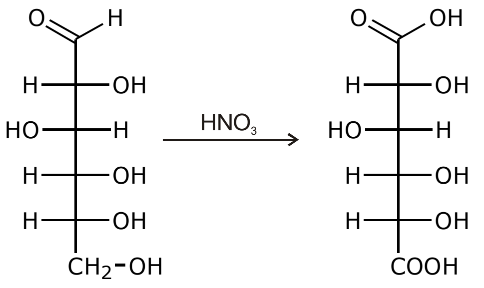


$$\begin{array}{c} CHO \\ | \\ (CHOH)_n \\ | \\ H_2C-OH \end{array} \xrightarrow[H_2O]{Br_2} \begin{array}{c} COOH \\ | \\ (CHOH)_n \\ | \\ H_2C-OH \end{array}$$

(Aldose) (Aldonic acid)

Nitric acid oxidation : Aldaric acid

Dilute nitric acid – a stronger oxidizing agent than bromine water – oxidizes both –CHO group and the terminal $-CH_2OH$ group of an aldose to $-CO_2H$ groups. These dicarboxylic acids are known as aldaric acids:



D-Glucose D-Glucaric acid

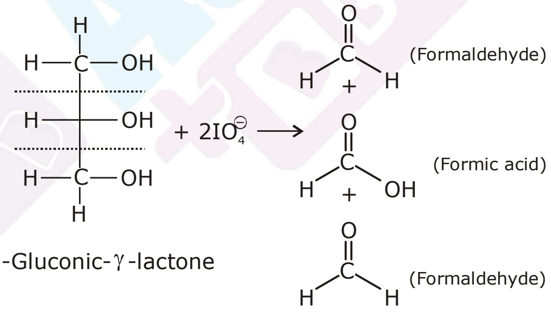
This aldaric acid obtained from D-glucose is called D-glucaric acid.

Periodate oxidation : oxidative cleavage of polyhydroxy compounds

Compounds that have hydroxyl groups onadjacent 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).

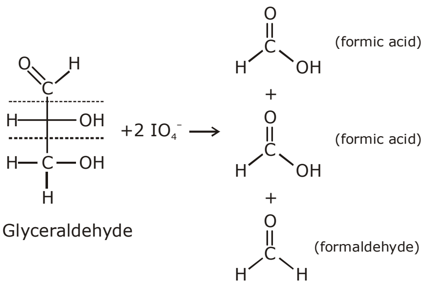
Before we discuss the use of periodic acid in carbohydrate chemistry, we should illustrate the course of the reaction with several simple examples. Notice in these periodate oxidations that for every C – C bond broken, a C – O bond is formed at each carbon.

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

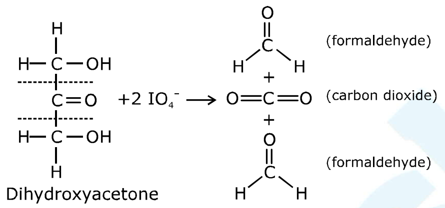


D-Gluconic-γ-lactone

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

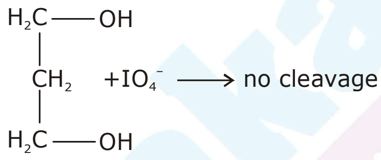


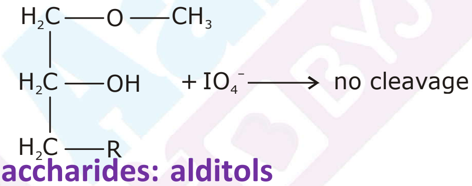
Glyceraldehyde



Dihydroxyacetone

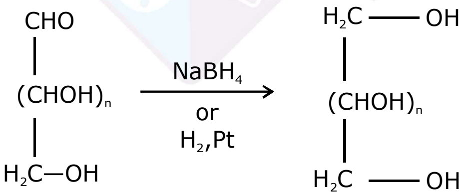
Periodic acid does not cleave compound in which the hydroxyl groups are separated by an intervening $-CH_2$ group, nor those in which a hydroxyl group is adjacent to an ether or acetal.





Reduction of monosaccharides: alditols

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

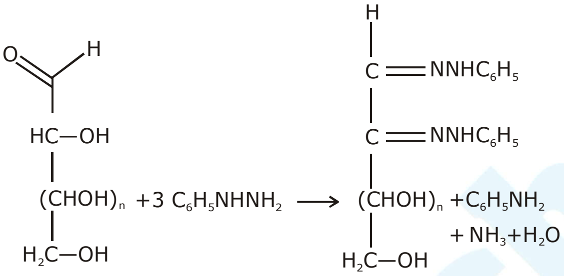


Aldose Alditol

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

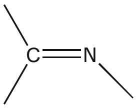
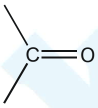
Reactions of monosaccharides with phenylhydrazine : osazone

The aldehyde group of an aldose reacts with some carbonyl reagents like hydroxylamine and phenylhydrazine. With hydroxylamine, the product is the expected oxime. With excess phenylhydrazine, three molar equivalents of phenylhydrazine are consumed and only two phenylhydrazone group is introduced. The product is called a phenylosazone. Phenylosazones crystallize readily (unlike sugars) and are useful derivatives for identifying sugars.



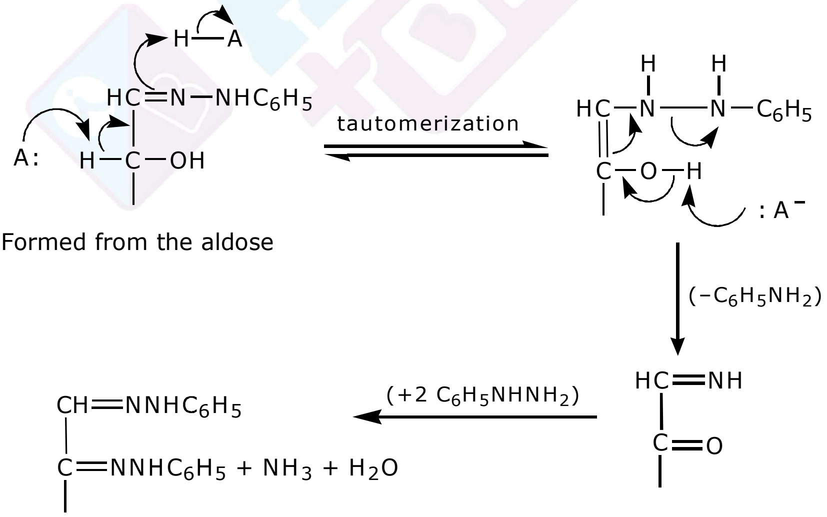
Aldose

Phenylosazone

The mechanism for osazone formation probably depends on a series of reaction in which  behaves very much like  in giving a nitrogen version of an enol.

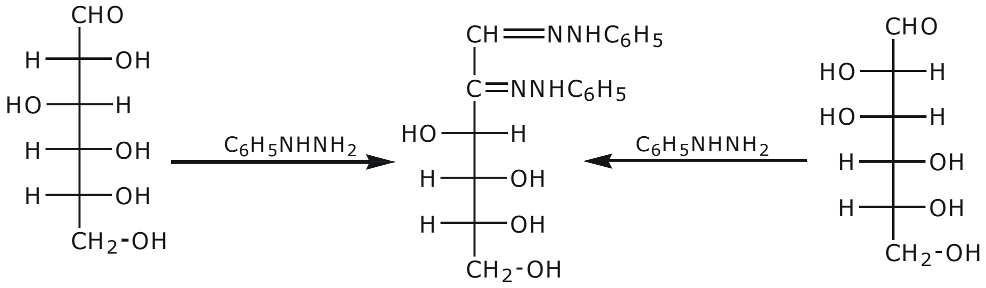
A Mechanism for the Reaction

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:

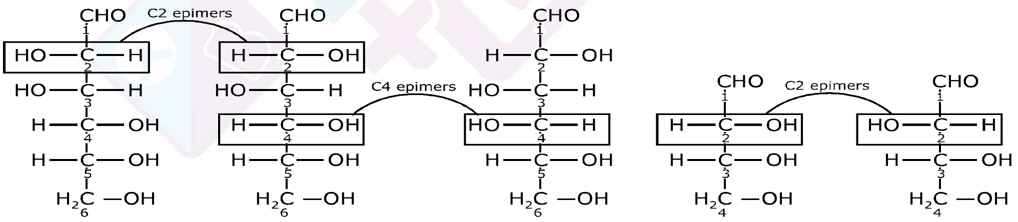


D-Glucose Phenylosazone D-Mannose

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 as epimers.

Epimers:

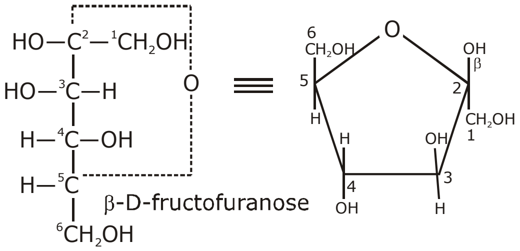
Many common sugars are closely related, differing only by the stereochemistry at a single carbon atom. For example, glucose and mannose differ only at C2, the first asymmetric carbon atom. Sugars that differs only by the stereochemistry at a single carbon are called ***epimers*** and the carbon atom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



D-mannose D-glucose D-galactose D-erythrose D-threose

Cyclic structure of Fructose:

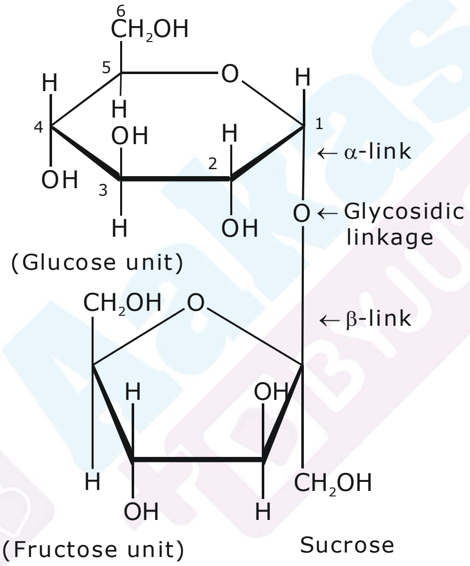
Like glucose, fructose also has a cyclic structure. Since fructose contains a keto group, it forms an intramolecular hemiketal. In the hemiketal formation, C5–OH of the fructose combines with C2-keto group. As a result, C2 becomes chiral and thus has two possible arrangements of CH_2OH and OH group around it. Thus,



β-D-fructofuranose

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

Hydroylsis of Sucrose:



Sucrose

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

$C_{12}H_{22}O_{11} \quad + \quad H_2O \xrightarrow{H^+}$ Sucrose

$[\alpha]_D = +66.5^\circ$

$C_6H_{12}O_6$ + $C_6H_{12}O_6$

D(+)-glucose D(–)-Fructose

$[\alpha]_D = +53^\circ$ $[\alpha]_D = -92^\circ$

Invert Sugar

$[\alpha]_D = (+53^\circ) + (-92^\circ) = -39^\circ$

Surose is dextrorotatory, its specific rotation being but D-fructose has a large negative rotation, $[\alpha]_D$ = –92°. 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

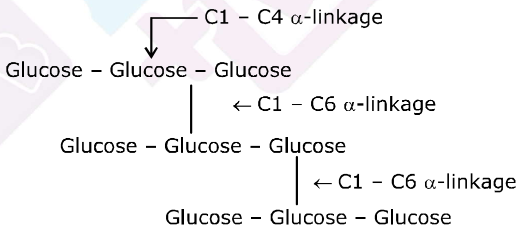
Polysaccharides are the polymers of monosaccharides. The natural polysaccharides generally contain about 100-3000 monosaccharide units. The three most abundant natural polysaccharides-cellulose, starch and glycogen are derived from the same monomer, i.e., glucose.

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

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

Amylose is a linear polymer of α-D glucose. It contains about 200 glucose units which are linked to one another through α-linkage involving C_1 of one gluose unit with C_4 of the other.

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

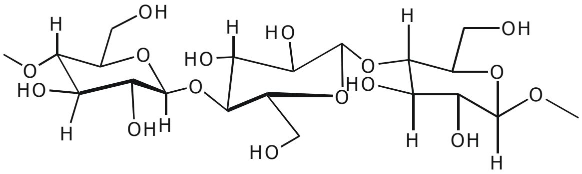


Hydrolysis:

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

Cellulose:

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



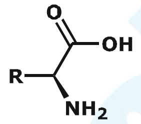
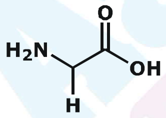
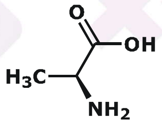
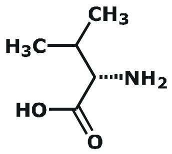
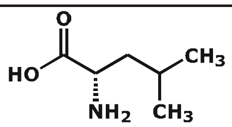
SECTION B

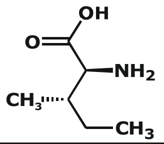
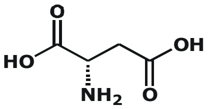
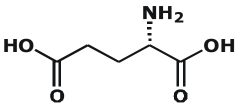
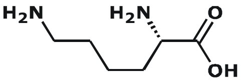
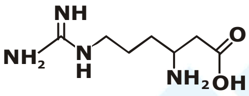
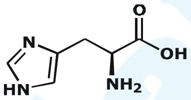
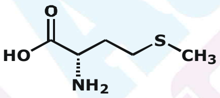
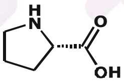
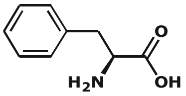
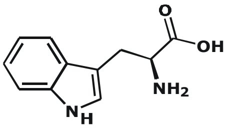
Amino Acids

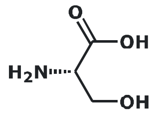
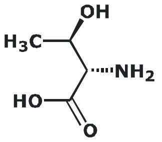
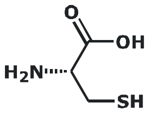
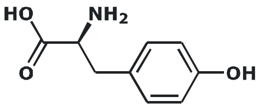
1. Introduction:

Amino acids are the compounds which contain both an amino group and a carboxy group in their molecules. They constitute particularly an 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 given in the table. These abbreviations are particularly useful in designating the sequence of amino acids in peptides and proteins which you will study.

Nature of amino acid	**E/N.E**		**Name**	**Abbreviation**
Neutral amino acid	**NE**		**Glycine**	**Gly**
Neutral amino acid	**NE**		**Alanine**	**Ala**
Neutral amino acid	**E**		**Valine**	**Val**
Neutral amino acid	**E**		**Leucine**	**Leu**

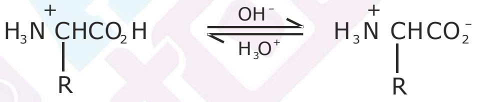
Neutral amino acid	**E**		**Isoleucine**	**Ile**
Acidic amino acid	**NE**		**Aspartic Acid**	**Asp**
Acidic amino acid	**NE**		**Glutamic Acid**	**Glu**
Basic amino acid	**E**		**Lysine**	**Lys**
Basic amino acid	**E**		**Arginine**	**Arg**
Basic amino acid	**E**		**Histidine**	**His**
Neutral amino acid	**E**		**Methionine**	**Met**
Neutral amino acid	**NE**		**Proline**	**Pro**
Neutral amino acid	**E**		**Phenylalanine**	**Phe**
Neutral amino acid	**E**		**Tryptophan**	**Trp**

Neutral amino acid	**NE**		**Serine**	**Ser**
Neutral amino acid	**E**		**Threonine**	**Thr**
Neutral amino acid	**NE**		**Cysteine**	**Cys**
Neutral amino acid	**NE**		**Tyrosine**	**Tyr**

E = Essential amino acid **NE** = Non essential amino acid

Amino acid as dipolar ions

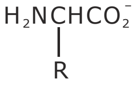
Amino Acids contain both a basic group ($–NH_2$) and an acidic group (–COOH). In the dry solid state, amino acids exist as dipolar ions, a form in which the carboxyl group is present as a carboxylate ion, $–CO_2^-$, and the amino group is present as an ammonium ion, $–NH_3^+$ (Dipolar ions are also called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



$$H_3\overset{+}{N}\underset{\substack{|\\R}}{C}HCO_2H \underset{H_3O^+}{\overset{OH^-}{\rightleftharpoons}} H_3\overset{+}{N}\,\underset{\substack{|\\R}}{C}HCO_2^-$$

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

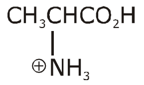
Dipolar ion



$$H_2N\underset{\substack{|\\R}}{C}HCO_2^-$$

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 exist mainly in 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). For a typical cationic form 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):



$$\underset{\overset{|}{\oplus NH_3}}{CH_3CHCO_2H}$$

Cationic form of alanine

$pK_{a1} = 2.3$

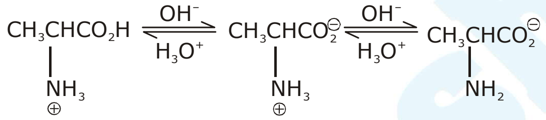
$CH_3CH_2CO_2H$

Propanoic acid

$pK_a = 4.89$

The reason for this enhanced acidity of the carboxyl group in an α-amino acid is due to the inductive effect of the neighboring aminium cation, which helps to stabilize the carboxylate anion formed after 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 equation given below.

The protonated amine group of an α-amino acid is also acidic, but less than that of 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 equation below. The carboxylic acid proton is always lost before the proton from the aminium group in an α-amino acid.



$$\underset{\overset{|}{\underset{\oplus}{NH_3}}}{CH_3CHCO_2H} \underset{H_3O^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\overset{|}{\underset{\oplus}{NH_3}}}{CH_3CHCO_2^{\ominus}} \underset{H_3O^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\overset{|}{NH_2}}{CH_3CHCO_2^{\ominus}}$$

Cationic form $pK_{a_1} = 2.3$ | Dipolar ion $pK_{a_2} = 9.7$ | Anionic form

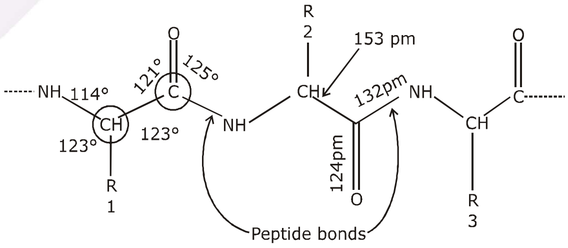
The state of an α-amino acid at any given pH is governed by a combination of two equilibrium, as shown in the above equation for alanine. The isoelectric point (pI) of an amino acid such as alanine is the average of pK_{a_1} and pK_{a_2};

pI = ½ (2.3 + 9.7) = 6.0 (isoelectric point of alanine)

Peptides and protein

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 carbóxy 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:



General Peptide Structure

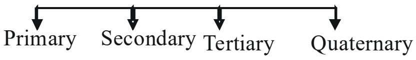
Peptides can be classified as dipeptides, tripeptides and tetrapeptides, depending on whether the number of amino acids, two, three or four, respectively. Peptides containing upto 50 amino acids are called polypeptides. Bradykinin is an important naturally occurring nonapeptide which is present in blood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

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

Configuration of proteins :

(a) Biological nature or function of protein was confirmed by its conformation.

(b) This conformation is of 4 types



1. Primary Structure :

⇒ This type of structure was given by **Frederick Sanger** in 1953 in Insulin (of one chain)

⇒ Primary structure is confirmed by a single polypeptide chain in a linear manner.

⇒ All amino acid are attached in a straight chain by peptide bond.

⇒ No biological importance & it will change to other forms.

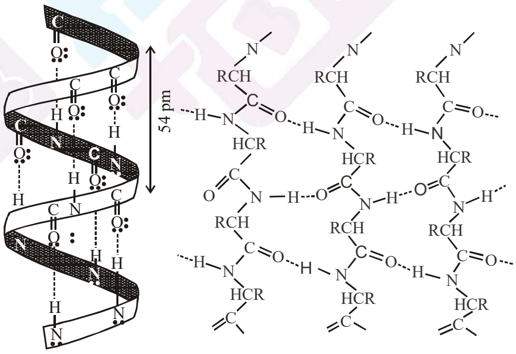
2. Secondary Structure :

⇒ In this structure straight chain undergoes irregular changes to form coils.

⇒ H-bond + peptide bond present in secondary structure.

⇒ This H bond is present between hydrogen of amino group and oxygen atom of carboxylic acid group.

⇒ This structure is of two types



(i) α-helix

⇒ Chain is spiral

⇒ 3.7 atoms in one coiling

⇒ Right handed circular.

Eg. → Myosin, Keratin etc.

(ii) β-pleated sheet

⇒ Structure of protein is not arranged in a sequence.

⇒ Polypeptide chains are parallel to each other

⇒ H - bond is formed by near chains

Eg. Silk fibres.

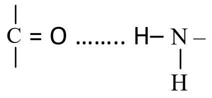
3. Tertiary structure :

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

Ex. Albumin

⇒ This structure is formed by 4 regular hydrogen bonds which makes a regularity in it

(i) Hydrogen bond :



$$\overset{|}{\underset{|}{C}} = O \,\ldots\ldots\, H - \underset{\underset{H}{|}}{N} -$$

Hydrogen bond

⇒ They are formed between oxygen of acidic amino acid and H of basic amino acid.

(ii) Hydrophobic bond :

⇒ Non - polar side chains of neutral amino acid tends to be closely associated with one another in proteins.

⇒ Present in between the amino acid.

⇒ These are not true bonds.

(iii) Ionic bond :

$$-COO^{-}\ldots\ldots H_3{}^{+}N-$$

Ionic bond

⇒ These are salt bonds formed between oppositely charged groups in side chains of amino acids

Eg. Aspartic acid, Glutamic acid

(iv) Disulphide bonds :

| ——— S - S —— |

⇒ Relatively stable bond and thus is not broken readily under usual conditions of denaturation.

⇒ Formed between the -SH group of amino acid Ex. Cysteine and Methionine .

4. Quaternary structure :

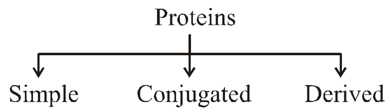
⇒ When 2 or more polypeptide chains united by forces other than covalent bonds (i.e. not peptide and disulphide bonds) are called Quaternary structure.

⇒ It is the most stable structure.

Ex. Haemoglobin

Types of proteins :

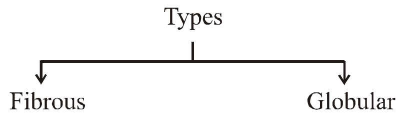
⇒ Classification of protein is based upon three general properties shape, solubility and chemical composition.



1. Simple proteins :

⇒ It is formed of only amino acids

⇒



(A) Fibrous :

⇒ It is insoluble

⇒ It is of elongated shape.

⇒ It is highly resistant to digestion by proteolytic enzymes.

⇒ Their main function - Protection.

Ex. Collagen, Keratin etc

(B) Globular :

⇒ These are spherical and oval in shape. Chains are highly coiled

⇒ These are soluble.

Ex. Albumin

Conjugated Proteins :

⇒ These are complex proteins in which protein molecule is combined with characteristic non-amino acid substance.

⇒ Non-amino acid or Non - protein part is called as prosthetic group

Ex. Nucleoproteins

(Protein + Nucleic acid),

Phosphoproteins (Protein + $(PO_4)^{3-}$)

Eg. → Casein of milk, Vitelline of egg - yolk

Derived proteins :

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

Eg. → Proteose, Metaproteins, Peptones

(b) Denaturation of Proteins

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

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

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

Test of Protein :

(a) Protein with conc. HNO_3 on heating gives yellow solution. Further addition of NH_4OH solution to the cooled solution gives a orange colour solution. It is **Xanthoproteic test**.

(b) (NH_4OH) + dil. $CuSO_4$ + protein give blue violet colour. It is a **biuret test**.

(c) **Millon reaction**. Proteins on adding Millon's reagent (a solution of mercuric and mercurous nitrates in nitric acid containing a little nitrous acid) followed by heating the solution give red precipitate or colour.

(d) **Ninhydrin reaction**. Proteins, peptides and α-amino acids give a characteristic blue colour on treatment with ninhydrin.

SECTION C

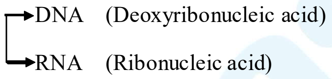
Nucleic Acid

(a) These are special type of acids which are present in nucleus & cytoplasma.

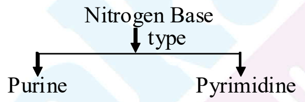
(b) Control the metabolic activities of cell.

(c) They are also found in mitochondria, centriole and chloroplast.

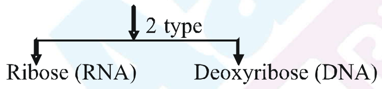
Types → These are of 2 types



(d) **Fischer** discovered Nitrogen bases in 1888



(e) **Levan** sugar

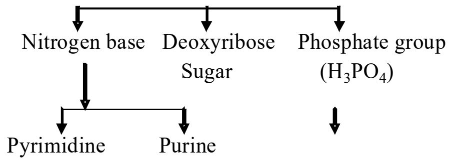


Deoxyribonucleic Acid (D.N.A.) :

(a) It is found in nucleus.

(b) They were also found on pneumococcus bacteria.

(c) DNA is made up of 3 units-



(i) Thymine	(i) Adenine
(ii) Cytosine	(ii) Guanine

(d) **Nucleoside**

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

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

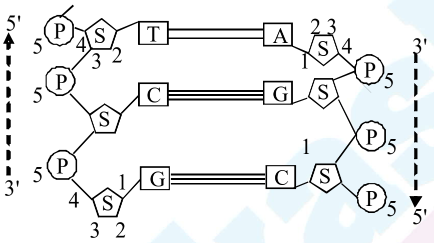
(i) Nucleotide

(a) Nitrogen base + Sugar + Phosphate → Nucleotide

(b) Nucleotide is a unit of DNA.

(c) All nucleotides combined and form a chain called polynucleotides by which RNA and DNA is formed.

Structure of DNA



(a) Double Helical model of DNA was proposed by biochemist **J.D.Watson**, British chemist **FHC Crick** in 1953.

(b) DNA in double stranded structure is made up of two chains of polynucleotides.

(c) DNA is a polymer of nucleotide.

(d) Nucleotide are joined by $3' \rightarrow 5'$ phosphodiester bonds.

(e) Sugar and phosphorous are alternately arranged.

(f) In both chains, in between A and T, 2 Hydrogen bonds are present while in C and G 3H bonds are present. $(A = T)$ $(C \equiv G)$

(g) A always attaches with T while C always attaches with G.

(h) Purine and pyrimidine are found in ratio 1 : 1.

(i) DNA is attached with histone protein.

(j) In prokaryotic cell and mitochondria circular DNA is present.

Function of DNA

(i) Self - Replication or Self -Duplication :

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

(ii) Protein Synthesis :

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

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

$$\text{DNA} \xrightarrow{\text{Replication}} \text{DNA} \xrightarrow{\text{Transcription}} \text{RNA} \xrightarrow{\text{Translation}} \text{Protein}$$

Ribonucleic Acid (RNA) :

⇒ Found in cytoplasm as well as in nucleus.

Cytoplasm → In the ribosome (heigher amount)

Chemical Nature :

⇒ Ribonucleic acid is a polymer of purine and pyrimidine ribonucleotides linked by 3' → 5' phosphodiester bridges. The number of nucleotides in RNA ranges from as **few as 75 to many thousands**. Although sharing many features with DNA, RNA possesses several specific difference.

⇒ As indicated by its name, sugar in RNA to which the phosphate and nitrogen- bases are attached is ribose rather than the deoxyribose of DNA.

⇒ Although RNA contains the ribonucleotides of adenine, guanine, and cytosine, it does not posses thymine. Instead of thymine, RNA contains the ribonucleotides of uracil. Thus the pyrimidine components of RNA differs from those of DNA.

⇒ RNA exists basically **as a single-stranded molecule** rather than as a double -stranded helical molecule, as DNA. However the single strand of RNA is capable of folding back on itself like a hairpin and thus acquiring double-stranded characteristics. In these regions, A pairs with U and G pairs with C.

Types of RNA and their Functions :

There are 3 main types of RNA molecules

(i) Messenger RNA (mRNA)
(ii) Transfer RNA (tRNA)
(iii) Ribosomal RNA (rRNA)

(i) Messenger RNA (mRNA) :

⇒ This type of RNA consists of **single strand** of variable length and serves as a template for protein synthesis. Codon in the chromosomes.

⇒ mRNA forms complementary copy of DNA as it carries **chemical messages in the form of nitrogen-base sequence from the nucleus to the ribosomes**, i.e. from **DNA to cytoplasm where proteins are synthesized**. Therefore, it is called messenger RNA or mRNA

⇒ mRNA is sythesised from DNA in the nucleus.

⇒ It is called **transcription**.

(ii) Ribosomal RNA (rRNA) :

⇒ A ribosome is a cytoplasmic nucleoprotein structure which serves as the organellar machinery for protein synthesis from mRNA templates.

⇒ On the ribosome, the mRNA and tRNA molecules interact to translate into a specific protein molecule, the information transcribed from the DNA.

⇒ rRNA constitutes the largest part of total RNA (Highest) - 80%

(iii) Transfer RNA (tRNA) :

⇒ These are also called **Soluble RNA**.

⇒ Single stranded.

⇒ 10-15% of the total RNA.

⇒ **Size** - **Smallest** → 75 - 80 nucleotides only.

⇒ **Synthesis** - Within **nucleus** from **DNA**.

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

Enzymes

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

Specific cheracteristics :

Enzymes have following two specific characters:

(i) Specificity (ii) Efficiency

Specificity of enzymes :

(a) Generally one enzyme can catalyze only one biochemical reaction.

(b) It can increase rate of reaction upto 10^{20} times.

(c) In some cases one enzyme can catalyzes more than one reaction and one reaction can be catalyzed by more than one enzyme.

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

Efficiency of enzymes :

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

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

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

Enzymes are denatured at higher temperature.

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

Importance of enzymes :

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

eg. Scarcity of **Phenylalanine** hydroxylase enzyme in human body can result in **Phenylketonuria** disease.

Factors affecting enzyme action :

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

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

(ii) Enzyme activators (co-enzymes). The activity of certain enzymes is increased in the presence of certain substances, called co-enzymes. It has been observed that if a protein contains a small amount of vitamin as the non-protein part, its activity is enhanced considerably. The activators are generally metal ions such as Na^+, Mn^{2+}, Cu^{2+}, Co^{2+} etc. These metal ions are weakly bonded to the enzyme molecules and increase their catalytic activity. For example, the enzyme, amylase, in presence of NaCl, which provides Na^+ ion, shows a very high catalytic activity.

(iii) **Enzyme inhibitors and poisons.** Just as in the case of catalysts, the activity of enzyme is slowed down in the presence of certain substance. Such substances are called inhibitors or poisons. They act by combining with the active functional group thereby reducing or completely destroying the catalytic activity of the enzymes. The use of many drugs is on account of their action as enzyme inhibitors in our body.

Zinc :

(i) Zinc is a constituent of carbonic anhydrase, present in RBCs helping in CO_2 transport.

(ii) Zinc is a component to lactic dehydrogenase, important for the interconversion between pyruvic acid and lactic acid

(iii) Zinc is a component part of some peptidases, therefore is is important for digestion of proteins in the alimentary canal

Cobalt

(i) Cobalt helps in erythropoiesis and in the activities of some enzymes.

(ii) It is present in vitamin B_{12}.

Copper

(i) Copper helps in the utilisation of iron.

(ii) Copper deficiency may produce anaemia because of failure in iron utilisation.

Molybdenum

(i) Molybdenum is a constituent of oxidase enzymes (xanthine oxidase)

(ii) Molybdenum plays an important role in biological nitrogen fixation

Fluorine

(i) Fluorine maintains normal dental enamel and prevents dental caries.

(ii) Excessive intake of fluorine cause fluorosis characterized by mottled teeth and enlarged bones.

Vitamins

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

Classification of Vitamins

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

(i) Fat soluble vitamins:

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

(ii) Water soluble vitamins:

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

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

S.N.	Name of Vitamins	Source	Deficiency Diseases
1	Vitamin A (Retinol)	Fish liver oil, carrots, butter and milk	Xerophthalmia (hardening of cornea of eye) Night blindness
2	Vitamin B1 (Thiamine)	Yeast, milk, Green vegetables and cereals and grams	Beri Beri (loss of appetite, retarded growth)
3	Vitamin B2 (Riboflavin)	Milk, egg white, liver, Kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin
4	Vitamin B6 (Pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
5	Vitamin B12 (Cyanocobal-amine)	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin)
6	Vitamin C (Ascorbic acid)	Citrus fruits, amla and green leafy vegetables	scurvy (bleeding gums)
7	Vitamin D (Calciferol)	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)
8	Vitamin E or Tocopherol (a, b and g) or Antisterility factor	Eggs, Milk, Fish, Wheat germ oil colton seed oil etc.	Sterility (loss of sexual power and reproduction)
9	Vitamin K	Green leafy vegetables, Broccoli, Cauliflower, Cabbage, Meat, Fish, Eggs	Bone dovelepment reduces, osteoporosis, Cardiovascular diseases, Increase time for blood clotting

SECTION D

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 molecules of a compound M, linking in a linear manner will form polymer x–M–$(M)_{n-2}$–M–y. The nature of linkages at the terminal units i.e. M–x and M–y depends upon the mode of reaction used in making the polymers.

Homopolymers and Copolymers :

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

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

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–6,6	Hexamethylene diamine and Adipic acid
Terylene	Terephthalic acid and ethylene glycol

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

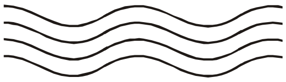
(3) Synthetic polymers :

Man-made polymers, i.e. polymers prepared in laboratory are known as synthetic polymers. Example are : PVC, polyethylene, polystyrene, nylon-6, nylon-6,6, nylon-6,10, terylene, synthetic rubbers etc.

(II) CLASSIFICATION BASED UPON SHAPE

(1) Linear polymers :

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



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

Note :

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

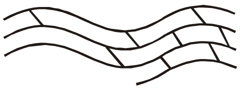
(ii) Linear polymers may be condensation as well as addition polymers. Examples are cellulose, polypeptide, nucleic acid, nylon, terylene etc.

(2) Branched chain polymers :

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

(3) Cross-linked or Three Dimensional network polymers

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



CLASSIFICATION BASED UPON SYNTHESIS

(1) Condensation polymerisation

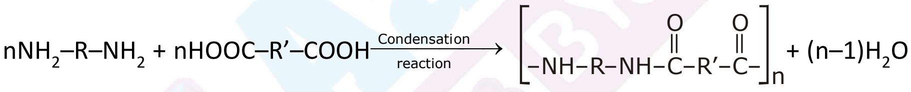
(i) They are formed due to condensation reactions.

(ii) Condensation polymerisation is also known as step growth polymerisation.

(iii) For condensation polymerisation, monomers should have at least two functional groups. Both functional groups may be same or different.

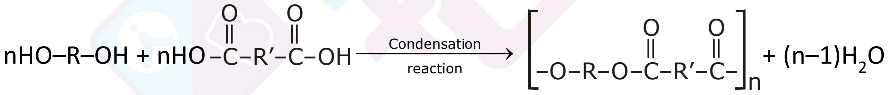
(iv) Monomers having only two functional group always give linear polymer.

For example,



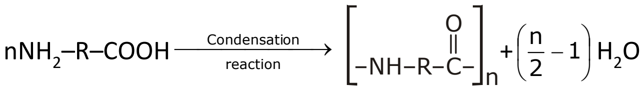
$$nNH_2{-}R{-}NH_2 + nHOOC{-}R'{-}COOH \xrightarrow[\text{reaction}]{\text{Condensation}} \left[-NH-R-NH-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}-\right]_n + (n-1)H_2O$$

Polyamide



$$nHO{-}R{-}OH + nHO-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\text{reaction}]{\text{Condensation}} \left[-O-R-O-\overset{O}{\overset{\|}{C}}-R'-\overset{O}{\overset{\|}{C}}-\right]_n + (n-1)H_2O$$

Polyester



$$nNH_2{-}R{-}COOH \xrightarrow[\text{reaction}]{\text{Condensation}} \left[-NH-R-\overset{O}{\overset{\|}{C}}-\right]_n + \left(\frac{n}{2}-1\right)H_2O$$

(v) Condensation polymers do not contain all atoms initially present in the monomers. Some atoms are lost in the form of small molecules.

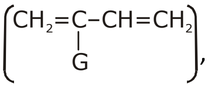
(vi) Monomer having three functional groups always gives cross-linked polymer. Examples are : Urea-formaldehyde resin, phenol-formaldehyde resin.

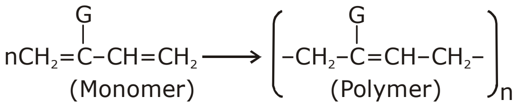
(2) Addition polymerisation :

(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  $\left(CH_2=\underset{\underset{G}{|}}{C}-CH=CH_2\right)$, then polymer is always branched chain polymer.



$$nCH_2=\overset{\overset{G}{|}}{C}-CH=CH_2 \longrightarrow \left[-CH_2-\overset{\overset{G}{|}}{C}=CH-CH_2-\right]_n$$

(Monomer) (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.

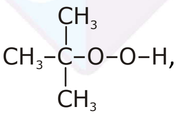
(vi) Addition polymers are called as chain growth polymers.

Types of Addition Polymerization

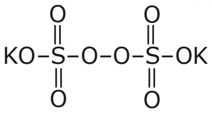
(A) Radical Polymerisation:

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

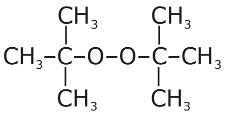
H_2O_2,



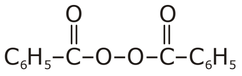
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-O-H$,



$KO-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-OK$

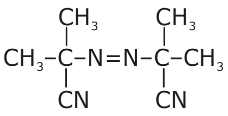


$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$



$C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5$

and



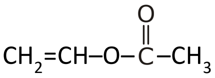
$CH_3-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-N=N-\underset{\underset{CN}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

(ii) Reaction intermediate of radical polymerization is a free radical.

(iii) Radical polymerization occures mostly in those monomers whose free radicals are more stable.

Examples are:

$C_6H_5-CH=CH_2$,	$CH_2=CH-Cl$,
Styrene	Vinyl chloride

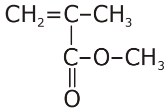


$$CH_2=CH-O-\overset{\overset{O}{\|}}{C}-CH_3$$

Vinyl acetate

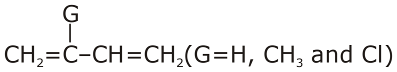
$CH_2=CH-CN$

Acrylonitrile
(vinyl cyanide)



$$\begin{array}{l} CH_2=C-CH_3 \\ \qquad\;\; | \\ \qquad\;\; C-O-CH_3 \\ \qquad\;\; \| \\ \qquad\;\; O \end{array}$$

Methyl methacrylate



$$CH_2=\overset{\overset{G}{|}}{C}-CH=CH_2 (G=H,\ CH_3 \text{ and } Cl)$$

2-substituted-1,3-butadiene

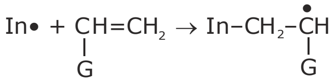
(iv) Radical polymer has linear as well as branched chain structure

Most of the commercial addition polymers are vinyl polymers obtained from alkenes and their derivatives $CH_2=\underset{\underset{G}{|}}{CH}$ [G is H, C_6H_5, R etc.]

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

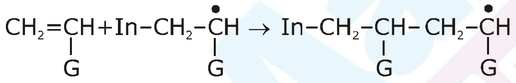
Chain initiation step :

Initiator → In •

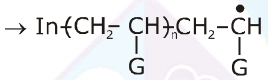


$$In\bullet + \underset{\underset{G}{|}}{CH}=CH_2 \rightarrow In-CH_2-\underset{\underset{G}{|}}{\overset{\bullet}{C}H}$$

Chain propagating step :

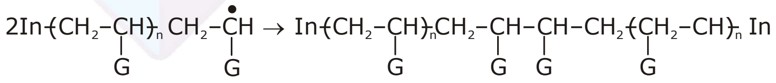


$$CH_2=\underset{\underset{G}{|}}{CH}+In-CH_2-\underset{\underset{G}{|}}{\overset{\bullet}{C}H} \rightarrow In-CH_2-\underset{\underset{G}{|}}{CH}-CH_2-\underset{\underset{G}{|}}{\overset{\bullet}{C}H}$$



$$\rightarrow In\{CH_2-\underset{\underset{G}{|}}{CH}\}_n CH_2-\underset{\underset{G}{|}}{\overset{\bullet}{C}H}$$

Chain terminating step :



$$2In\{CH_2-\underset{\underset{G}{|}}{CH}\}_n CH_2-\underset{\underset{G}{|}}{\overset{\bullet}{C}H} \rightarrow In\{CH_2-\underset{\underset{G}{|}}{CH}\}_n CH_2-\underset{\underset{G}{|}}{CH}-\underset{\underset{G}{|}}{CH}-CH_2\{\underset{\underset{G}{|}}{CH_2-CH}\}_n In$$

Polymer

(i) Addition polymerisation which takes place in the presence of Ziegler- Natta catalyst [$(C_2H_5)_3Al$ and $TiCl_4$] is known as Ziegler- Natta polymerisation or co-ordination polymerisation.

(ii) Ziegler- Natta polymerisation always gives linear, stereo-regular polymers.

(iii) Ziegler- Natta catalyst revolutionised the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers (due to linear geometry) that have greater resistance to cracking and heat. High density polyethylene is prepared using a Ziegler- Natta catalyst.

Classification based on intermolecular forces (secondary forces)

(i) Intermolecular forces present between polymeric chains are (a) Vander waals forces (b) Hydrogen bonds and (c) Dipole - dipole attractions.

(ii) Mechanical properties such as tensile strength, elasticity, toughness etc. depend upon the secondary force present between the polymeric chains.

(iii) Magnitude of secondary forces depends upon the size of the molecule and the number of functional groups along the polymeric chains.

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

(1) Elastomers :

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

When elastomers are stretched, the random chains stretch out, but there are insufficient Vander 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

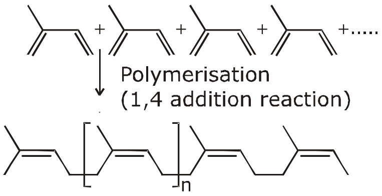
S.N.	**Thermoplastic polymers**	**Themosetting polymers**
1.	Soften and melt on heating and become hard on cooling i.e. process is reversible	Become hard on heating and process is irreversible.
2.	Can be moulded and remoulded and or reshaped.	They can be moulded once and cannot be remoulded reshaped.
3.	They are addition polymers polymers.	They are condensation
4.	Structure is generally linear	Structure is cross - linked.

Rubber

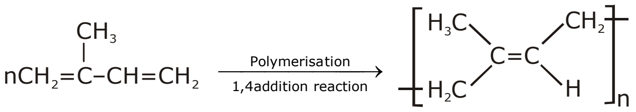
1. Natural Rubber :

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

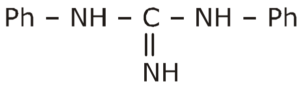
The raw natural rubber is a soft gummy and sticky mass. It is insoluble in water, dilute acids and alkalies but soluble in non-polar solvents. It has low elasticity and low tensile strength. Natural rubber is a polymer of 2-methyl-1, 3-butadiene (isoprene). On average, a molecule of rubber contains 5000 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 are trans. Thus, gutta-percha is trans-polyisoprene.

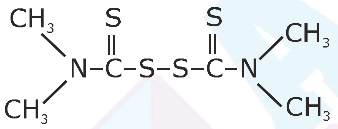


It is harder and more brittle than rubber. It is filling material that dentists use in root canal treatment. In order to give strength and elasticity to natural rubber, it is vulcanized. Heating of rubber with sulphur or sulphur as vulcanisation. The essential feature of the vulcanisation is the formation 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:



$$Ph-NH-\underset{\underset{NH}{\parallel}}{C}-NH-Ph$$

Diphenyl guanidine



Tetramethylthioureadisulphide

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

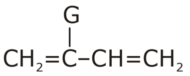
Syntehic rubber or polymerisation of dienes

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.

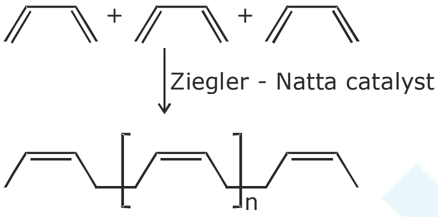
1. **Homopolymers :**

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



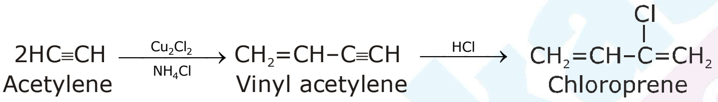
$CH_2=\overset{\overset{\displaystyle G}{|}}{C}-CH=CH_2$ where G=H, CH_3 or Cl.

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



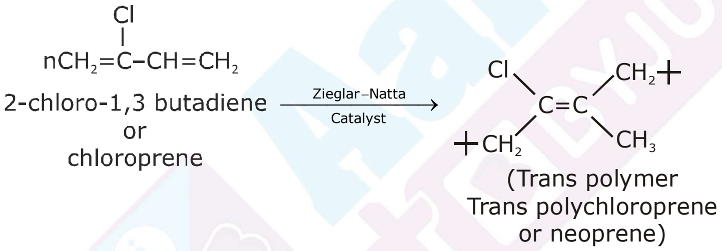
cis poly (1,3 butadiene)

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



$$\underset{\text{Acetylene}}{2HC\equiv CH}\xrightarrow[NH_4Cl]{Cu_2Cl_2}\underset{\text{Vinyl acetylene}}{CH_2=CH-C\equiv CH}\xrightarrow{HCl}\underset{\text{Chloroprene}}{CH_2=CH-\overset{\overset{\displaystyle Cl}{|}}{C}=CH_2}$$

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



(Trans polymer
Trans polychloroprene
or neoprene)

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 along with Monomers

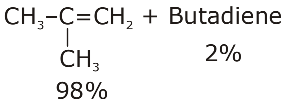
1. Buna-S, SBR (styrene-Butadiene rubber)

$C_6H_5-CH=CH_2$ + $CH_2=CH-CH=CH_2$
(25%) (75%)

2. Buna-N, NBR (Nitrile-Butadiene rubber)

$CH_2=CH-CN$ + $CH_2=CH-CH=CH_2$
(25%) (75%)

3. Butyl rubber



$$\underset{98\%}{CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2} + \underset{2\%}{\text{Butadiene}}$$

4. ABS; Acrylonitrile, Butadiene, Styrene

$CH_2=CH–CN + CH_2=CH–CH=CH_2 + C_6H_5CH=CH_2$

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

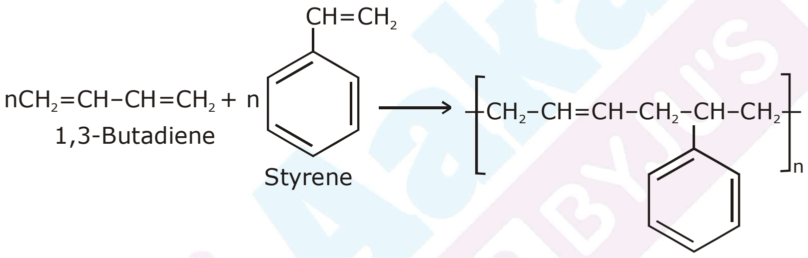
$$Cl-CH_2-CH_2-Cl + Na-S-S-Na + Cl-CH_2-CH_2-Cl$$
$$\Big\downarrow \text{Polymerisation}$$
$$-CH_2-CH_2-S-S-CH_2-CH_2-S-S-CH_2-CH_2-$$

Thiokol rubber

The repeating unit is $–CH_2–S–S–CH_2–$

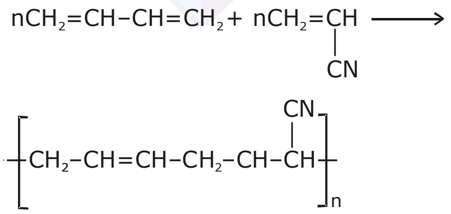
Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

(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 GSR).



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

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



$$nCH_2=CH-CH=CH_2 + nCH_2=\underset{CN}{\underset{|}{CH}} \longrightarrow \left[CH_2-CH=CH-CH_2-CH-\overset{CN}{\overset{|}{CH}}\right]_n$$

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

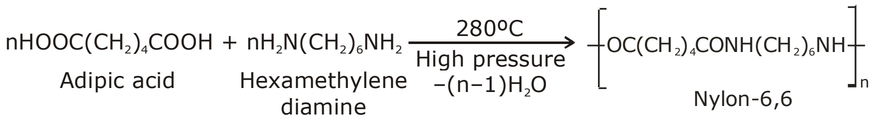
(d) Cold Rubber : Cold rubber is obtained by polymerization of butadiene and styrene at –18° to 5°C temperature in the presence of redox system. Cold rubber has a greater tensile strength and greater resistance to abrasion than SBR.

Nylon

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

(1) NYLON -6,6 (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).

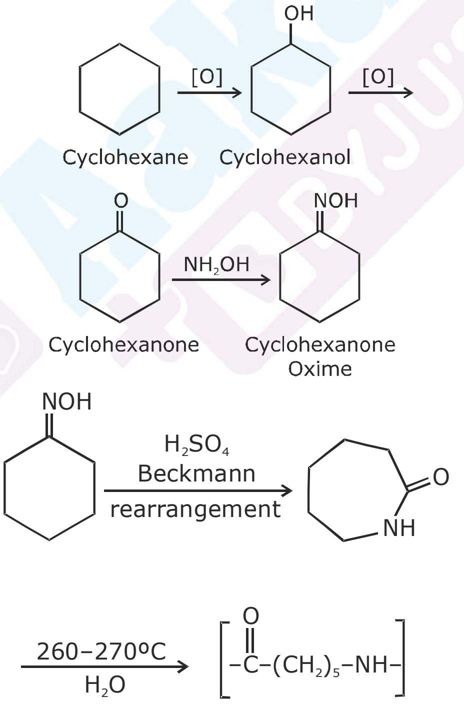


$$\underset{\text{Adipic acid}}{nHOOC(CH_2)_4COOH} + \underset{\substack{\text{Hexamethylene}\\ \text{diamine}}}{nH_2N(CH_2)_6NH_2} \xrightarrow[\substack{\text{High pressure}\\ -(n-1)H_2O}]{280^oC} \underset{\text{Nylon-6,6}}{\left[OC(CH_2)_4CONH(CH_2)_6NH \right]_n}$$

(2) 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 260º-270ºC. 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, which 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 to form the polyamide polymer.

Carpolactam is obtained by Backmann rearrangement of cyclohexanone oxime.



(six carbon atoms in the repeating units)
Nylon-6

(3) NYLON-2 – NYLON-6

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

Polyethelene

Polyethylene is of two types:

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

$$nCH_2{=}CH_2 \xrightarrow[\text{1500 atm.}]{200^\circ C} \left[CH_2{-}CH_2 \right]_n$$

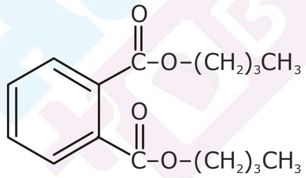
The polyethylene produced has a molecular mass of about 20,000 and has a branched structure. Due to this, polyethylene has a low density (0.92) and low melting point (110ºC). That is why polyethylene prepared by free radical polymerisation is called low density polyethylene. It is a transparent polymer 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 160ºC under pressure of 6 to 7 atmosphere.

The polymer is linear chain, hence it has high density (0.97) and has high melting point (130ºC). 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.

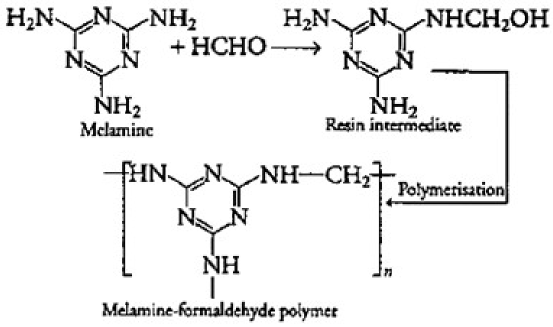
Plasticier

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

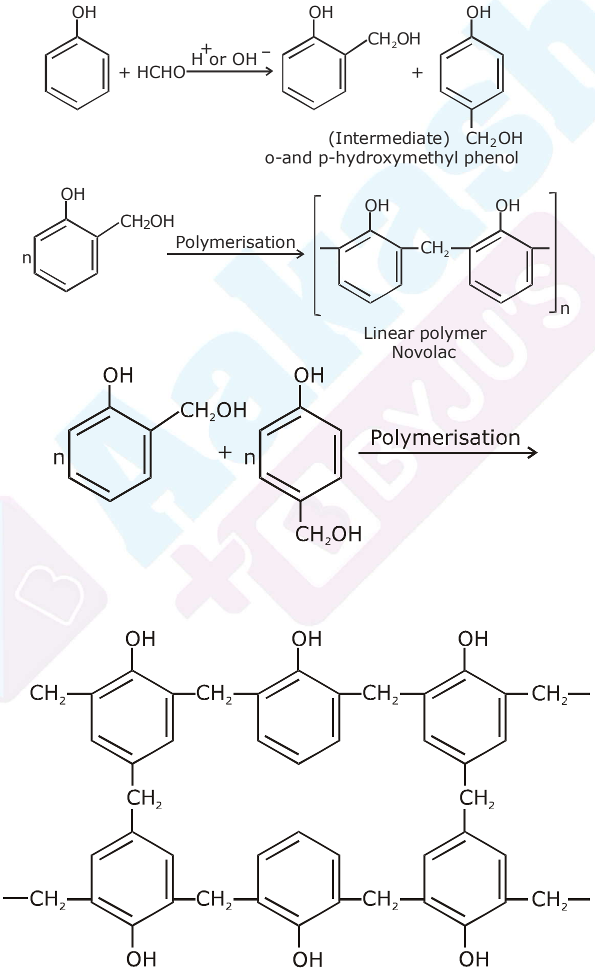
This resin is formed by condensation polymerisation of melamine and formaldehyde.



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

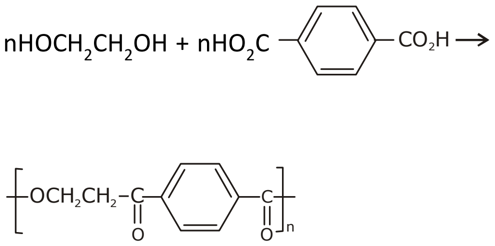
Phenol-formaldehyde resins are obtained by the reaction of phenol and formaldehyde in the presence of either an acid or a basic catalyst. The reaction starts with the initial formation of ortho and para-hydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with –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.



Cross-linked polymer (Bakelite)

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.



Dacron

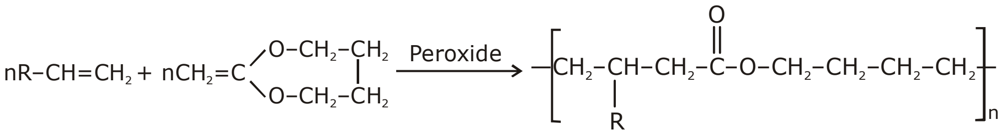
The terylene fibre (Dacron) is crease resistant and has low moisture absorption. It has high tensile strength. It is mainly used in making wash and wear garments, in blending with wood to provide better crease and wrinkle resistance.

Biodegradable polymers

By far the largest use of synthetic polymers is as plastic. A major portion of it is used as throwaway containers and packing materials. Since plastics do not disintegrate by themselves, they are not biodegradable over a period of time. Non-biodegradability is due 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.



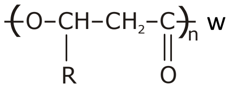
Ester linkage attacked by enzyme

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

(1) Poly - β -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.

$CH_3–CH(OH)–CH_2–COOH+ CH_3–CH_2–CH(OH)–CH_2–COOH \rightarrow$



$$\left(\!\!-O-\underset{\displaystyle R}{\underset{|}{C}}H-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-\!\!\right)_n$$ where R = CH_3, C_2H_5

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

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

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

MOLECULAR MASS OF POLYMER

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

The molecular mass of a polymer is expressed as

$(\overline{M}_n)$

$$\overline{M}_n = \frac{\sum N_i M_i}{\sum_i N_i}$$ Where N_i is the number of molecules of molecular mass M_i

(b) Weight average molecular mass $(\overline{M}_w)$

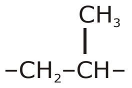
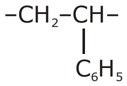
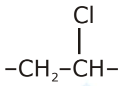
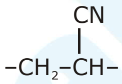
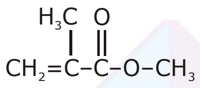
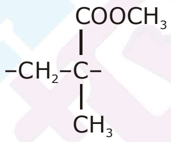
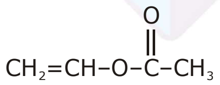
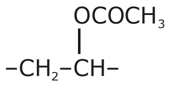
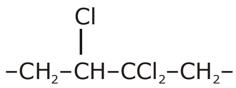
$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum_i N_i M_i}$$

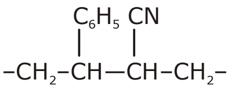
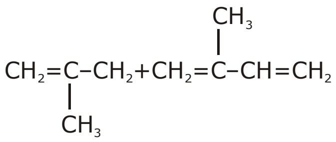
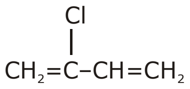
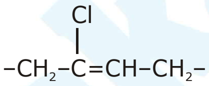
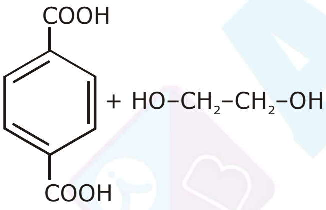
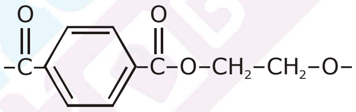
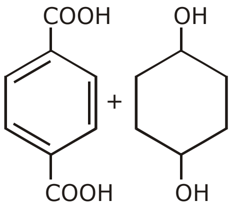
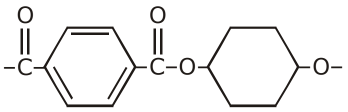
Where N_i is the number of molecules of molecular mass M_i. Methods such as light scattering and ultracentrifuge depend on the mass of individual molecules and yield weight average molecular masses. $\overline{M}_n$ is determined by employing methods which depend upon the number of molecules present in the polymer sample viz. colligative properties like osmotic pressure.

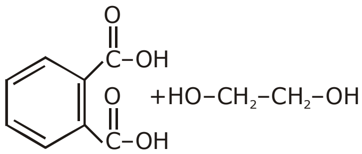
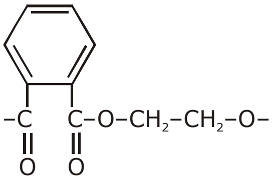
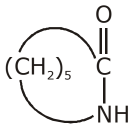
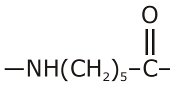
The ratio of the weight and number average molecular masses $(\overline{M}_w/\overline{M}_n)$ is called Poly Dispersity Index (PDI). Some natural polymers, which are generally monodispersed, the PDI is unity (i.e. $\overline{M}_w = \overline{M}_n$).

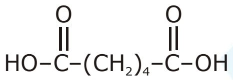
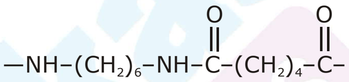
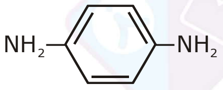
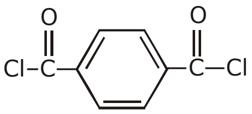
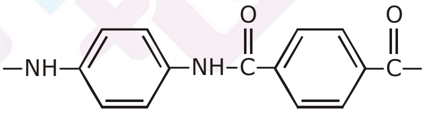
In synthetic polymers, which are always polydispersed, PDI > 1 because it is always higher than $\overline{M}_n$.

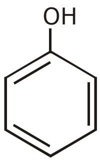
3.35 COMMON POLYMERS

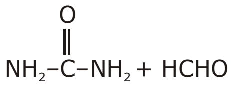
	Monomer	**Repeating unit**	**Polymer**
1.	$CH_2=CH_2$ Ethylene	$-CH_2-CH_2-$	Polyethylene
2.	$CH_3-CH=CH_2$ Propene	 $-CH_2-\overset{CH_3}{\overset{\vert}{CH}}-$	Polypropene
3.	$C_6H_5-CH=CH_2$ Styrene	 $-CH_2-\underset{C_6H_5}{\underset{\vert}{CH}}-$	Polystyrene
4.	$CF_2=CF_2$ Tetrafluoroethylene	$-CF_2-CF_2-$ ethylene (PTFE), Teflon	Polytetrafluoro
5.	$CH_2=CH-Cl$ Vinyl chloride	 $-CH_2-\overset{Cl}{\overset{\vert}{CH}}-$	Polyvinyl Chloride (PVC)
6.	$CH_2=CH-CN$ Vinyl cyanide	 $-CH_2-\overset{CN}{\overset{\vert}{CH}}-$ poly acrylonitrile,	Polyvinyl cyanide, Acrylonitrile Orlon.
7.	 $CH_2=\overset{H_3C}{\overset{\vert}{C}}-\overset{O}{\overset{\Vert}{C}}-O-CH_3$ Methyl methacrylate	 $-CH_2-\overset{COOCH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{C}}}}-$ Plexiglas, Lucite	Polymethyl methacrylate,
8.	 $CH_2=CH-O-\overset{O}{\overset{\Vert}{C}}-CH_3$ Vinyl acetate	 $-CH_2-\overset{OCOCH_3}{\overset{\vert}{CH}}-$	Polyvinyl Acetate
9.	$CH_2=CH-CH=CH_2$ 1, 3-butadiene	$-CH_2-CH=CH-CH_2-$ Buna rubber	Polybutadiene,
10.	$CH_2=CH-Cl$ (vinyl chloride) + $CH_2=CCl_2$ (Vinylidene chloride)	 $-CH_2-\overset{Cl}{\overset{\vert}{CH}}-CCl_2-CH_2-$	Saran

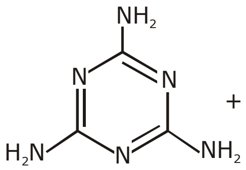
11.	$C_6H_5-CH=CH_2$ (Styrene) + $CH_2=CH-CN$ (acrylonitrile)	 $-CH_2-\overset{\overset{C_6H_5}{\vert}}{CH}-\overset{\overset{CN}{\vert}}{CH}-CH_2-$	SAN
12.	$CH_2=CH-CN + CH_2=CH-CH=CH_2$ + $C_6H_5-CH=CH_2$	–	ABS
13.	 $CH_2=\underset{\underset{CH_3}{\vert}}{C}-CH_2+CH_2=\overset{\overset{CH_3}{\vert}}{C}-CH=CH_2$	–	Butyl rubber
14.	$C_6H_5-CH=CH_2+CH_2=CH-CH=CH_2$	–	Buna-S, SBR
	Monomer	**Repeating unit**	**Polymer**
15.	$CH_2=CH-CN + C_6H_5-CH=CH_2$	–	Buna-N, NBR
16.	 $CH_2=\overset{\overset{Cl}{\vert}}{C}-CH=CH_2$ Chloroprene	 $-CH_2-\overset{\overset{Cl}{\vert}}{C}=CH-CH_2-$	Neoprene
17.			Poly(ethylene terephthalane) Terylene, Dacron or Mylar
18.			Kodel Polyster

19.	 phthatate alkyd resin (Glyptal)		Polyethylene
20.	 Caprolactam	 $-NH(CH_2)_5-\overset{O}{\overset{\|}{C}}-$	Nylon-6

	Monomer	**Repeating unit**	**Polymer**
21.	$NH_2(CH_2)_6-NH_2$ Hexamethylenediamine +  $HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH$ Adipic Acid	 $-NH-(CH_2)_6-NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-$	Nylon-6,6
22.	 1, 4-Diaminobenzene +  Terephthaloyl chloride		Kelvar

23.  + HCHO – Bakelite or resol

24. 
$NH_2-\overset{\overset{O}{\|}}{C}-NH_2$ + HCHO – Urea-formaldehyde resin

25.  + HCHO – Melamine formaldehyde resin

Malamine

Practical organic chemistry

(A) FUNCTIONAL GROUP ANALYSIS

1. Unsaturation : Alkenes & alkynes :

(a) Baeyers test : Cold dilute alk. $KMnO_4$ decolourisation test
Purple colour → Colourless + MnO_2 (Brown ppt)

(b) Br_2 water decolourisation test
Violet colour of Br_2 → Colourless

2. Terminal alkynes :
Confirmed by precipitate of Acetylide ion with $NaNH_2$ or $AgNO_2$ or Cu_2Cl_2/NH_4OH

3. Alkyl halides :

(a) If they are capable of carbocation formation then they will give ppt with $AgNO_3$.

(b) Beilstein's test : A green colour is imported to the flame if small amount of organic compound is taken on copper wire.

4. Alcohol :

(a) Cerric ammonium nitrate → Give red colour

(b) Boil with acetic acid & conc. H_2SO_4 → fruity smell

(c) 2-alkanol & ethanol also give Iodoform test → Yellow ppt. of CH_3I on reaction with $I_2 + {}^{-}OH$

5. Aldehyde & ketones :
2,4-Dinitrophenyl hydrazine (or) Brady's reagent give yellow, orange or red colour with aldehyde & ketones (2, 4-DNP)

6. Aldehydes :

(a) Tollen's test → Silver mirror

(b) Fehling's test {except benzaldehyde} → Red colour

(c) Benedicts test → Red colour

(d) Schiff's dye colour regeneration test → Pink colour

(e) Grey or black precipitate 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 → 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 → Isonitriles have very distinctive foul odour

(b) Hoffmann mustard oil reaction → Oily liquid with mustard like smell.

11. Aromatic 1º amine → diazo test

12. Amide boil with NaOH → NH_3

13. Nitrobenzene → Mullikan Baker test → Treat it with Zn + NH_4Cl then boil with Tollen's reagent → Silver mirror will appear

14. Proteins :

(a) Biuret test : Also used for urea → Alkaline solution of protein treated with a drop of aq $CuSO_4$, bluish violet colour is obtained

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

DIFFERENTIATION TEST

D1. 1º, 2º & 3º alcohols :

(a) Lucas test : Lucas reagent is conc. HCl + $ZnCl_2$

(b) Victor Meyer's test (RBC test)

(i) 1º Alcohol → Blood red colour

(ii) 2º Alcohol → Blue

(iii) 3º Alcohol → Colourless

D2. 1º, 2º & 3º amines :

(a) Hinsberg’s reagent

(i) 1º Amine yield a clear solution from which upon acidification an insoluble material was separated.

(ii) 2º Amine yield an insoluble compound which is unaffected by acid

(iii) 3º Amine yield insoluble compound

(b) Reaction with HNO_2.

1. Natural rubber is a polymer of:

(1) Chloroprene (2) Isoprene

(3) 1,3-Butadiene (4) None

Ans. **(2)**

Sol. Isoprene (2-methyl-1,3-butadiene) is the monomer of natural rubber.

2. Hydroylsis of sucrose is called:

(1) Saponification (2) Inversion

(3) Esterification (2) Hydration

Ans. **(2)**

Sol. When sucrose is hydrolysed, the direction of rotation of plane polarised light is inverted so it called inversion of sucrose.

3. In vulcanization of rubber:

(1) Sulphur reacts to form a new compound

(2) Sulphur cross-links are introduced

(3) Sulphur forms a very thin protective layer over rubber.

(4) All statements are correct.

Ans. **(2)**

Sol. In vulcanization of rubber sulphur cross-links are introduced.

4. Which of the following belong to the class of natural polymers ?

(1) Proteins (2) Cellulose

(3) Rubber (4) All of the above

Ans. **(4)**

Sol. Naturally occuring polymers are silk, natural rubber, wool, cellulose and protiens.

5. The reaction of glucose and red P + HI is called:

(1) Sandmeyer’s reaction (2) Reformatsky reaction

(3) Gattermann’s reaction (4) Reduction

Ans. **(4)**

Sol. The reaction of glucose and red P + HI is called reduction.

Red P + HI $\longrightarrow$ Reducing agent.

6. The reagent used in Ruff degradation is :

(1) Baeyer’s reagent (2) Tollen’s reagent

(3) Fenton’s reagent (4) Benedict’s reagent

Ans. (3)

Sol. The reagent used in Ruff degradation is Fenton's reagent.

Fenton's reagent $\longrightarrow H_2O_2, Fe_2(SO_4)_3$

Ruff's degradation is the shootening of carbohydrate chain.

7. Number of possible isomers of glucose is:

(1) 10 (2) 14 (3) 16 (4) 20

Ans. (3)

Sol. Number of possible isomer of glucose is 16.

Number of chiral carbon in glucose is 4.

So, number of possible isomers is $4^2 = 16$.

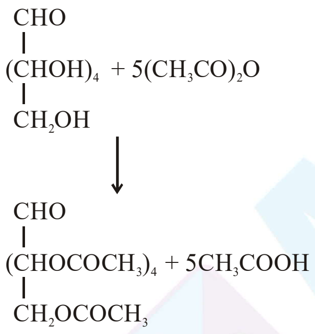
8. Glucose reacts with acetic anhydride to form:

(1) Monoacetate (2) Tetra acetate

(3) Penta acetate (4) Hexa acetate

Ans. (3)

Sol. Glucose has five hydroxy group in it.



$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 + 5(CH_3CO)_2O \\ | \\ CH_2OH \end{array} \longrightarrow \begin{array}{l} CHO \\ | \\ (CHOCOCH_3)_4 + 5CH_3COOH \\ | \\ CH_2OCOCH_3 \end{array}$$

9. Glucose or aldohexose contains:

(1) One –CHO group

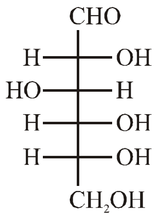
(2) Five –OH groups

(3) One primary alcoholic group and four secondary alcoholic groups

(4) All are correct

Ans. (4)

Sol.



Glucose

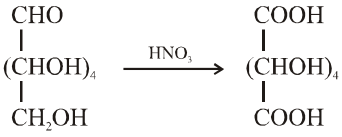
10. When glucose is heated with nitric acid, the product is:

(1) Gluconic acid (2) Glucaric acid

(3) Glycolic acid (4) Oxalic acid

Ans. **(2)**

Sol.



$$\begin{array}{c} \text{CHO} \\ | \\ (\text{CHOH})_4 \\ | \\ \text{CH}_2\text{OH} \end{array} \xrightarrow{\text{HNO}_3} \begin{array}{c} \text{COOH} \\ | \\ (\text{CHOH})_4 \\ | \\ \text{COOH} \end{array}$$

Glucaric acid
or
Saccharic acid

11. Cane sugar is made of:

(1) 5 membered glucose ring and 5 membered fructose ring

(2) 6 membered glucose ring and 6 membered fructose ring

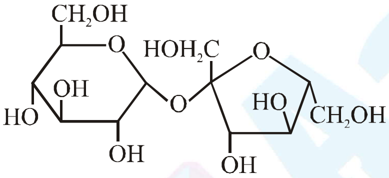
(3) 6 membered glucose ring and 5 membered fructose ring

(4) 6 membered galactose ring and 6 membered fructose ring

Ans. **(3)**

Sol. Cane sugar is sucrose.

It composed of 6 membered glucose ring and 5 membered fructose ring.



Sucrose

CHEMISTRY IN EVERYDAY LIFE

Chemical in Medicines

Chemotherapy :

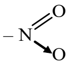
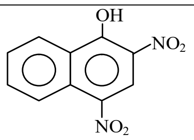
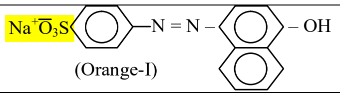
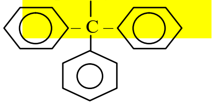
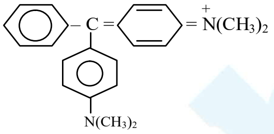
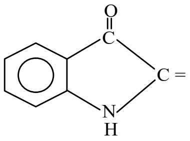
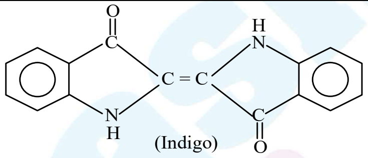
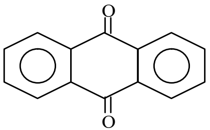
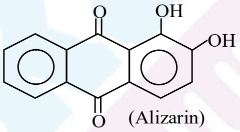
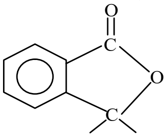
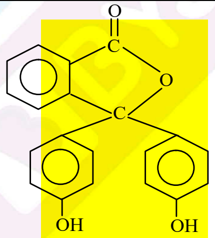
The branch of science which deals with the treatment of diseases using suitable chemicals is known as **chemotherapy**.

Classification of Medicines :

Medicines are generally classified according to the purpose for which they are used. The different terms thus used along with examples are given below :

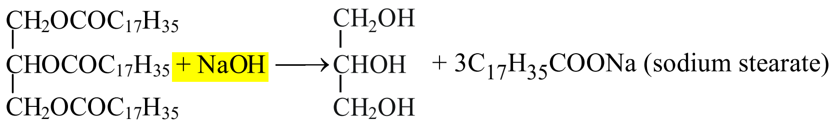
Class of Drugs	Mode of action and Uses	Example
Antipyretics	Bring down the body temperature during high fever	Antipyretics are Aspirin, Phenacetin, Paracetamol, Novalgin, and Quinine
Antimalarials	Bring down the body temperature during malaria fever	Quinine, Nowadays, Chloroquine, Paraquine, and Primaquine etc
Analgesics	Getting relief from pain	
(i) Narcotics	Produce sleep and unconsciousness	Morphine (commonly known as heroin), Codeine
(ii) Non-narcotics	Give immediate relief from pain and fever	Aspirin, Phenacetin, Novalgin, butazolidine and ibuprofen
Antiseptics	Kill or prevent the growth of micro-organisms Safely applied on wounds, cuts, ulcers, diseased skin surfaces	0.2% solution of phenol, Chloroxylenol, dettol, bithional, tincture of iodine, some organic dyes (Gentian violet and methylene blue), chlorine.
Disinfectants	Kill micro-organisms but cannot be applied on living tissues Commonly applied to inanimate objects such as floors, instruments	1% solution of phenol
Tranquilizers	They are neurologically active drugs. Acts on the central nervous system by blocking the neurotransmitter dopamine in the brain. **Uses :** Treatment of stress, anxiety, depression, sleeps disorders and severe mental diseases like schizophrenia	
(i) Hypnotics	Reduce mental tension and anxiety, induced sleep	Barbituric acid, luminal, Haloperiodol, clozapine
(ii) Non-hypnotics	Reduce tension and anxiety, do not induced sleep	Chlordiazepoxide, Meprobamate, Diazepam (Valium), alprazolam
Antidepressants	Mood booster drugs	Vitalin, Cocaine, Methedrine

Class of Drugs	Mode of action and Uses	Example
Antibiotics	In microorganism, fungi and moulds or even destroy them. **Uses :** Relief allergy (Sensitivity), Gonorrhoea, rheumatic fever, local infections	Penicilline, Streptomycin, Ampicillin and Amoxycillin
Broad spectrum antibiotics	Used for curing typhoid, acute fever, dysentery, whooping cough, pneumonia, eye infection, certain urine infection	Tetracycline chloromycetin and chloramphenicol
Sulpha drugs	Used against pneumonia, tuberculosis, diphtheria	Sulphadiazine, sulphanilamide
Germicides	Kill germs, fungi and virus	Phenol, cresols, formaldehyde, DDT, potassium permanganate solution, (1%) chlorine, bleaching powder, hydrogen peroxide
Anti-–fertility drugs	These synthetic hormones that suppresses ovulation/fertilisation. **Uses :** Used in birth control pills	**Synthetic oestrogen :** Ethynylestradiol, menstranol **Progesterone :** Norethindrone, Norethynodrel
Antihistamines	Used to fight allergy, hay fever, conjunctivitis, nasal discharges, irradation sickness, motion sickness (air, sea, road), nausea in pregnancy and post operative vomiting	Diphenhydramine hydrochloride, Cetrizine, Chlorpheniramine, Promethazine hydrochloride
Antacids **(i) Systemic antacids** (Sodium bicarbonate) **(ii) Non-systemic antacids** ($Al(OH)_3$, $Mg(OH)_2$, $MgCO_3$, $CaCO_3$)	They have acid (hydrochloric acid) neutralising capacity	

Dyes	
Classification of dyes	**Example**
(i) Natural dyes	Indigo (a blue dye) and alizarin (a red dye)
(ii) Synthetic dyes	Coal-tar dye
Classification of Dyes based on their Constitution (Chemical classification)	
1. Nitro dyes 	 (Martius yellow)
2. Azo dyes $-N=N-$ (Azo)	 (Orange-I)
3. Triphenylmethane dyes  (Triphenylmethane)	 (Malachite green)
4. Indigoid dyes  (Indigoid)	 (Indigo)
5. Anthraquinone dyes  (Anthraquinone)	 (Alizarin)
6. Phthalein dyes  (Phthalein)	 (Phenolphthalein)

Classification of dyes on the basis of their applications	Uses	Example
(i) Acid dyes	Used to dye wool, silk, nylon and acrylic fibres	orange – I, orange – II, methyl orange, methyl red and congo red
(ii) Basic dyes	Modified nylons and polyesters can be dyed	aniline yellow, butter yellow, chrysodine G (structures given below) and malachite green
(iii) Direct dyes	Usually used for dyeing cotton, wool, silk, rayon and nylon	Stilben, phthalocyanine and dioxazine.
(iv) Disperse dyes	Used to dye synthetic fibres such as nylons, polyesters and polyacrylonitrile fibres	monoazo dyes and anthraquinone dyes [(i) Celliton fast pink B and (ii) Celliton fast blue B]
(v) Fibre reactive dyes	Cotton, wool or silk can be dyed	Derivative of 2, 4–Dichloro–1, 3, 5– triazine
(vi) Ingrain dyes	Cotton, silk, nylon and polyester can be dyed	para red
(vii) Vat dyes	Used to dye cotton fibres	Indigo
(viii) Mordant dyes	Used to dye wool	Alizarin

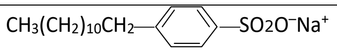
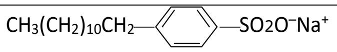
Soap : Soaps are prepared by hydrolysis of higher fatty acids (stearic acid, oleic acid, palmitic acid).



$$\begin{array}{l} CH_2OCOC_{17}H_{35} \\ | \\ CHOCOC_{17}H_{35} + NaOH \\ | \\ CH_2OCOC_{17}H_{35} \end{array} \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3C_{17}H_{35}COONa \text{ (sodium stearate)}$$

Saponification reaction

Soap	
1. Types of soaps	
(i) Hard soaps (Contain free alkali)	Obtained from cheap oils and fats using sodium hydroxide **Used :** washing purposes
(ii) Soft soaps (do not contain free alkali)	Obtained from good oils using potassium hydroxide **Used :** Used as toilet soaps, shaving cream, shaving sticks and shampoo
(iii) Transparent soaps (Contain glycerol)	Dissolving toilet soaps in alcohol and evaporating the filtrate
(iv) Medicated soaps	Containing some medicinal important substance
(v) Metallic soaps	Soaps of metals other than sodium and potassium
2. Manufacture of soap	
The cold process	Made by combining oils and sodium hydroxide lye. It is expansive method, formed soaps is not in good quality.
The hot process	Similar to cold process soap, hot process soap is also made with oils and lye- but instead of stick blending unit it hits trace (a thick batter), the essential oils or fragrance/additives are added after gel phase and being poured into a mold
Modern method	Glycerides of fatty acids are hydrolysed by water at higher temperatures in presence of catalyst to give glycerol and higher fatty acids. These are separated and fatty acids are reacted with NaOH or Na_2CO_3 at higher temperature to form its sodium salt. When lime or ZnO are used as catalyst, the method is known as **Ittner process** and if sulphuric acid or aromatic sulphonic acids are used as catalyst it is called **Twitchell method.**

Detergent		
Types of detergent on the basis of hydrocarbon chain	**Composition**	**Example**
(i) Sodium alkyl sulphates	Half esters of an inorganic acid (H_2SO_4) rather than an organic acid	$CH_3(CH_2)_{10}CH_2OSO_2O^-Na^+$ sodium lauryl sulphate
(ii) Alkylbenzenesulphonates	Sodium salts of long chain (linear) alkyl substituted benzene sulphonic acids	 $CH_3(CH_2)_{10}CH_2$—C_6H_4—$SO2O^-Na^+$ sodium dodecylbenzene sulphate
Types of detergent on the basis of charge		
(i) Anionic detergents	Large part of their molecules are anions	
(a) Sodium alkyl sulphates	Half esters of an inorganic acid (H_2SO_4) rather than an organic acid	$CH_3(CH_2)_{10}CH_2OSO_2O^-Na^+$ sodium lauryl sulphate
(b) Alkylbenzenesulphonates	Sodium salts of long chain (linear) alkyl substituted benzene sulphonic acids	 $CH_3(CH_2)_{10}CH_2$—C_6H_4—$SO2O^-Na^+$ sodium dodecylbenzene sulphate
(ii) Cationic detergents	Large part of their molecules are cations	
(iii) Non-ionic detergents	Large part of their molecules are neutral	$HO(CH_2CH_2O)_nCH_2CH_2OH$ (Polyethylene glycol), $CH_3(CH_3)_{16}COO(CH_2CH_2O)_nCH_2CH_2OH$ Polyethylene glycol stearate

Chemicals in food

Chemicals are added to food for
(i) their preservation
(ii) enhancing their appeal, and
(iii) adding nutritive value in them.

Main categories of food additives are as follows

(i) Flavours and sweeteners
(ii) Fat emulsifiers and stabilising agents
(iii) Flour improvers - antistaling agents and bleaches
(iv) Antioxidants
(v) Preservatives
(vi) Sweetner : Aspartame, Alitame and Sucralose
(vii) Food preservative : Table salt, sugar, vegetable oil and sodium benzoate