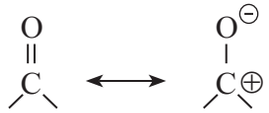
1. Choose the most correct option.

i. In the following resonating structures A and B, the number of unshared electrons in valence shell present on oxygen respectively are



(A) (B)

a. 2, 4 b. 2, 6

c. 4, 6 d. 6, 4

ii. In the Wolf -Kishner reduction, alkyl aryl ketones are reduced to alkyl benzenes. During this change, ketones are first converted into

a. acids b. alcohols

c. hydrazones d. alkenes

iii. Aldol condensation is

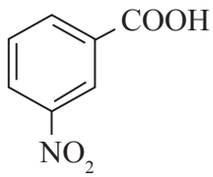
a. electrophilic substitution reaction

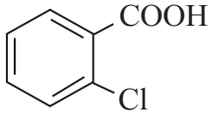
b. nucleophilic substitution reaction

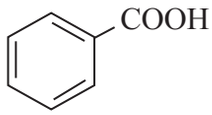
c. elimination reaction

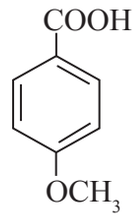
d. addition - elimination reaction

iv. Which one of the following has lowest acidity ?

a. 

b. 

c. 

d. 

v. Diborane reduces

a. ester group b. nitro group

c. halo group d. acid group

vi. Benzaldehyde does NOT show positive test with

a. Schiff reagent

b. Tollens' ragent

c. Sodium bisulphite solution

d. Fehling solution

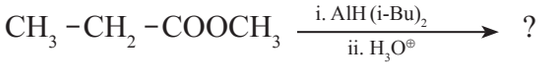
2. Answer the following in one sentence

i. What are aromatic ketones?

ii. Is phenyl acetic acid an aromatic carboxylic acid ?

iii. Write reaction showing conversion of ethanenitrile into ethanol.

iv. Predict the product of the following reaction:



v. Name the product obtained by reacting toluene with carbon monoxide and hydrogen chloride in presence of anhydrous aluminium chloride.

vi. Write reaction showing conversion of Benzonitrile into benzoic acid.

vii. Name the product obtained by the oxidation of 1,2,3,4-tetrahydronaphthalene with acidified potassium permanganate .

viii. What is formalin ?

ix. Arrange the following compounds in the increasing order of their boiling points :

Formaldehyde, ethane, methyl alcohol.

x. Acetic acid is prepared from methyl magnesium bromide and dry ice in presence of dry ether. Name the compound which serves not only reagent but also as cooling agent in the reaction.

3. Answer in brief.

i. Observe the following equation of reaction of Tollens' reagent with aldehyde. How do we know that a redox reaction has taken place. Explain.

$$R-CHO + 2\ Ag(NH_3)_2^+ + OH^- \xrightarrow{\Delta} R-COO^- + 2\ Ag\downarrow + 4\ NH_3 + 2\ H_2O$$

ii. Formic acid is stronger than acetic acid. Explain.

iii. What is the action of hydrazine on cyclopentanone in presence of ---.

KOH in ethylene glycol ?

iv. Write reaction showing conversion of Acetaldehyde into acetaldehyde dimethyl acetal.

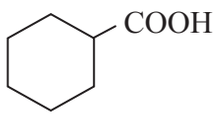
v. Aldehydes are more reactive toward nucleophilic addition reactions than ketones. Explain.

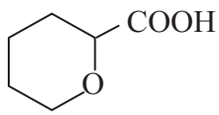
vi. Write reaction showing the action of the following reagent on propanenitrile –

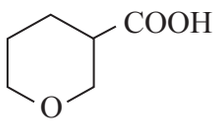
a. Dilute NaOH

b. Dilute HCl ?

vi. Arrange the following carboxylic acids with increasing order of their acidic strength and justify your answer.







4. Answer the following

i. Write a note on –

a. Cannizaro reaction

b. Stephen reaction.

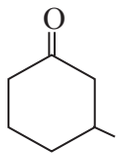
ii. What is the action of the following reagents on toluene ?

a. Alkaline $KMnO_4$, dil. HCl and heat

b. CrO_2Cl_2 in CS_2

c. Acetyl chloride in presence of anhydrous $AlCl_3$.

iii. Write the IUPAC names of the following structures :

a. 

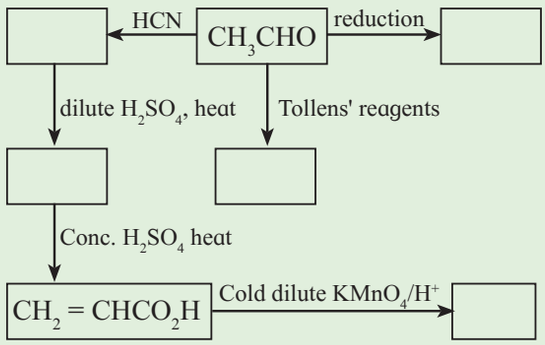
b. 

iv. Write reaction showing conversion of p- bromoisopropyl benzene into p-Isopropyl benzoic acid (3 steps).

v. Write reaction showing aldol condensation of cyclohexanone.

Activity :

Draw and complete the following reaction scheme which starts with acetaldehyde. In each empty box, write the structural formula of the organic compound that would be formed.



13 AMINES

Can you recall ?

- Write some examples of nitrogen containing organic compounds.
- What are the types of amines?

Amines are nitrogen containing organic compounds having basic character. Amines are present in many natural compounds like proteins, vitamins, hormones and plant products like nicotine.

13.1 Classification of Amines : Amines are classified as primary (1°), secondary (2°) and tertiary (3°) amines. Their structures are obtained in simple way by replacing one, two or three hydrogen atoms of NH_3 molecule by alkyl/aryl groups (see Table 13.1).

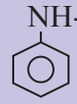
Secondary and tertiary amines are further classified as simple / symmetrical amines and mixed / unsymmetrical amines. When all the alkyl or aryl groups on nitrogen are same, it is a simple amine. If these groups are different, then the amine is a mixed amine.

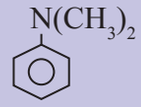
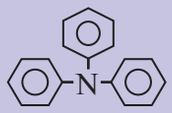
Amines are also divided into two major classes, namely, aliphatic and aromatic amines on the basis of nature of the groups attached to the nitrogen atom.

Use your brain power

Classify the following amines as simple/mixed; 1°, 2°, 3° and aliphatic or aromatic.

$(C_2H_5)_2NH$, $(CH_3)_3N$, $C_2H_5\text{-}NH\text{-}CH_3$,

$C_6H_5\text{-}NH_2$, $CH_3\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}H\text{-}NH_2$,  ,

$CH_3\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}\text{-}NH_2$,  , 

Remember...

Other organic compopunds like alkyl halides or alcohols are classified as 1°, 2°, 3° depending upon the nature of the carbon atom to which functional group is attached where as amines are classified depending upon the number of alkyl or aryl groups directly attached to the nitrogen atom. Thus, isopropyl amine is 1^0 amine, but isopropyl alcohol is 2^0 alcohol.

Table 13.1 Types of amines

Type	Functional group		Examples	
	Name	Formula	Formula	Common Name
Primary amine, (1^0)	Amino	$-NH_2$	$C_2H_5\text{-}NH_2$	Ethylamine
Secondary amine, (2^0)	Imino	$>NH$	$CH_3\diagdown\!\!\diagup NH$ (with CH_3)	Dimethylamine
Tertiary amine, (3^0)	Tertiary nitrogen	$\geqslant N$	CH_3, CH_3, CH_3 on N	Trimethylamine

13.2 Nomenclature of Amines :

13.2.1 Common names : Common names of aliphatic amines are given by writing the name of alkyl group followed by suffix-amine, that is, 'alkyl amine'. In the case of mixed amines, the names of alkyl groups are written in alphabetical order. If two or three identical alkyl groups are attached to nitrogen atom, the prefix 'di-' or 'tri-' is added before the name of alkyl group. The parent arylamine, C_6H_5-NH_2, is named as aniline. Other aromatic amines are named as derivatives of aniline (see Table 13.2).

13.2.2 IUPAC names : In IUPAC system, primary amines are named by replacing the ending 'e' of the parent alkane by suffix -amine (alkanamine). A locant indicating the position of amino group is added before the suffix amine. When two or more amino groups are present, the prefix 'di-', 'tri-' etc. are used with proper locant. In this case the ending 'e' of parent alkane is retained.

Secondary or tertiary amines are named as N-substituted derivatives of primary amines. The largest alkyl group attached to nitrogen is taken as the parent alkane and other alkyl groups as N-substituents. While naming arylamines ending 'e' of arene is replaced by 'amine'. The common name of aniline is also accepted by IUPAC (see Table 13.2).

Remember...

The name of amine (common or IUPAC) is always written as one word. For example : C_2H_5-NH_2 Ethylamine (Ethanamine)

Try this...

Draw possible structures of all the isomers of $C_4H_{11}N$. Write their common as well as IUPAC names.

13.3 Preparation of Amines :

13.3.1 : By ammonolysis of alkyl halides :

When alkyl halide is heated with alcoholic solution of excess ammonia it undergoes nucleophilic substitution reaction in which the halogen atom is replaced by an amino (-NH_2) group to form primary amine. This process of breaking of C-X bond by ammonia is known as ammonolysis. The reaction is also known as alkylation of ammonia. The reaction is carried out in a sealed tube at 373 K. It may be noted that the primary amine obtained in the 1st step is stronger nucleophile than ammonia. Hence, it further reacts with alkyl halide to form secondary and tertiary amines and finally quaternary ammonium salt if NH_3 is not used in large excess.

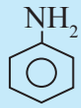
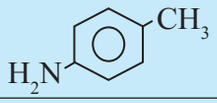
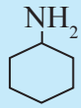
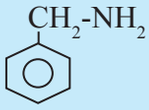
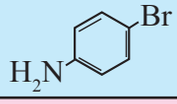
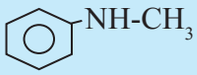
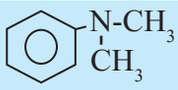
$$\underset{}{R\text{-}X} + \underset{\text{(excess)}}{NH_3(alc).} \xrightarrow{\Delta} \underset{1^0 \text{ amine}}{R\text{-}NH_2}$$

The order of reactivity of alkyl halides with ammonia is R-I > R-Br > R-Cl.

Use your brain power

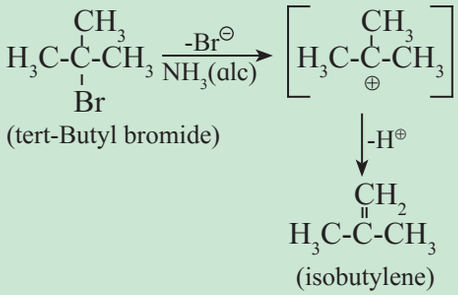
- Write chemical equations for
  1. reaction of alc. NH_3 with C_2H_5I.
  2. Ammonolysis of benzyl chloride followed by the reaction with two moles of CH_3-I.
- Why is ammonolysis of alkyl halide not a suitable method for the preparation of primary amine ?

Table 13.2 : Common and IUPAC names of some alkyl and arylamines

Amines	Common names	IUPAC names
a. Primary amines :		
CH_3-NH_2	Methylamine	Methanamine
CH_3-CH_2-CH_2-NH_2	n-Propylamine	Propan-1-amine
CH_3-CH(NH_2)-CH_3	Isopropylamine	Propan-2-amine
H_2N-CH_2-CH_2-NH_2	Ethylenediamine	Ethane-1, 2-diamine
CH_2=CH-CH_2-NH_2	Allylamine	Prop-2-en-1-amine
	Aniline/ Phenylamine	Aniline or Benzenamine
H_2N-$(CH_2)_6$-NH_2	Hexamethylenediamine	Hexane-1, 6-diamine
	p-Toluidine	4-Methylaniline
	Cyclohexylamine	Cyclohexanamine
	Benzylamine	Phenylmethanamine
	p-Bromoaniline	4-Bromoaniline or 4-Bromobenzenamine
b. Secondary Amines		
CH_3-NH-CH_3	Dimethylamine	N-methylmethanamine
CH_3-CH_2-NH-CH_3	Ethylmethylamine	N-methylethanamine
	Methylphenylamine	N-methylaniline or N-methylbenzenamine
C_6H_5-NH-C_6H_5	Diphenylamine	N-Phenylbenzenamine
c. Tertiary Amines		
CH_3-N(CH_3)-CH_3	Trimethylamine	N, N-Dimethylmethanamine
C_2H_5-N(CH_3)-CH_3	Ethyldimethylamine	N, N-Dimethylethanamine
CH_3-N(C_3H_7)-C_2H_5	Ethylmethyln-propylamine	N-Ethyl-N-methyl propan-1-amine
CH_3-CH(CH_3)-C_2H_5-N-CH_3	Ethylmethylisopropylamine	N-Ethyl-N-methyl propan-2-amine
	N, N-Dimethylaniline	N, N-Dimethylbenzenamine

Do you know ?

When tert-butyl bromide is treated with alcoholic NH_3, isobutylene is formed. This is the result of elimination reaction preferred over nucleophilic substitution through the stable tertiary butyl carbocation intermediate.



(tert-Butyl bromide) (isobutylene)

13.3.2 Reduction of nitrocompounds :

Aliphatic and aromatic nitrocompounds can be reduced to primary amines by using metal-acid mixture (Sn/HCl or Fe/HCl or Zn/HCl) or catalytic hydrogenation (H_2/Ni or Pt or Pd) or $LiAlH_4$ in ether.

$$R\text{-}NO_2 + 6[H] \xrightarrow{Sn/HCl} R\text{-}NH_2 + 2H_2O$$

13.3.3 Reduction of alkyl cyanide (alkanenitriles) :

Can you recall ?

- How is alkyl halide converted into alkyl cyanide ?

Primary amines can be obtained by the reduction of alkyl cyanide with sodium and ethanol. This is known as **Mendius reduction**. The reaction can also be brought about by lithium aluminium hydride.

$$R\text{-}C\equiv N + 4[H] \xrightarrow[\text{or } LiAlH_4]{Na/C_2H_5OH} \underset{1^\circ \text{ amine}}{R\text{-}CH_2\text{-}NH_2}$$

Problem 13.1 : Write reaction to convert methyl bromide into ethyl amine ? Also, comment on the number of carbon atoms in the starting compound and the product.

Solution : Methyl bromide can be converted into ethyl amine in two stage reaction sequence as shown below.

$$CH_3\text{-}Br + KCN \longrightarrow CH_3\text{-}CN + KBr$$

$$CH_3\text{-}CN \xrightarrow[\text{(reduction)}]{Na/C_2H_5OH} CH_3\text{-}CH_2\text{-}NH_2$$

The starting compound methyl bromide contains one carbon atom while the product ethylamine contains two carbon atoms. A reaction in which number of carbons increases involves a step up reaction. The overall conversion of methyl bromide into ethyl amine is a step up conversion.

Use your brain power

Use your brain power:

Identify 'A' and 'B' in the following conversions.

(i) $CH_3\text{-}I \xrightarrow{KCN} A \xrightarrow{Na/C_2H_5OH} B$

(ii) $CH_3\text{-}Br \xrightarrow{AgNO_2} A \xrightarrow{Sn/HCl} B$

(iii) $C_2H_5\text{-}I \xrightarrow{AgCN} A \xrightarrow{Na/C_2H_5OH} B$

13.3.4 By reduction of amides :

Primary amines having same number of carbon atoms can be obtained by the reduction of amides by $LiAlH_4$ in ether or by Na/C_2H_5OH.

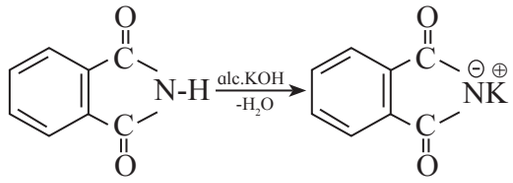
$$\underset{\text{(Acetamide)}}{CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2} + 4[H] \xrightarrow[\text{or } Na/C_2H_5OH]{LiAlH_4, ether\, H_3O^\oplus} \underset{\text{(Ethylamine)}}{CH_3\text{-}CH_2\text{-}NH_2} + H_2O$$

13.3.5 Gabriel phthalimide synthesis : This method is used for the synthesis of primary amine. It involves the following three stages.

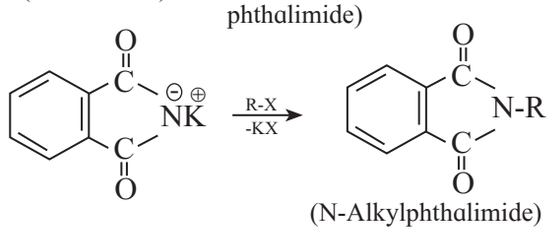
i. Formation of potassium salt of phthalimide from phthalimide on reaction with alcoholic potassium hydroxide.

ii. Formation of N-alkyl phthalimide from the potassium salt by reaction with alkyl halide.

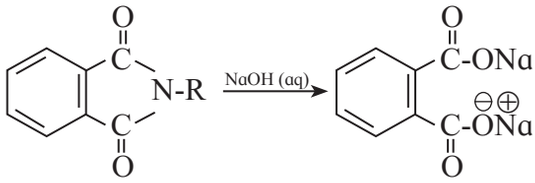
iii. Alkaline hydrolysis of N-alkyl phthalimide to form the corresponding primary amine.

i. 

(Phthalimide) (Potassium salt of phthalimide)

ii. 

(N-Alkylphthalimide)

iii. 

(sodium phthalate)

+ **R-NH$_2$**
(1° amine)

Aromatic amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

13.3.6 By Hofmann degradation (Hofmann rearrangement / Hofmann bromamide degradation / Hofmann hypobromite degradation) :

This is a good laboratory method for the conversion of an amide into primary amine containing one carbon less. The reaction is brought about by warming the amide with bromine and concentrated aqueous KOH solution.

$$\underset{\text{(Amide)}}{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2} + Br_2 + 4KOH(aq) \xrightarrow{\Delta} R\text{-}NH_2 + 2KBr + K_2CO_3 + 2H_2O$$
(1° amine)

For example :

$$\underset{\text{(Acetamide)}}{CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2} + Br_2 + 4KOH\ (aq) \xrightarrow{\Delta} \underset{\text{(methylamine)}}{CH_3\text{-}NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

The overall result is removal of the $-\overset{O}{\overset{\|}{C}}-$ group from the amide. As the product contains one carbon atom less than the original amide. It is a **step down** reaction.

Use your brain power

Write the chemical equations for the following conversions :

i. Methyl chloride to ethylamine.

ii. Benzamide to aniline.

iii. 1, 4 - Dichlorobutane to hexane - 1, 6 - diamine.

iv. Benzamide to benzylamine.

13.4 Physical properties of Amines :

13.4.1 Intermolecular forces, boiling points and solubility : The N-H bond in amines is polar because the electronegativities of Nitrogen (3.0) and Hydrogen (2.1) are different. Due to the polar nature of N-H bond primary and secondary amines have intermolecular hydrogen bonding. The intermolecular hydrogen bonding is to greater extent in primary amine than in secondary amines, because primary amines have two hydrogen atoms bonded to nitrogen for hydrogen bond formation (see Fig 13.1).

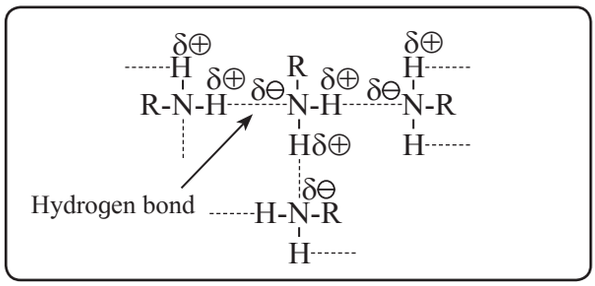


Fig. 13.1 : Intermolecular hydrogen bonding in primary amines

Tertiary amines do not have intermolecular hydrogen bonding as there is no hydrogen atom on nitrogen of tertiary amine. But due to polar N-C bonds, tertiary amines are polar molecules, and have intermolecular dipole-dipole attractive forces. Thus intermolecular forces of attraction are strongest in primary amines and weakest in tertiary amines.

The observed order of boiling points of isomeric amines is : primary amine > secondary amine > tertiary amine (see Table 13.3 serial numbers 1, 2, 3). It can be explained on the basis of the intermolecular forces in them.

The lower aliphatic amines are gases with fishy odour, middle members are liquids and higher members are solids under ordinary temperature and pressure.

Aniline and other arylamines are usually colourless liquids but get coloured as they are easily oxidised by air.

Due to their ability to form hydrogen bond with water molecule, lower aliphatic amines are soluble in water (see Fig. 13.2). Solubility of amines decreases with increase in molar mass of amines due to increase in size of hydrophobic alkyl group. Aromatic amines and higher aliphatic amines are insoluble in water.

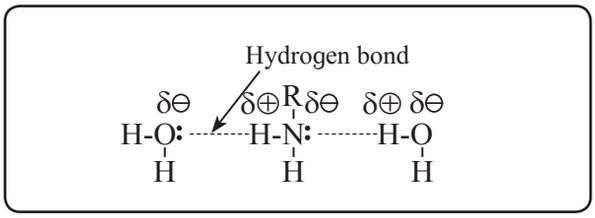


Fig. 13.2 : Hydrogen bonding between amine and water molecule

Since N-H bonds in amines are less polar than O-H bond in alcohol, water solubilities of alcohols, amines and alkanes of comparable molar mass in water are in the decreasing order: **alcohols > amines > alkanes.**

The order of boiling points of alkanes, amines, alcohols and carboxylic acid of comparable molar mass is as follows :

Alkanes < Amines < Alcohols < Carboxylic acid. (Table 13.3, serial number 4, 5, 6, 7)

Use your brain power

Arrange the following :

a. In decreasing order of the b.p.
C_2H_5-OH, C_2H_5-NH_2, $(CH_3)_2NH$

b. In increasing order of solubility in water:
C_2H_5-NH_2, C_3H_7-NH_2, C_6H_5-NH_2

Table 13.3 Boiling points of alkane, alcohol and amines of similar molar masses

Sr. No	Compound	Molar mass	B.P. (K)
1	n-$C_4H_9NH_2$	73	350.8
2	$(C_2H_5)_2NH$	73	329.3
3	$C_2H_5N(CH_3)_2$	73	310.5
4	C_2H_5COOH	74	414.4
5	n-C_4H_9OH	74	390.3
6	$(CH_3)_3C$-NH_2	73	318.15
7	$C_2H_5CH(CH_3)_2$	72	300.8

13.5 Basicity of Amines

The basic nature of amines is due to presence of a lone pair of electrons on the nitrogen atom. In terms of Lewis theory, amines are bases because they can share a lone pair of electrons on 'N' atom with an electron deficient species. For example : Trimethylamine shares its lone pair of electrons with the electron deficient boron trifluoride.

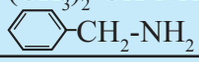
$$Me_3N: + BF_3 \longrightarrow Me_3\overset{\oplus}{N}\text{-}\overset{\ominus}{BF_3}$$

Basic strength of amines is expressed quantitatively as K_b or pK_b value. In terms of Lowry-Bronsted theory, the basic nature of amines is explained by writing the following equilibrium.

$$\underset{\text{(amine)}}{\geqslant N:} + H_2O \rightleftharpoons \underset{\text{(conjugate acid)}}{\geqslant \overset{\oplus}{N}\text{-}H} + \overset{\ominus}{O}H \quad \ldots\ldots\ldots (13.1)$$

In this equilibrium amine accepts $H^{\oplus}$, hence an amine is a Lowry-Bronsted base. For stronger base, this equilibrium shifts towards right, thereby the K_b value is larger and pK_b value is smaller and vice versa (refer to Chapter 3). Table 13.4 gives pK_b values of some amines.

Table 13.4 : pK_b Values of some amines in aqueous medium

Amine	Structural Formula	pK_b value
Primary alkanamines :		
Methanamine	CH_3-NH_2	3.38
Ethanamine	CH_3-CH_2-NH_2	3.29
Propan-2-amine	$(CH_3)_2$-CH-NH_2	3.40
Phenylmethanamine		4.70
Secondary alkanamines :		
N-Methylmethanamine	$(CH_3)_2NH$	3.27
N-Ethylethanamine	$(CH_3CH_2)_2NH$	3.00
Tertiary alkanamines :		
N, N-Dimethylmethanamine	$(CH_3)_3N$	4.22
N, N-Diethylethanamine	$(CH_3CH_2)_3N$	3.25
Ammonia	NH_3	4.75
Arylamines :		
Benzenamine (aniline)		9.38
N-Methylaniline		9.30
N, N-Dimethylaniline		8.92

13.5.1 : Basic strength of aliphatic amines :

The trend in the observed pK_b values (see table 13.4) and basic strength of 1°, 2°, 3° amines and NH_3 can be represented as shown below :

Order of pK_b values:

$NH_3 > R\text{-}NH_2 > R_2NH < R_3N$

Order of basic strength :

$NH_3 < R\text{-}NH_2 < R_2NH > R_3N$ ..... (13.2)

Thus as per the observed pK_b values of the aliphatic amines, **secondary amines are the strongest bases**. Basic strength increases as we move from NH_3 to R-NH_2 and from R-NH_2 to R_2NH, but basic strength decreases as we move from R_2NH to R_3N (Table 13.4).

The basic strength and the corresponding pK_b value depends upon the position of the equilibrium shown in Eq. (13.1). Greater the stabilization of the conjugate acid more on right side the equilibrium will lie and stronger will be the base and smaller will be its pK_b value.

Can you recall ?

- What is meant by +I effect ?
- Which of the following species is better stabilized and by which effect ?

$CH_3\text{-}\overset{\oplus}{C}H_2$ and $CH_3\text{-}\overset{\oplus}{C}H\text{-}CH_3$

Basicity of amines is related to the structural effects which influence stabilization of various species. Greater is the stabilization of the protonated amine, that is, the conjugate acid, greater is the basicity of the amine.

Use your brain power

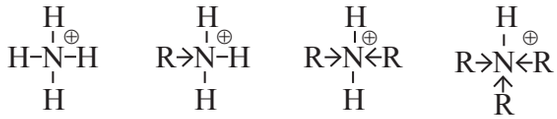
Refer to pK_b values from Table 13.4 and answer which compound from the following pairs is stronger base ?

i. $CH_3\text{-}NH_2$ and $(CH_3)_2NH$

ii. $(C_2H_5)_2NH$ and $(C_2H_5)_3N$

iii. NH_3 and $(CH_3)_2CH\text{-}NH_2$

a. Influence of +I effect on stabilization of conjugate acids of aliphatic amines and NH_3 can be represented as shown below :



An alkyl group exerts electron releasing inductive effect (+I) which stabilizes positive charge on atom bonded to it. As we move from conjugate acid of ammonia ($NH_4^{\oplus}$) to that of tertiary amine ($R_3NH^{\oplus}$), the number of alkyl groups (R) bonded to Nitrogen goes on increasing steadily. This results in increasing stabilization of the conjugate acids and thereby an increasing order of basic strength is expected.

Order of stabilization :

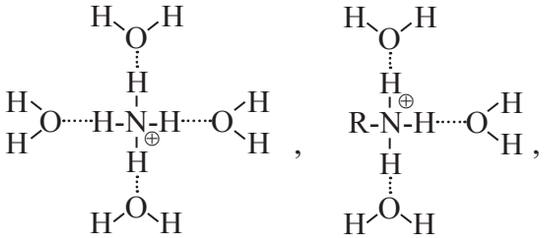
$$\overset{\oplus}{N}H_4 < R\text{-}\overset{\oplus}{N}H_3 < R_2\overset{\oplus}{N}H_2 < R_3\overset{\oplus}{N}\text{-}H$$

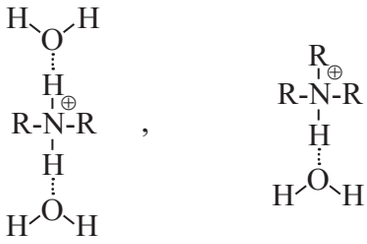
Expected order of basic strength :

$$NH_3 < R\text{-}NH_2 < R_2NH < R_3N$$

The expected order of basic strength on the basis of +I effect differs from the observed order (Eq.13.2). It is seen that the observed increasing basic strength from ammonia to 1° amine and from 1° amine to 2° amine is explained on the basis of increased stabilization of conjugate acids by +I effect of increased number of alkyl (R) groups. However, decreased basic strength of 3° amine implies that the conjugate acid of 3° amine is less stabilized even though the +I effect of three alkyl groups in $R_3\overset{\oplus}{N}H$ is expected to be large. This is suggestive of existance of another influencing factor in stabilization of conjugate acids of amines.

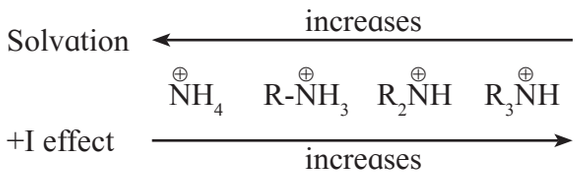
b. Influence of solvation by water on stabilization of conjugate acids of aliphatic amines and ammonia can be represented as shown below :





The solvent water stabilizes the conjugate acid by hydrogen bonding through the 'H' bonded to the '$N^{\oplus}$'. The number of 'H' atoms bonded to the '$N^{\oplus}$' decreaes from 4 in $NH_4^{\oplus}$ to 1 in $R_3NH^{\oplus}$. As a result $NH_4^{\oplus}$ is best stabilized by solvation while the stabilization by solvation is very poor in $R_3NH^{\oplus}$.

c. Combined influence of +I effect and solvation on stabilization if conjugate acids of aliphatic amines decides the observed basic strength and pK_b value. These two influencing factors operate in opposite directions.



The net results is that as we move from NH_3 to RNH_2 to R_2NH, the basic strength increases due to better stabilization of the corresponding conjugate acids. But 3° amine is weaker base than 2° amine because the stabilization of conjugate acid of 3° amine by solvation is very poor.

13.5.2 Basicity of arylamines :

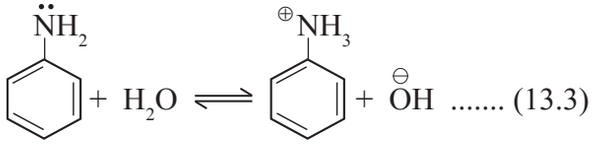
Can you recall ?

Refer to Table 13.4 and answer :

Are the pK_b values of aniline, N-methylaniline and N, N-dimethylaniline larger or smaller than those of NH_3 and CH_3NH_2 ?

Which one of the two, aniline or CH_3NH_2, is a stronger base ?

From the pK_b values we understand that arylamines in general are weaker bases than ammonia and aliphatic amines. Strength of arylamines is explained in accordance with Lowery Bronsted theory by writing the following equilibrium (Eq. 13.3) For aniline (similar to eq. 13.1).

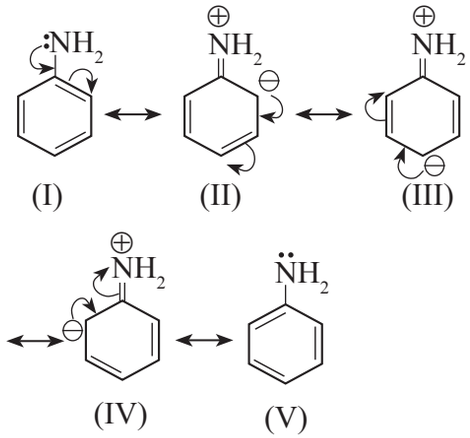


..... (13.3)

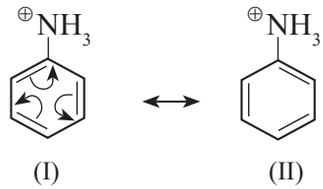
(Base) (Conjugate acid)

Here, both the species base and conjugate acid, are resonance stabilized but to different extent.

In arylamines, the $-NH_2$ group is attached directly to an aromatic ring. The lone pair of electrons on nitrogen is conjugated to the aromatic ring and is less available for protonation. Aniline is resonance stabilized by the following five resonance structures.



On the other hand anilinium ion obtained by accepting a proton does not have lone pair of electrons on nitrogen. Hence it can be stabilized by only two resonance structures and therefore less stabilized than aniline.



As a result the equilibrium (13.3) is shifted towards left side. This makes aniline (and also other arylamines) weaker bases than aliphatic amines and ammonia.

Use your brain power

Arrange the following amines in decreasing order of their basic strength -

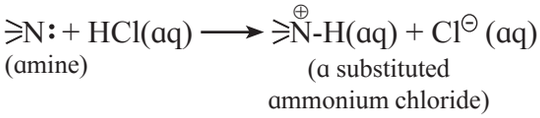
NH_3, CH_3-NH_2, $(CH_3)_2NH$, $C_6H_5NH_2$.

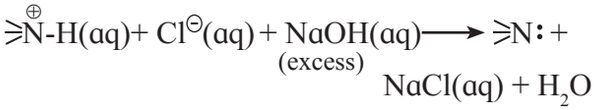
13.6 Chemical properties of amines

13.6.1 Laboratory test for amines :

a. Test for amines as the 'base' : All amines 1°, 2° and 3° are basic compounds. Aqueous solution of water soluble amines turns red litmus blue.

The 'basic' nature of amines is detected in laboratory by reaction with aqueous solution of strong mineral acid HCl.





Water insoluble amine dissolves in aqueous HCl due to formation of water soluble substituted ammonium chloride, which on reaction with excess aqueous NaOH regenerates the original insoluble amine.

b. Diazotization reaction/ Orange dye test: In a sample of aromatic primary amine, 1-2 mL of conc. HCl is added. The aqueous solution of $NaNO_2$ is added with cooling. This solution is transfered to a test tube containing solution of β naphthol in NaOH. Formation of orange dye indicates presence of aromatic primary amino group. (It may be noted that temperature of all the solutions and reaction mixtures is maintined near 0°C throughout the reaction).

The reactions involved in this test will be discussed in section 13.7.2.

13.6.2: Alkylation of amines : Hofmann's exhaustive alkylation : When a primary amine is heated with excess of primary alkyl halide it gives a mixture of secondary amine, tertiary amine along with tetraalkylammonium halide (also refer to sec. 13.3.1).

$$R\text{-}NH_2 \xrightarrow[-HX]{R\text{-}X} R_2NH \xrightarrow[-HX]{R\text{-}X} R_3N \xrightarrow[-HX]{R\text{-}X} R_4\overset{\oplus}{N}X^{\ominus}$$

(1° Amine) (2° Amine) (3° Amine) (Tetraalkyl ammonium halide)

If excess of alkyl halide is used tetraalkyl ammonium halide is obtained as major product. The reaction is known as exhaustive alkylation of amines.

The tetraalkylammonium halides are called quaternary ammonium salts which are crystalline solids. They are the derivatives of ammoium salts in which all the four hydrogen atoms attached to nitrogen in $\overset{\oplus}{N}H_4$ are replaced by four alkyl groups (same or different). Primary, secondary and tertiary amines consume three, two and one moles of alkyl halide respectively to get converted into quaternary ammonium salt. The reaction is carried out in presence of mild base $NaHCO_3$, to neutralize the large quantity of HX formed. If the alkyl halide is methyl iodide, the reaction is called exhaustive methylation of amines.

For example : When methylamine is heated with excess methyl iodide, it gives tetramethyl ammonium iodide.

$$CH_3\text{-}NH_2 + CH_3\text{-}I \xrightarrow{\Delta} (CH_3)_2NH + HI$$

$$(CH_3)_2NH + CH_3\text{-}I \xrightarrow{\Delta} (CH_3)_3N + HI$$

$$(CH_3)_3N + CH_3\text{-}I \xrightarrow{\Delta} (CH_3)_4\overset{\oplus}{N}I^{\ominus}$$

Use your brain power

$$C_2H_5\text{-}NH_2 + C_2H_5\text{-}I \xrightarrow[\text{excess}]{\Delta} ?$$

$$(C_2H_5)_2NH + CH_3\text{-}I \xrightarrow[\text{excess}]{\Delta} ?$$

$$C_6H_5\text{-}NH_2 + CH_3\text{-}I \xrightarrow[\text{excess}]{\Delta} ?$$

13.6.3 Hofmann Elimination :

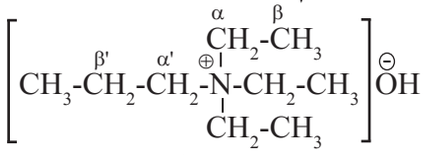
When tetraalkylammonium halide is hetated with moist silver oxide, it gives quanternary ammonium hydroxide which is a deliquescent crystalline solid, and strongly basic like NaOH or KOH. Quaternary ammonium hydroxides on strong heating undergo β-elimination to give an alkene, the reaction is called Hofmann elimination. The least substituted alkene is obtained as major product (in contrast to Saytzeff elimination)

For example :

$CH_3CH_2CH_2\text{-}\overset{\oplus}{N}(CH_2CH_3)_3\ I^{\ominus} + AgOH$

(N,N,N-triethylpropylammonium iodide)

$\xrightarrow[\text{moist } Ag_2O]{\Delta}$



(N,N,N-triethylpropanammonium hydroxide)

$\xrightarrow[-H_2O]{\Delta}$

$CH_2{=}CH_2 + CH_3CH_2CH_2\text{-}\ddot{N}\text{-}CH_2CH_3$ (with CH_2CH_3 on N)

(ethene) (N,N-diethylpropan-1-amine)

Use your brain power

Complete the following reaction:

$$CH_3\text{-}CH_2\text{-}\overset{\oplus}{N}(CH_3)_3I^{\ominus} \xrightarrow[Ag_2O]{\text{Moist}} ? \xrightarrow{\Delta}$$

Do you know ?

- Acetylcholine is a quaternary ammonium salt which occurs in nervous system and functions as neurotransmitter

  $CH_3\text{-}CO\text{-}O\text{-}CH_2\text{-}CH_2\text{-}\overset{\oplus}{N}(CH_3)_3$

- Quaternary ammonium salts are also present in cationic detergents.

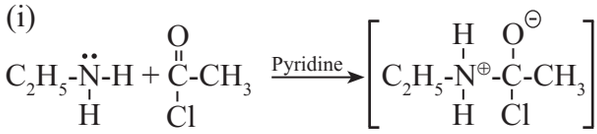
13.6.4 Acylation of amines :

Can you recall ?

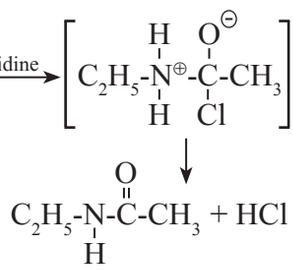
- What is an acyl group ?
- How are alcohols acylated ?

Aliphatic and aromatic primary and secondary amines undergo acylation reaction. These amines contain replaceable hydrogen atoms (positively polarised H) on the nitrogen atom. These hydrogen atoms are replaced by acyl groups such as acetyl group. On reaction of amines with acetyl chloride or acetic anhydride, acetyl derivative of amine is obtained. It is also called amide. Amide is less basic than the amine. Acylation is a nucleophilic substitution reaction. The reaction is carried out in presence of strong base like pyridine, which neutralizes the acid produced during the reaction. For example :

(i)

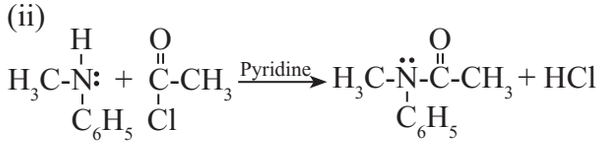


(Ethanamine) (Ethanoyl chloride)



(N-Ethylethanamide)

(ii)



(N-Methylaniline) (N-methyl-N-phenylethanamide)

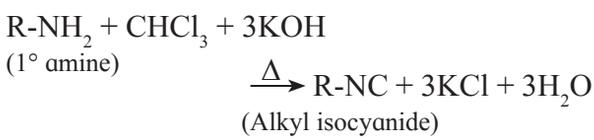
Benzoyl chloride also gives similar reaction with amines.

Use your brain power

- $CH_3\text{-}NH_2 + Ph\text{-}CO\text{-}Cl \longrightarrow$?
- $(CH_3)_3N + Ph\text{-}CO\text{-}Cl \longrightarrow$?

13.6.5 Carbylamine reaction :

Aliphatic or aromatic primary amines on heating with chloroform give foul (offensive) smelling products called alkyl/aryl isocyanides or carbylamines. This reaction is a test for primary amines. Secondary and tertiary amines do not give this test.



(1° amine) (Alkyl isocyanide)

Use your brain power

Write the carbylamine reaction by using aniline as starting material.

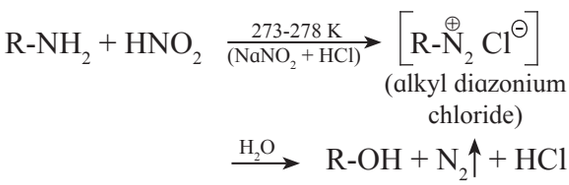
13.6.6 Reaction with nitrous acid : Primary, secondary and tertiary amines react differently with nitrous acid. Reactions of only primary amines will be considered here.

Can you tell ?

- What is the formula of nitrous acid ?
- Can nitrous acid be stored in bottle ?

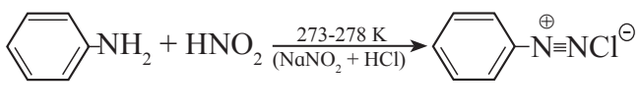
Nitrous acid is an unstable compound. Hence it is prepared *in situ* by adding aqueous sodium nitrite to hydrochloric acid already mix with the substrate, that is amine.

a. Aliphatic primary amines on reaction with nitrous acid form aliphatic diazonium salts as very unstable intermidiates which decompose immediately by reaction with solvent water. Corresponding alcohol is formed as the product of the reaction and nitrogen gas is liberated .



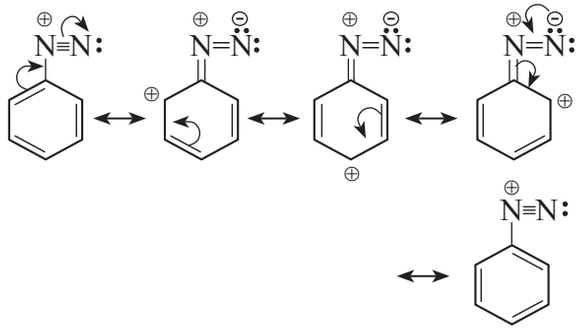
(alkyl diazonium chloride)

b. Aromatic primary amines react with nitrous acid to form diazonium salts which have reasonable stability at 273 K.



(benzene diazonium chloride)

Aryl diazonium salts are resonance stabilized and useful as versatile intermidiates to obtain a variety of products.



13.7 Reactions of arene diazonium salts:

Aryl diazonium salts show two types of reactions.

13.7.1 Reactions involving displacement of diazo group : The diazonium group ($-N_2^{\oplus}$) is a very good leaving group due to the positive charge on nitrogen atom bonded to aromatic ring. As a result, the arene diazonium salts undergo nucleophilic substitution reaction with a variety of nucleophiles. Table 13.5 shows reactions of diazonium salts involving displacement of diazo group.

Table 13.5 Reactions of arene diazonium salts

Title of reaction	Substrate	Reagent	Products
Sandmeyer reaction (good yield)	$Ar\text{-}N_2^{\oplus}X^{\ominus}$	$CuCl/HCl$	$Ar\text{-}Cl + N_2$
	$Ar\text{-}N_2^{\oplus}X^{\ominus}$	$CuBr/HBr$	$Ar\text{-}Br + N_2$
	$Ar\text{-}N_2^{\oplus}X^{\ominus}$	$CuCN/KCN$	$Ar\text{-}CN + N_2$
Gatterman reaction	$Ar\text{-}N_2^{\oplus}X^{\ominus}$	Cu powder / HCl	$Ar\text{-}Cl + N_2$
	$Ar\text{-}N_2^{\oplus}X^{\ominus}$	Cu powder / HBr	$Ar\text{-}Br + N_2$
Iodoarene formation	$Ar\text{-}N_2^{\oplus}Cl^{\ominus}$	KI	$Ar\text{-}I + N_2$
Mild Reduction	$Ar\text{-}N_2^{\oplus}Cl^{\ominus}$	H_3PO_2 / H_2O	$Ar\text{-}H + N_2 + H_3PO_3 + HCl$
	$Ar\text{-}N_2^{\oplus}Cl^{\ominus}$	$CH_3\text{-}CH_2\text{-}OH$	$Ar\text{-}H + N_2 + CH_3CHO + HCl$
Phenol formation	$Ar\text{-}N_2^{\oplus}Cl^{\ominus}$	H_2O / 283 K	$Ar\text{-}OH + N_2 + HCl$

Reaction with fluoroboric acid :

Arene diazonium salt on reaction with fluoroboric acid gives precipitate of diazonium fluoroborate which on heating decomposes to yield fluoroarene. On the other hand when heated with aqueous sodium nitrite in presence of copper it gives nitroarene.

$$Ar\text{-}N_2^{\oplus}Cl^{\ominus} \xrightarrow{HBF_4} Ar\text{-}N_2^{\oplus}BF_4^{\ominus}$$

$$Ar\text{-}N_2^{\oplus}BF_4^{\ominus} \xrightarrow{\Delta} Ar\text{-}F + N_2\uparrow + BF_3$$

$$Ar\text{-}N_2^{\oplus}BF_4^{\ominus} \xrightarrow[\Delta, Cu]{aq.\ NaNO_2} Ar\text{-}NO_2 + N_2\uparrow + BF_3$$

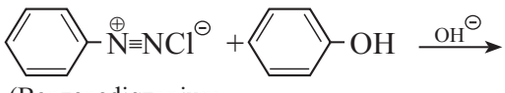
Use your brain power

Complete the following reactions :

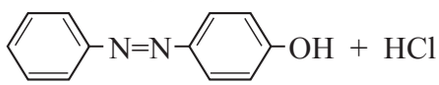
- $Ar\text{-}NH_2 \xrightarrow{?} Ar\text{-}N_2^{\oplus}Cl^{\ominus} \xrightarrow[\text{Cupprous chloride}]{HCl} ?$
- $Ar\text{-}N_2^{\oplus}Cl^{\ominus} \xrightarrow{H_3PO_2} ?$

13.7.2 Reactions involving retention of diazo group: (Coupling reactions) :

Arene diazonium salts when treated with certain reactive aromatic compounds such as phenols or aromatic amines, give azo compounds. These have extended conjugated system of double bonds in which two aromatic rings are joined through azo group -N=N-. This reaction is called **azo coupling**. Azo compounds are brightly coloured and are used as dyes. This is an example of electrophilic aromatic substitution reaction. Here the electrophiles are positively charged diazonium ions. Substitution usually occurs para to the ring activating group. For example : Benzenediazonium chloride reacts with phenol in mild alkaline medium to give p-Hydroxy-azobenzene (orange dye).

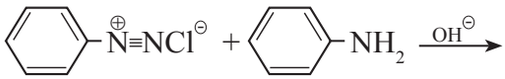


(Benzenediazonium chloride)

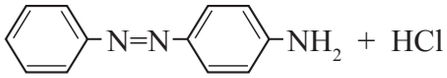


(p-Hydroxyazobenzene)

Azo coupling with β-naphthol in NaOH is used as a confirmatory test for primary aromatic amines. Benzenediazonium chloride reacts with aniline in mild alkaline medium to give p-aminoazo-benzene (yellow dye.)



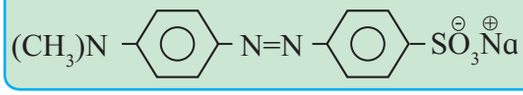
(Benzenediazonium chloride) (Aniline)



(p-Aminoazobenzene)

Do you know ?

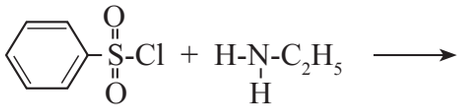
The acid-base indicator methyl orange is an azo dye.



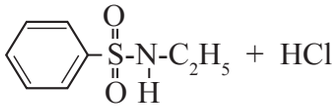
13.8 Reaction with arenesulfonyl chloride :

(Hinsberg's test) : Benzenesulfonyl chloride ($C_6H_5SO_2Cl$) is known as **Hinsberg's reagent**.

a. Ethyl amine (primary amine) reacts with benzenesulfonyl chloride to form N-ethyl benzenesulfonyl amide.



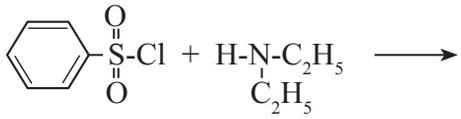
(Benzenesulfonyl chloride) (1° amine)



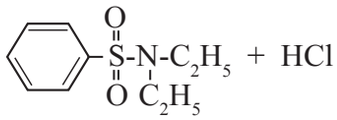
(N-Ethylbenzene sulfonamide)
(Soluble in alkali)

The hydrogen attached to nitrogen in sulfonamide ethanamine (a primary amine) is strongly acidic. Hence it is soluble in alkali.

b. Diethyl amine reacts with benzene-sulfonyl chloride to give N, N- diethyl benzene sulfonamide.



(2° amine)



(N, N-diethylbenzene sulfonamide)

N,N-diethylbenzenesulfonamide does not contain any H-atom attached to nitrogen atom. Hence it is not acidic and does not dissolve in alkali.

Can you tell ?

- Do tertiary amines have 'H' bonded to 'N' ?
- Why do tertiary amines not react with benzene sulfonyl chloride ?

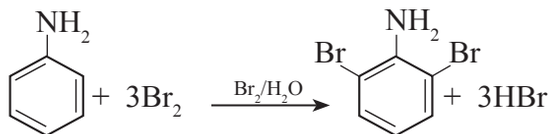
Use your brain power

How will you distinguish between methylamine, dimethylamine and trimethylamine by Hinsberg's test ?

13.9 Electrophilic aromatic substitution in aromatic amines :

Amino group is ortho and para directing and powerful ring activating group. As a result aromtic amines readily undergo electrophilic substitution reactions.

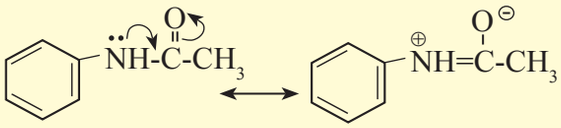
a. Bromination : Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6- tribromoaniline.



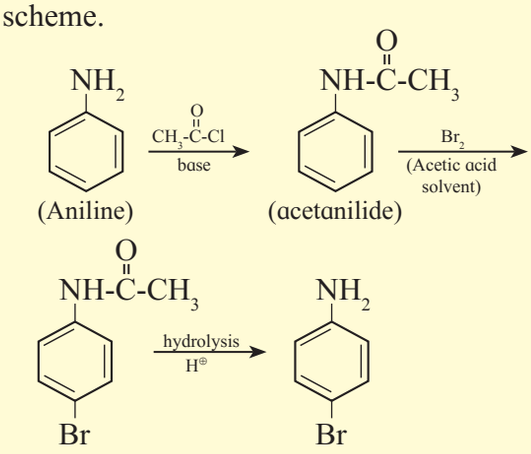
(Aniline) (2,4,6-tribromoaniline)

Problem 13.1 : Write the scheme for preparation of p-bromoaniline from aniline. Justify your answer.

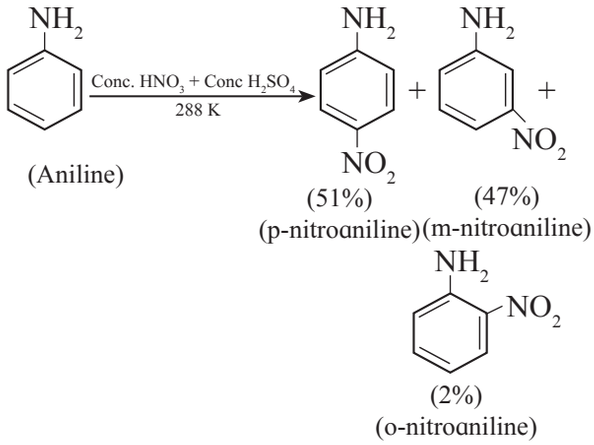
Solution : NH_2- group in aniline is highly ring activating and o-/p- directing due to involvement of the lone pair of electrons on 'N' in resonace with the ring. As a result, on reaction with Br_2 it gives 2,4,6-tribromoniline. To get a monobromo product, it is necessary to decrease the ring activating effect of -NH_2 group. This is done by acetylation of aniline. The lone pair of 'N' in acetanilide is also involved in resonance in the acetyl group. To that extent ring activation decreases.



Hence, acetanilide on bromination gives a monobromo product p-bromoacetanilide. After monobromination the original -NH_2 group is regenerated. The protection of -NH_2 group in the form of acetyl group is removed by acid catalyzed hydrolysis to get p-bromoaniline, as shown in the following scheme.



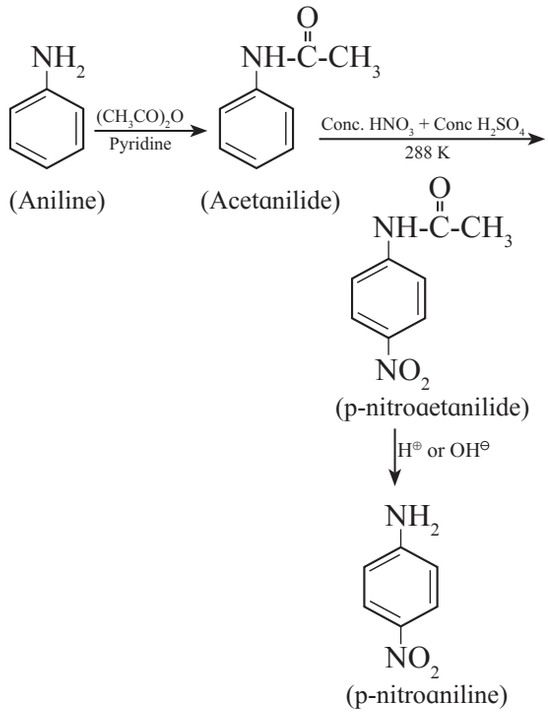
b. Nitration : Direct nitration of aniline yeilds a mixture of ortho, meta and para nitroanilines. In acidic medium -NH_2 group is protonated to -$\overset{\oplus}{N}H_3$ group which is meta-directing and deactivating. Hence considerable amount of m-nitroaniline is obtained.



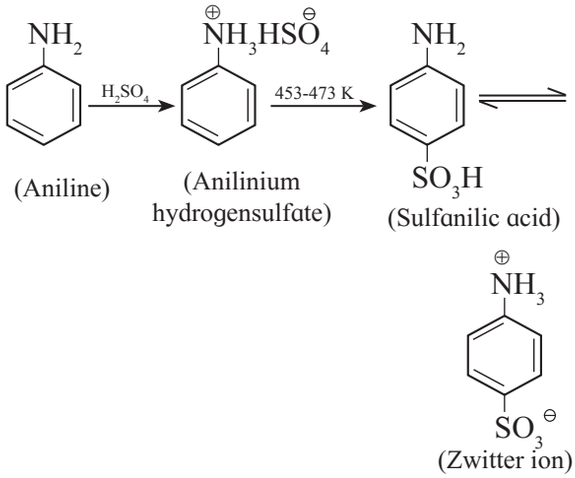
Internet my friend

Search the pK_a or pK_b values of ortho, meta and para nitroaniline on internet and arrange them in increasing order of their basic strength.

However, to get p-nitroaniline as major product, -NH_2 group is first protected by acetylation, nitration is carried out and then amide is hydrolysed.



c. Sulfonation : Aniline reacts with concerntrated sulfuric acid to form anilinium hydrogen sulfate which on heating with sulfuric acid at 453-473K produces p-aminobenzene sulfonic acid (sulfanilic acid) as major product.



Sulfanilic acid exists as a salt; called **dipolar ion or zwitter ion**. It is produced by the reaction between an acidic group and a basic group present in the same molecule.

Use your brain power

- Can aniline react with a Lewis acid ?
- Why aniline does not undergo Friedel Craft's reaction using aluminium chloride ?

Exercises

1. Choose the most correct option.

i. The hybridisation of nitrogen in primary amine is .....

a. sp b. sp^2 c. sp^3 d. sp^3d

ii. Isobutylamine is an example of .....

a. 2° amine b. 3° amine

c. 1° amine

d. quaternary ammonium salt.

iii. Which one of the following compounds has the highest boiling point ?

a. n-Butylamine b. sec-Butylamine

c. isobutylamine d. tert-Butylamine

iv. Which of the following has the highest basic strength ?

a. Trimethylamine b. Methylamine

c. Ammonia d. Dimethylamine

v. Which type of amine does produce N_2 when treated with HNO_2 ?

a. Primary amine b. Secondary amine

c. Tertiary amine

d. Both primary and secondary amines

vi. Carbylamine test is given by

a. Primary amine

b. Secondary amine

c. Tertiary amine

d. Both secondary and tertiary amines

vii. Which one of the following compounds does not react with acetyl chloride ?

a. CH_3-CH_2-NH_2 b. $(CH_3$-$CH_2)_2NH$

c. $(CH_3$-$CH_2)_3N$ d. C_6H_5-NH_2

viii. Which of the following compounds will dissolve in aqueous NaOH after undergoing reaction with Hinsberg reagent ?

a. Ethylamine b. Triethylamine

c. Trimethylamine d. Diethylamine

ix. Identify 'B' in the following reactions

CH_3-C≡N $\xrightarrow{Na/C_2H_5OH}$ A $\xrightarrow{NaNO_2/dilHCl}$ B

a. CH_3-CH_2-NH_2 b. CH_3-CH_2-NO_2

c. CH_3-$CH_2N_2^{\oplus}Cl^{\ominus}$ d. CH_3-CH_2-OH

x. Which one of the following compounds contains azo linkage ?

a. Hydrazine

b. p-Hydroxyazobenzene

c. N-Nitrosodiethylamine

d. Ethylenediamine

2. Answer in one sentence.

i. Write reaction of p-toluenesulfonyl chloride with diethylamine.

ii. How many moles of methylbromide are required to convert ethanamine to N, N-dimethyl ethanamine ?

iii. Which amide does produce ethanamine by Hofmann bromamide degradation reaction?

iv. Write the order of basicity of aliphatic alkylamine in gaseous phase.

v. Why are primary aliphatic amines stronger bases than ammonia ?

vi. Predict the product of the following reaction.

Nitrobenzene $\xrightarrow{\text{Sn/Conc. HCl}}$?

vii. Write the IUPAC name of benzylamine.

viii. Arrange the following amines in an increasing order of boiling points.

n-propylamine, ethylmethyl amine, trimethylamine.

ix. Write the balanced chemical equations for the action of dil H_2SO_4 on diethylamine.

x. Arrange the following amines in the increasing order of their pK_b values.

Aniline, Cyclohexylamine, 4-Nitroaniline

3. Answer the following

i. Identify A and B in the following reactions.

$C_6H_5CH_2Br \xrightarrow[KCN]{\text{alco.}} A \xrightarrow{Na/\text{ethanol}} B.$

ii. Explain the basic nature of amines with suitable example.

iii. What is diazotisation ? Write diazotisation reaction of aniline.

iv. Write reaction to convert acetic acid into methylamine.

v. Write a short note on coupling reactions.

vi. Explain Gabriel phthalimide synthesis.

vii. Explain carbylamine reaction with suitable examples.

viii. Write reaction to convert (i) methanamine into ethanamine (ii) Aniline into p-bromoaniline.

ix. Complete the following reactions :

a. $C_6H_5N_2^{\oplus}Cl^{\ominus} + C_2H_5OH \longrightarrow$

b. $C_6H_5NH_2 + Br_2(aq) \longrightarrow$?

x. Explain Ammonolysis of alkyl halides.

xi. Write reaction to convert ethylamine into methylamine.

4. Answer the following.

i. Write the IUPAC names of the following amines :

a. $CH_3\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{N}}\text{-}CH_2\text{-}CH_2\text{-}CH_3$

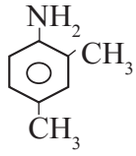
b. $CH_3\text{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}\text{-}CH_2\text{-}CH_2\text{-}NH_2$

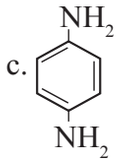
c. $CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}NH\text{-}CH_2\text{-}CH_3$

ii. What are amines ? How are they classified ?

iii. Write IUPAC names of the following amines.

a. $H_2N\text{-}(CH_2)_6\text{-}NH_2$

b. 

c. 

iv. Write reactions to prepare ethanamine from

a. Acetonitrile b. Nitroethane

c. Propionamide

v. What is the action of acetic anhydride on ethylamine, diethylamine and triethylamine ?

vii. Distinguish between ethylamine, diethylamine and triethylamine by using Hinsberg's reagent ?

viii. Write reactions to bring about the following conversions :

a. Aniline into p-nitroaniline

b. Aniline into sulphanilic acid ?

Activity :

- **Prepare a chart of azodyes, colours and its application.**
- **Prepare a list of names and structures of N-containing ingredients of diet.**

14. BIOMOLECULES

Can you recall ?

- What are the constituents of balanced diet ?
- What are the products of digestion of carbohydrates?
- Which constituent of diet is useful for building muscles?
- Which constituent of diet is a source of high energy?
- What is the genetic material of organisms?

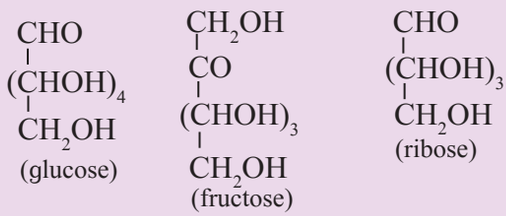
14.1 Introduction : Principal molecules of the living world : Bodies of living organisms contain large number of different molecules which constitute their structure. They are also part of various physiological processes taking place in them. Primary structural materials of organisms are proteins and cellulose. By means of the unique process of photosynthesis plants produce carbohydrates. Plants utilize the minerals absorbed by their roots to produce proteins. Lipids are the main ingredient of vegetable oils and milk fats. Nucleic acids constitute the genetic material of organisms.

In this chapter we are going to study some aspects of three principal biomolecules, namely, carbohydrates, proteins and nucleic acids.

14.2 Carbohydrates : From the simple chemical reactions of many carbohydrates it is understood that carbohydrates are polyhydroxy aldehydes or ketones or compounds which give rise to such units on hydrolysis. Some carbohydrates like glucose, fructose are sweet in taste, and are called sugars. The most commonly used sugar is sucrose which is obtained from sugarcane or sugar beet. The sugar present in milk is called lactose.

Try this...

Observe the following structural formulae carefully and answer the questions.



1. How many OH groups are present in glucose, fructose and ribose respectively?
2. Which other functional groups are present in these three compounds?

Greek word for sugar is sakkharon. Hence carbohydrates are also called **saccharides**. Origin of the term carbohydrate lies in the finding that molecular formulae of many of them can be expressed as $C_x(H_2O)_y$(hydrates of carbon). For example: glucose ($C_6H_{12}O_6$ Or $C_6(H_2O)_6$, sucrose ($C_{12}H_{22}O_{11}$ or $C_{12}(H_2O)_{11}$), starch $[(C_6H_{10}O_5)_n$ or $[C_6(H_2O)_5]_n]$.

14.2.1 Classification of carbohydrates :

Carbohydrates are clssified into three broad groups in accordance with their behaviour on hydrolysis. These are monosaccharides, oligosaccharides and polysaccharides (Fig. 14.1).

Monosaccharides do not hydrolyse further into smaller units of polyhydroxy aldehydes or ketones. **Oligosaccharides** on hydrolysis yield two to ten units of monosaccharides and accordingly they are further classified as **disaccharides**, **trisaccharides** and so on. **Polysaccharides** give very large number of monosaccharide units on complete hydrolysis.

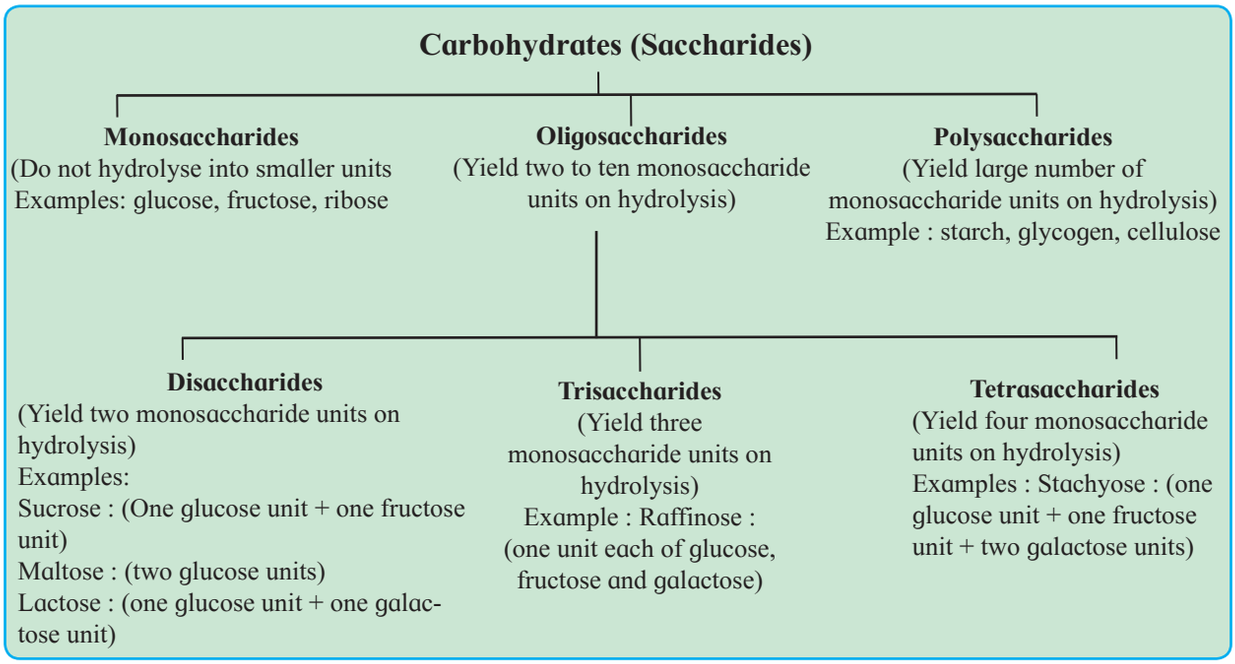


Fig. 14.1 : Classification of carbohydrates

Remember...

- About **twenty different monosaccharides** are found in carbohydrates.
- **Disaccharides** are the most common oilgosacchrides. The two monosaccharide units in disaccharides may be same or different.
- **Polysaccharides** : **Starch** is common ingredient of food grains. **Cellulose** is constituent of cell wall of plant cells. Animals store polysaccharides in their body in the form of **glycogen**.

14.2.2 Nomenclature of monosaccharides :

According to IUPAC system of nomenclature, general name for monosaccharide is **glycose**. Monosaccharide with one aldehydic carbonyl group is called **aldose** while that with one ketonic carbonyl group is called **ketose**. These names are further modified in accordance with the total number of carbon atoms in the monosaccharide. For example, glucose ($C_6H_{12}O_6$) is an aldose with six carbons, and is thereby, an **aldohexose**. Fructose ($C_6H_{12}O_6$) is a ketose with six carbons, and is, thereby, a **ketohexose**.

Use your brain power

Give IUPAC names to the following monosaccharides.

1. $CH_2OH-CHOH-CHO$
2. $CH_2OH-(CHOH)_3-CHO$
3. $CH_2OH-CO-(CHOH)_3-CH_2OH$

14.2.3 Glucose : Glucose occurs in nature in free as well as in combined state. Glucose can be obtained from sucrose or starch by acid catalysed hydrolysis as shown below.

a. Prepartion of glucose from sucrose :

Sucrose is hydrolysed by warming with dilute hydrochloric acid or sulfuric acid for about two hours. This hydrolysis converts sucrose into mixture of glucose and fructose. Glucose is separated from fructose by adding ethanol during cooling. Glucose being almost insoluble in alcohol crystallizes out first. The solution is filltered to obtain crystals of glucose.

$$\underset{\text{(Sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\Delta]{H^{\oplus}} \underset{\text{(Glucose)}}{C_6H_{12}O_6} + \underset{\text{(Fructose)}}{C_6H_{12}O_6}$$

b. Prepartion of glucose from starch :

Commercially glucose is obtained by hydrolysis of starch by boiling it with dilute sulfuric acid at 393K under 2 to 3 atm pressure.

$$(C_6H_{10}O_5)_n + n\,H_2O \xrightarrow[393K,\ 2\text{-}3\ atm]{H^{\oplus}} n\,C_6H_{12}O_6$$

(Starch) (Glucose)

14.2.4 Structure and properties of glucose

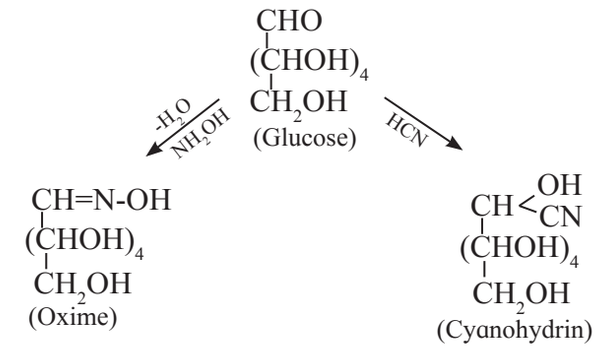
Glucose has an aldohexose structure. In other words, glucose molecule contains one aldehydic, that is, formyl group and the remaining five carbons carry one hydroxyl group (-OH) each. The six carbons in glucose form one straight chain. This aldohexose structure of glucose was established on the basis of the following **chemical properties**.

1. Molecular formula of glucose was found to be $C_6H_{12}O_6$, on the basis of its elemental compostion and colligative properties.

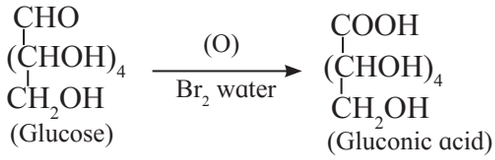
2. The six carbons in glucose molecule form a straight chain. This was inferred from the following observation : Glucose gives n-hexane on prolonged heating with HI.

$$\underset{\text{(Glucose)}}{CHO\text{-}(CHOH)_4\text{-}CH_2OH} \xrightarrow{HI,\ \Delta} \underset{\text{(n-Hexane)}}{CH_3\text{-}(CH_2)_4\text{-}CH_3}$$

3. Glucose molecule contains one carbonyl group. This was inferred from the observation that glucose forms oxime by reaction with hydroxylamine and gives cyanohydrin on reaction with hydrogen cyanide.



4. The carbonyl group in glucose is in the form of aldehyde. This was inferred from the observation that glucose gets oxidised to a six carbon monocarboxylic acid called gluconic acid on reaction with bromine water which is a mild oxidizing agent.



Problem 14.1 :
An alcoholic compound was found to have molcular mass of 90 u. It was acetylated. Molecular mass of the acetyl derivative was found to be 174 u. How many alcoholic (-OH) groups must be present in the original compound?

Solution : In acetylation reaction H atom of an (-OH) group is replaced by an acetyl group ($-COCH_3$). This results in an increase in molcular mass by [(12+16+12+3×1)-1], that as, 42 u.

In the given alcohol,

increase in molecular mass = 174 u - 90 u
= 84 u

$$\therefore \text{ Number of -OH groups} = \frac{84\ u}{42\ u} = 2$$

Can you recall ?

What are the products of reaction of

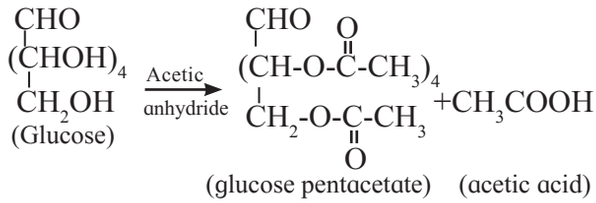
i. $CH_3\text{-}CO\text{-}CH_3$ with $NH_2\text{-}OH$?

ii. $CH_3\text{-}CHO$ with HCN?

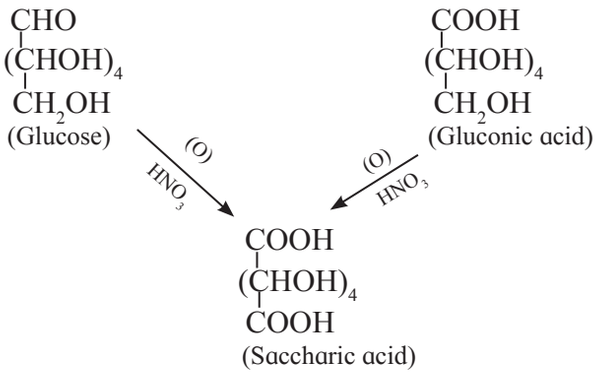
iii. $CH_3\text{-}OH$ with $CH_3\text{-}CO\text{-}O\text{-}CO\text{-}CH_3$?

5. Glucose contains five hydoxyl groups :

This was inferred from the observation that Glucose reacts with five moles of acetic anhydride to form glucose pentaacetate. As glucose is a stable compound, it was further inferred that the five hydroxyl groups are bonded to five different carbon atoms in glucose molecule.



6. Glucose contains one primary alcoholic (- CH_2OH) group : This was inferred from the following observation : Glucose and gluconic acid both on oxidation with dilute nitric acid give the same dicarboxylic acid called saccharic acid.



Use your brain power

- Write structural formula of glucose showing all the bonds in the molecule.
- Number all the carbons in the molecules giving number 1 to the (-CHO) carbon.
- Mark the chiral carbons in the molecule with asterisk (*).
- How many chiral carbons are present in glucose?

14.2.5 Optical isomerism in glucose :

Structural formula of glucose shows that it contains four chiral carbon atoms. You have learnt that every chiral carbon can have two distinct spatial arrangements of groups around it (section 10.5.1). In other words, two distinct configurations are possible for each of the four chiral carbons of glucose. Stereostructure of glucose is therefore one out of several possible stereostructures of an aldohexose.

Do you know ?

A structural formula containing 'n' number of chiral carbon can have maximum '2^n' numbers of stereostructures or optical isomers. An aldohexose therefore, can exist as sixteen ($2^4 = 16$) optical isomers, and glucose is one of them.

Can you recall ?

- What are the ways to represent three dimensional structure of an organic molecule?
- How is a Fischer projection formula drawn?

On the basis of very elaborate chemical evidence and measurement of optical activity of various chemicals involved, Emil Fischer, a German Nobel laureate (1902), determined the configuration of the four chiral carbons (C-2, C-3, C-4, C-5) in glucose.

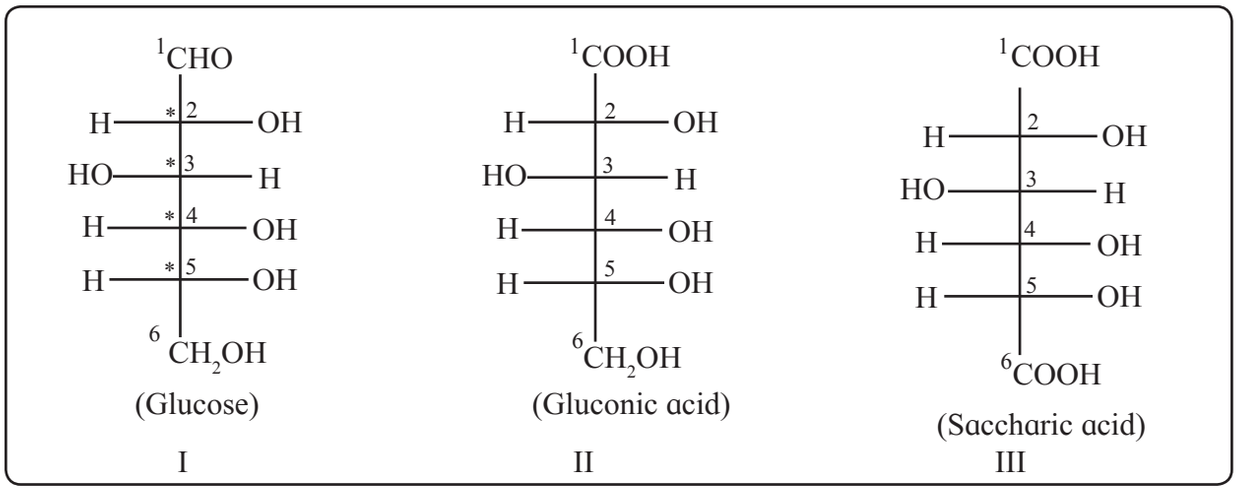


Fig 14.2 : Fischer projection formulae of glucose, gluconic acid and saccharic acid

Figure 14.2 shows the Fisher projection formulae of glucose (I), gluconic acid (II) and saccharic acid (III).

Glucose is an optically active compound and has its specific rotation, $[\propto]_D^{20}$, equal to $+52.7^0$. Due to its dextrorotation glucose is also called **dextrose**. The designations **(+)-glucose** or **d-glucose** imply the dextrorotatory nature of glucose. **D-glucose** is another designation of glucose, which is more common. This designation indicates the configuration of glucose rather than the sign of its optical rotation.

D/L configuration system : The prefix D- or L- in the name of a compound indicates relative configuration of a stereoisomer. It refers to a particular enantiomer of glyceraldehyde. **Glyceraldehyde** has one chiral carbon(C-2) and exists as two enantiomers. These are represented by two Fischer projection formulae (see Fig. 14.3).

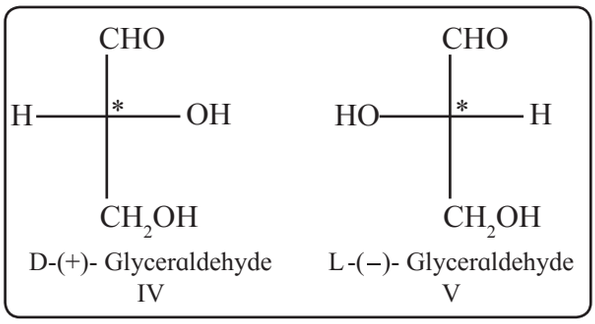
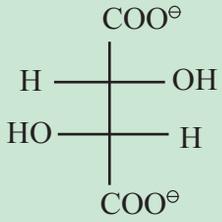


Fig. 14.3 : Enantiomers of glyceraldehyde

Conventionally (+)-glyceraldehyde is represented by the Fischer projection formula having OH group attached to C-2 on right side (IV) and this configuration is denoted by symbol '**D**'. Similarly, configuration of (-) glyceraldehyde (V) is denoted by symbol '**L**'. All the compounds which can be correlated by a series of chemical reactions to (+) - glyceraldehyde are said to have D-configuration. The compounds which are chemically correlated to (-) - glyceraldehyde are said to have L- configuration. This is the system of **relative configuration** of chiral compounds.

Do you know ?

Optical rotation is an experimentally measurable property of a compound. Configuration of chiral carbon, on the other hand, is difficult to observe by simple experiment. In 1951 X-ray crystallographic studies of (+) - sodium rubidium tartarate established its configuration as :



This was the first instance of determining absolute configuration.

A monosaccharide is assigned D/L configuration on the basis of the configuration of the lowest chiral carbon in its Fischer projection formula. Figure 14.4 illustrates the D-configuration of (+) - glucose.

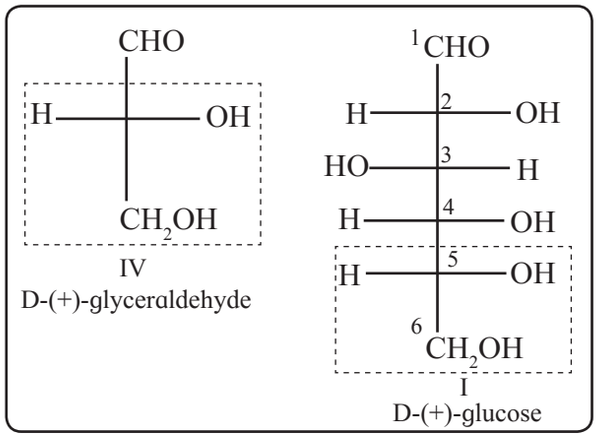
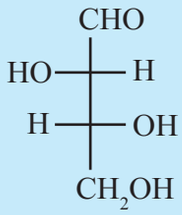


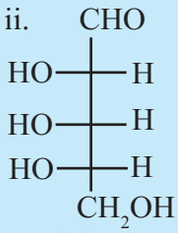
Fig. 14.4 : Relative configuration of (+) - glucose

14.2.6 Ring structure of glucose : On the basis of chemical evidence stereostructure of D-glucose was represented by the Fischer projection formula **I** (Fig. 14.2 and Fig. 14.4). Glucose, however, was found to exhibit some more chemical properties which could not be explained on the basis of the structure **I.** It was necessary to write another structure for glucose which will explain all the properties. Ring structure of glucose fulfils this requirement.

Problem 14.2 : Assign D/L configuration to the following monosaccharides.

i. 

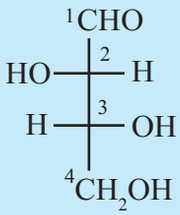
(Threose)

ii. 

(Ribose)

Solution :

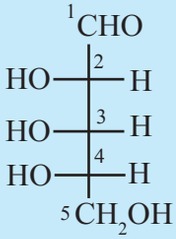
D/L configuration is assigned to Fischer projection formula of monosaccharide on the basis of the lowest chiral carbon.

i. 

(Threose)

Threose has two chiral carbons C-2 and C-3. The given Fischer projection formula of threose has -OH groups at the lowest C-3 chiral carbon on right side.

∴ It is D-threose.

ii. 

(Ribose)

Ribose has three chiral carbons C-2, C-3 and C-4. The given Fischer projection formula of ribose has -OH group at the lowest C-4 chiral carbon on left side.

∴ It is L-ribose

Glucose is found to have two cyclic structures (VI and VII) which are in equilibrium with each other through the open chain structure (I) in aqueous solution (Fig.14.5).

The ring structure of glucose is formed by reaction between the formyl (-CHO) group and the alcoholic (-OH) group at C-5. Thus, the ring structure is a **hemiacetal** structure (section 12.8.2 c). The two hemiacetal structures (VI and VII) differ only in the configuration of C-1 (Fig. 14.5), the additional chiral centre resulting from ring closure. The two ring structures are called **∝- and β- anomers** of glucose and C-1 is called the anomeric carbon. The ring of the cyclic structure of glucose contains five carbons and one oxygen. Thus, it is a six membered ring. It is called pyranose structure, in analogy with the six membered heterocyclic compound pyran (Fig. 14.6). Hence glucose is also called **glucopyranose**. Haworth formula is a better way than Fischer projection formula to represent structure of glucopyranose (Fig. 14.6). In the **Haworth formula** the pyranose ring is considered to be in a perpendicular plane with respect to the plane of paper. The carbons and oxygen in the ring are in the places as they appear in Fig. 14.6. The lower side of the ring is called **∝-side** and the upper side is the **β-side**. The ∝-anomer has its anomeric hydroxyl (-OH) group (at C-1) on the ∝-side, whereas the β-anomer has

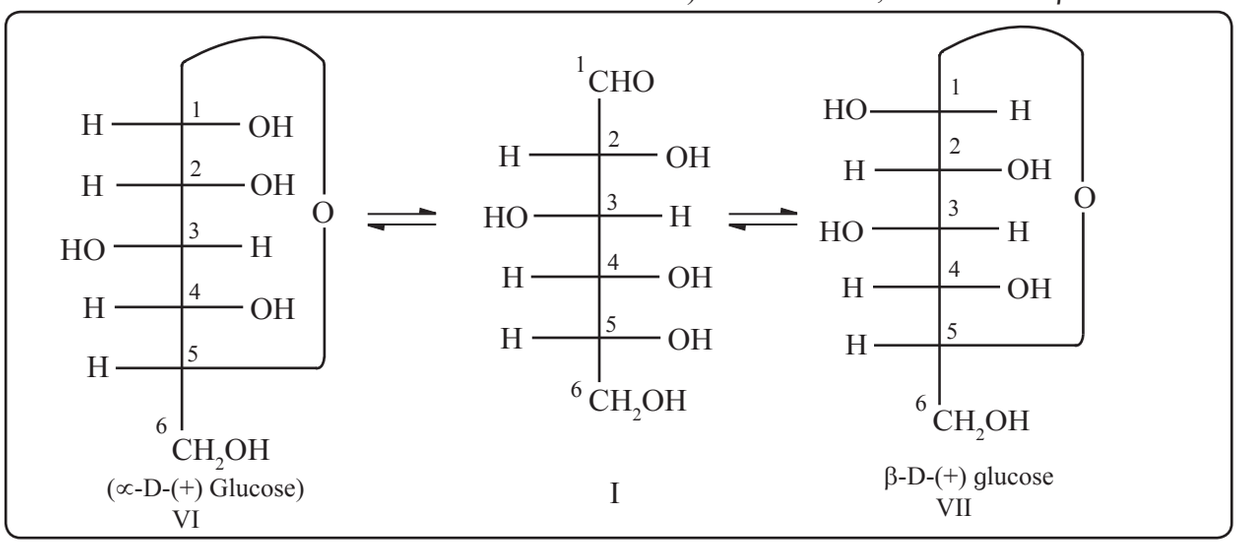


Fig. 14.5 Ring structures of glucose: Fischer projection formulae

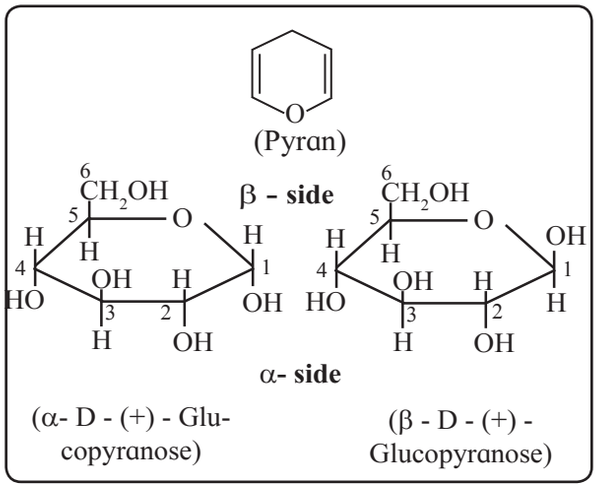


Fig. 14.6 : Haworth formula of anomers of glucopyranose

its anomeric hydroxyl (-OH) group (at C-1) on the β-side. The groups which appear on right side in the Fischer projection formula appear on α-side in the Haworth formula, and viceversa.

14.2.7 Reducing nature of glucose :

Hemiacetal group of glucopyranose structure is a **potential aldehyde group**. It imparts reducing properties to glucose. Thus, glucose gives **positive Tollens test and positive Fehling test** (Section 12.8.1 a).

14.2.8 Representation of Fructose structure

Fructose ($C_6H_{12}O_6$) is a laevorotatory ketohexose. Fructose is also called laevulose due to its laevorotation $[\propto]_D^{20}$ = -92.4^0. Being an ∝-hydroxy keto compound fructose is a **reducing sugar**. In free state it exists as mixture of fructopyranose (major) and fructofuranose. In combined state fructose is found in the form of **fructofuranose** ring structre (as in sucrose, see section 14.2.9). The name furanose is given by analogy with furan, a five membered heterocyclic compound. Figure 14.7 shows representations of open chain structure of fructose and ring structures of ∝- and β- anomers of fructofuranose. Ring structure of fructose is a hemiketal (section 12.8.2 c).

14.2.9 Disaccharides : Disaccharides give rise to two units of same or different monosaccharides on hydrolysis with dilute acids or specific enzymes. The two monosaccharide units are linked together by an ether oxide linkage (-O-), which is termed as **glycosidic linkage** in carbohydrate chemistry. Glycosidic linkage is formed by removal of a water molecule by reaction of two hydroxyl

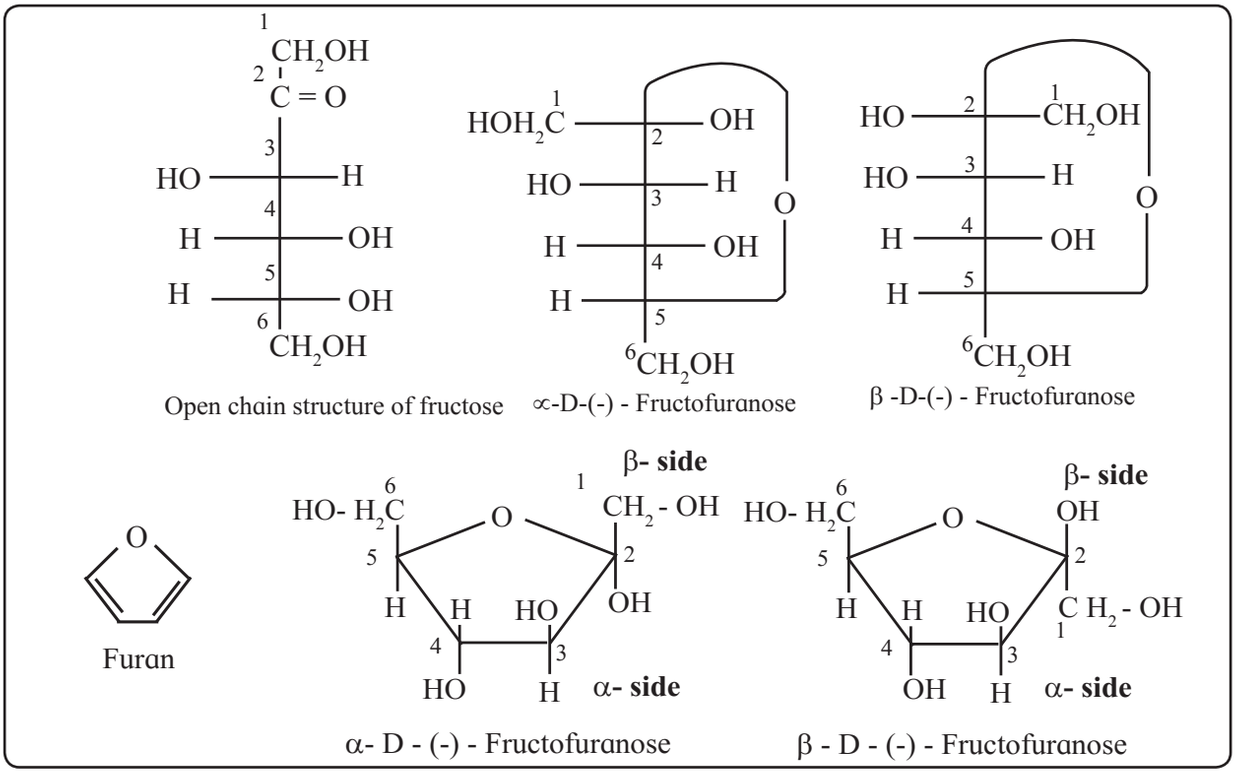


Fig. 14.7 : Representations of fructose structure

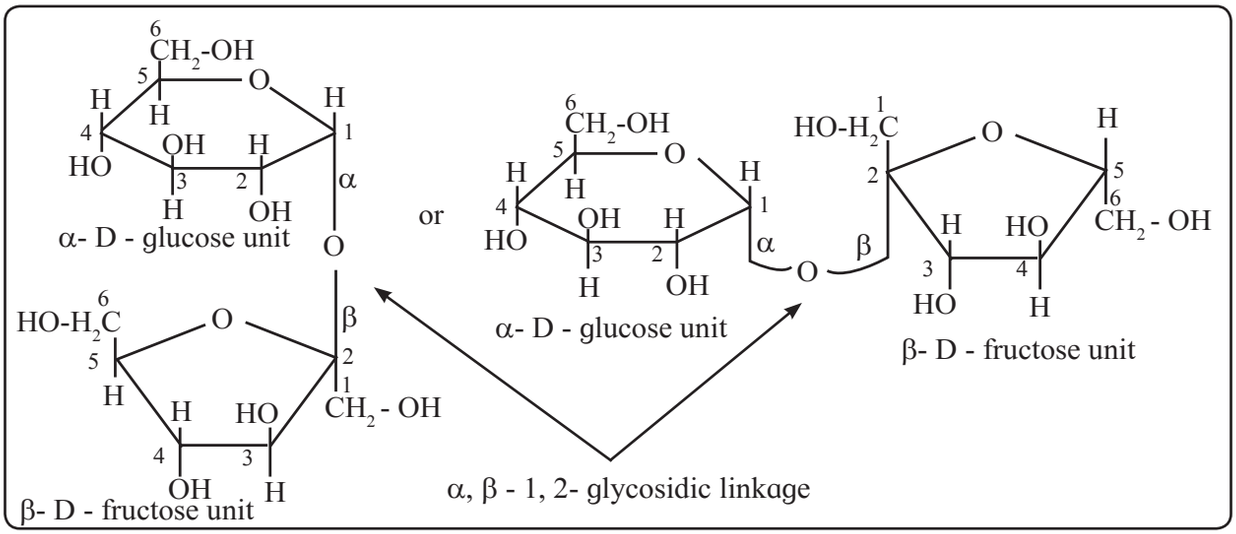


Fig. 14.8 : Haworth formula of sucrose

(-OH) groups from two monosaccharide units. At least one of the two monosaccharide units must use its anomeric hydroxyl group in formation of the glycosidic linkage. Three most common disaccharides are sucrose, maltose and lactose.

a. Sucrose : Sucrose ($C_{12}H_{22}O_{11}$) is dextrorotatory ($+66.5^0$). On hydrolysis with dilute acid or an enzyme called invertase sucrose gives equimolar mixture of D-(+) glucose and D-(-) fructose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{or invertase}]{H^{\oplus}} C_6H_{12}O_6 + C_6H_{12}O_6$$

(Sucrose) (D-(+) glucose) (D-(-)fructose)

Since the laevoratotion of fructose (-92.4^0) is larger than the dextrorotation of glucose ($+52.7^0$), the hydrolysis product has net laevorotation. Hence hydrolysis of sucrose is also called **inversion of sucrose**, and the product is called **invert sugar**. Structure of sucrose contains glycosidic linkage between C-1 of ∝-glucose and C-2 of β-fructose (Fig. 14.8).

Try this...

Make models corresponding to the two Haworth formulae of sucrose in Fig. 14.8. Check that both are identical.

Since the potential aldehyde and ketone groups of both the monosaccharide units are involved in formation of the glycosidic bond, sucrose is a **non reducing sugar**.

b. Maltose : Maltose ($C_{12}H_{22}O_{11}$) is a disaccharide made of two units of D-glucose. The glycosidic bond in maltose is formed between C-1 of one glucose ring and C-4 of the other. The glucose ring which uses its hydroxyl group at C-1 is ∝-glucopyranose. Hence the linkage is called ∝-1,4-glycosidic linkage. The hemiacetal group at C-1 of the second ring is not involved in glycosidic linkage. Hence maltose is a **reducing sugar**. Maltose gives glucose on hydrolysis with dilute acids or the enzyme maltase. Figure 14.9 shows Haworth formula of maltose.

Do you know ?

Invert sugar is commerically available as invert syrup. It is used as sweetene in bakery and confectionary products and also in fruit **preserves** and beverages. It is sweeter than sucrose and glucose. It is resistant to crystallization and promotes retention of moisture, enhances flavour and texture and also prolongs shelf life.

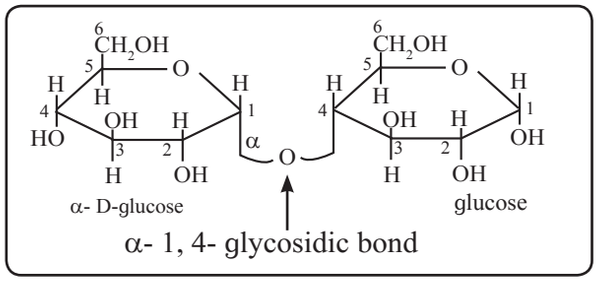


Fig. 14.9 : Haworth formula of maltose

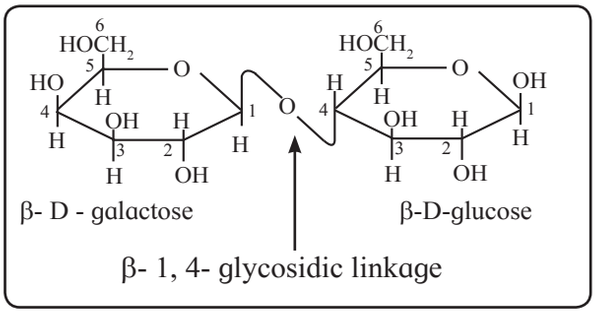


Fig. 14.10 : Haworth formula of lactose

c. Lactose : Lactose ($C_{12}H_{22}O_{11}$) is a disaccharide present in milk. It is formed from two monosaccharide units, namely D-galactose and D-glucose. The glycosidic linkage is formed between C-1 of β-D-galactose and C-4 of glucose. Therefore the linkage in lactose is called β-1,4-glycosidic linkage. The hemiacetal group at C-1 of the glucose unit is not involved in glycosidic linkage but is free. Hence lactose is a **reducing sugar**. Figure 14.10 shows Haworth formula of lactose.

14.2.10 Polysaccharides : Polysaccharides are formed by linking large number of monosaccharide units by glycosidic linkages.

Use your brain power

- Is galactose an aldohexose or a ketohexose?
- Which carbon in galactose has different configuration compared to glucose?
- Draw Haworth formulae of ∝-D-galactose and β-D-galactose.
- Which disaccharides among sucrose, maltose and lactose is/are expected to give positive Fehling test?
- What are the expected products of hydrolysis of lactose?

Starch, cellulose and glycogen are the most common natural polysaccharides. Starch is storage carbohydrate of plants and important nutrient for humans and other animals. Cellulose is the main constituent of cell wall of plant and bacterial cells. It is also main constituent of wood and cotton. Glycogen constitutes storage carbohydrate of animals and is present in liver, muscles and brain. It is also found in yeast and fungi.

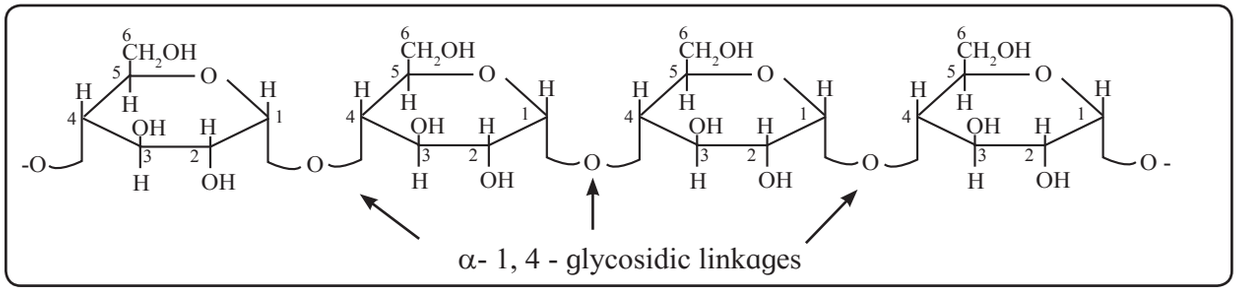


Fig. 14.11 : Amylose

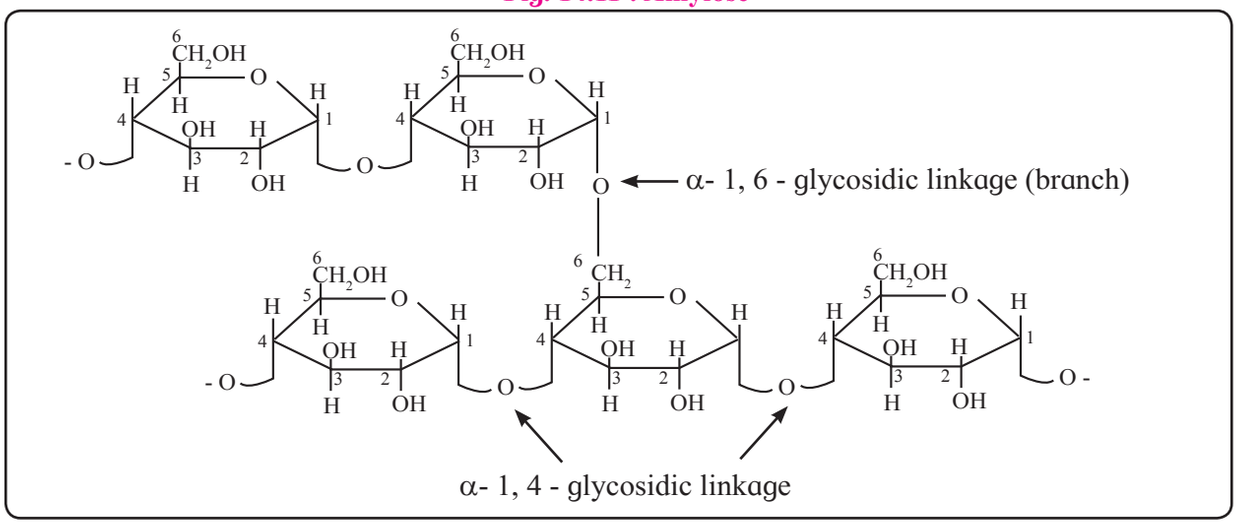


Fig. 14.12 : Amylopectin

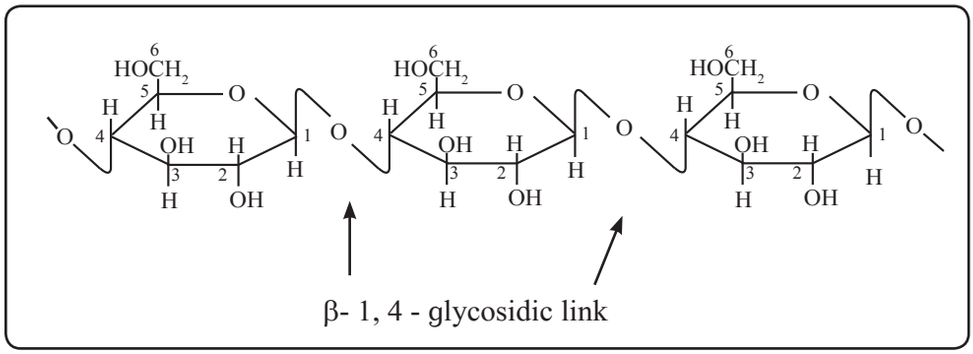


Fig. 14.13 : Cellulose

Can you think ?

When you chew plain bread, *chapati* or *bhaakari* for long time, it tastes sweet. What could be the resason ?

a. Starch : Starch is a polymer of ∝-D-glucose.Starch has two components, namely, **amylose** (15-20%) and **amylopectin** (80-85%). Amylose is soluble in water and forms blue coloured complex with iodine. It contains 200-1000 ∝-glucose units linked by ∝-1,4- glycosidic linkages giving rise to unbranched chain of variable length (Fig. 14.11). Amylopectin is water insoluble component of starch which forms blue-violet coloured complex with iodine. It is a branched chain polysaccharide. In amylopectin, chains are formed by ∝-1,4- glycosidic linkages between ∝-glucose units, where as branches are formed by ∝-1,6- glycosidic linkages (Fig. 14.12).

b. Cellulose : Cellulose is a straight chain polysaccharide of β-glucose units linked by β-1,4- glycosidic bonds. Chemical hydrolysis of cellulose requires use of concerntrated strong acids at high temperature and pressure. This implies that the β-1,4- glycosidic bond is very strong and difficult to hydrolyse. Humans do not have enzymes which can hydrolyse this linkage. Hence cellulose cannot be digested by human beings; it serves as the fibrous content of food useful for bowel movement. Figure 14.13 shows the Haworth formula of cellulose.

c. Glycogen : Glycogen has its structure similar to that of amylopectin, but it is more highly branched.

Do you know ?

The symbiotic bacteria in guts of insects called termites have enzymes that can hydrolyse β-1,4- glycosidic linkage in cellulose.

14.3 Proteins

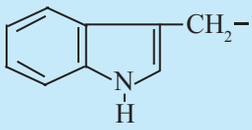
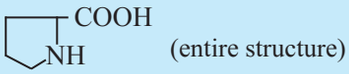
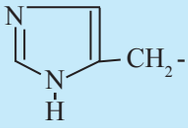
Can you recall ?

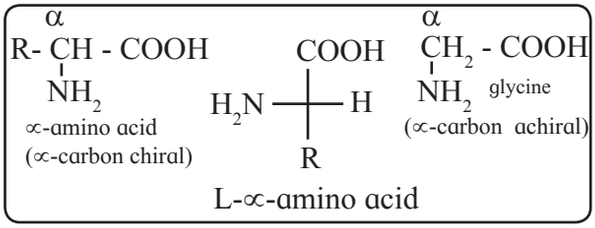
- What is the product of reaction of acetic acid with ammonia ?
- Write the structural formula of N-methyl acetamide. What is the name of the functional group in this compound?
- What are the nitrogenous nutrients in human diet?

Proteins are the fundamental structural materials of animal bodies. Proteins in the form of enzymes play prime role in all the physiological reactions. The name protein is derived form the Greek word, 'proteios' which means 'primary' or 'of prime importance'. Nutritional sources of proteins are milk, pulses, nuts, fish, meat, etc. Chemically proteins are polyamides which are high molecular weight polymers of the monomer units called ∝-amino acids.

14.3.1 ∝-Amino acids : Proteins on complete hydrolysis give rise to a mixture of ∝-amino acids. ∝-Amino acids are carboxylic acids having an amino ($-NH_2$) group bonded to

Table 14.1 Natural α - amino acids : L - RCH (NH_2) COOH (* Essential α - amino acids)

Type	Name	R	Three letter symbol	One letter symbol
Neutral ∝-amino acids	1. Glycine	H-	Gly	G
	2. Alanine	CH_3-	Ala	A
	3. Valine*	Me_2CH-	Val	V
	4. Leucine*	Me_2CH-CH_2 -	Leu	L
	5. Isoleucine*	$CH_3-CH_2-CH(Me)$-	Ile	I
	6. Asparagine	$H_2N-CO-CH_2$ -	Asn	N
	7. Glutamine	$H_2N-CO-CH_2-CH_2$-	Gin	Q
	8. Serine	$HO-CH_2$-	Ser	S
	9. Threonine*	CH_3-CHOH-	Thr	T
	10. Cysteine	$HS-CH_2$ -	Cys	C
	11. Methionine*	$Me-S-CH_2-CH_2$	Met	M
	12. Phenyalanine*	$Ph-CH_2$-	Phe	F
	13. Tyrosine	p-$HO-C_6H_4-CH_2$-	Tyr	Y
	14. Tryptophan*		Trp	W
	15. Proline	 (entire structure)	Pro	P
Acidic	16. Aspartic acid	$HOOC-CH_2$ -	Asp	D
	17. Glutamic acid	$HOOC-CH_2-CH_2$-	Glu	G
Basic	18. Lysine*	$H_2N-(CH_2)_4$-	Lys	K
	19. Arginine*	$HN = C(NH_2) - NH - (CH_2)$-	Arg	R
	20. Histidine*		His	H



L-∝-amino acid

Fig. 14.14 : Natural ∝-amino acids

the ∝-Carbon, that is, the carbon next to the carboxyl (- COOH) group (Fig. 14.14). ∝-carbon in all the ∝-amino acids (except glycine) is chiral. It is found that the ∝- carbon in ∝-amino acids obtained by hydrolysis of proteins has 'L' configuration. The L-∝-amino acids are represented by the Fischer projection formula as shown in Fig. 14.14.

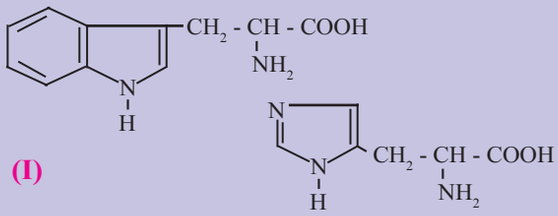
The symbol 'R' in the structure of ∝-amino acids respresents side chain and may contain additional functional groups. If 'R' contains a carboxyl (-COOH) group the amino acid is **acidic amino acid**. If 'R' contains an amino (1^0,2^0 or 3^0) group, it is called **basic amino acid**. The other amino acids having neutral or no functional group in 'R' are called **neutral amino acids**.

∝-Amino acids have trivial names and are generally represented by three letter symbols or sometimes by one letter symbol. Table 14.1 lists the twenty ∝-amino acids, often referred to as simply amino acids, commonly found in proteins with their symbols and also their

types as neutral, acidic or basic. Ten ∝-amino acids from this list cannot be synthesised in human body and have to be obtained through diet. These are called **essential amino acids** and are marked with asterisk (*) in Table 14.1.

Use your brain power

Tryptophan and histidine have the structures (I) and (II) respectively. Classify them into neutral/ acidic/basic ∝-amino acids and justify your answer.(Hint : Consider involvement of lone pair in resonance).



(I) (II)

Can you think ?

Compare the molecular masses of the following compounds and explain the observed melting points.

Formula	Molecular mass	Melting point
$CH_3 - CH(NH_2) - COOH$	89	293.5^0C
$C_5H_{11} - NH_2$	87	-55^0C
$C_3H_7 - COOH$	88	-7.9^0C

∝-Amino acids are high melting, water soluble crystalline solids, unlike simple amines or carboxylic acids. These properties are due to a peculiar structure called **zwitter ion structure** of ∝-amino acids. An ∝-amino acid molecule contains both acidic carboxyl (-COOH) group as well as basic amino ($-NH_2$) group. Proton transfer from acidic group to basic group of amino acid forms a salt, which is a dipolar ion called zwitter ion (Fig. 14.15).

Amino acid can exist in different forms depending upon the pH of the aqueous solution in which it is dissolved. Consider, for example, zwitter ion and the other forms of alanine (Fig. 14.16).

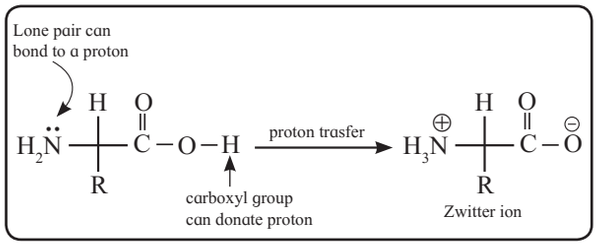


Fig. 14.15 : Zwitter ion

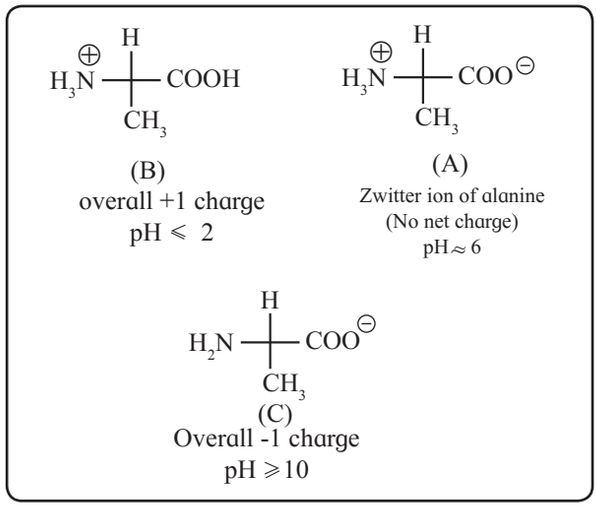


Fig. 14.16 : Three forms of alanine

Do you know ?

At the physiological pH of 7.4, neutral ∝-amino acids are primarily in their zwitterionic forms. On the other hand, at this pH acidic ∝-amino acids exist as anion (due to deprotonation of the carboxyl group), while basic ∝-amino acids exist as cation (due to protonation of the amino groups). Ionic structures of constituent ∝-amino acids result in ionic nature of proteins.

Can you recall ?

- What does the enzyme pepsin do?
- What are the initial and final products of digestion of proteins?

14.3.2 Peptide bond and protein :

Proteins are known to break down into peptides in stomach and duodenum under the influence of enzymes, pepsin being one of them which is secreted by stomach. Polypeptides are further broken down to ∝-amino acids. This implies that proteins are formed by connecting ∝-amino acids to each other. The bond that connects ∝-amino acids to each other is called **peptide bond**. Consider, for example, linking of a molecule of glycine with that of alanine. One way of doing this is to combine carboxyl group of glycine with ∝-amino group of alanine. This results in elimination of a water molecule and formation of a **dipeptide** called **glycylalanine** in which the two amino acid units are linked

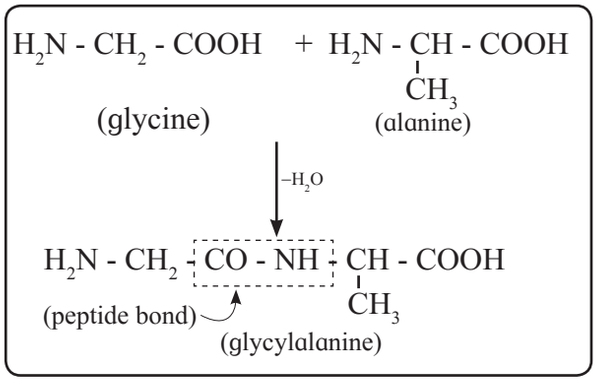


Fig. 14.17 : Peptide bond

by a peptide bond (Fig. 14.17). It can be seen that a peptide bond or peptide linkage is same as what is described as **secondary amide** in organic chemistry. Combination of a third molecule of an ∝-amino acid with a dipeptide would result in formation of a **tripeptide**. Similarly linking of four, five or six ∝-amino acids results in formation of tetrapeptide, pentapeptide or hexapeptide respectively. When the number of ∝-amino acids linked by peptide bonds is more than ten, the products are called **polypeptides**. The -CHR- units linked by peptide bonds are referred to as '**amino acid residues**'. Proteins are polypeptides having more than hundred amino acid residues linked by peptide bonds. It may be, however, noted that distinction between proteins and polypeptides is not sharp. The two ends of a polypeptide chain of protein are not identical. The end having free carboxyl group is called **C-terminal** while the other end having free amino group is called **N-terminal**. In the dipeptide glycylalanine glycine residue is N-terminal and alanine residue is C-terminal.

Use your brain power

- Write the structural formula of dipeptide formed by combination of carboxyl group of alanine and amino group of glycine.
- Name the resulting dipeptide.
- Is this dipeptide same as glycyalanine or its structural isomer?

14.3.3 Types of proteins :

Depending upon the molecular shape proteins are classified into two types.

a. Globular proteins : Molecules of globular proteins have spherical shape. This shape results from coiling around of the polypeptide chain of protein. Globular proteins are usually soluble in water. For example : insulin, egg albumin, serum albumin, legumelin (protein in pulses)

b. Fibrous proteins : Molecules of fibrous proteins have elongated, rod like shape. This shape is the result of holding the polypeptide chains of protein parallel to each other. Hydrogen bonds and disulfide bonds are responsible for this shape. Fibrous proteins are insoluble in water. For example : keratin (present in hair, nail, wool), myosin (protein of muscles).

The shapes of protein molecules are the result of **four level structure of proteins**.

14.3.4 Structure of proteins :

Proteins are responsible for a variety of functions in organisms. Proteins of hair, muscles, skin give shape to the structure, while enzymes are proteins which catalyze physiological reactions. These diverse functions of proteins can be understood by studying the **four**

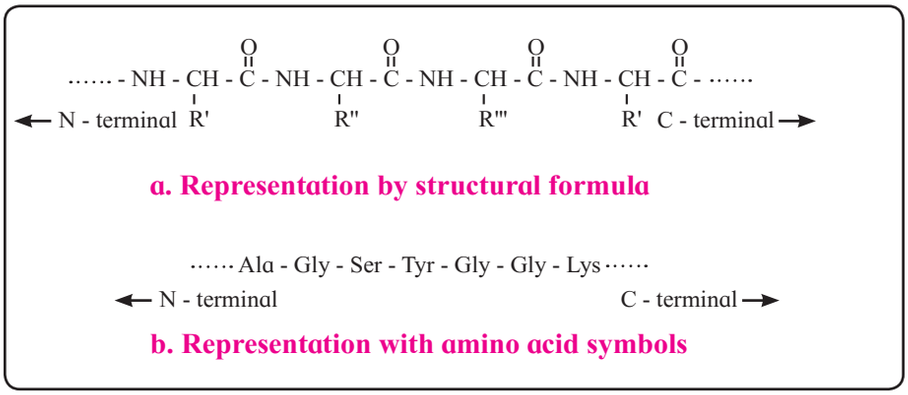


Fig. 14.18 : Representation of primary structure of protein

level structure of proteins, namely primary, secondary, tertiary and quaternary structure of proteins.

a. Primary structure of proteins : Primary structure of proteins is **the sequence of constituent ∝-amino acid residues linked by peptide bonds**. Any change in the sequence of amino acid residuce results in a different protein. Primary structure of proteins is represented by writing the three letter symbols of amino acid residuces as per their sequence in the concerned protein. The symbols are separated by dashes. According to the convention, the N-terminal amino acid residue as written at the left end and the C-terminal amino acid residue at the right end (Fig. 14.18).

Problem 14.3

Chymotrypsin is a digestive enzyme that hydrolyzes those amide bonds for which the carbonyl group comes from phenylalanine, tyrosine or tryptophan. Write the symbols of the amino acids and peptides smaller than pentapeptide formed by hydrolysis of the following hexapeptide with chymotrypsin.

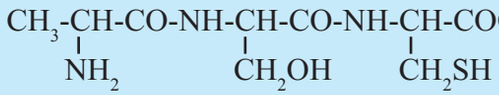
Gly-Tyr-Gly-Ala-Phe-Val

Solution : In the given hexapeptaide hydroylsis by chymotripsin can take place at two points, namely, Phe and Tyr. The carbonyl group of these residuces is towards right side, that is, toward the C-terminal. Therefore the hydrolysis products in required range will be :

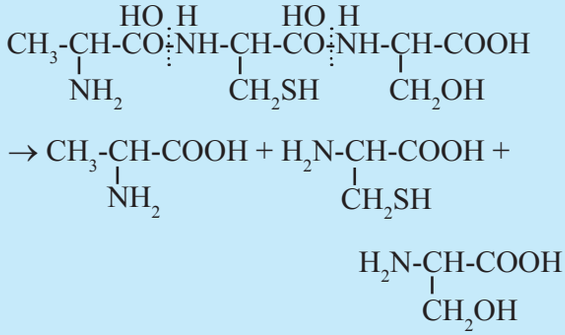
Gly-Tyr, Gly-Ala-Phe and Val

(a dipeptide) (a tripeptide) (∝-amino acid)

Problem 14.4 : Write down the structures of amino acids constituting the following peptide.



Solution : The given peptide has two amide bonds linking three amino acids. The structures of these amino acids are obtained by adding one H_2O molecule across the amide bond as follows :



b. Secondary structure of proteins :

The three-dimensional arrangement of localized regions of a protein chain is called the secondary structure of protein. Hydrogen bonding between N-H proton of one amide linkage and C=O oxygen of another gives rise to the secondary structure. Two types of secondary structures commonly found in proteins are **∝-helix** and **β-pleated sheet**.

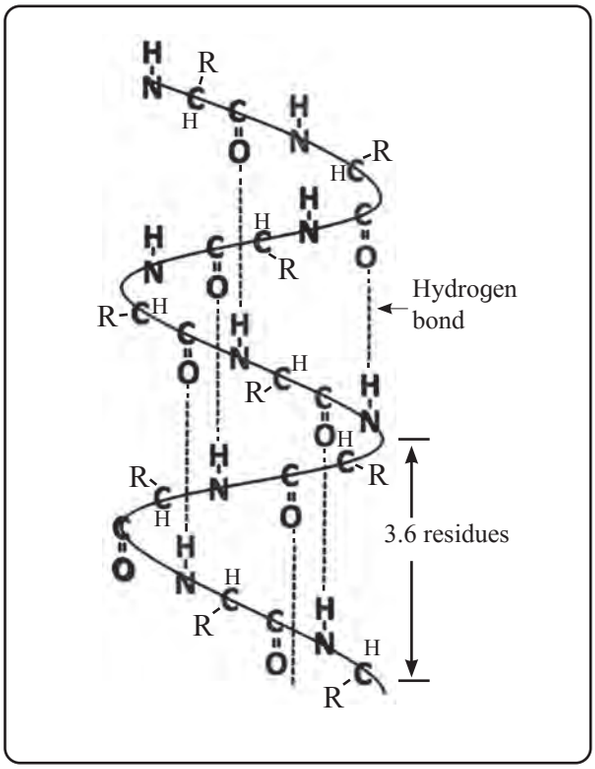


Fig. 14.19 : Backbone of ∝ - Helix

∝-Helix : The ∝-helix forms when a polypeptide chain twists into a **right handed or clockwise spiral** (Fig. 14.19). Some characteristic features of ∝-helical structure of protein are:

- Each turn of the helix has 3.6 amino acids.
- A C=O group of one amino acid is hydrogen bonded to N-H group of the fourth amino acid along the chain.
- Hydrogen bonds are parallel to the axis of helix while R groups extend outward from the helix core.

Myosin in muscle and ∝-keratin in hair are proteins with almost entire ∝-helical secondary structure.

Do you know ?

In collagen, the protein of connective tissue, the polypeptide chains have **unusual left-handed helix structure**. Three strands of these chains wind around each other in a right-handed triple helix.

β-Pleated sheet : The secondary structure is called β-pleated sheet when **two or more polypeptide chains, called strands, line up side-by-side** (Fig. 14.20). The β-pleated sheet structure of protein consists of extended strands of polypeptide chains held together by hydrogen bonding. The characteristics of β-pleated sheet structure are :

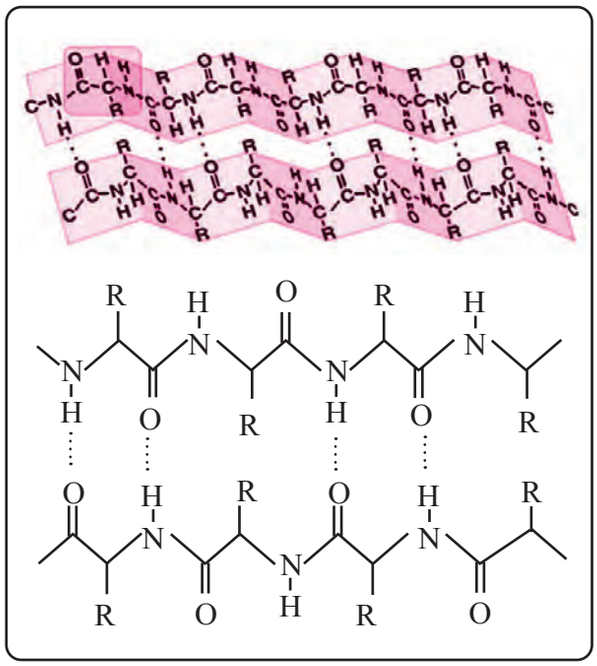


Fig. 14.20 : β - pleated sheet

- The C=O and N-H bonds lie in the plane of the sheet.
- Hydrogen bonding occurs between the N-H and C=O groups of nearby amino acid residues in the neighbouring chains.
- The R groups are oriented above and below the plane of the sheet.

The β-pleated sheet arrangement is favoured by amino acids with small R groups.

Most proteins have regions of ∝-helix and β-pleated sheet, in addition to other random regions that cannot be characterised by either of these secondary structures. For example: Spider dragline silk protein is strong due to β-pleated sheet region, yet elastic due to ∝-helical regions in it.

c. Tertiary structure of proteins : The three-dimensional shape adopted by the entire polypeptide chain of a protein is called its tertiary structure. It is the result of folding of the chain in a particular manner that the structure is itself stabilized and also has attractive interaction with the aqueous environment of the cell. The **globular** and **fibrous** proteins represent two major molecular shapes resulting from the tertiary structure. The forces that stabilize a particular tertiary structure include **hydrogen bonding**, **dipole-dipole attraction** (due to polar bonds in the side chains), **electrostatic attraction** (due to the ionic groups like $-COO^{\ominus}$, $NH_3^{\oplus}$ in the side chain) and also **London dispersion forces**. Finally, **disulfide bonds** formed by oxidation of nearby -SH groups (in cysteine residues) are the **covalent bonds** which stabilize the tertiary structure (Fig. 14.21).

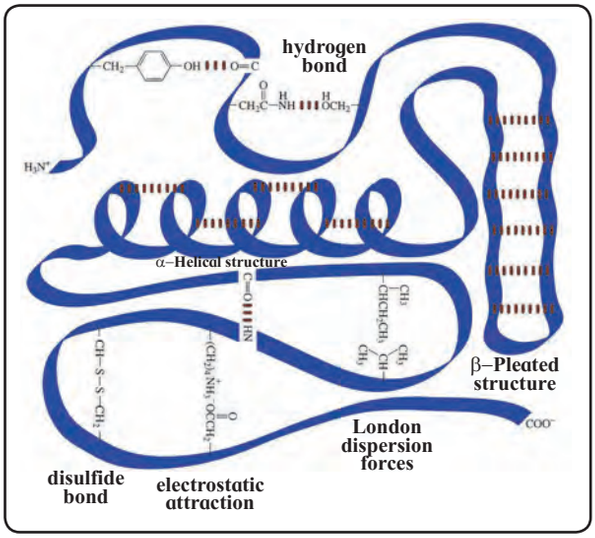


Fig. 14.21 : Tertiary structure of protein

d. Quaternary structure of proteins : When two or more polypeptide chains with folded **tertiary structures come together into one protein complex**, the resulting shape is called quaternary structure of the protein. Each individual polypeptide chain is called a subunit of the overall protein. For example: **Haemoglobin** consists of **four subunits** called haeme held together by intermolecular forces in a compact three dimensional shape. Haemoglobin can do its function of oxygen transport only when all the four subunits are together. Figure 14.22 summerizes schematically the four levels of protein structure.

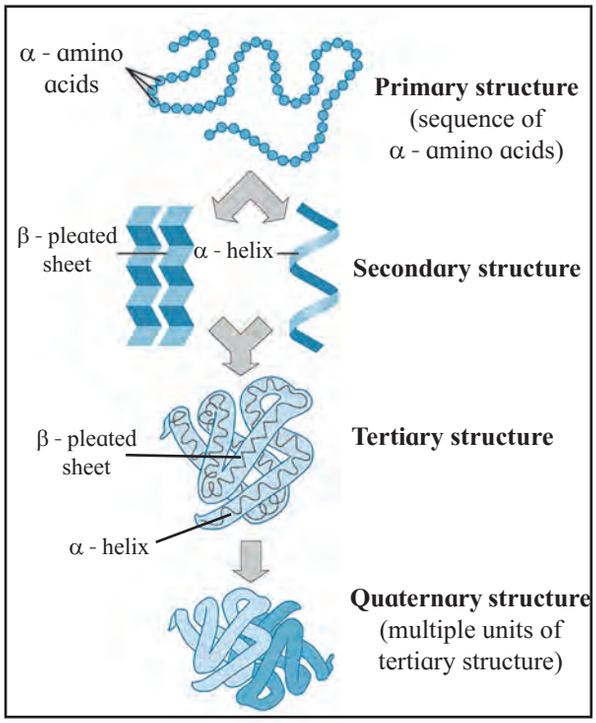


Fig. 14.22 : Four levels of protein structure

Use your brain power

A protein chain has the following amino acids residues. Show and label the interactions that can be present in various pairs from these giving rise to tertiary level structure of protein.

$$-HN-\underset{\displaystyle CH_2OH}{\underset{|}{CH}}-CO- \quad , \quad -HN-\underset{\displaystyle CH_2-Ph}{\underset{|}{CH}}-CO- \quad ,$$

$$-HN-\underset{\displaystyle CH_2-CO-NH_2}{\underset{|}{CH}}-CO- \quad , \quad -HN-\underset{\displaystyle CH_2-CH-Me_2}{\underset{|}{CH}}-CO- \quad ,$$

Can you tell ?

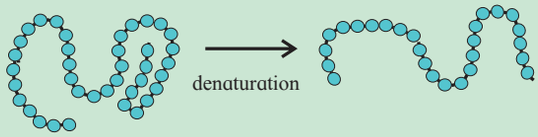
What is the physical change observed when (a) egg is boiled, (b) milk gets curdled on adding lemon juice ?

14.3.5 Denaturation of proteins

High temperature, acid, base and even agitation can disrupt the noncovalent interactions responsible for a specific shape of protein. This is denaturation of protein. **Denaturation is the process by which the molecular shape of protein changes without breaking the amide/peptide bonds that form the primary structre.**

Do you know ?

Globular proteins are typically folded with hydrophobic side chains in the interior and polar residues on the outside, and thereby are water soluble. Denaturation exposes the hydrophobic region of globular proteins and makes them water insoluble.



coiled globular protein — loose coils and loops

Denaturation results in disturbing the secondary, tertiary or quaternary structure of protein. This causes change in properties of protein and the biological activity is often lost.

14.3.6 Enzymes :

Can you recall ?

- Which parameter, equilibrium constant or activation energy, decides the rate of a chemical reaction?
- What is the influence of a catalyst on activation energy?

A very large number of chemical reactions take place in our bodies. These are brought about at the physiological pH of 7.4 and the body temperature of 37^0 C with the help of biological catalysts called enzymes. For example : insulin, harmone secreted by pancreas, controls blood sugar level; amylase, an enzyme present in saliva, hydrolyzes starch. Chemically enzymes are proteins. Every living cell contains at least 1000 different enzymes. Most enzymes catalyse only one reaction or one group of similar reactions. Thus, enzyme catalysis is **highly specific**. You have learnt that a mineral acid can catalyse hydrolysis of many types of compounds such as esters, acetals and amides. In contrast, an enzyme that catalyses hydrolysis of amide will not work on ester or acetal.

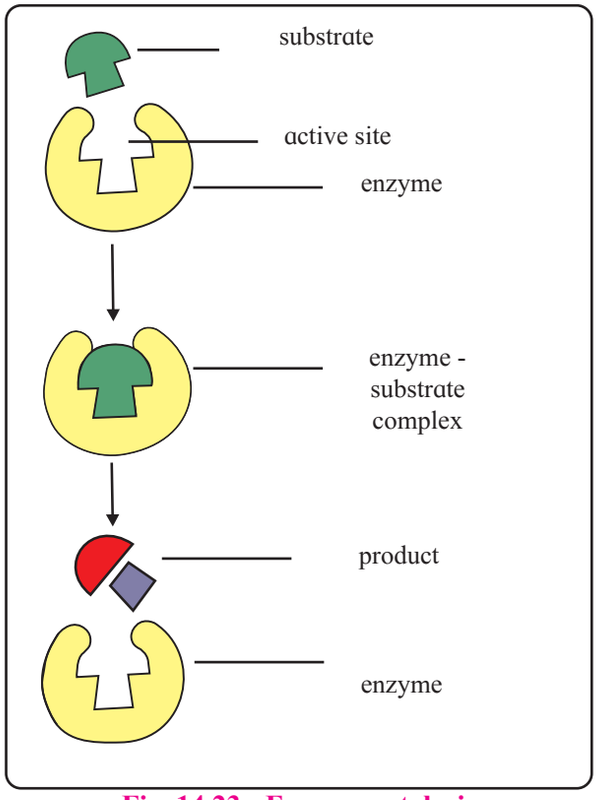


Fig. 14.23 : Enzyme catalysis

Mechanism of enzyme catalysis

Action of an enzyme on a substrate is described as **lock-and-key mechanism** (Fig.14.23). Accordingly, an enzyme has an active site on its surface. A substrate molecule can attach to this active site only if it has the right size and shape. Once in the active site, the substrate is held in the correct orientation to react and forms the products of reaction.

The products leave the active site and the enzyme is then ready to act as catalyst again. Formation of enzyme-substrate complex has very low activation energy. That is how the rate of the reaction is very high. Some enzymes are so **efficient** that one enzyme molecule can catalyse the reaction of 10000 substrate molecules in one second.

Several enzymes have been isolated from organisms (such as bacteria), purified and crystallised,and amino acid sequences of many of them have been determined. In many **industrial processes** specific reactions are carried out by use of enzymes extracted from organisms, and also by use of **new enzymes** made using genetic engineering.

Some examples of **industrial application** of enzyme catalysis are :

- Conversion of glucose to sweet-tasting fructose, using glucose isomerase.
- Manufacture of new antibiotics, using pencillin G acylase.
- Manufacture of laundry detergents, using proteases.
- Manufacture of esters used in cosmetics, using genetically engineered enzyme.

14.4 Nucleic acids :

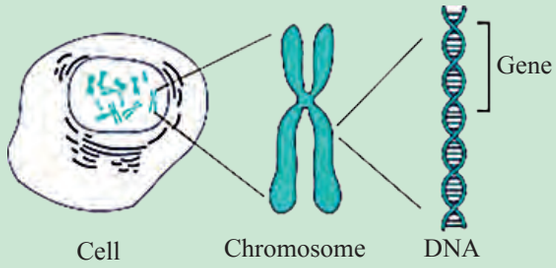
Can you tell ?

- What is the single term that answers all the following questions ?
- What decides whether you are blue eyed or brown eyed ?
- Why does wheat grain germinate to produce wheat plant and not rice plant ?
- Which acid molecules are present in nuclei of living cells ?

One of the most remarkable properties of living cells is their ability to produce their replicas through thousands of generations. This becomes possible because certain type

Do you know ?

Synthesis of protein, the fundamental structural material of body, is the process in which genetic information is transferred. DNA governs this process. DNA is present in the chromosomes of the cell nucleus. Each chromosome has a different type of DNA. An individual chromosome is composed of many **genes**. Gene is a portion of DNA molecule responsible for synthesis of a single protein. **DNA stores the genetic information**, while **RNA translates** this into synthesis of proteins needed by cells for proper function and development.



of information is passed unchanged from one generation to the next. Such information is called **genetic information** and its transfer to new cells is accomplished by **nucleic acids**.

There are two types of nucleic acids : **ribonucleic acids (RNA) and deoxyribonucleic acids (DNA)**. RNA are found mainly in the fluid of living cells (cytoplasm) while DNA are found primarily in the nuclei of living cells.

Knowledge of structure of nucleic acids is essential to understand their biological functions. In this chapter we are going to look at the **structural aspects of nucleic acids**.

14.4.1 Nucleotides : Nucleic acids are unbranched polymers of **repeating monomers** called nucleotides. In other words, nucleic acids have a polynucleotide structure. DNA molecules contain several million nucleotides while RNA molecules contain a few thousand

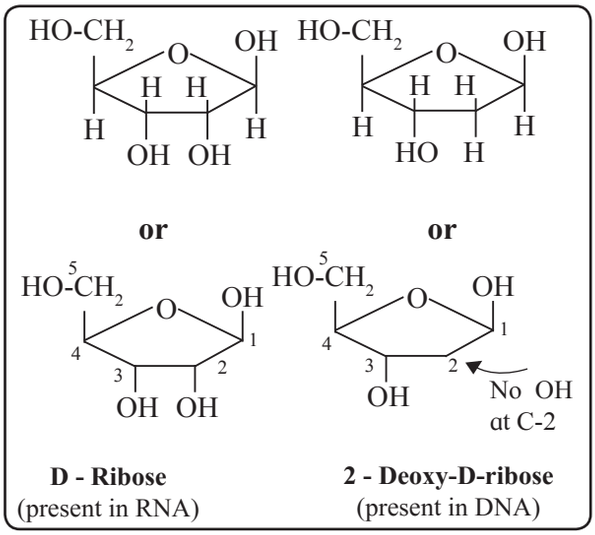


Fig 14.24 : Sugar Components of nucleic acids

nucleotides.

The nucleotide monomers consist of three components : a **monosaccharide**, a **nitrogen-containing base** and a **phosphate group**.

Nucleotides of both RNA and DNA contain five-membered ring monosaccharide (furanose), often called simply sugar component. In RNA, the sugar component of nucleotide unit is D-ribose, while in DNA, it is 2-deoxy-D-ribose (Fig. 14.24).

Total five nitrogen - containing bases are present in nucleic acids. Three bases with one ring (**cytosine**, **uracil** and **thymine**) are derived from the parent compound **pyrimidine**. Two

Remember...

RNA contains : D-ribose, A, G, C, U

DNA contains : D-2-deoxyribose, A, G, C, T

bases with two rings (**adenine** and **guanine**) are derived from the parent compound **purine**. Each base in designated by a one-letter symbol (Fig. 14.25). Uracil (U) occurs only in RNA while thymine (T) occurs only in DNA.

A **nucleoside** is formed by joining the anomeric carbon of the furanose with nitrogen of a base. While numbering the atoms in a nucleoside, primes (') are used for furanose numbering to distinguish them from the atoms of the base (Fig. 14.26). With pyrimidine bases, the nitrogen atom at the 1 position bonds with the 1' carbon of the sugar. With purine bases, the nitrogen atom at the 9 position bonds with 1' carbon of the sugar.

Nucleotides are formed by adding a phosphate group to the 5'-OH of a nucleoside (Fig. 14.27). Thus, **nucleotides are monophosphates of nucleosides**. Abridged names of some nucleotides are AMP, dAMP, UMP, dTMP and so on. Here, the first capital letter is derived from the corresponding base.

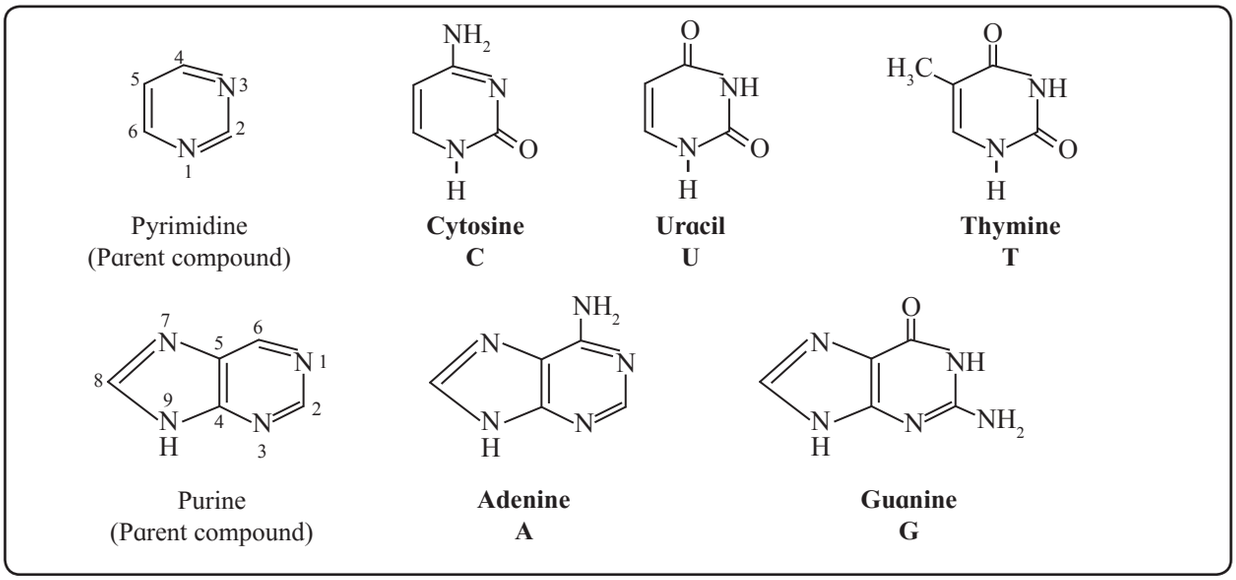


Fig 14.25 : Bases in nucleic acids

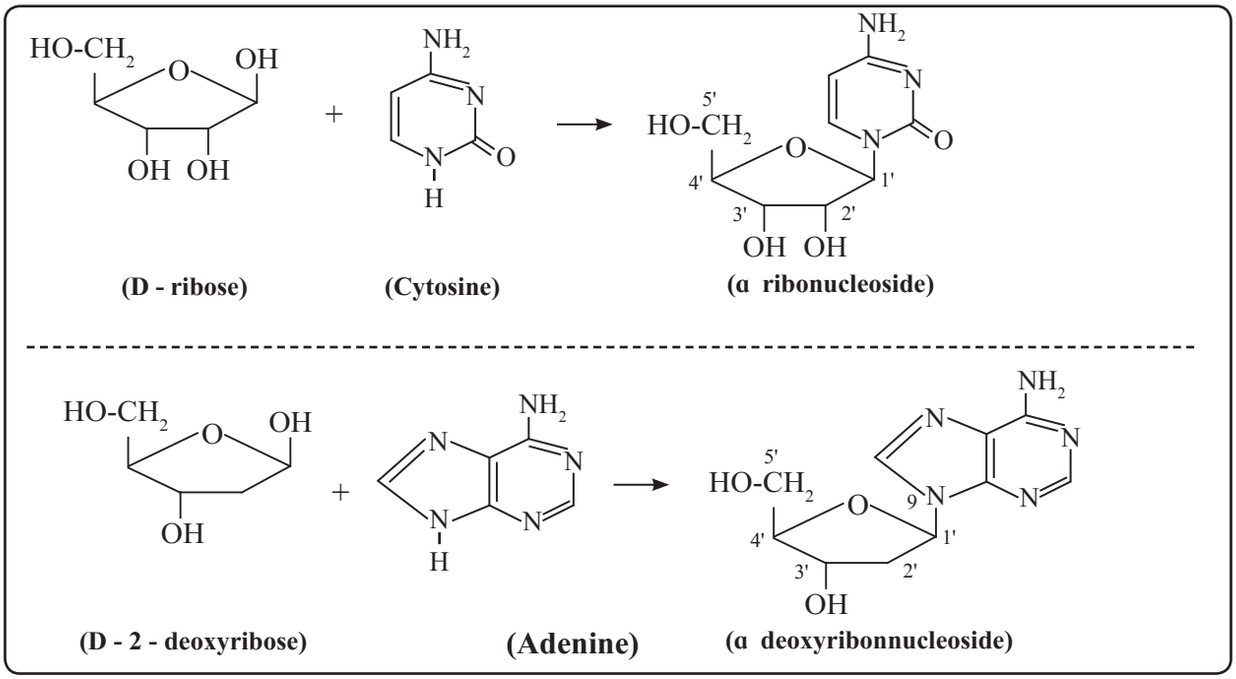


Fig 14.26 : Formation of nucleoside

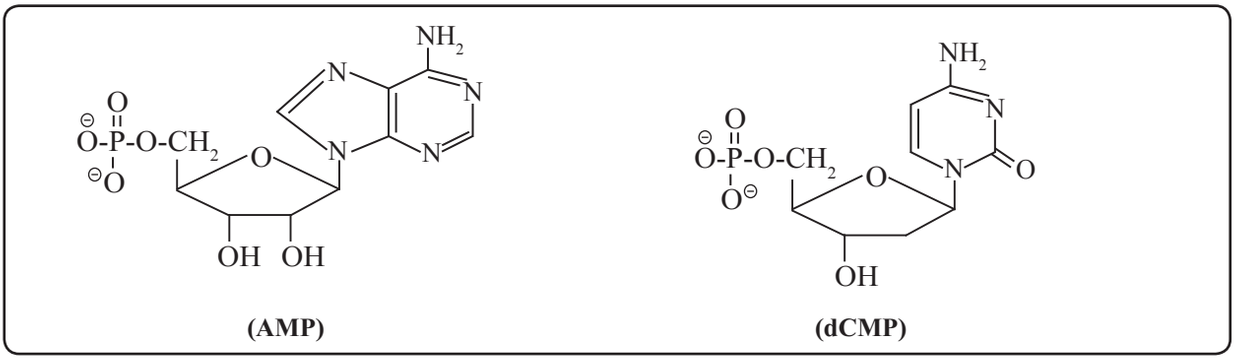


Fig 14.27 : Structures of nucleotides

Use your brain power

Draw structural formulae of nucleosides formed from the following sugars and bases.

i. D-ribose and guanine

ii. D-2-deoxyribose and thymine

MP stands for monophosphate. Small letter 'd' in the beginning indicates deoxyribose in the nucleotide.

14.4.2 Structure of nucleic acids : Nucleic acids, both DNA and RNA, are polymers of nucleotides, formed by joining the 3' - OH group of one nucleotide with 5'-phosphate of another nucleotide (Fig. 14.28). Two ends of polynucleotide chain are distinct from each other. One end having free phosphate group of 5' position is called 5' end. The other end is 3' end and has free OH- group at 3' position.

The polynucleotide structure of nucleic acids can be represented schematically as in Fig. 14.29 (a and b).

The primary structure of nucleic acids is the sequence of the nucleotides in it. This, in turn, is determined by the identity of the bases in the nucleotides. Different nucleic acids have distinct primary structure. **It is the sequence of bases in DNA which carries the genetic information of the organism.** The polynucleotide chains of nucleic acids are named by the sequence of the bases, beginning at the 5' end and using the one letter symbols of the bases. For example the

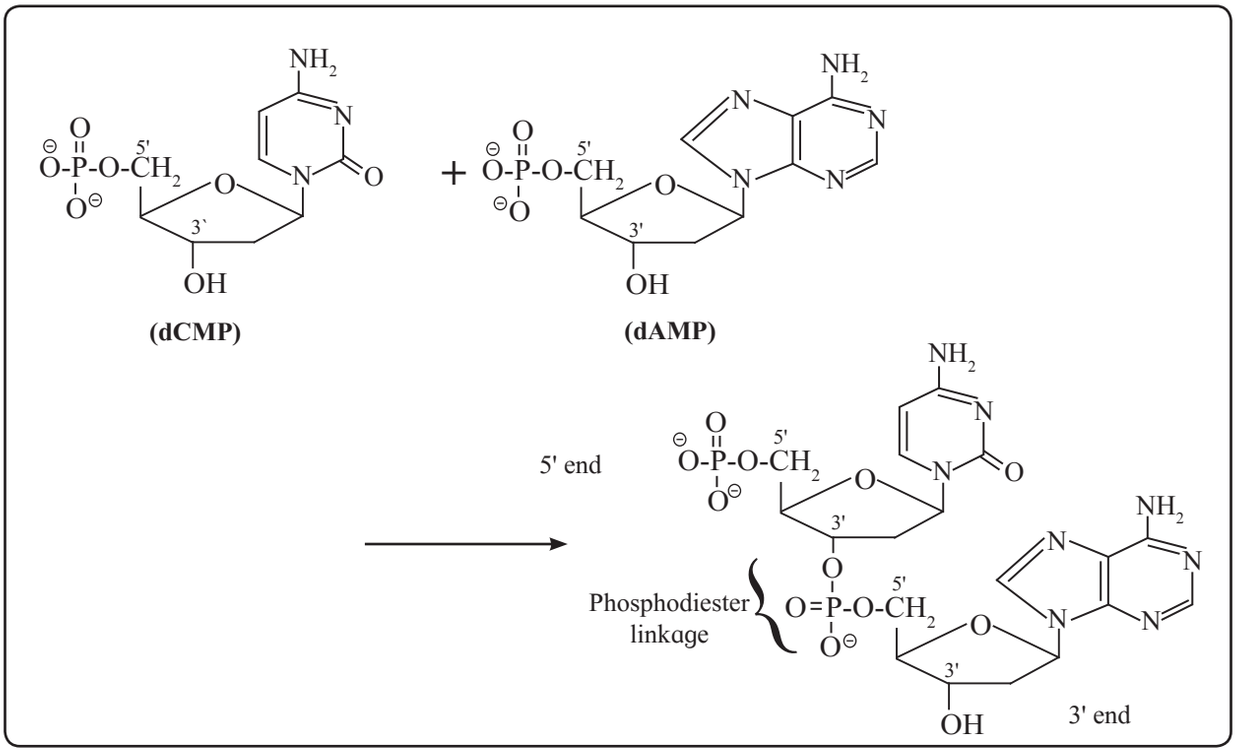


Fig 14.28 : Formation of a dinucleotide

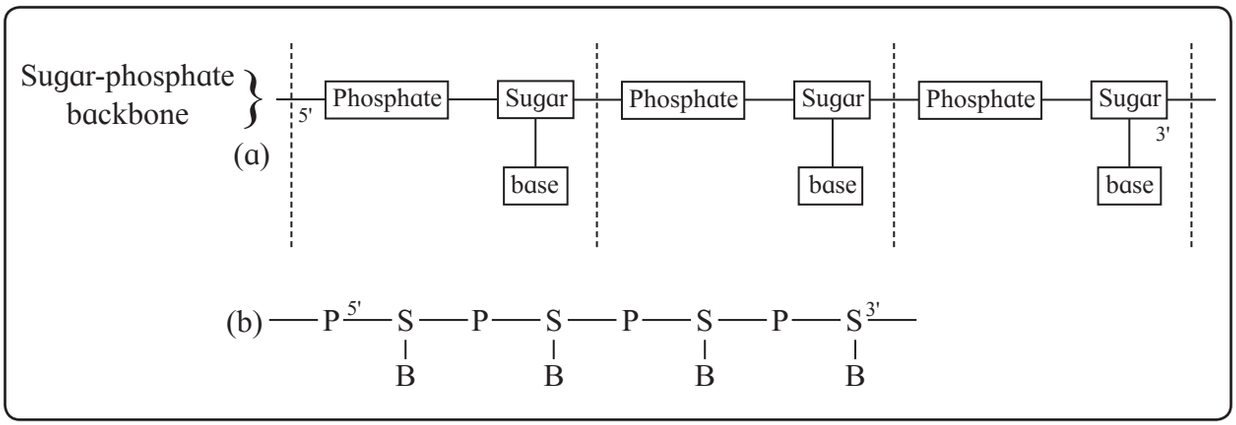
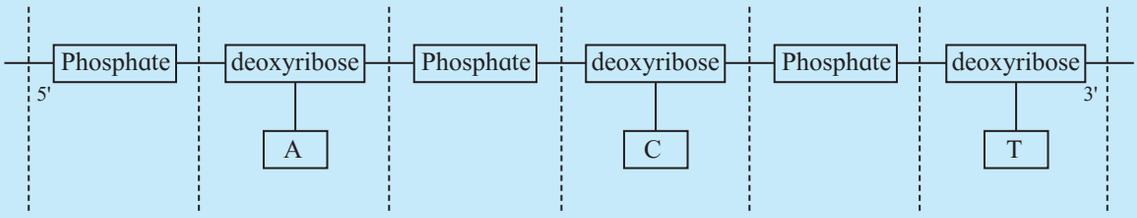


Fig 14.29 : Polynucleotide structure of nucleic acids : Schematic representations (a) and (b)

Problem 14.5 : Draw a schematic representation of trinucleotide segment 'ACT' of a DNA molecule.

Solution : In DNA molecule sugar is deoxyribose. The base 'A' in the given segment is at 5' end while the base 'T' at the 3' end. Hence the schematic representation of the given segment of DNA is



name CATG means there are four nucleotides in the segment containing the bases cytosine, adenine, thymine and guanine, in the indicated order from the 5' end.

Remember...

- A nucleic acid contains a backbone consisting of alternating sugar and phosphate groups.
- Backbone of all types of DNA contains the sugar 2-deoxy-D-ribose while that of RNA contains the sugar D-ribose.
- The identity and sequence of bases distinguish one polynucleotide from the other.
- A polynucleotide has one free phosphate group at the 5' end.
- A polynucleotide has a free OH group at the 3' end.

14.4.3 DNA double helix : James Watson and Francis Crick put forth in 1953 a double helix model for DNA structure, which was later verified by electron microscopy. Salient features of the Watson and Crick model of DNA are :

- DNA consists of two polynucleotide strands that wind into a **right-handed double helix**.
- The two strands run in opposite directions; one from the 5' end to the 3' end, while the other from the 3' end to the 5' end.
- The sugar- phosphate backbone lies on the outside of the helix and the bases lie on the inside, perpendicular to the axis of the helix.
- The double helix is stabilized by hydrogen bonding between the bases of the two DNA strands. This gives rise to a ladder-like structure of DNA double helix.
- Adenine always forms two hydrogen bonds with thymine, and guanine forms three hydrogen bonds with cytosine. Thus **A - T and C - G are complementary base pairs** and the two strands of the double helix are complementary to each other.

It may be noted that RNA exists as single stranded structure.

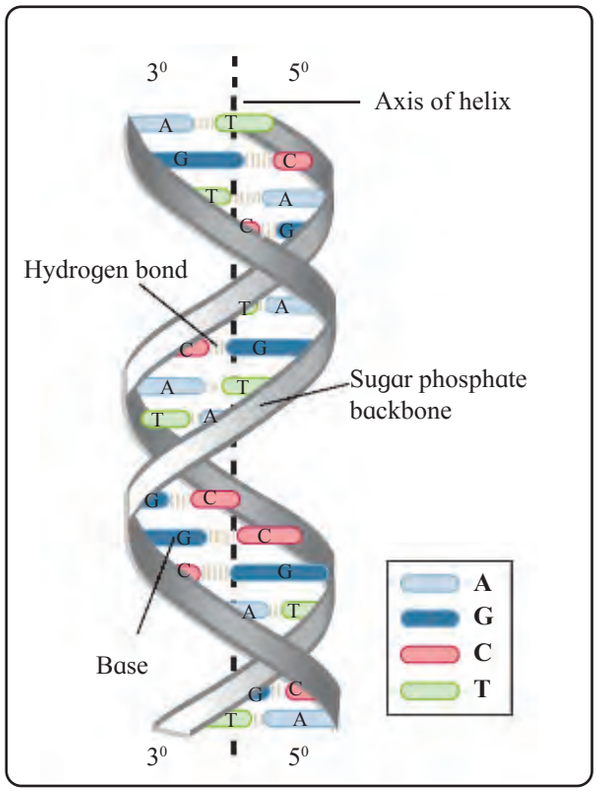
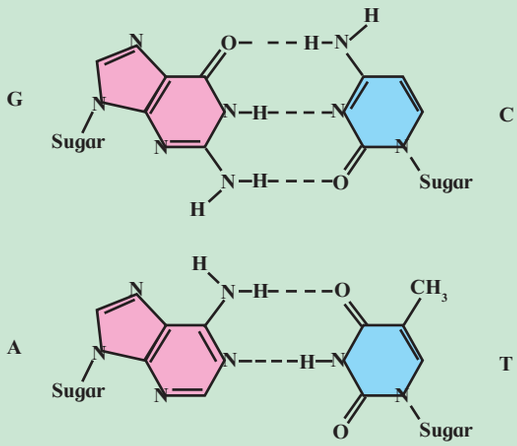


Fig. 14.30 : DNA double helix

Do you know ?

Hydrogen bonding between complementary base pairs.



Problem 14.6 : Write the sequence of the complementary strand of the following portion of a DNA molecule : 5' - ACGTAC-3'

Solution : The complementary strand runs in opposite direction from the 3' end to the 5' end. It has the base sequence decided by complementary base pairs A - T and C - G.

Original strand 5' - A C G T A C - 3'

Complementary strand 3' - T G C A T G - 5'

Exercises

1. Select the most correct choice.

i. $CH_2OH\text{-}CO\text{-}(CHOH)_4\text{-}CH_2OH$ is an example of

a. Aldohexose b. Aldoheptose
c. Ketotetrose d. Ketoheptose

ii. Open chain formula of glucose does not contain

a. Formyl group
b. Anomeric hydroxyl group
c. Primary hydroxyl group
d. Secondary hydroxyl group

iii. Which of the following does not apply to CH_2NH_2 - COOH

a. Neutral amino acid
b. L - amino acid
c. Exists as zwitter ion
d. Natural amino acid

iv. Tryptophan is called essential amino acid because

a. It contains aromatic nucleus.
b. It is present in all the human proteins.
c. It cannot be synthesised by human body.
d. It is essential constituent of enzymes.

v. A disulfide link gives rise to the following structure of protein.

a. Primary
b. Secondary
c. Tertiary
d. Quaternary

vi. RNA has

a. A - U base pairing
b. P-S-P-S backbone
c. double helix
d. G - C base pairing

2. Give scientific reasons :

i. The disaccharide sucrose gives negative Tollens test while the disaccharide maltose gives positive Tollens test.

ii. On complete hydrolysis DNA gives equimolar quantities of adenine and thymine.

iii. α - Amino acids have high melting points compared to the corresponding amines or carboxylic acids of comparable molecular mass.

iv. Hydrolysis of sucrose is called inversion.

v. On boiling egg albumin becomes opaque white.

3. Answer the following

i. Some of the following statements apply to DNA only, some to RNA only and some to both. Lable them accordingly.

a. The polynucleotide is double stranded. (.....)

b. The polynucleotide contains uracil. (.....)

c. The polynucleotide contains D-ribose (.....).

d. The polynucleotide contains Guanine (.....).

ii. Write the sequence of the complementary strand for the following segments of a DNA molecule.

a. 5' - CGTTTAAG - 3'

b. 5' - CCGGTTAATACGGC - 3'

iii. Write the names and schematic representations of all the possible dipeptides formed from alanine, glycine and tyrosine.

iv. Give two evidences for presence of formyl group in glucose.

4. Draw a neat diagram for the following:

i. Haworth formula of glucopyranose

ii. Zwitter ion

iii. Haworth formula of maltose

iv. Secondary structure of protein

v. AMP

vi. dAMP

vii. One purine base from nucleic acid

viii. Enzyme catalysis

Activity :

- **Draw structure of a segment of DNA comprising at least ten nucleotides on a big chart paper.**
- **Make a model of DNA double stranded structure as group activity.**

15. INTRODUCTION TO POLYMER CHEMISTRY

Can you recall ?

i. Classify the following materials as bio-degradable and non-bio-degradable : Thermocol, glass, wood, cotton clothes, paper bags, polythene bags, nylon ropes, fruit peels.

ii. Give examples of man made materials we use in our daily life.

iii. Which material is used in manufacture of toys, combs ?

iv. Write examples of thermosetting plastic articles.

v. List various properties of plastic.

15.1 Introduction : Today the overall development in polymer science and technology has enriched human life. The world would be at totally different place without polymers such as artificial fibres, plastics and elastomers. From the throwaway candy wrapper to the artificial heart, polymers touch our lives as does no other class of material.

In short we are living in the world of polymers. Polymer chemistry emerged as a separate branch of chemistry during the last several decades due to the voluminous knowledge built up in this field and the ever increasing applications in everyday life.

Chemically polymers are complex, giant macromolecules made from the repeating units which are derived from small molecules called 'monomers'. The term 'polymer' originates from Greek word 'poly' meaning many and 'mer' meaning part or unit. Interlinking of many units constitutes polymers.

Polymers are high molecular mass macromolecules (10^3 - 10^7 u).

Both inorganic as well as organic polymers are known. In this chapter we will study some aspects of organic polymers. You have learnt in Chapter 14 about carbohydrates, proteins and nucleic acids which are important organic biopolymers playing crucial role in living world.

In this chapter we will consider mainly man made organic polymers with reference to aspects such as types, preparation and applications.

Do you know ?

Nobel prizes for pioneering work in 'Polymers' :

- The polymeric substances, that we know today as macromolecules, were considered hundred years ago as associated molecules. Staudinger received Nobel prize (1953) for his work which established macromolecular nature of polymers.
- In 1963 Natta received Nobel prize for recognizing stereospecific regularity in vinyl polymers.
- In 1974 Flory received Nobel prize for elucidating the three step mechanism of chain-reaction in polymerization involving initiation, propagation and termination.

15.2 Classification of polymers : Polymers are classified in number of ways on the basis of their source, chemical structures, mode of polymerization, molecular forces, type of monomers and biodegradability.

15.2.1 Classification of polymers on the basis of source or origin : Poylmers are divided into three categories : a. Natural b. Synthetic c. Semisynthetic

a. Natural polymers : The polymers obtained from natural source are said to be natural polymers. They are further subdivided into two types.

i. Plant polymers : These are obtained from plants. For example, cotton and linen are obtained from cotton plant and flax plant respectively. Natural rubber is another example of natural polymer which is manufactured from the latex obtained from bark of rubber trees.

ii. Animal polymers : These are derived from animal sources. For example, wool is obtained from hair of sheep. Silk is obtained from silkworm.

b. Synthetic Polymers : These are man- made polymers. These polymers are artificially prepared by polymerization of one monomer or copolymerization of two or more monomers. Nylon, terylene, neoprene are synthetic polymers. These are further divided into three subtypes, namely, fibres, synthetic rubbers and plastics.

c. Semisynthetic polymers : These are derived from natural polymers. These are also called regenerated fibres.Cellulose derivatives such as cellulose acetate rayon, cellulose nitrate, viscose rayon, cuprammonium rayon are a few examples of this category.

Semisynthetic polymers are used in preparation of non-inflammable photographic films, cinema films, varnishes, etc.

Use your brain power

- Differentiate between natural and synthetic polymers.

15.2.2 Classification of polymers on the basis of structure : Depending upon how the monomers are linked together, that is, the chain configuration, polymers are classified in three general types : a. linear b. branched and c. three dimensional cross - linked polymers (Fig. 15.1). The nature of linking the monomers depends upon the nature and number of functional groups in them.

a. Linear or straight chain polymers : When the monomer molecules are joined together in a linear arrangement the resulting polymer is straight chain polymer. It is obtained from bifunctional monomers or alkenes. (Fig. 15.1(a)). For example : PVC, high density polythene.

b. Branched chain polymers : The second most common arrangement is that of branched chain. Monomer having 3 functional groups or already having side chains give rise to branched chain polymers. (Fig. 15.1 (b)). For example : low density polythene.

c. Cross-linked polymers : Third type of arrangement is said to be cross linked or network polymers where cross links are produced between linear chains as shown in Fig. 15.1 (c). Cross linking results from polyfunctional monomers. For example, bakelite, melamine.

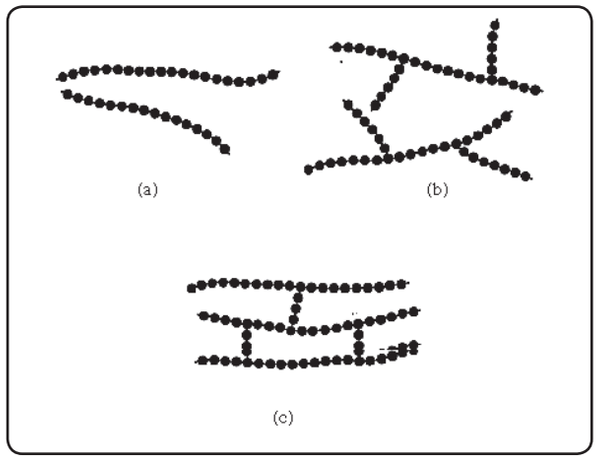


Fig. 15.1 : Different chain configurations of polymers

15.2.3 Classification of polymers on the basis of mode of polymerization : Polymerization is the fundamental process by which low molecular mass compounds are converted into high molecular weight compounds by linking together of repeating structural units with covalent bonds. This process is illustrated below.

Low molecular mass material (Possessing reactive groups) $\xrightarrow[\text{and/or catalyst}]{\text{High temprature and/or pressure}}$ High molecular mass material

There are three modes of polymerization according to the types of reactions taking place between the monomers.

a. Addition polymerization (or chain growth polymerization)

b. Condensation polymerization (or step growth polymerization)

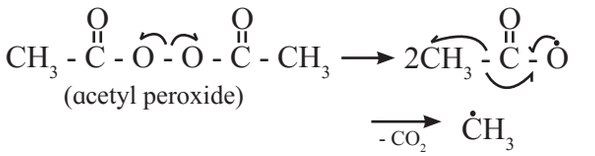
c. Ring opening polymerization

a. Addition polymerization : Addition polymerization is a process of formation of polymers by addition of monomers without loss of any small molecules. The repeating unit of an addition polymer has the same elemental composition as that of original monomer.

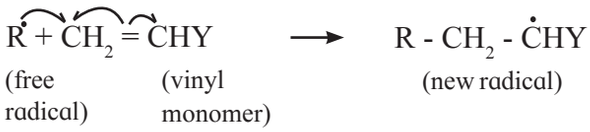
Compounds containing double bond undergo addition polymerization. It is also referred as vinyl polymerization, since majority of monomers are from vinyl category. For example : vinyl chloride (CH_2=CHCl), acrylonitrile (CH_2=CHCN). Formation of polyethylene from ethylene is well known example of addition polymerization. Addition polymerization produces high molecular mass polymeric materials without formation of any intermediate low molecular mass polymeric materials.

Free radical mechanism is most common in addition polymerisation. It is also called chain reaction which involves three distinct steps chain initiation, chain propagation and chain termination.

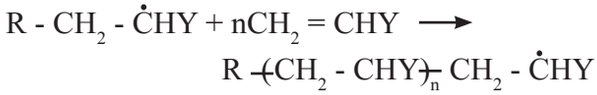
Step 1 : Chain initiation : The chain reaction is initiated by a free radical. An initiator (catalyst) such as benzoyl peroxide, acetyl peroxide, tert-butyl peroxide, etc. can be used to produce free radical. For example acetyl peroxide generates methyl radical as shown below :



The free radical (say $\dot{R}$) so formed attaches itself to the olefin (vinyl monomer) and produces a new radical, made up of two parts, namely, the attached radical and the monomer unit.

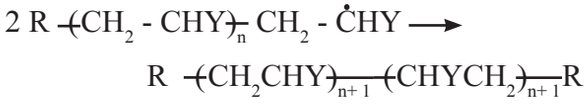


Step 2 : Chain propagation : The new radical formed in the initiation step reacts with another molecule of vinyl monomer, forming another still bigger sized radical, which in turn reacts with another monomer molecule. The repetition of this sequence takes place very rapidly. It is called chain propagation.



This step is very rapid and leads to high molecular mass radical.

Step 3 : Chain termination : Ultimately, at some stage,termination of the growing chain takes place. It may occur by several processes. One mode of termination is by combination of two growing chain radicals.

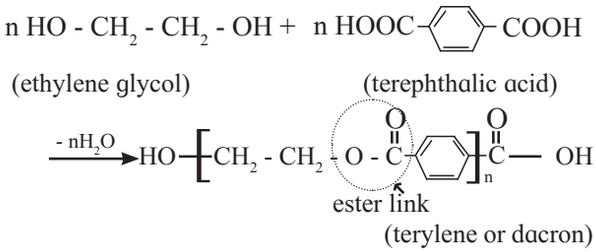


Internet my friend

Study audiovisual free radical mechanism of addition polymerization. (Refer/search for free radical polymerization.Animation (IQOG-CSIC) on youtube channel)

b. Condensation polymerization :

Consider the formation of terylene, a poly ester polymer, from ethylene glycol and terephthalic acid.



In this reaction an alcoholic OH group in ethylene glycol condenses with a carboxyl group in terephthalic acid by eliminating a water molecule to form an ester linkage.

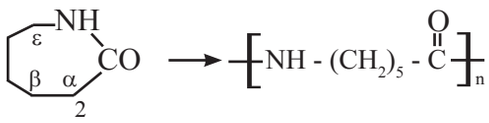
The process of formation of polymers from polyfunctional monomers with the elimination of some small molecules such as water, hydrochloric acid, methanol, ammonia is called condensation polymerization.

In this type of polymerization the chain growth occurs by a series of condensation steps. Therefore it is also referred to as **step growth polymerization**. This process is continued until a high molecular mass polymer is obtained.

Remember...

Repeating units of condensation polymer do not have the same elemental composition as that of monomer.

c. Ring opening polymerization : The third type of polymerization is ring opening polymerization. Cyclic compounds like lactams, cyclic ethers, lactones, etc. polymerize by ring opening polymerization. Strong acid or base catalyze this reaction. For example : polymerization of ε-caprolactam. (For more details see section 15.3.5 (b).



Elemental composition of the repeating unit in the polymer resulting from ring opening polymerization is same as that of the monomers, as in the case of addition polymerization. Addition polymerizations are often very rapid. But ring opening polymerization proceeds by addition of a single monomer unit (but never of larger units) to the growing chain molecules. In this sense, ring opening polymerization is a step growth polymerization similar to condensation polymerization.

Use your brain power

What is the type of polymerization in the following examples ?

(i)

$$2n\ CH_2 = CH - CH_3 \xrightarrow{\dot{C}H_3}$$

$$H_3C - (CH_2 - \underset{CH_3}{CH})_n - (\underset{CH_3}{CH} - CH_2)_n - CH_3$$

(ii)

$$nHO\text{-}(CH_2)_x\text{-}OH + nHOOC - (CH_2)_y - COOH \longrightarrow HO\text{-}[(CH_2)_x\text{-}O\text{-}CO - (CH_2)_y - CO]_n\text{-}OH$$

15.2.4 Classification of polymers on the basis of intermolecular forces : Mechanical properties of polymers such as tensile strength, toughness, elasticity differ widely depending upon the intermolecular forces. Polymers are classified into various categories on the basis of intermolecular forces as follows.

a. Elastomers : Elasticity is a property by which a substance gets stretched by external force and restores its original shape on release of that force. Elastomers, the elastic polymers, have weak van der Waals type of intermolecular forces which permit the polymer to be stretched. A few crosslinks between the chains help the stretched polymer to retract to its original position on removal of applied force. For example : vulcunized rubber, buna-S, buna-N, neoprene, etc.

b. Fibres : Polymeric solids which form threads are called fibres. The fibres possess high tensile strength which is a property to have resistance to breaking under tension. This characteristic is due to the strong intermolecular forces like hydrogen bonding and strong dipole-dipole forces. Due to these strong intermolecular

forces the fibres are crystalline in nature. For example : polyamides (nylon 6, 6), polyesters (terylene), etc.

c. Thermoplastic polymers : Plasticity is a property of being easily shaped or moulded. Thermoplastic polymers are capable of repeated softening on heating and hardening on cooling. These polymers possess moderately strong intermolecular forces that are intermediate between elastomers and fibres. For example : polythene, polystyrene, polyvinyls, etc. :

d. Thermosetting polymers : Themosetting polymers are rigid polymers. During their formation they have property of being shaped on heating; but they get hardened while hot. Once hardened these become infusible; cannot be softened by heating and therefore cannot be remoulded. This characteristic is the result of extensive cross linking by covalent bonds formed in the moulds during hardening/setting process while hot. For example : bakelite, urea formaldehyde resin, etc.

15.2.5 Classification of polymers on the basis of type of different monomers : Polymers are divided into two classes :

a. Homopolymers : The polymers which have only one type of repeating unit are called homopolymers. Usually they are formed from a single monomer. In some cases the repeating unit is formed by condensation of two distinct monomers. For example : polythene, polypropene, Nylon 6, polyacrylonitrile, Nylon 6, 6.

b. Copolymers : The polymers which have two or more types of repeating units are called copolymer. They are formed by polymerization of two or more different types of monomers in presence of each other. The different monomer units are randomly sequenced in the copolymer. For example : Buna-S, Buna-N.

Problem 15.1 : Refer to the following table listing for different polymers formed from respective monomer. Identify from the list whether it is copolymer or homopolymer.

Sr. No.	Monomer	Polymers
1.	Ethylene	Polyethylene
2.	Vinyl chloride	Polyvinyl chloride
3.	Isobutylene	Polyisobutylene
4.	Acrylonitrile	Polyacrylonitrile
5.	Caprolactum	Nylon 6
6.	Hexamethylene diammonium adipate	Nylon 6, 6
7.	Butdiene + styrene	Buna-S

Solution : In each of first five cases, there is only one monomer which gives corresponding homopolymer. In the sixth case hexamethylene diamine reacts with adipic acid to form the salt hexamethylene diammonium adipate which undergoes condensation to form Nylon 6, 6. Hence nylon 6, 6 is homopolymer. The polymer Buna-S is formed by polymerization of the monomers butadiene and styrene in presence of each other. The repeating units corresponding to the monomers butadiene and styrene are randomly arranged in the polymer. Hence Buna-S in copolymer.

Fig. 15.2 Shows all the classes of polymers in the form of a tree diagram.

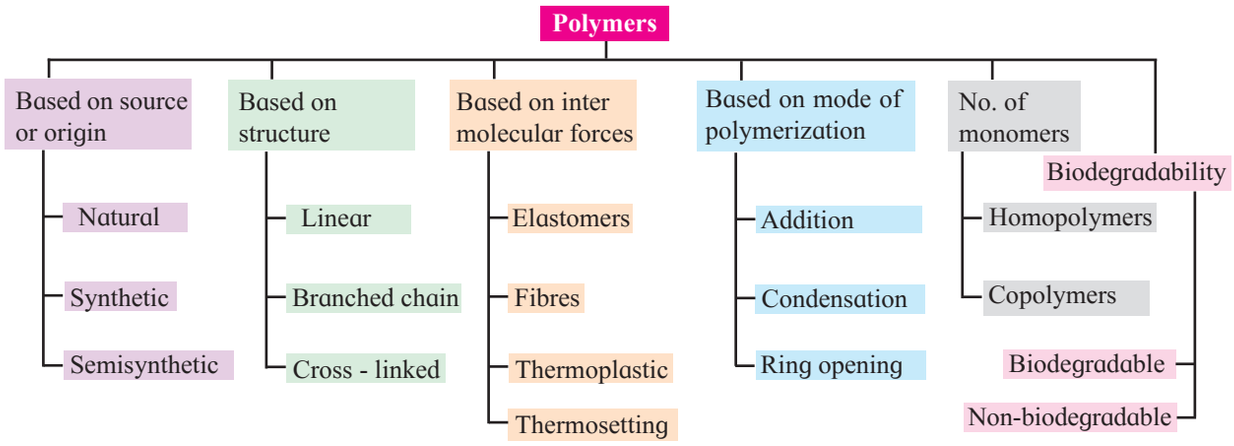


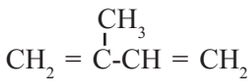
Fig. 15.2 : Classification of polymers

15.2.6 Classification of polymers on the basis of biodegradability : Most of the synthetic polymers are not affected by microbes. These are called non-biodegradable polymers. These, in the form of waste material which stays in the environment for very long time and pose pollution hazards. Most natural fibres in contrast are biodegradable. In attempt to tackle the environmental problem, scientists have developed bio-degradable synthetic polymers. More details will be described in section 15.5.

15.3 Some important polymers :

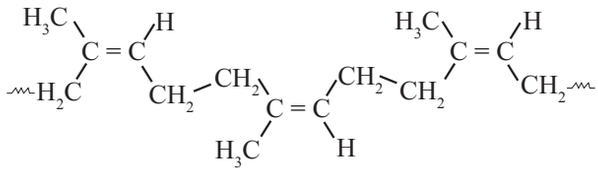
15.3.1 Rubber : Elastomers are popularly known as **rubbers**. For example, balloons, shoesoles, tyres, surgeon's gloves, garden hose, etc. are made from elastomeric material or rubber.

Natural rubber : Monomer of natural rubber is isoprene (2-methyl - 1, 3-butadiene).



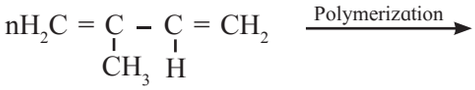
(isoprene)

Natural rubber is a high molecular mass linear polymer of isoprene. Its molecular mass varies from 130, 000u to 340, 000u (that is number of monomer units varies from 2000 to 5000).

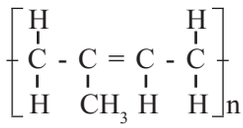


Natural rubber

Reaction involved in formation of natural rubber by the process of addition polymerization is as follows.



(isoprene)



(polyisoprene/rubber)

Properties of Natural rubber :

1. Polyisoprene molecule has cis configuration of the C = C double bond. It consists of various chains held together by weak van der Waals forces and has coiled structure.
2. It can be stretched like a spring and exhibits elastic property.

Vulcanization of rubber : To improve the physical properties of natural rubber, a process of vulcanization is carried out. In 1839 Charles Goodyear, an American inventor invented the process of vulcanization.

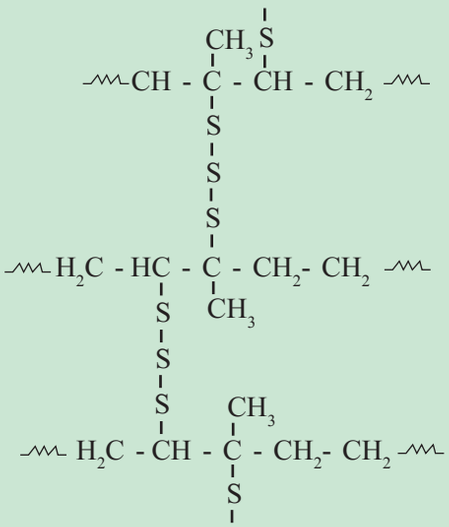
The process by which a network of cross links is introduced into an elastomers is called vulcanization. The profound effect of vulcanization enhances the properties like tensile strength, stiffness, elasticity, toughness; etc. of natural rubber. Sulfur vulcanization is the most frequently used process. Sulfur forms crosslinks between polyisoprene chains which results in improved properties of natural rubber.

Do you know ?

Vulcanizing is carried out by heating raw rubber with sulfur powder in presence of some organic compounds called accelerators at about 150 ^{0}C. (The most common accelerator is ZBX or zincbutyl xanthate). By increasing amount of sulfur the rubber can be hardened. For example when the amount of sulfur is raised to 40-45 % a non-elastic hard material known as **ebonite** is obtained.

One or more sulfur atoms cross-link two polyisoprene chains. Cross-linking takes place by opening of a double bond and produces three dimensional vulcanised rubber.

Probable 3-D structure of vulcanized rubber is



Use your brain power

- From the cis-polyisoprene structure of natural rubber explain the low strength of van der Waals forces in it.
- Explain how vulcanization of natural rubber improves its elasticity ? (Hint : consider the intermolecular links.)

Do you know ?

Natural Rubber first came into the market in early 19 th century. It was entirely recovered from wild *Hevea brasiliensis* trees which usually grew on the banks of Amazon river and its tributaries in South America. The amount of hydrocarbon present in Hevea Tree is very high (35%). As per the demand the production of natural rubber increased by leaps and bounds and at present 1.5 million tons of natural rubber is sent to the market.

The latex is collected from a mature Hevea tree by making deep cuts on the bark and by allowing the latex stream in a pot attached below the cut. The latex is an emulsion like milk.

When a coagulant like acetic acid is added to the latex the rubber hydrocarbon gets coagulated in the amorphous solid form.

15.3.2 Polythene :

Can you recall ?

How is ethylene prepared ?

Polythene is the simplest and most commonly used hydrocarbon thermoplastic and has following structure.

$$-\left[CH_2 - CH_2\right]_n-$$

The IUPAC name of polyethylene is polythene. Polythene is of two kinds, namely low density polythene (LDP) and high density polythene (HDP) .

a. Low density polyethylene (LDP) :

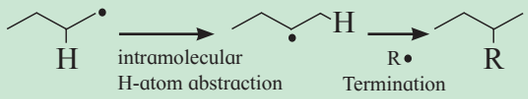
LDP is obtained by polymerization of ethylene under high pressure (1000 - 2000 atm) and temperature (350 - 570 K) in presence of traces of O_2 or peroxide as initiator.

$$CH_2 = CH_2 \xrightarrow[\text{peroxide at 350 - 370K,}\ 1000 - 2000\ \text{atm}]{\text{Traces of } O_2} \text{LDP}$$

The mechanism of this reaction involves free radical addition and H-atom abstraction. The latter results in branching. As a result the chains are loosely held and the polymer has low density.

Do you know ?

In the H-atom abstraction, process involved in formation of LDP; the terminal carbon radical abstracts H-atom from an internal carbon atom in the form of an internal carbon radical. Termination step in addition polymerization gives rise to branching of these internal carbons.



Properties of LDP : LDP films are extremely flexible, but tough, chemically inert and moisture resistant. It is poor conductor of electricity with melting point 110 ^{0}C.

Uses of LDP : LDP is mainly used in preparation of pipes for agriculture, irrigation, domestic water line connections as well as insulation to electric cables. It is also used in submarine cable insulation. It is used in producing extruded films, sheets, mainly for packaging and household uses like in preparation of squeeze bottles, attractive containers etc.

b. High density polyethylene (HDP) : It is essentially a linear polymer with high density due to close packing.

$$CH_2 = CH_2 \xrightarrow[6 - 7\ \text{atm, catalyst}]{333\ \text{K} - 343\ \text{K}} \text{HDP}$$

HDP is obtained by polymerization of ethene in presence of Zieglar-Natta catalyst which is a combination of triethyl aluminium with titanium tetrachloride at a temperature of 333K to 343K and a pressure of 6-7 atm.

Properties of HDP : HDP is crystalline, melting point in the range of 144 - 150 ^{0}C. It is much stiffer than LDP and has high tensile strength and hardness. It is more resistant to chemicals than LDP.

Uses of HDP : HDP is used in manufacture of toys and other household articles like buckets, dustbins, bottles, pipes etc. It is used to prepare laboratory wares and other objects where high tensile strength and stiffness is required.

Internet my friend

Where is polythene manufactured in India ?

15.3.3 Teflon : Chemically teflon is polytetrafluoroethylene. The monomer used in preparation of teflon is tetrafluoroethylene, ($CF_2 = CF_2$) which is a gas at room temperature.

Tetrafluoroethylene is polymerized by using free radical initiators such as hydrogen peroxide or ammonium persulphate at high pressure.

$$nCF_2 = CF_2 \xrightarrow[\text{Peroxide}]{\text{Polymerization}} \text{-}[CF_2 - CF_2]\text{-}_n$$

(Tetrafluoroethene) (Teflon)

Properties : Telflon is tough, chemically inert and resistant to heat and attack by corrosive reagents.

C - F bond is very difficult to break and remains unaffected by corrosive alkali, organic solvents.

Uses : Telflon is used in making non-stick cookware, oil seals, gaskets, etc.

Internet my friend

Collect the information of Teflon coated products used in daily life and in industries.

15.3.4 Polyacrylonitrile : Polyacrylonitrile is prepared by addition polymerization of acrylonitrile by using peroxide initiator.

$$nCH_2 = CHCN \xrightarrow[\text{Peroxide}]{\text{Polymerization}} \left[CH_2 - \underset{CN}{CH}\right]_n$$

(Acrylonitrile) (Polyacrylonitrile)

Polyacrylonitrile resembles wool and is used as wool substitute and for making orlon or acrilan.

Do you know ?

Orlon is used to make blankets, shawls, sweat shirts, sweaters.

15.3.5 Polyamide polymers : Polyamide polymers are generally known as nylons. Nylon is the generic name of the synthetic linear polyamides obtained by the condensation polymerization between dicarboxylic acids and diamines, the self condensation of an amino acid or by the ring opening polymerization of lactams.

Polyamides contain - CO - NH - groups as the inter unit linkages. Two important polyamide polymers are nylon 6, 6 and nylon 6.

a. Nylon 6,6 : The monomers adipic acid and hexamethylendiamine on mixing forms nylon salt, which upon condensation polymerization under conditions of high temperature and pressure give the polyamide fibre nylon 6,6.

$$n\ HOOC\text{-}(CH_2)_4\text{-}COOH + n\ H_2N\text{-}(CH_2)_6\text{-}NH_2$$

(adipic acid) (hexamethylene diamine)

$$n\left[\overset{\ominus}{O}\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{\ominus}{O}H_3\overset{\oplus}{N}\text{-}(CH_2)_6\text{-}\overset{\oplus}{N}H_3\right]$$

(nylon salt)

$$\xrightarrow[-nH_2O]{553K\text{ high pressure}}$$

$$\left[\text{-}\overset{O}{\overset{\|}{C}}\text{-}(CH_2)_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}(CH_2)_6\text{-}\overset{H}{N}\text{-}\right]_n$$

(nylon 6,6)

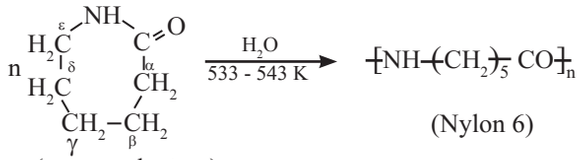
The numerals 6,6 in the name of this polymer stand for the number of carbon atoms in the two bifunctional monomers, namely, adipic acid and hexamethylenediamine.

Nylon 6,6 is high molecular mass (12000-50000 u) linear condensation polymer. It possesses high tensile strength. It does not soak in water. It is used for making sheets, bristles for brushes, surgical sutures, textile fabrics, etc.

Do you know ?

- When an amino group and carboxyl group present in the same molecule react intramolecularly the resulting amide is cyclic and is called **lactam**.
- A cyclic ester formed by intramolecular reaction of hydroxyl and carboxyl groups is called **lactone**.

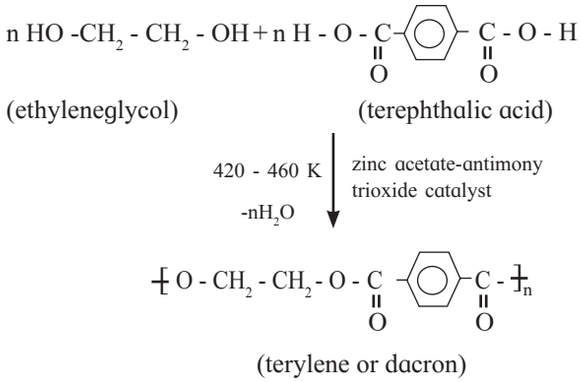
b. Nylon 6 : When epsilon (ε)-caprolactam is heated with water at high temperature it undergoes ring opening polymerization to give the polyamide polymer called nylon 6.



(ε - caprolactam)

The name nylon 6 is given on the basis of six carbon atoms present in the monomer unit. Due to its high tensile strength and luster nylon 6 fibres are used for manufacture of tyre cords, fabrics and ropes.

15.3.6 Polyesters : The polyester polymers have ester linkage joining the repeating units. Commercially the most important polyester fibre is 'terylene' (also called dacron). It is obtained by condensation polymerization of ethylene glycol and terephthalic acid in presence of catalyst at high temperature.



(terylene or dacron)

Terylene has relatively high melting point (265^{0}C) and is resistant to chemicals and water. It is used for making wrinkle free fabrics by blending with cotton (terycot) and wool (terywool), and also as glass reinforcing materials in safety helmets. PET is the most common thermoplastic which is another trade name of the polyester polyethyleneterephthalate. It is used for making many articles like bottles, jams, packaging containers.

Polycarbonates are also a kind of polyester polymers. These are high melting thermosetting resins.

15.3.7 Phenol - formaldehyde and related polymers :

a. Bakelite : Bakelite, the thermosetting polymer obtained from reaction of phenol and formaldehyde is the oldest synthetic polymer. Phenol and formaldehyde react in presence of acid or base catalyst to form thermosetting/ moulding powder (novolac) in two stages. In the third stage, various articles are shaped from novolac by putting it in appropriate moulds and heating at high temperature (138^{0}C to 176^{0}C) and at high pressure. The reactions involved are represented in the Fig. 15.3.

During the third stage of thermosetting in the moulds, many crosslinks are formed which results in formation of rigid polymeric material, called bakelite which is insoluble and infusible and has high tensile strength. It can also serve as substitute for glass. Bakelite is used for making articles like telephone instrument, kitchenware, electric insulators.

b. Melamine-formaldehyde polymer : Decorative table tops like formica and plastic dinner-ware are made from heat and moisture resistant themosetting plastic called melamine - formaldehyde resin. The reactions are shown in Fig. 15.4. Melamine and formaldehyde undergo condensation polymerisation to give cross linked melamine formaldehyde.

Internet my friend

Find applications of bakelite in day to day life.

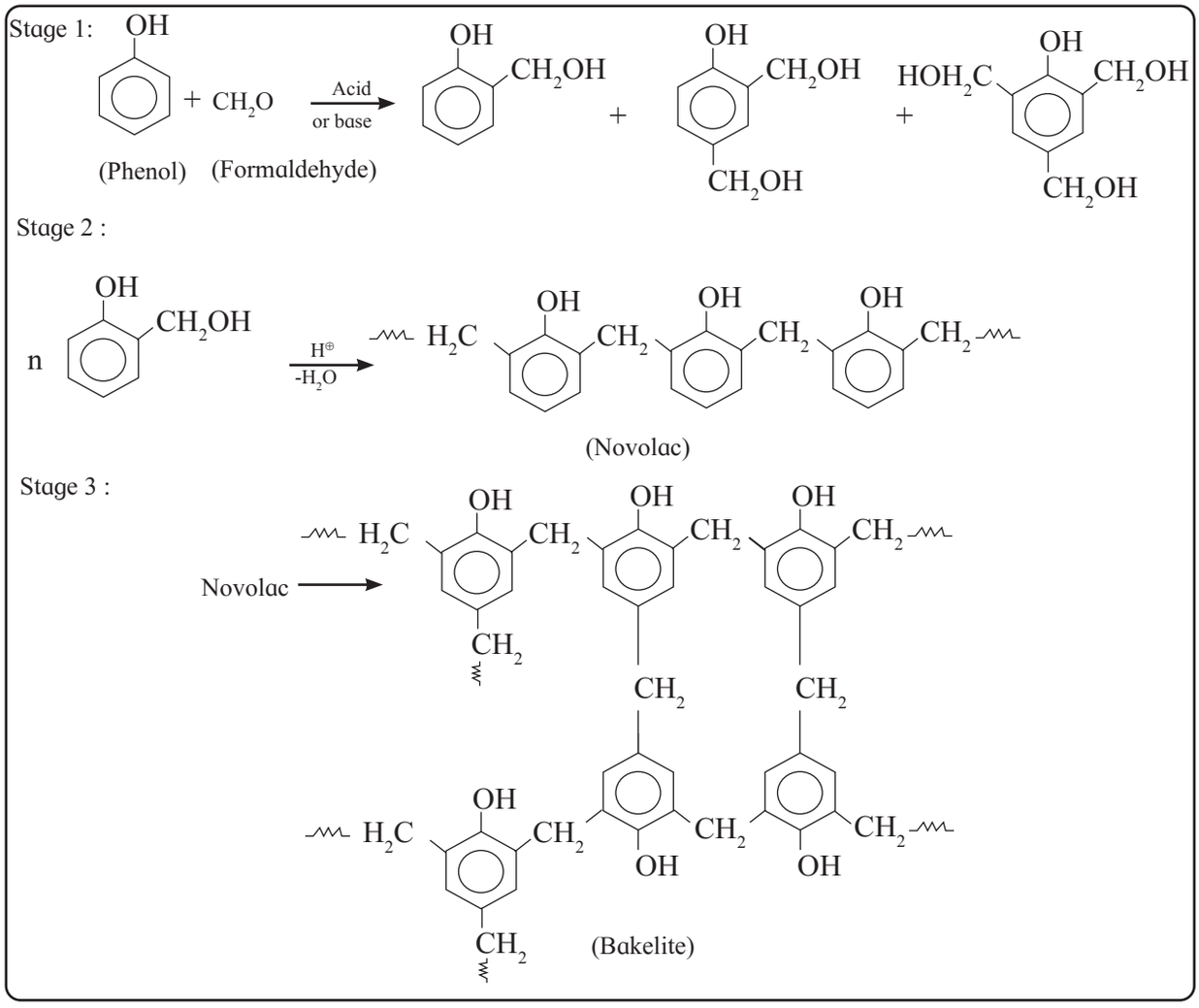


Fig. 15.3 Preparation of Bakelite

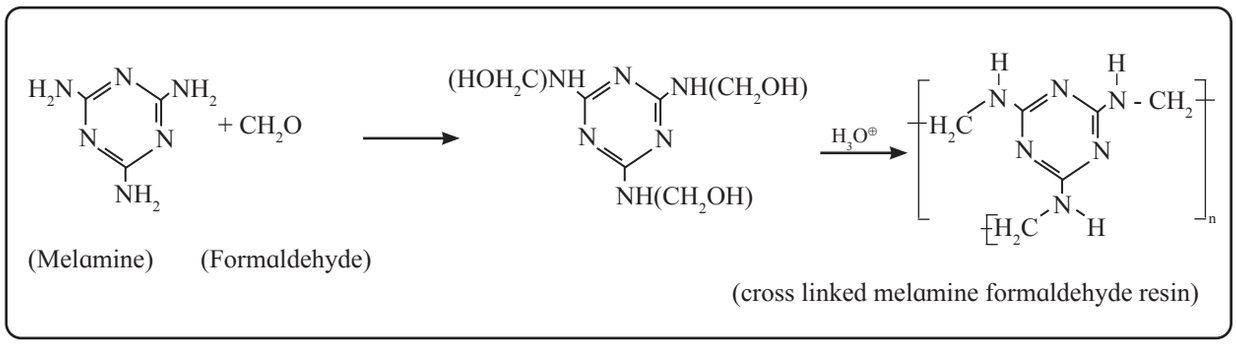


Fig. 15.4 Formation of cross linked melamine formaldehyde resin

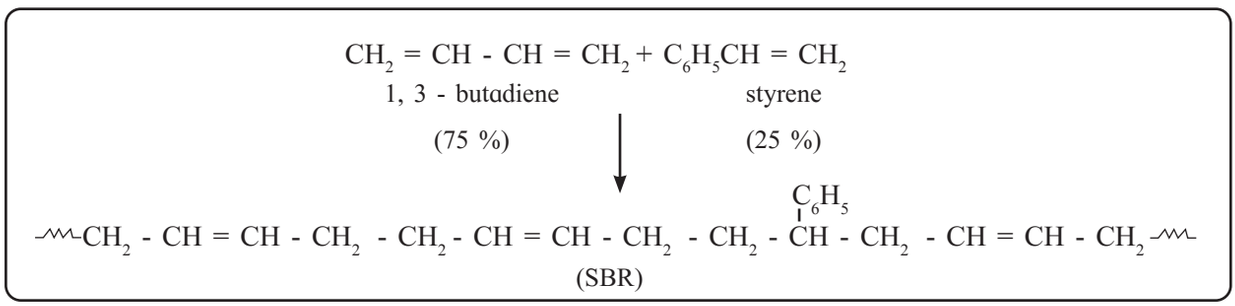


Fig. 15.5 Formation of SBR (Buna - S)

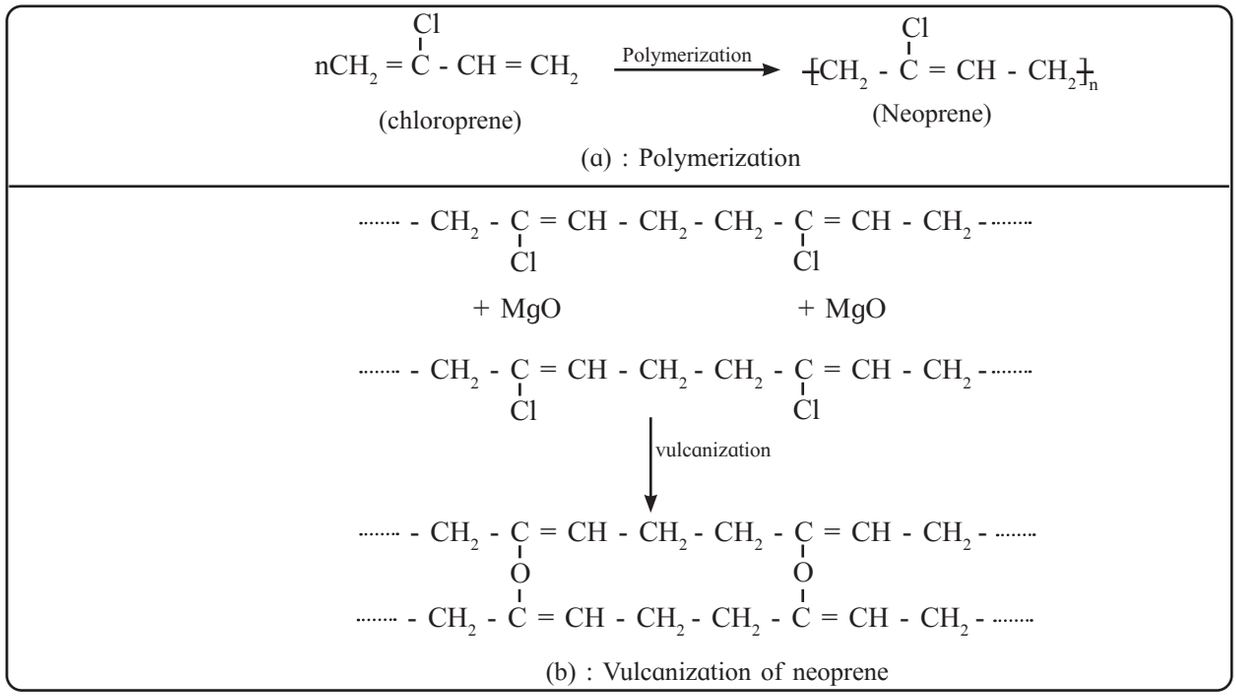


Fig. 15.6 Neoprene and vulcanization

15.3.8 Buna-S rubber : Buna-S is an elastomer which is a copolymer of styrene with butadiene (Fig.15.5). Its trade name is SBR (styrene-butadiene rubber). The copolymer is usually obtained from 75 parts of butadiene and 25 parts of styrene subjected to addition polymerization by the action of sodium. It is vulcanized with sulfur.

Buna-S is superior to natural rubber with regard to mechanical strength and has abrasion resistance. Hence it is used in tyre industry.

15.3.9 Neoprene : Neoprene, a synthetic rubber, is a addition polymer of chloroprene (2-chloro-1,3-butadiene). Chloroprenepolymerizes rapidly in presence of oxygen. Vulcanization of neoprene takes place in presence of magnesium oxide. The reactions involved can be represented in Fig. 15.6.

Neoprene is particularly resistant to petroleum, vegetable oils, light as well as heat. Neoprene is used in making hose pipes for transport of gasoline and making gaskets. It is used for manufacturing insulator cable, jackets, belts for power transmission and conveying.

15.3.10 Viscose rayon : Viscose rayon is a semisynthetic fibre which is regenerated cellulose. Cellulose in the form of wood pulp is transformed into viscose rayon. Cellulose is a linear polymer of glucose units and has molecular formula $(C_6H_{10}O_5)_n$. A modified representation of the molecular formula of cellulose Cell-OH, is used in the reactions involved in viscose formation, as shown in Fig. 15.7. Cellulose in the form of wood pulp is treated with concentrated NaOH solution to get fluffy alkali cellulose. It is then converted to xanthate by treating with carbon disulphide. On mixing with dilute NaOH it gives viscose solution which is extruded through spinnerates

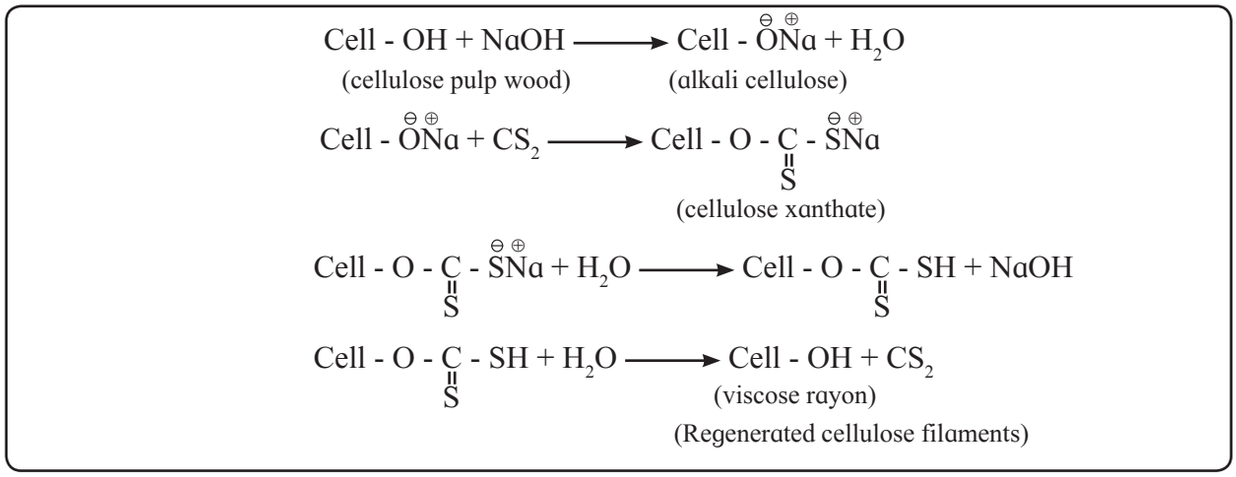


Fig. 15.7 : Formation of viscose rayon

of spining machine into acid bath when regenerated cellulose fibres precipitate.

Use your brain power

- Write structural formulae of styrene and polybutadiene.

15.4 Molecular mass and degree of polymerization of polymers : A polymer is usually a complex mixture of molecules of different molecular masses. Hence, molecular mass of a polymer is an average of the molecular masses of constituent molecules. Molecular mass of polymer depends upon the degree of polymerization (DP). DP is the number of monomer units in a polymer molecule.

Most of the mechanical properties of polymers depend upon their molecular mass. Low molecular mass polymers are liable to be brittle and have low mechanical strength. If a polymer is allowed to attain very high molecular mass it becomes tough and unmanageable. Both these ends are undesirable. A polymer must possess a molecular mass more than certain minimum value in order to exhibit the properties needed for a particular application. This minimum molecular mass corressponds to the critical degree of polymerization. But the polymerization process has to be controlled after certain stage. For polymers containing hydrogen bonding the critical degree of polymerization is lower than those containing weak intermolecular forces.

Can you tell ?

1. Classify the following polymers as addition or condensation.

   i. PVC ii. Polyamides iii. Polystyrene iv. Polycarbonates v. Novolac

2. Complete the following table :

Condensation polymers	Repeating unit	Name of monomer	Formula of monomer	Uses
1. Nylon 6				
2. Nylon 6, 6				
3. Terylene				
4. Melamine				

Problem 15.2 : The critical degree of polymerization is low for nylon 6 while high for polythene. Explain.

Solution : Nylon 6 is a polyamide polymer, and has strong intermolecular hydrogen bonding as inter molecular forces. On the other hand polythene chains have only weak van der Waals forces as intermolecular interaction. Because of the stronger intermolecular forces the critical DP is lower for nylon 6 than polythene.

15.5 Biodegradable polymers :

Can you recall ?

- Name some materials which undergo degradation after use.
- List the materials which do not decay even after a long time.
- How is the environment affected by non decaying substances ?
- Which bonds are broken during digestion of proteins and carbohydrates ?
- What happens to disposed natural wastes such as stale food, fruit peels, torn cotton cloth ?

Inspite of large number of useful applications, polymers are blamed for creating environmental pollution. To strike the golden mean, certain new biodegradable synthetic polymers have been developed.

Aliphatic polyesters and polyamides with large proportion of polar linkages are one of the important classes of biodegradable polymers. Some important examples are discussed below.

Disposed natural wastes are usually attacked by soil microbes and get degraded to humus. But most synthetic polymers and plastics cannot be degraded by microbes and stay in the environment for very long period of time posing pollution problems. To overcome this problem biodegradable polymers are being developed. These polymers contain functional groups similar to those in biopolymers such as proteins. Aliphatic polyesters are also an important class of biodegradable polymers.

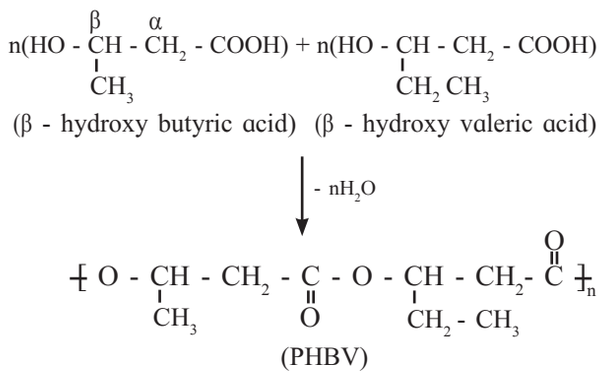
Can you recall ?

- What are the structural formulae of glycine and ε - amino caproic acid ?

Use your brain power

- Represent the copolymerization reaction between glycine and ε - amino caproic acid to form the copolymer nylon 2- nylon 6.
- What is the origin of the numbers 2 and 6 in the name of this polymer ?

15.5.1 PHBV : PHBV is a copolymer of two bifunctional β- hydroxy carboxylic acids, namely, β- hydroxybutyric acid (3 - hydroxybutanoic acid) and β- hydroxyvaleric acid (3 - hydroxypentanoic acid). Hydroxyl group of one monomer forms ester link by reacting with carboxyl group of the other. Thus PHBV is an aliphatic polyester with name poly β- hydroxy butyrate - co - β- hydroxy valerate (PHBV). PHBV is degraded by microbes in the environment.

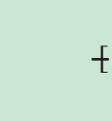
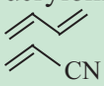
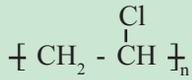
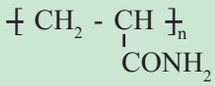
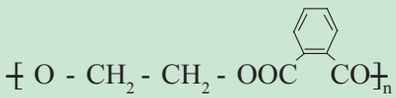
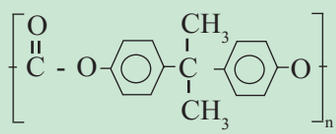
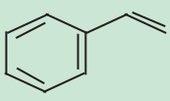
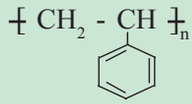


(PHBV)

15.5.2 Nylon 2 - nylon 6 : Nylon 2 - nylon 6 is a polyamide copolymer of two amino acids, namely, glycine and ε - amino caproic acid. It is a biodegradable polymer.

15.6 Commercially important polymers : Apart from the polymers already discussed in this chapter, many more polymers are used extensively. Structures and applications of some of them are given in the Table 15.1.

Table 15.1 : Commercially important polymers

Trade name	Monomer	Polymer structure	Applications
Perspex/acrylic glass	methyl methacrylate 		lenses, paint, security barrier, LCD screen, shatter resistant glass
Buna N	Butadiene and acrylonitrile 		adhesives, rubber belts, shoe soles, O-rings, gaskets
PVC (polyvinyl chloride)	vinyl chloride 		water pipes, rain coats, flooring
Polyacrylamide	acrylamide 		Polyacrylamide gel used in electrophoresis
Urea-formaldehyde resin	a. urea b. formaldehyde		unbreakable dinner ware, decorative laminates
Glyptal	a. ethyleneglycol b. phthalic acid		paints and lacquers
Polycarbonate	a. bisphenol b. phosgene		electrical and telecommunication hardware, food grade plastic containers
Thermocol (made from airfilled thin walled beads of polystyrene	Styrene 		non-biodegradable styrene can leach when heated. Therefore it is banned.

Exercises

1. Choose the correct option from the given alternatives.

i. Nylon fibres are ----

A. Semisynthetic fibres

B. Polyamide fibres

C. Polyester fibres

D. Cellulose fibres

ii. Which of the following is naturally occurring polymer ?

A. Telfon B. Polyethylene

C. PVC D. Protein

iii. Silk is a kind of ---- fibre

A. Semisynthetic

B. Synthetic

C. Animal

D. Vegetable

iv. Dacron is another name of ----

A. Nylon 6 B. Orlon

C. Novolac D. Terylene

v. Which of the following is made up of polyamides ?

A. Dacron B. Rayon

C. Nylon D. Jute

vi. The number of carbon atoms present in the ring of ε - caprolactam is

A. Five B. Two

C. Seven D. Six

vii. Terylene is ----

A. Polyamide fibre

B. Polyester fibre

C. Vegetable fibre

D. Protein fibre

viii. PET is formed by ----

A. Addition B. Condensation

C. Alkylation D. Hydration

ix. Chemically pure cotton is ----

A. Acetate rayon

B. Viscose rayon

C. Cellulose nitrate

D. Cellulose

x. Teflon is chemically inert, due to presence of .....

A. C-H bond B. C-F bond

C. H- bond D. C=C bond

2. Answer the following in one sentence each.

i. Identify 'A' and 'B' in the following reaction ----

a. $HO\text{-}CH_2\text{-}CH_2\text{-}OH + H\text{-}O\text{-}C(=O)\text{-}C_6H_4\text{-}C(=O)\text{-}O\text{-}H \xrightarrow[\Delta]{533K}$ 'A'

b. $H_2N\text{-}(CH_2)_6\text{-}NH_2 + HOOC\text{-}(CH_2)_4COOH \xrightarrow[533K]{N_2}$ 'B'

ii. Complete the following statements

a. Caprolactam is used to prepare--------

b. Novolak is a copolymer of ---------- and ---------

c. Terylene is ----------polymer of terephthalic acid and ethylene glycol.

d. Benzoyl peroxide used in addtion polymerisation acts as ----------

e. Polyethene consists of polymerised ----------

iii. Draw the flow chart diagram to show classification of polymers based on type of polymerisation.

iv. Write examples of Addition polymers and condensation polymers.

v. Name some chain growth polymers.

vi. Define the terms :

1) Monomer

2) Vulcanisation

3) Synthetic fibres

vii. What type of intermolecular force leads to high density polymer ?

viii. Give one example each of copolymer and homopolymer.

ix. Identify Thermoplastic and Thermosetting Plastics from the following -----

1. PET

2. Urea formaldehyde resin

3. Polythene

4. Phenol formaldehyde

3. Answer the following.

i. Write the names of classes of polymers formed according to intermolecular forces and describe briefly their structural characteristics.

ii. Write reactions of formation of :

a. Nylon 6 b. Terylene

iii. Write structure of natural rubber and neoprene rubber along with the name and structure of thier monomers.

iv. Name the polymer type in which following linkage is present.

v. Write structural formula of the following synthetic rubbers :

a. SBR rubber

b. Buna-N rubber

c. Neoprene rubber

vi. Match the following pairs :

Name of polymer	Monomer
1. Teflon	a. $CH_2=CH_2$
2. PVC	b. $CF_2=CF_2$
3. Polyester	c) $CH_2=CHCl$
4. Polythene	d) C_6H_5OH and HCHO
5. Bakelite	e) Dicarboxylic acid and polyhydoxyglycol

vii. Draw the structures of polymers formed from the following monomers

1. Adipic acid + Hexamethylenediamine

2. ε - Aminocaproic acid + Glycine

viii. Name and draw structure of the repeating unit in natural rubber.

ix. Classify the following polymers as natural and synthetic polymers

a. Cellulose b. Polystyrene

c. Terylene d. Starch

e. Protein f. Silicones

g. Orlon (Polyacrylonitrle)

h. Phenol-formedehyde resins

x. What are synthetic resins? Name some natural and synthetic resins.

xi. Distinguish between thermosetting and thermoplastic resins. Write example of both the classes.

xii. Write name and formula of raw material from which bakelite is made.

4. Attempt the following :

i. Identify condensation polymers and addition polymers from the following.

a. $-(CH_2-\underset{\displaystyle C_6H_5}{\underset{|}{CH}}-)_n$

b. $-(CH_2-CH=CH-CH_2)_n$

c. $-(CO(CH_2)_4-CONH(CH_2)_6NH-)_n$

d. $-(OCH_2-CH_2-O-CO-C_6H_4-CO-)_n$

ii. Write the chemical reactions involved in manufacture of Nylon 6,6

iii. Explain vulcanisation of rubber. Which vulcanizing agents are used for the following synthetic rubber.

a. Neoprene b. Buna-N

iv. Write reactions involved in the formation of --- 1) Teflon

2) Bakelite

v. What is meant by LDP and HDP? Mention the basic difference between the same with suitable examples.

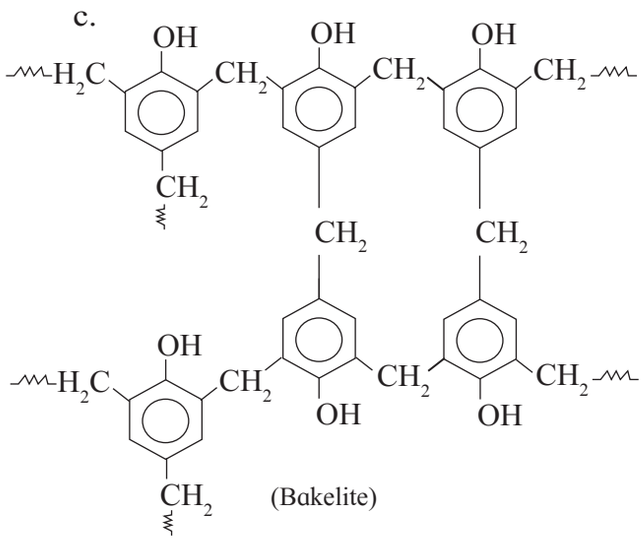
vi. Write preparation, properties and uses of Teflon.

vii. Classify the following polymers as straight chain, branched chain and cross linked polymers.

a. $-(CH_2-\underset{\underset{CN}{|}}{CH}-)_n$

b. $-(CH_2-CH_2-\underset{\underset{CH_2}{|}}{CH}-CH_2-CH_2-)_n$ with CH_2

c.



(Bakelite)

5. Answer the following.

i. How is polythene manufactured ? Give their properties and uses.

ii. Is synthetic rubber better than natural rubber ? If so, in what respect?

iii. Write main specialities of Buna-S, Neoprene rubber?

iv. Write the structure of isoprene and the polymer obtained from it.

v. Explain in detail free radical mechanism involved during preparation of addition polymer.

Activity :

i. Collect the information of the process like extrusion and moulding in Textile Industries.

ii. Make a list of polymers used to make the following articles

a. Photographic film

b. Frames of spectacles

c. Fountain pens

d. Moulded plastic chains

e. Terywool or Terycot fabric

iii. Prepare a report on factors responsible for degradation of polymers giving suitable example.

iv. Search and make a chart/note on silicones with reference to monomers, structure, properties and uses.

v. Collect the information and data about Rubber industry, plastic industry and synthetic fibre (rayon) industries running in India.

16. GREEN CHEMISTRY AND NANOCHEMISTRY

Can you recall ?

1. What do you mean by environment?
2. Which are the factors affecting the environment?
3. What is pollution? Which are the types of pollution?
4. Why it occurs?

16.1 Introduction

Chemistry plays an important role to improve the quality of our life. Unfortunately, due to this achievement our health and global environment are under threat. Also, due to increase in human population and the industrial revolution, energy crises and environmental pollution are highlighted major global problems in the 21st century. To minimize the problems of energy crises and pollution, we have to adapt **green chemistry**.

Do you know ?

Paul T. Anastas (Born on May 16, 1962) is the director of Yale university's Center for green chemistry and green engineering. He is known as father of green chemistry.

Green Chemistry is an approach to chemistry that aims to maximize efficiency and minimize hazardous effects on human health and environment. The concept of green chemistry was coined by **Paul T. Anastas**.

Definition : Green Chemistry is the use of chemistry for pollution prevention by environmentally conscious design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

To reduce the impact of energy crises, pollution and to save natural resources, we need to implement 12 principles of green chemistry enunciated by Paul Anastas whereever possible.

16.2 Sustainable development : Green chemistry plays an important role in sustainable development. We can achieve sustainable development by adapting the twelve principles of green chemistry. **Sustainable development** is development that meets the needs of the present, without compromising the ability of future generations to meet their own need. Sustainable development has been continued to evolve as that protecting the world's resources.

16.3 Principles of green chemistry :

1. Prevention of waste or by products :

To give priority for the prevention of waste rather than cleaning up and treating waste after it has been created.

Illustration : To develop the zero waste technology (ZWT). In terms of ZWT, in a chemical synthesis, waste product should be zero or minimum. It also aims to use the waste product of one system as the raw material for other system. For example : 1. bottom ash of thermal power station can be used as a raw material for cement and brick industry. 2. Effluent coming out from cleansing of machinery parts may be used as coolant water in thermal power station.

2. Atom economy : Atom economy is a measure of the amount of atoms from the starting materials that are present in the useful products at the end of chemical process. Good atom economy means most of the atoms of the reactants are incorporated in the desired products and only small amounts of unwanted byproducts are formed and hence lesser problems of waste disposal.

Illustration : The concept of atom economy gives the measure of the unwanted product produced in a particular reaction.

$$\% \text{ atom economy} = \frac{\text{Formula weight of the desired product}}{\text{sum of formula weight of all the reactants used in the reaction}} \times 100$$

For example : conversion of Butan-1-ol to 1 - bromobutane

$$CH_3CH_2CH_2CH_2OH + NaBr + H_2SO_4 \longrightarrow CH_3CH_2CH_2CH_2\text{-}Br + NaHSO_4 + H_2O$$

$$\% \text{ atom economy} = \frac{\text{mass of } (4C + 9H + 1Br) \text{ atoms}}{\text{mass of } (4C + 12H + 5O + 1Br + 1Na + 1S) \text{atoms}} \times 100$$

$$= \frac{137 \text{ u}}{275 \text{ u}} \times 100$$

$$= 49.81 \%$$

3. Less hazardous chemical synthesis :

Designed chemical reactions and synthesis routes should be as safe as possible. So that we can avoid formation of hazardous waste from chemical processes.

Illustration : Earlier DDT (Dichlorodiphenyl trichloroethane) was used as insecticide and which was effective in controlling diseases like typhoid and malaria carrying mosquitos. It was realized that DDT is harmful to living things. Nowadays benzene hexachloride (BHC) is used as insecticide. One of the ϒ-isomer (gamma) of BHC is called gammexane or lindane.

4. Desigining Safer Chemicals : This principle is quite similar to the previous one. To develop products that are less toxic or which require less toxic raw materials.

Illustration : In Chemical industries workers are exposed to toxic environment. In order to prevent the workers from exposure to toxicity, we should think of designing safer chemicals. For example : Adipic acid is widely used in polymer industry. Benzene is the starting material for the synthesis of adipic acid but benzene is carcinogenic and benzene being volatile organic compound (VOC) pollutes air. In green technology developed by Drath and Frost, adipic acid is enzymatically synthesised from glucose.

5. Use Safer solvent and auxilaries :

Choose the safer solvent available for any given step of reaction. Minimize the total amount of solvents and auxilary substances used, as these make up a large percentage of the total waste created.

Illustration : The main aim behind this principle is to use green solvents. For example, water, supercritical CO_2 in place of volatile halogenated organic solvents, for example, CH_2Cl_2, $CHCl_3$, CCl_4 for chemical synthesis and other purposes. Solvents as chemicals that dissolve solutes and form solutions, facilitate many reactions. Water is a safe benign solvent while dichloromethane is hazardous. Use of toxic solvent affects millions of workers every year and has implications for consumers and the environment as well. Many solvents are used in high volumes and many are volatile organic compounds. Their use creates large amounts of waste, air pollution and other health impacts. Finding safer, more efficient alternatives or removing solvents altogether is one of the best ways to improve a process or product.

6. Design for energy efficiency : Chemical synthesis should be designed to minimize the use of energy. It is better to minimize the energy by carrying out reactions at room temperature and pressure.

This can be achieved by use of proper catalyst, use of micro organisms for organic synthesis, use of renewable materials, ... ,etc.

Illustration : The biocatalyst can work at the ambient condition. Similarly, in chemical synthesis, refluxing conditions require less

energy, improving the technology of heating system, use microwave heating, ... , etc.

7. Use of renewable feedstocks : The perspective of this principle is largely toward petrochemicals. Use chemicals which are made from renewable (plant based) sources rather than other (for example : Crude Oil).

Illustration : Overexploitation of nonrenewable feed stocks will deplete the resources and future generation will be deprived. Moreover, use of these nonrenewable resources puts burden on the environment.

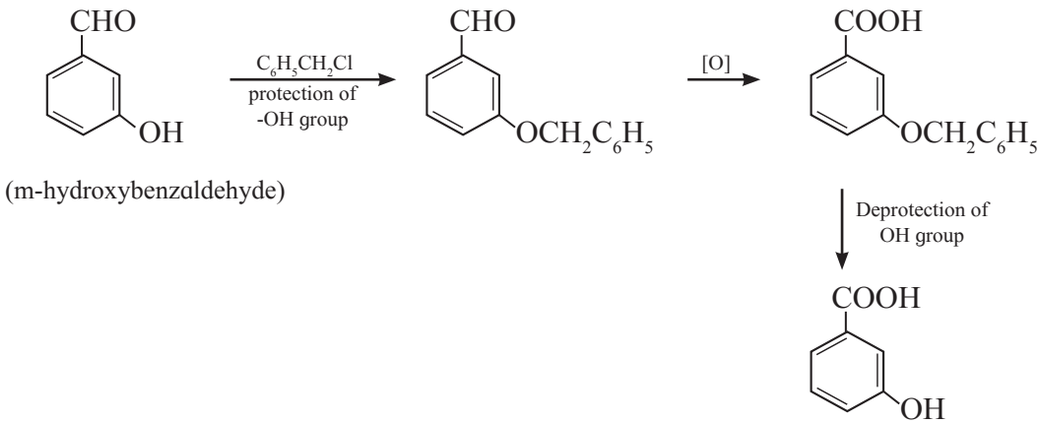
On the other hand, use of renewable resources for example agricultural or biological product ensures the sharing of resources by future generation. This practice generally does not put much burden on environment. The products and waste are generally biodegradable.

8. Reduce derivatives : [Minimization of steps]

A commonly used technique in organic synthesis is the use of protecting or blocking group. Unnecessary derivatization (for example installation / removal of use of protecting groups) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

Illustration : In organic synthesis, we need very often protection of some functional groups. Finally, we again need their deprotection. It is explained in the following example of synthesis of m-hydroxybenzoic acid from m-hydroxy benzaldehyde.

Obviously, in such cases, atom economy is also less. The green chemistry principle aims to develop the methodology where unnecessary steps should be avoided, if practicable biocatalytic reactions very often need no protection of selective group.



(m-hydroxybenzaldehyde)

(m-hydroxybenzoic acid)

9. Use of catalysis : Use of catalyst in the chemical reaction speeds up its rate. Catalyst helps to incease selectivity, minimize waste and reduce reaction times and energy demands.

Complete the chart

Reaction	Name of Catalyst used
1. Hydrogenation of oil (Hardening)	.....
2. Haber's process of manufature of ammonia	.....
3. Manufacture of HDPE polymer	.....
4. Manufacture of H_2SO_4 by contact process	.....
5. Fischer-Tropsch process (synthesis of gasoline)	.....

Do you know ?

Does plastic packaging impact the food they wrap ?

Phthalates leach into food through packaging so you should avoid microwaving food or drinks in plastic and not use plastic cling wrap and store your food in glass container whenever possible. Try to avoid prepackaging, processed food so that you will reduce exposure to harmful effect of plastic.

10. Design for degradation : Design chemicals that degrade and can be discarded easily. Ensure that both chemicals and their degradation products are not toxic, bioaccumulative or environmentally persistent.

Illustration : The aim behind this principle is that the waste product should degrade automatically to clean the environment. Thus, the biodegradable polymers and pesticides are always preferred. To make separation easier for the consumer an international plastic recycle mark is printed on larger items.

Use this chart to sort plastic materials in daily life

11. Real-time Analysis Pollution Prevention: Analytical methods need to be further developed to allow for real-time, in process monitoring and control prior to the formation of hazardous substances.

Illustration : Analytical methodologies should be developed or modified, so that continuous monitoring of the manufacturing and processing units is possible. This is very much important for the chemical industries and nuclear reactors.

12. Safer chemistry for Accident prevention:

We need to develop chemical processes that are safer and minimize the risk of accidents.

Illustration : The substances to be used in a chemical reaction should be selected in such a way that they can minimize the occurrence of chemical accidents, explosions, fire and emission. For example, if the chemical process works with the gaseous substances, then the possibility of accidents including explosion is relatively higher compared to the system working with non volatile liquid and solid substances.

16.4 The role of Green chemistry : The green chemistry approach recognizes that the Earth does have a natural capacity for dealing with much of the waste and pollution that society generates, it is only when that capacity is exceeded that we become unsustainable.

To promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and use of chemical products.

Green chemistry helps to reduce capital expenditure, to prevent pollution. Green chemistry incorporates pollution prevention practices in the manufacture of chemicals and promotes pollution prevention and industrial ecology. Green chemistry is a new way of looking at chemicals and their manufacturing process to minimize any negative environmental effects. Right now the green chemistry revolution is beginning and it is an exciting time with new challenges for chemists involved with the discovery, manufacture and use of chemicals.

Green chemistry helps to protect the presence of ozone in the stratosphere essential for the survival of life on the earth. Green chemistry is useful to control green house effect (Global warming). So we should think about save environment and save earth.

Can you recall ?

1. What are the shapes of a bacillus and coccus? (Refer to chapter from Biology, Std. XI)
2. Which instrument is used to observe the cells ? (Refer to chapter 5 from Biology, Std. XI)
3. What is the size range of molecules of lipids and proteins ?

16.5 Introduction to nano chemistry : From clothes, sunglasses you wear to computer hard drives and even cleaning products, nanotechnology plays a big role in the manufacture of many materials. We have been using Lasers in DVD, CD players for a long time which contain nanosize components. Look at Fig. 16.1 which shows comparative scales from macro-materials to atoms.

Also observe another Fig. 16.2 which depicts the materials in nature, as well as devices that are man made. In both figures some objects like tennis ball (Fig. 16.1), ant, human hair (Fig. 16.2) we can see with our own eyes whereas bacteria, virus, red blood cell, we can not observe with naked eye. These are known as nanomaterials.

a. What is nanoscience ?

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales where properties differ significantly from those at a larger scale.

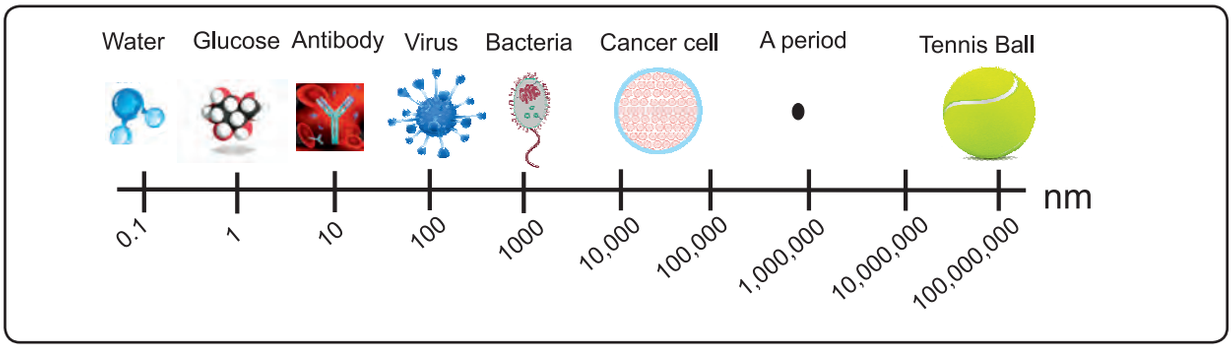


Fig. 16.1 Macro-materials to atoms

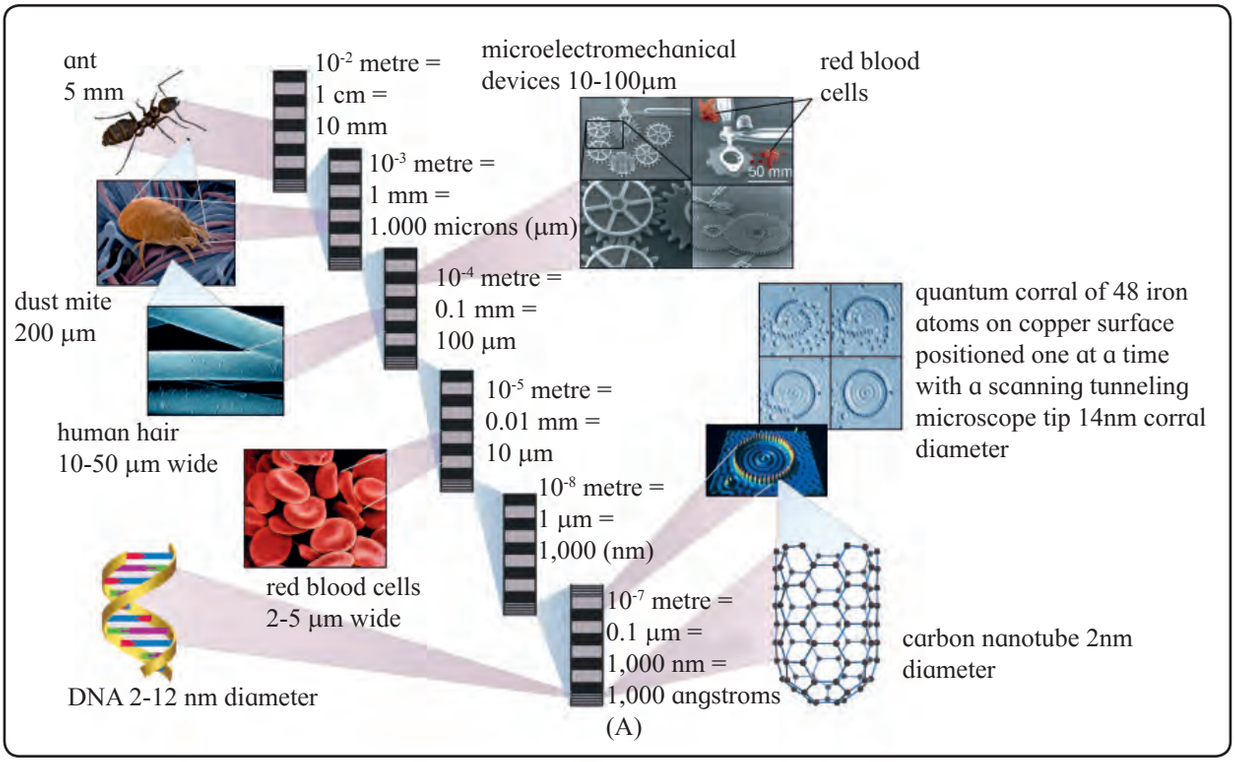


Fig. 16.2 Scale of nanomaterials

b. How do we define nanotechnology ?

Nanotechnology is the design, characterization, production and application of structures, device and system by controlling shape and size at nanometer scale.

c. Why Nano ?

The nanometer scale : 'Nano' in Greek means dwarf but in actual case 'nano' is even smaller than dwarf. Conventionally, the nanometer scale is defined as 1-100 nm. One nanometer is one billionth of a meter. (that is 1nm = 10^{-9}m).

The materials we see around us are bulk materials that possess macroscopic physical properties. Grain of sand that is micron-sized material also possesses same bulk properties. But material synthesized at nanoscale (1nm - 100nm) possesses unique optical, structural, thermal, catalytic, magnetic and electrical properties. These properties change as a function of size and are very different from their bulk materials.

d. What is a nanomaterial ?

The nanomaterial is a material having structural components with atleast one dimension in the nanometer scale that is 1-100 nm. Nanomaterials are larger than single atoms but smaller than bacteria and cells. These may

be nanoparticles, nanowires and nanotubes according to dimensions. Nanostructured materials may be large organic molecules, inorganic cluster compounds and metallic or semiconductor particles.

What are zero, one and two dimensional nanoscale system ?

i. Zero-Dimensional Nanostructures : For example, Nanoparticles.

A zero dimensional structure is one in which all three dimensions are in the nanoscale.

ii. One-Dimensional Nanostructures : For example, Nanowires and Nano rods.

A one dimensional nanostructure is one in which two dimensions are in the nanoscale.

iii. Two-Dimensional Nanostructures : For example, Thin films.

A two-dimensional nanostructure is one in which one dimension is in the nanoscale.

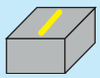
Nanomaterial Dimension	Nanomaterial Type	Example
All three dimensions < 100 nm	Nanoparticles, Quantum dots, nanoshells, nanorings, microcapsules	
One dimensions < 100 nm	Nanotubes, fibres, nanowires	
Two dimension < 100 nm	Thin films, layers and coatings	

Fig. 16.3 Illustration of zero, one, two dimensions

e. Definition of Nanochemistry : It is the combination of chemistry and nanoscience. It deals with designing and synthesis of materials of nanoscale with different size, shape, structure and composition and their organization into functional architectures. Nanochemistry is used in chemical, physical, materials science as well as engineering, biological and medical applications.

Do you know ?

A very highly useful application of nanochemistry is 'medicine'. A simple skin care product of nanochemistry is sunscreen. Sunscreen contains nanoparticles of Zinc oxide, (ZnO) and Titanium dioxide, (TiO_2). These chemicals protect the skin against harmful UV (ultraviolet) rays by absorbing or reflecting the light and prevent the skin from damage.

Internet my friend

Find out similar applications in medicine related to wounds, healing process. Also find out applications of TiO_2 and ZnO in other areas.

16.6 Characteristic features of Nanoparticles : What makes the science at nanoscale special is that at such a small scale, different laws dominate over those that we experience in our everyday life.

16.6.1 Colour : It is an optical property that is different at nanoscale. Elemental gold as we know, has nice shining yellow colour. However, if you had only 100 gold atoms arranged in cube, its colour would be red.

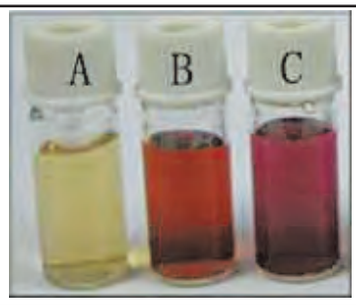


Fig. 16.4 Formation of gold nanoparticles solution

16.6.2 Surface area : High surface-to-volume ratio is a very important characteristic of nanoparticles. If a bulk material is sub divided into a group of individual nanoparticles, the total volume remains the same, but the

collective surface area is largely increased. With large surface area for the same volume, these small particles react much faster because more surface area provides more number of reaction sites, leading to more chemical reactivity. Explanation of increase in surface area with decrease in particle size.

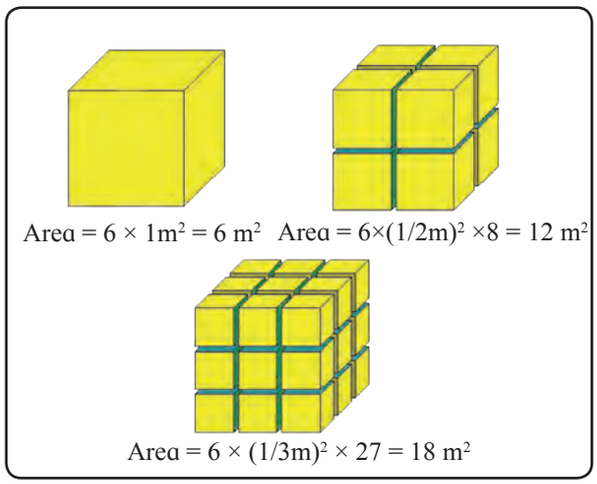


Fig. 16.5 : Surface area of nanoparticles

Fig. 16.5 shows the surface areas when a cube of $1m^3$ were progressively cut into smaller cube until cube of $1nm^3$ formed.

16.6.3 Catalytic activity : Due to increase in surface area with decrease in particle size, nanomaterial-based catalysts show increased catalytic acitivity. Usually they are heterogeneous catalysts that means catalysts are in solid form and the reactions occur on the surface of the catalyst. Nanoparticle catalysts can be easily separated and can be recycled. Example, Pd, Pt metal nanoparticles used in hydrogenation reactions.

TiO_2, ZnO are used in photocatalysis. Gold in bulk form is unreactive, but gold nanoparticles are found to be very good catalyst for various organic reactions.

Internet my friend

Find out various applications or use of gold nanoparticles.

16.6.4 Thermal properties : melting point

The melting point of nanomaterial changes drastically and depends on size. For example, sodium clusters (Na_n) of 1000 atoms appeared to melt at 288 K while cluster of 10,000 atoms melted at 303 K and bulk sodium melts at 371K.

16.6.5 Mechanical properties

Mechanical strength : Nanosized copper and palladium clusters with diameter in the size range of 5-7 nm can have hardness upto 500% greater than bulk metal.

16.6.6 Electrical conductivity : Electrical conductivity is observed to change at nanoscale. For example, carbon nanotube can act as a conductor or semiconductor in behaviour.

16.7 Synthesis of nanomaterials

16.7.1 : There are two approaches to the synthesis of nanomaterials. Bottom up and Top down. Fig. 16.6 shows schematic illustration of the preparation methods of nanoparticles.

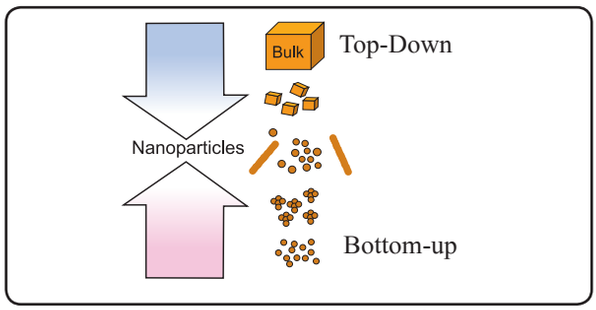


Fig. 16.6 : Schematic illustration of the preparation of nanoparticles

In the bottom up approach, molecular components arrange themselves into more complex assemblies atom by atom, molecule by molecule and cluster by cluster from the bottom. Example : synthesis of nanoparticles by colloidal dispersion.

In the top-down approach, nanomaterials are synthesized from bulk material by breaking the material. The bulk solids are dis-assembled into finer pieces until they are constituted of only few atoms.

16.7.2 Wet chemical synthesis of Nanomaterials : Sol-gel process : Sols are dispersions of colloidal particles in a liquid. Colloids are solid particles with diameters of 1-100nm. A gel is interconnected rigid network

with pores of submicrometer dimensions and polymeric chains whose average length is greater than a micrometer.

A sol-gel process is based on inorganic polymerization reactions. It is generally carried out at room temperature and includes four steps : hydrolysis, polycondensation, drying and thermal decomposition. This method is widely employed to prepare oxide materials.

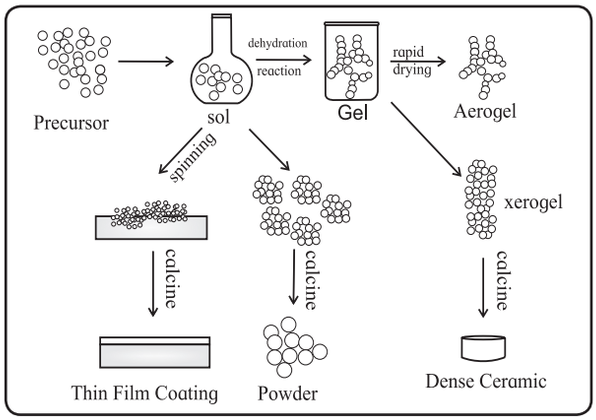


Fig. 16.7 : Schematic representation of sol-gel process of synthesis of nanoparticles

The rections involved in the sol-gel process can be described as follows :

$MOR + H_2O \longrightarrow MOH + ROH$ (hydrolysis)

metal alkoxide

$MOH + ROM \longrightarrow M\text{-}O\text{-}M + ROH$

(condensation)

1. Formation of different stable solution of the alkoxide or solvated metal precursor.
2. Gelation resulting from the formation of an oxide or alcohol-bridged network (gel) by a polycondensation reaction.
3. Aging of the gel means during that period gel transforms into a solid mass.
4. Drying of the gel : In this step, water and other volatile liquids are removed from the gel network.
5. Dehydration : The material is heated at temperatures upto 800 ^{0}C.

16.7.3 Analysis or characterization of nanomaterials :

The synthesized material is analyzed by various analytical tools or techniques. The name of the technique and its use is described in the following Table 16.1.

16.7.4 Photographs of instruments

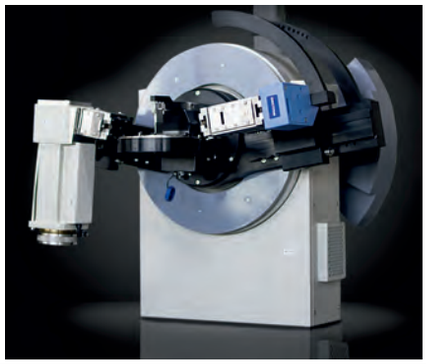


Fig. 16.8 Photograph of X-ray diffractometer

Table 16.1

Name of Technique	Instrument used	Information
1. UV-visible spectroscopy	UV-visible spectrophotometer	Preliminary confirmation of formation of nanoparticles
2. Xray Diffraction (XRD)	Xray diffractometer	particle size, crystal structure, geometry
3. Scanning electron microscopy	Scanning electron microscope (SEM)	Structure of surface of material that is morphology
4. Transmission electron microscopy	Transmission electron microscope (TEM)	particle size
5. FTIR Fourier transform infrared spectroscopy	Fourier transform infrared spectrophotometer	Absorption by functional groups, Binding nature.

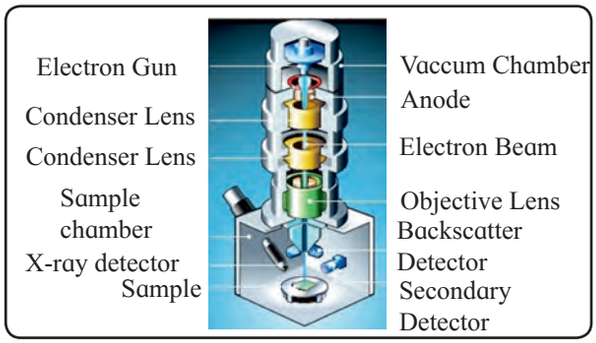


Fig. 16.9 Schematic diagram of scanning electron microscope

Fig. 16.10 Scanning electron microscope

16.8 History of nanotechnology :

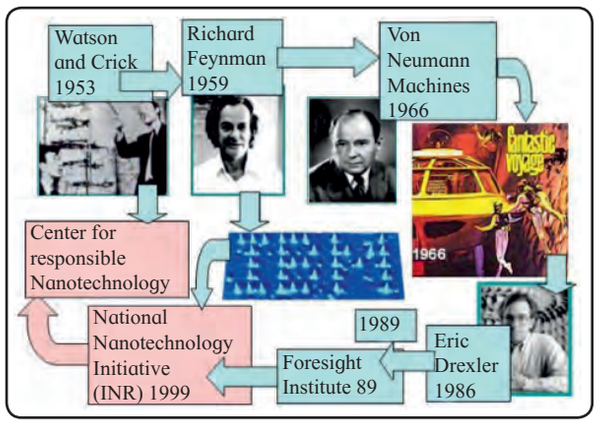


Fig. 16.13 : Scientists contributed to nanotechnology

Nanomaterials have been produced and used by humans for hundreds of years. However, understanding of certain materials as nanostructured materials is relatively recent. Due to the development of advanced tools that is sophisticated instruments, it has been possible to reveal the information at nanoscale.

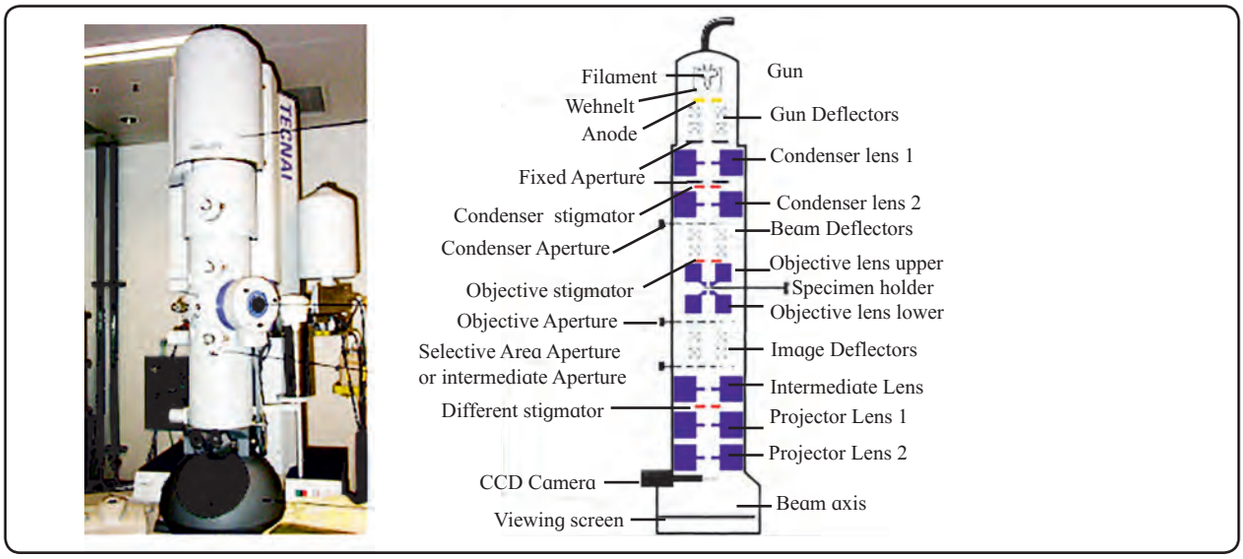


Fig. 16.11Transmission electron microscope (TEM)

Fig. 16.12 FTIR spectrophotometer

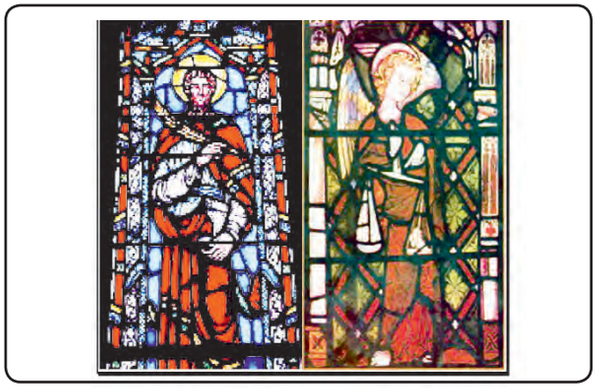


Fig. 16.14 Ruby red colour

a. Beautiful ruby red colour of some ancient glass paintings is due to gold and silver nanoparticles trapped in the glass matrix.

b. The decorative glaze or metallic film known as lustre found on some medieval pottery is due to certain spherical metallic nanoparticles.

c. Carbon black is a nanostructured material that is used in tyres of car to increase the life of tyre. (Discovery in 1900). Carbon nanotubes are made up of graphite sheets with nanosized diameter. They have highest strength.

d. Fumed silica, a component of silicon rubber, coatings, sealants and adhesives is also a nanostructured material.

Internet my friend

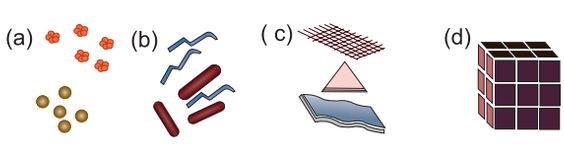
Find out more number of nanostructured materials in day to day used products.

Do you know ?

1. The term '**nanotechnology**' was defined by Tokyo science University Professor, Nario Taniguchi in 1974.
2. Invention of Scanning Tunneling Microscope (STM) in 1980, led to the discovery of fullerenes in 1986 and carbon nanotubes a few years later.

Internet my friend

Collect the information about the scientists who discovered SEM, STM, TEM instruments.



(a) 0D spheres and clusters, (b) 1D nanofibers, wires and rods (c) 2D films, plates and networks, (d) 3D nanomaterials

Fig. 16.15 Classification of nanomaterials

Can you think ?

Visualize the size effect : Size difference between the earth and an apple is equal to the size difference between atoms (30 nm) and an apple.

16.9 Applications of nanomaterials :

Nanochemistry has already contributed to number of innovative products in various disciplines because of their unique physical, chemical, optical, structural, catalytic properties and so on. Few applications are given below :

a. Nanoparticles can contribute to stronger, lighter, cleaner and smarter surfaces and systems. They are used in the manufacturing of scratchproof eyeglasses, transport, sunscreen, crack resistant paints and so on.

b. Used in electronic devices. For example, Magnetoresistive Random Acess memory (MRAM)

c. Nanotechnology plays an important role in water purification techniques.

Water contains waterborne pathogens like viruses, bacteria. 1.1 billion people are without access to an improved water supply. The provision of safe drinking water is currently high priority. Recently, cost effective filter materials coated with silver nanoparticles (AgNps) is an alternative technology. (For example : water purifier) Silver nanoparticles act as highly effective bacterial disinfectant, remove E.Coli from water.

d. Self cleaning materials : Lotus is an example of self cleaning. The lotus plant (*Nelumbo nucifera*) although grows in muddy water, its leaves always appear clean. The plants' leaves are superhydrophobic. Nanostructures on lotus leaves repel water which carries dirt as it rolls off. Lotus effect is the basis of self cleaning windows.

Do you know ?

Sol-gel processes are used in the motor vechicle industry to produce water repellent coatings for wind screens or exterior mirrors.

16.10 Nanoparticles and Nanotechnology :

Advantages :

1. Revolution in electronics and computing.

2. Energy sector - nanotechnology will make solar power more economical. Energy storage devices will become more efficient.

3. Medical field :

Manufacturing of smart drugs, helps cure faster and without side effects. Curing of life threatening diseases like cancer and diabetes.

Disadvantages : Despite the possibilities and the advancements that the nanotechnology offers to the world, there also exist certain potential risks involved with the disadvantages of it.

Nanotechnology has raised the standard of living but at the same time, it has increased the pollution which includes air pollution. The pollution caused by nanotechnology is known as nano pollution. This kind of pollution is very dangerous for living organisms.

Nanoparticles can cause lung damage. Inhaled particulated matter can be deposited throughout the human respiratory tract and then deposit in lungs.

The characteristics of nanoparticles that are relevant for health effects are size, chemical composition and shape.

Exercises

1. Choose the most correct option.

i. The development that meets the needs of present without compromising the ability of future generations to meet their own need is known as

a. Continuous development

b. Sustainable development

c. True development

d. Irrational development

ii. Which of the following is ϒ-isomer of BHC?

a. DDT b. lindane

c. Chloroform

d. Chlorobenzene

iii. The prefix 'nano' comes from

a. French word meaning billion

b. Greek word meaning dwarf

c. Spanish word meaning particle

d. Latin word meaning invisible

iv. Which of the following information is given by FTIR technique ?

a. Absorption of functional groups

b. Particle size

c. Confirmation of formation of nanoparticles

d. Crystal structure

v. The concept of green chemistry was coined by

a. Born Haber

b. Nario Taniguchi

c. Richard Feynman

d. Paul T. Anastas

2. Answer the following

i. Write the formula to calculate % atom economy.

ii. Name the ϒ-isomer of BHC.

iii. Ridhima wants to detect structure of surface of materials. Name the technique she has to use.

iv. Which nanomaterial is used for tyres of car to increase the life of tyres ?

v. Name the scientist who discovered scanning tunneling microscope (STM) in 1980.

vi. 1 nm = ...m ?

3. Answer the following

i. Define (i) Green chemistry (ii) sustainable development.

ii. Explain the role of green chemistry.

iii. Give the full form (long form) of the names for following instruments.

a. XRD b. TEM. c. STM

d. FTIR e. SEM

iv. Define the following terms :

a. Nanoscience

b. Nanotechnology

c. Nanomaterial

d. Nanochemistry

v. How nanotechnology plays an important role in water purification techniques?

vi. Which nanomaterial is used in sunscreen lotion ? Write its use.

vii. How will you illustrate the use of safer solvent and auxiliaries ?

viii. Define catalyst. Give two examples.

4. Answer the following

i. Explain any three principles of green chemistry.

ii. Explain atom economy with suitable example.

iii. How will you illustrate the principle, minimization of steps ?

iv. What do you mean by sol and gel? Describe the sol-gel method of preparation for nanoparticles.

v. Which flower is an example of self cleaning ?

Activity :

- **Collect information about application of nanochemistry in cosmetics and pharmaceuticals**

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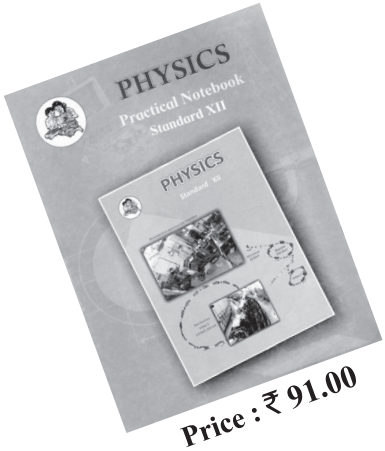

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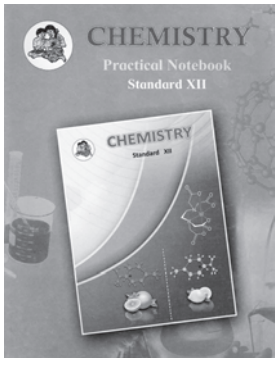

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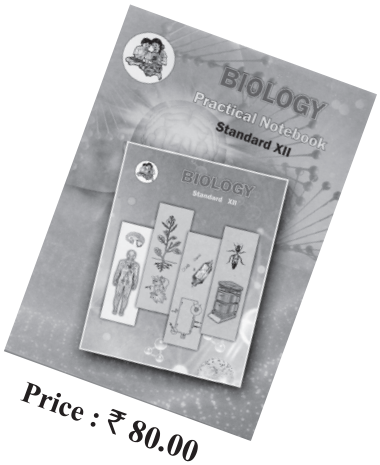

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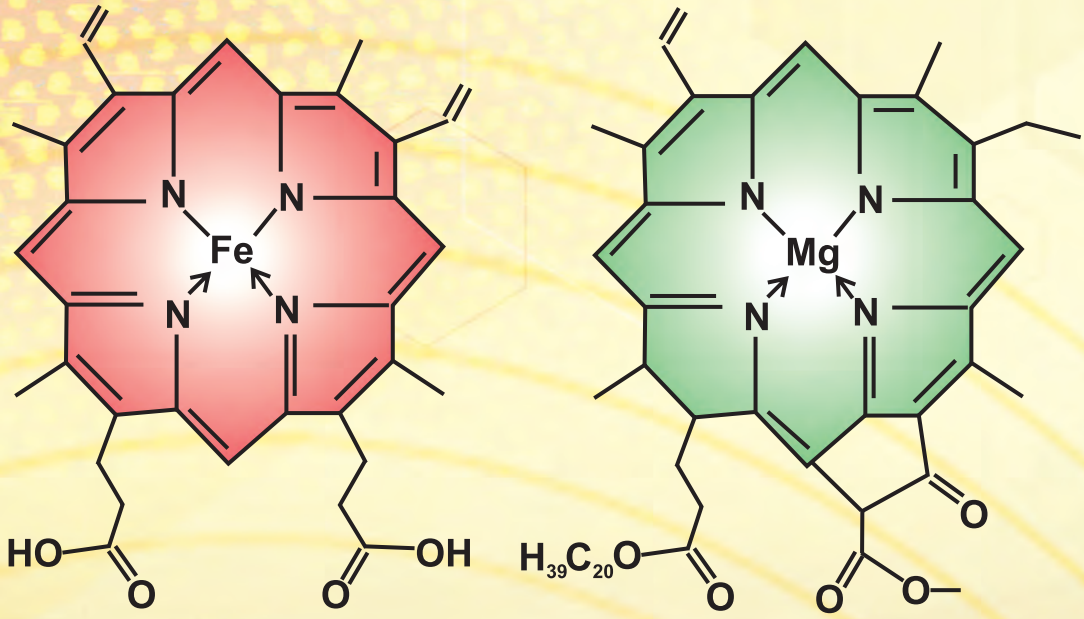

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