

**POLYMERS AND PRACTICAL ORGANIC CHEMISTRY NOTES**

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

Homopolymers and Copolymers

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

Homopolymer	Monomer
Starch	Glucose
Cellulose	Glucose
Glycogen	Glucose
Dextrin	Glucose
Inulin	Fructose
Polyethylene	Ethylene
Polyvinyl chloride	Vinyl chloride
Teflon	Tetrafluoro ethylene
Nylon-6	Caprolactam
Polystyrene	Styrene
Orlon (Acrilan)	Acrylonitrile
Plexiglas (Lucite)	Methyl methacrylate
Polyvinyl acetate	Vinyl acetate

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



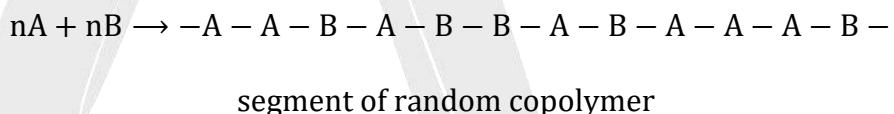
Copolymer	Monomers
Saran	Vinyl chloride and vinylidene chloride
SAN	Styrene and acrylonitrile
ABS	Acrylonitrile, butadiene and styrene
Butyl rubber	Isobutylene and Isoprene
Buna-S, SBR	Styrene and Butadiene
Buna-N, NBR	Acrylonitrile and Butadiene
Nylon-66	Hexamethylenediamine and Adipic acid
Terylene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

Types of copolymers

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

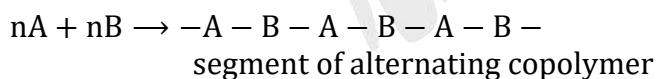
(1) Random Copolymer

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



(2) Alternating Copolymer

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

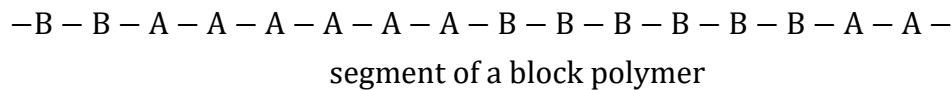


The exact distribution depends upon the proportion of the two reactant monomers and their relative reactivities. In practice neither perfectly random nor perfectly alternating copolymers are usually formed. However, most copolymers tend more towards alternating type but have many random imperfections.

(3) Block copolymer

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

For example,

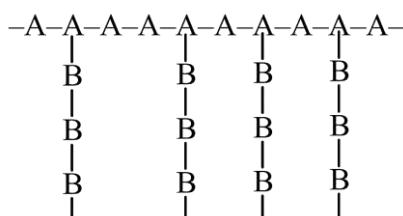




Block copolymer can be prepared by initiating the radical polymerisation of one monomer to grow homopolymer chains, followed by addition of an excess of the second monomer.

(4) Graft copolymer

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



(Segment of a graft copolymer)

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

CLASSIFICATION OF POLYMERS

Polymers are classified in following ways :

(I) CLASSIFICATION BASED UPON SOURCE

(1) Natural polymers

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

Natural polymer

- | | |
|--------------------------------------|-----------------------------------|
| 1. Polysaccharide | Monosaccharide |
| 2. Proteins | α -L-Amino acids |
| 3. Nucleic acid | Nucleotide |
| 4. Silk | Amino acids |
| 5. Natural Rubber (cis polyisoprene) | Isoprene (2-Methyl-1,3-butadiene) |
| 6. Gutta purcha (trans polyisoprene) | Isoprene |

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

(2) Semisynthetic polymers

Polymers which are prepared from natural polymers are known as semisynthetic polymers. Most of the semisynthetic polymers are prepared from cellulose. Examples are: cellulose acetate, cellulose nitrate, cellulose xanthate and Rayon.

(3) Synthetic polymers

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

(II) CLASSIFICATION BASED UPON SHAPE**(1) Linear polymers**

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



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

Note :

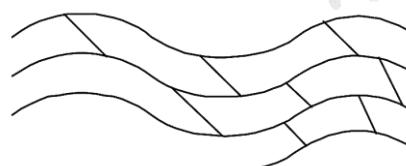
- (i) All fibers are linear polymers. Examples are cellulose, silk, nylon, terylene etc.
- (ii) Linear polymers may be condensation as well as addition polymers. Examples are cellulose, polypeptide, nucleic acid, nylon, terylene etc.

(2) Branched chain polymers

Branched chain polymers are those in which the monomeric units constitute a branched chain. Due to the presence of branches, these polymers do not pack well. As a result branched chain polymers have lower melting points, low densities and tensile strength as compared to linear polymers. Branched chain polymers may be formed due to addition as well as condensation polymerisation. Examples are amylopectin, glycogen, low density polyethylene and all vulcanised rubbers.

**(3) Cross-linked or Three Dimensional network polymers**

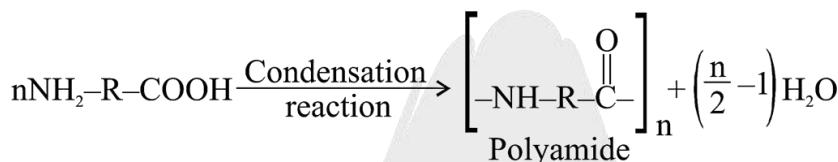
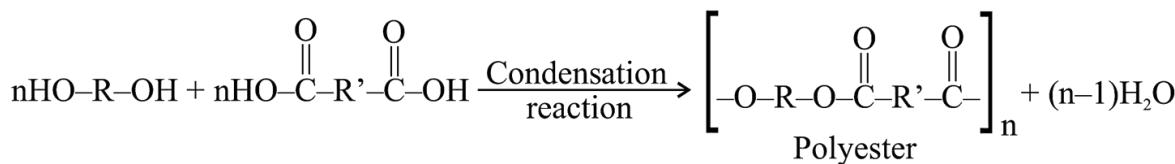
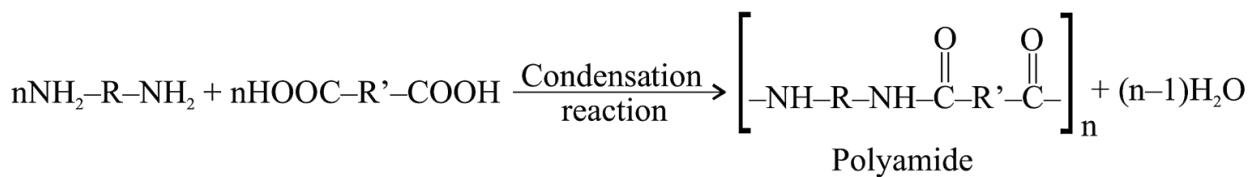
In these polymers the initially formed linear polymeric chains are joined together to form a three dimensional network structure. These polymers are hard, rigid and brittle. Cross-linked polymers are always condensation polymers. Resins are cross linked polymers.

**CLASSIFICATION BASED UPON SYNTHESIS****(1) Condensation polymerisation**

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



For example,



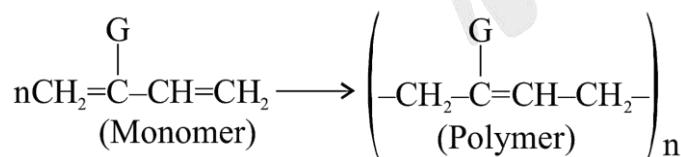
Condensation polymers do not contain all atoms initially present in the monomers. Some atoms are lost in the form of small molecules. Monomer having three functional groups always gives crosslinked polymer.

Examples are : Urea-formaldehyde resin, phenol-formaldehyde resin.

(3) Addition polymerisation

Polymers which are formed by addition reaction are known as addition polymers. If monomer is ethylene or its derivative, then addition polymer is either linear polymer or branch-chain polymer. Examples are : polystyrene, polytetrafluoroethylene, polyacrylonitrile etc. If monomer is 1, 3-butadiene or 2-substituted-1, 3-butadiene ($\text{CH}_2 = \underset{\text{G}}{\underset{\text{C}}{\text{||}}} \text{CH} = \text{CH}_2$), then polymer

is always branched chain polymer.



(Monomer)

- (i) G = H: 1,3 - Butadiene
- (ii) G = CH₃; 2 - Methyl-1,3-butadiene or isoprene
- (iii) G = Cl; 2 -Chloro-1,3-butadiene or chloroprene

(Polymer)

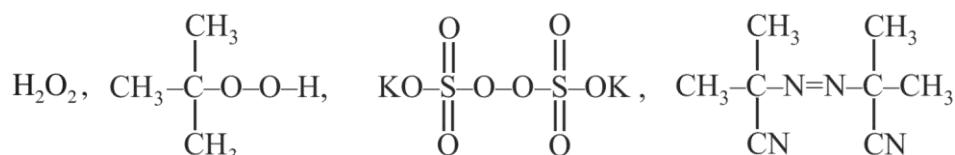
- (i) Polybutadiene
- (ii) Polyisoprene
- (iii) Plychloroprene (Neoprene)

Addition polymers retain all the atoms of the monomer units in the polymer. Addition polymerisation takes place in three steps. Initiation, chain propagation and chain termination.

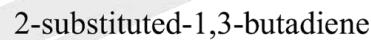
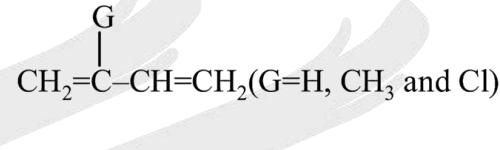
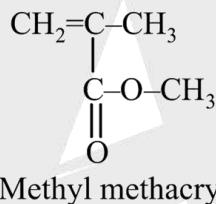
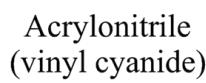
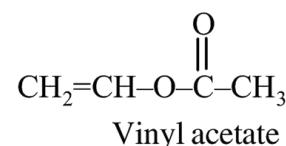
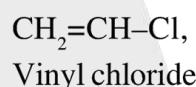
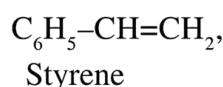
Addition polymers are called as chain growth polymers.

**Types of Addition Polymerisation****(A) Radical Polymerisation :**

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



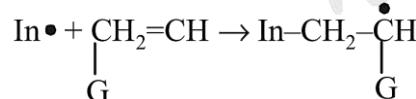
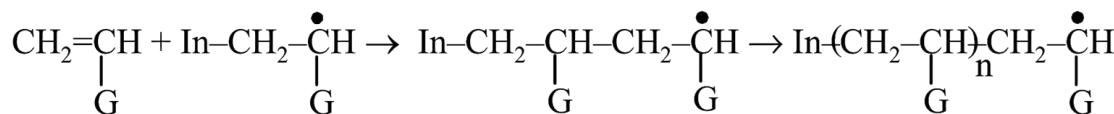
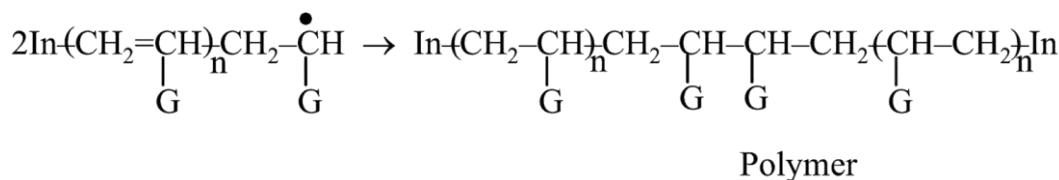
Reaction intermediate of radical polymerisation is a free radical. Radical polymerization has more chance for those monomers whose free radicals are more stable.

Examples are :

Radical polymer has linear as well as branched chain structure.

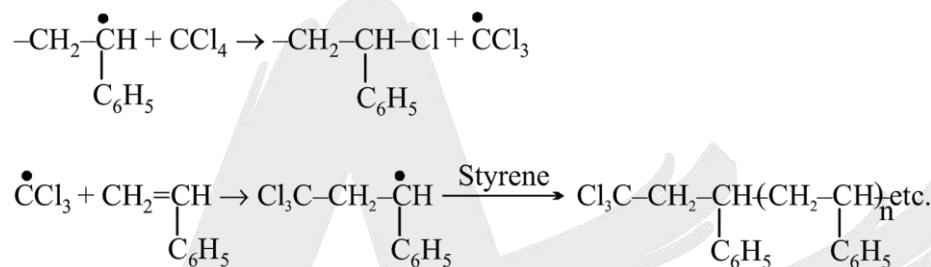
Most of the commercial addition polymers are vinyl polymers obtained from alkenes and their derivatives $\text{CH}_2=\underset{\text{G}}{\text{CH}}$ [G is H, C_6H_5 , R etc.]. This type of polymerisation is performed by heating

the monomer with only a very small amount of the initiator or by exposing the monomer to light. the general mode of radical polymerisation of vinyl monomers is depicted below :

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

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

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

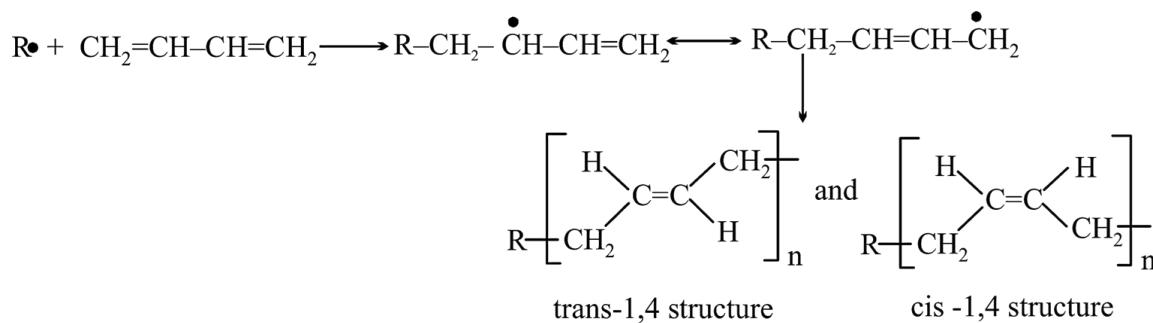


If the chain transfer agent a radical, which is highly unreactive, the reaction chain gets terminated such a compound thus inhibits or arrests polymerisation. Many amines, phenols, quinones etc. act as inhibitors. So, even traces of certain impurities, which can act as chain transfer agent or an inhibitor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

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

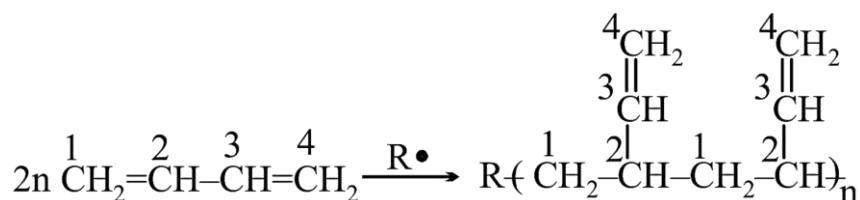
(1) 1,4 - polymerisation.

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



(2) 1,2-Polymerisation

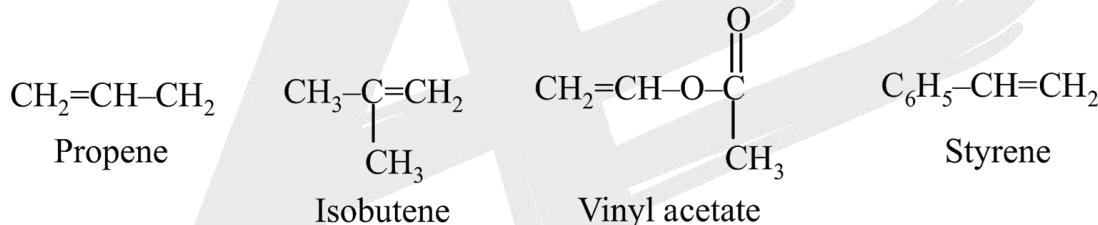
Alternatively, 1,3 -butadiene can undergo polymerisation at C_1 and C_2 to yield the polymeric product, polyvinyl polythene.



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

(B) Cationic Polymerisation :

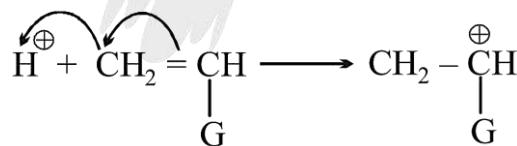
Polymerisation which is initiated by an electrophile is known as cationic polymerisation. Reaction intermediate of cationic polymerisation is a carbocation. Carbocations can undergo rearrangement leading to the formation of a more stable carbocation. The electrophile commonly used for initiation is $\text{BF}_3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



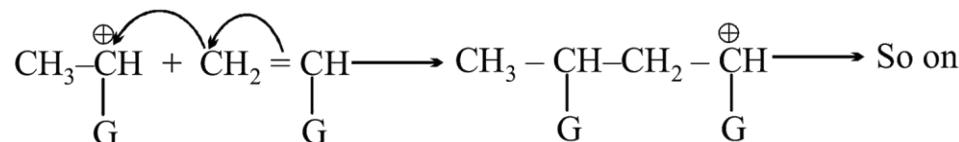
It is terminated by a base.

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

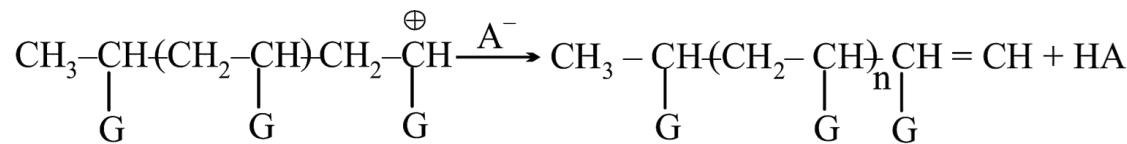
Chain initiation step :



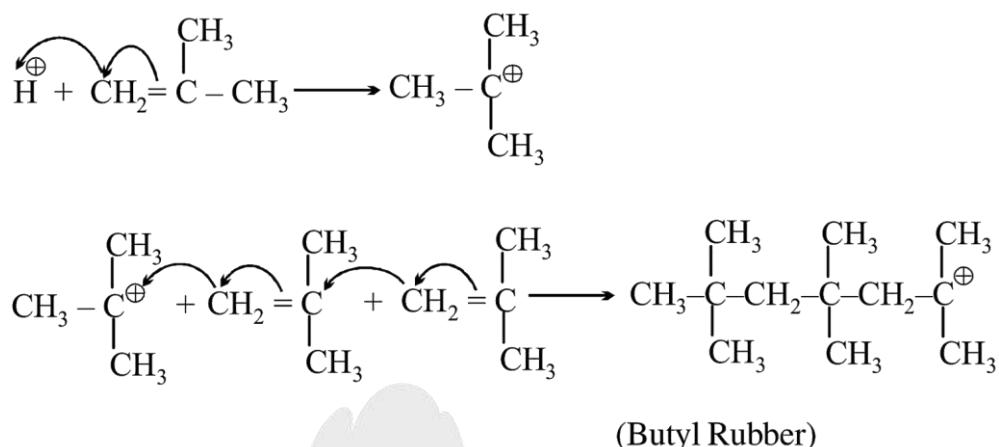
Chain propagating step :



Chain terminating step :



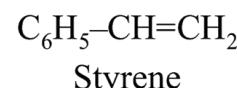
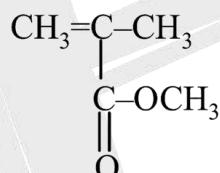
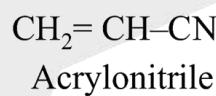
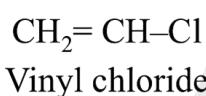
Cationic polymerisation is facilitated in monomers containing electron - releasing groups. Thus, isobutylene undergoes cationic polymerisation easily as it has two electron releasing $-\text{CH}_3$ groups that will stabilize the intermediate carbocation.



(C) Anionic Polymerisation :

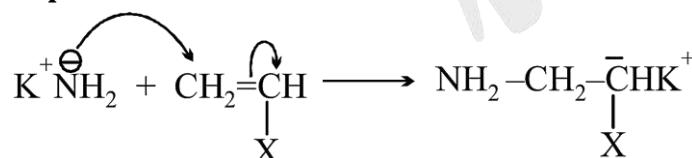
Anionic polymerisation takes place in the presence of base or nucleophile, which is initiator in this polymerization. Reaction intermediate in propagation steps are carboanion. The suitable initiator can be NaNH_2 or RLi . Those monomers undergo anionic polymerisation reaction whose anion is stable.

Example of monomers are :

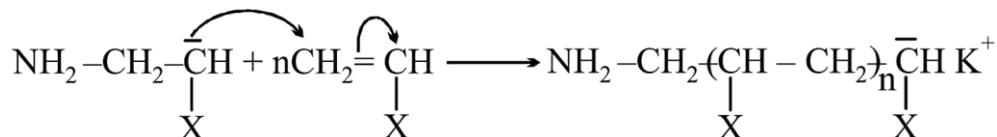


Anionic polymerisation always gives linear polymer. Anionic polymerisation terminated by an acid. The formation of polystyrene from styrene in the presence of potassium amide is an important example of this category of polymerisation. The mode of anionic polymerisation is depicted below:

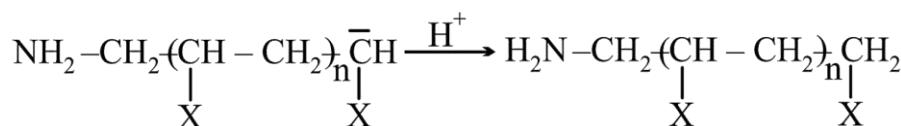
Chain initiation step :



Chain propagating step :



Chain terminating step :



**(D) Ziegler- Natta polymerisation :**

Addition polymerisation which takes place in the presence of Ziegler- Natta catalyst $[(C_2H_5)_3Al$ and $TiCl_4$] is known as Ziegler- Natta polymerisation or coordination polymersation. Ziegler- Natta polymerisation always gives linear, stereo-regular polymers. Ziegler- Natta catalyst revolutionised the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers (due to linear geometry) that have greater resistance to cracking and heat. High density polyethylene is prepared using a Ziegler- Natta catalyst.

CLASSIFICATION BASED ON INTERMOLECULAR FORCES**(SECONDARY FORCES)**

Intermolecular forces present between polymeric chains are (a) Van der waals forces (b) Hydrogen bonds and (c) Dipole - dipole attractions. Mechanical properties such as tensile strength, elasticity, toughness etc. depend upon the secondary forces present between the polymeric chains. Magnitude of secondary forces depends upon the size of the molecule and the number of functional groups along the polymeric chains. Magnitude of secondary forces is directly proportional to the length of the polymeric chain. On the basis of magnitude of secondary forces, polymers can be divided into the following following categories.

(1) Elastomes

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

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

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

(2) Fibres

Fibres are linear polymers in which the individual chains of a polymer are held together by hydrogen bonds and / or dipole-dipole attraction. In the fibres, the polymeric chains are highly ordered with respect to one another. Due to strong intermolecular forces of attraction and highly ordered geometry, fibres have high tensile strength and least elasticity. they have crystalline character and have high melting points and low solubility. Examples are cellulose, nylon, terylene, wool, silk etc.

Note :

- (i) Condensation polymers formed from bifunctional monomers are fibres in character.
- (ii) Addition polymers of alkene derivatives having strong- I group are fibres in character.

**(3) Thermoplastic Polymers**

Thermoplastic polymers are polymers that have both ordered crystalline regions (the regions of the polymer in which the chains are highly ordered with respect to one another) and amorphous, non crystalline regions (the regions of the polymer in which the chains are randomly oriented). The intermolecular forces of attraction are in between elastomers and fibres. There are no cross links between the polymeric chains. Thermoplastic polymers are hard at room temperature, but when they are heated, the individual chains can slip past one another and the polymer become soft and viscous. This soft and viscous material becomes rigid on cooling. The process of heating softening and cooling can be repeated as many times as desired without any change in chemical composition and mechanical properties of the plastic. As a result, these plastics can be moulded into toys, buckets, telephone and television cases. Some common examples are : polyethene, polypropylene, polystyrene, polyvinyl chloride, teflon etc.

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

(4) Thermosetting Polymers

Polymers which become hard on heating are called thermosetting polymers. Thermosetting polymers can be heated only once when it permanently sets into a solid, which cannot be remelted by heating. Thermosetting polymers are cross-linked polymers. Greater the degree of cross-linking that exists, the more rigid is the polymer. Cross-linking reduces the mobility of the polymer chains, causing them to be relatively brittle materials. The hardening on heating is due to the extensive cross-linking between different polymer chains to give a three-dimensional network solid. Examples are : phenol-formaldehyde resin, urea-formaldehyde resin, melamine-formaldehyde resin.

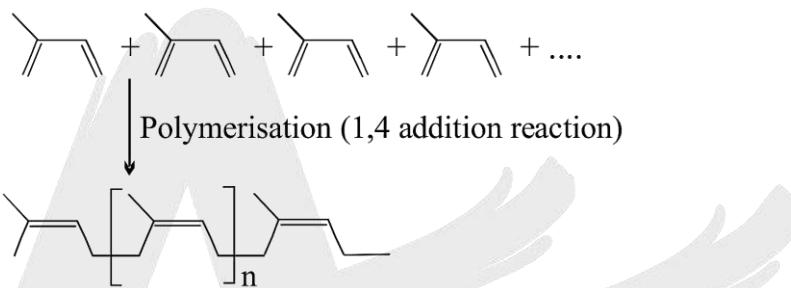
DIFFERENCE BETWEEN THERMOPLASTIC AND THERMOSETTING POLYMERS

S.NO.	Thermoplastic polymers	Thermosetting polymers
1.	Softens and melts on heating and becomes hard on cooling i.e. process is reversible	Become hard on heating and process is irreversible.
2.	Can be moulded and remoulded and reshaped.	They can be moulded once and cannot be remoulded or reshaped. They are addition polymers
3.	They are addition polymers	They are condensation polymers.
4.	Structure is generally linear	Structure is cross-linked.

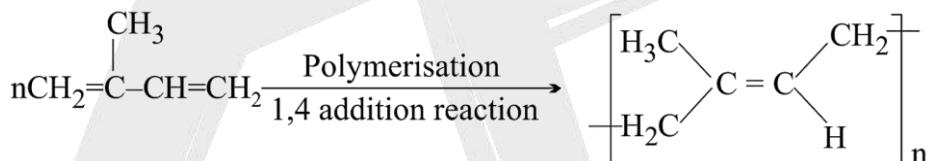
RUBBER**1. Natural Rubber**

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

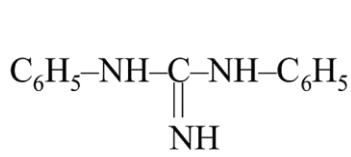
The raw natural rubber is a soft gummy and sticky **mass**. It is insoluble in water, dilute acids and alkalies but soluble in non-polar solvents. It has low elasticity and low tensile strength. Natural rubber is a polymer of 2-methyl-1,3-butadiene (isoprene). On average, a molecule of rubber contains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



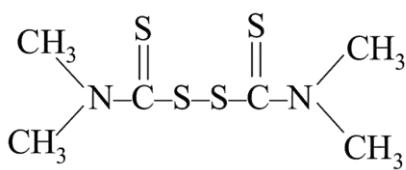
Gutta - percha is a naturally occurring isomer of rubber in which all the double bonds are *trans*. Thus, gutta-percha is *trans*-polyisoprene.



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



Diphenyl guanidine



Tetramethylthioureadisulph

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

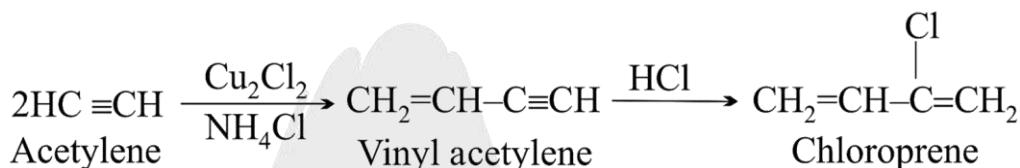
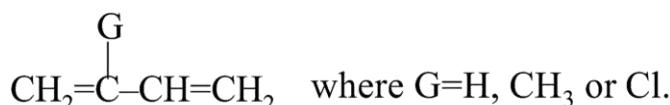
Natural rubber is used for making shoes, water - proof coats and golf balls. Vulcanised rubber is used for manufacture of rubber bands, gloves tubing and car tyres.

SYNTHETIC RUBBER OR POLYMERISATION OF DIENES

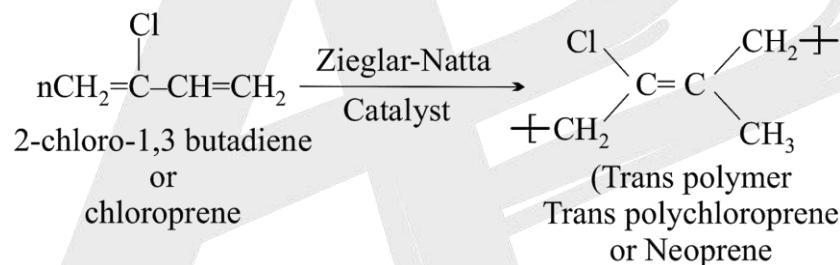
Polymers of 1,3 - butadienes are called synthetic rubbers because they have some of the properties of natural rubbers including the fact that they are water proof and elastic. Synthetic rubbers have some improved properties. They are more flexible, tougher and more durable than natural rubber.

1. Homopolymers

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



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



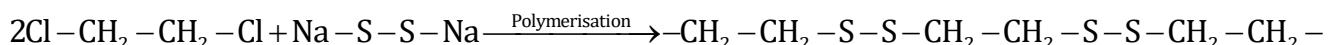
Many of the properties of neoprene are similar to natural rubber but neoprene is more resistant to action of oils, gasoline and other hydrocarbons. It is also resistant to sunlight, oxygen, ozone and heat. It is non - inflammable. It is used for making automobile and refrigerator parts, hoses for petrol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

2. Copolymers

The following synthetic rubbers are example of copolymers.

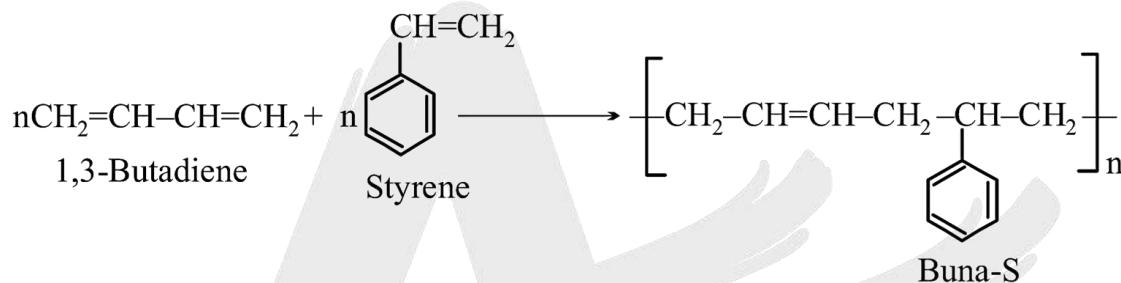
Synthetic rubber	Monomers
1. Buna-S, SBR (Styrene-butadiene rubber)	$\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ (25%) (75%)
2. Buna-N, NBR (Nitrile-butadiene rubber)	$\text{CH}_2=\text{CH}-\text{CN} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ (25%) (75%)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

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



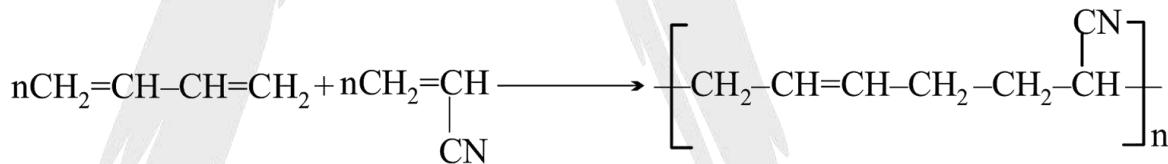
The repeating unit is $-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-$. Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

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



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

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



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

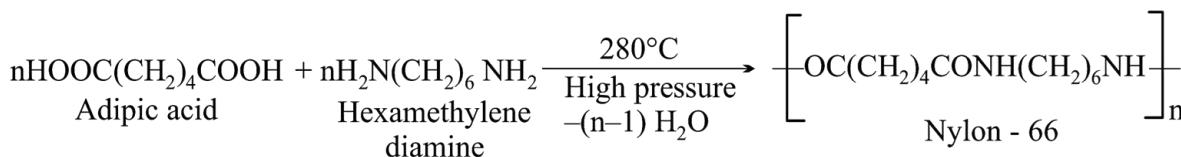
- (d) Cold Rubber :** Cold rubber is obtained by polymerisation of butadiene and styrene at -18° to 5°C temperature in the presence of redox system. Cold rubber has a greater tensile strength and greater resistance of abrasion than SBR.

NYLON

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

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

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

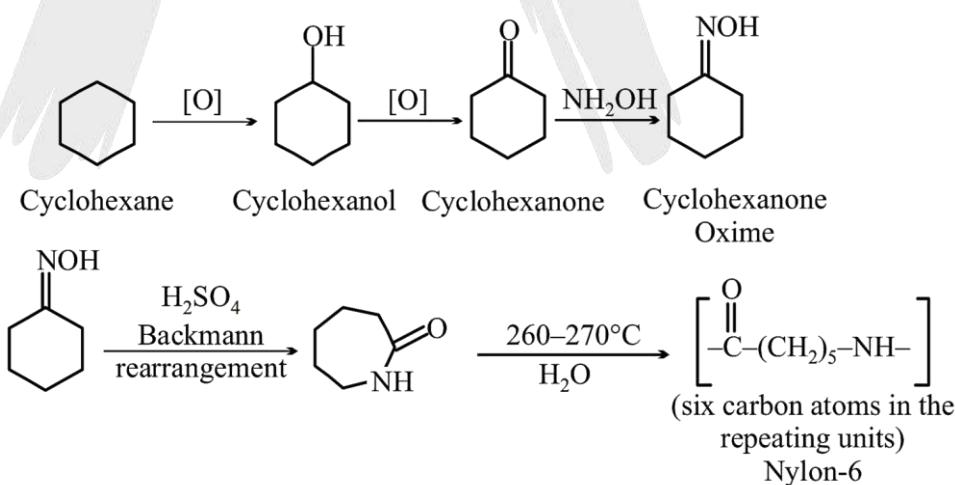
**(2) NYLON-610 (Nylon six, ten)**

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

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

(3) NYLON-6 (Perlon L)

A polyamide closely related to nylon is known as perlon L (Germany) or Nylon - 6 (USA). It is prepared by prolonged heating of caprolactum at $260 - 270^\circ\text{C}$. It is formed by self condensation of a large number of molecules of amino caproic acid. Since, caprolactum is more easily available, it is used for polymerization, with is carried out in the presence of H_2O that first hydrolyses the lactam to amino acid. Subsequently, the amino acid can react with the lactam and the process goes on and onto form the polyamide polymer. Caprolactam is obtained by Backmann rearrangement of cyclohexanone oxime.

**(4) NYLON-2-NYLON-6**

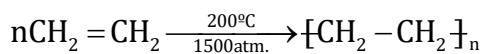
It is an alternating polyamide copolymer of glycine and amino caproic acid and is biodegradable.



POLYETHYLENE

Polyethylene is of two types :

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



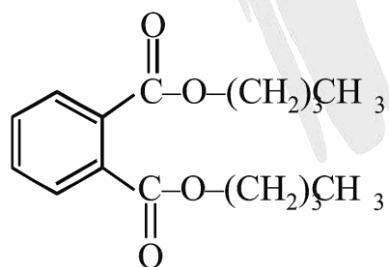
The polyethylene produced has a molecular mass of about 20,000 and has a branched structure. Due to this, polyethylene has a low density (0.92) and low melting point (110°C). That is why polyethylene prepared by free radical polymerisation is called low density polyethylene. It is a transparent polymer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

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

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

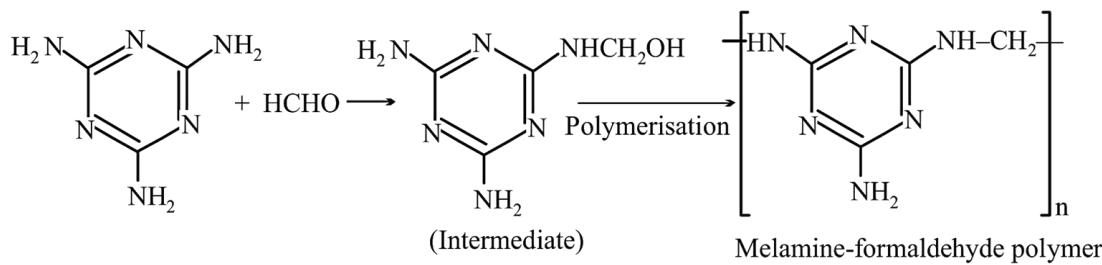
PLASTICISER

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



MELAMINE - FORMALDEHYDE RESIN

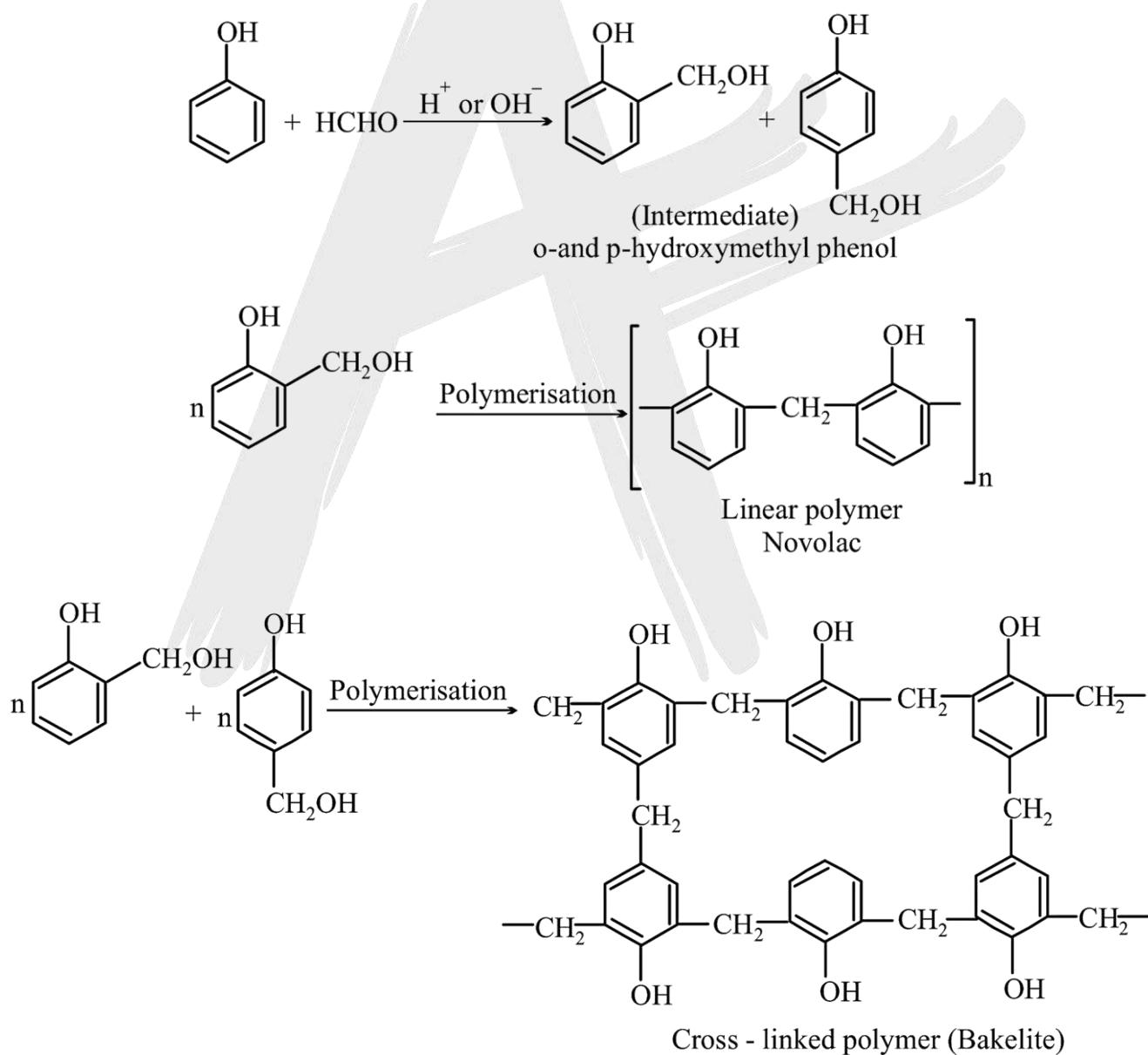
This resin is formed by condensation polymerisation of melamine and formaldehyde.



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

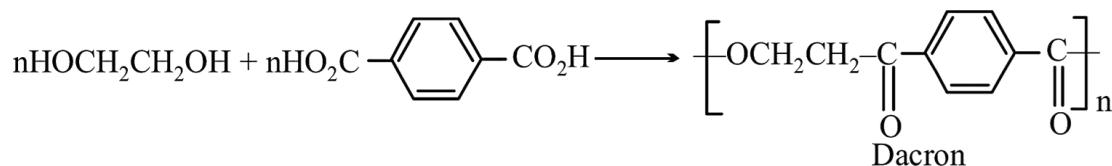
BAKELITE

Phenol-formaldehyde resins are obtained by the reaction of phenol and formaldehyde in the presence of either an acid or a basic catalyst. The reaction starts with the initial formation of ortho and parahydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with $-\text{CH}_2-$ groups. The reaction involves the formation of methylene bridges in ortho, para or both ortho and para positions. Linear or cross-linked materials are obtained depending on the conditions of the reaction.



**POLYESTERS**

Dacron is a common polyester, prepared using ethylene glycol and terephthalic acid. The reaction is carried out at 140° to 180°C in the presence of zinc acetate and Sb_2O_3 as catalyst.



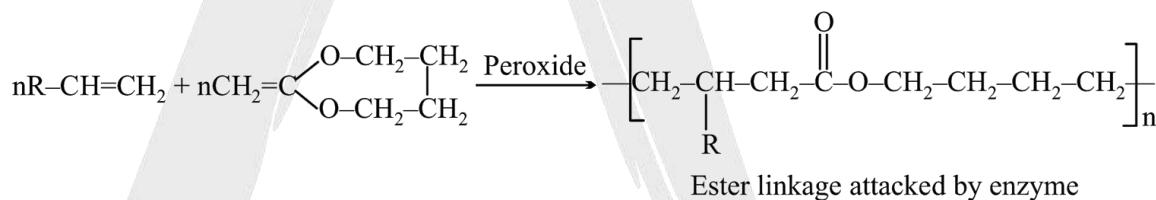
The terylene fibre (Dacron) is crease resistant and has low moisture absorption. It has high tensile strength. It is mainly used in making wash and wear garments, in blending with wood to provide better crease and wrinkle resistance.

BIODEGRADABLE POLYMERS

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

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

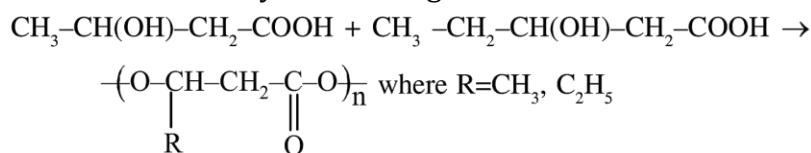
One method involves inserting hydrolysable ester group into the polymer. For example, when acetal (I) is added during the polymerization of alkene, ester group is inserted into the polymeric chains.



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

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

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



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

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

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

MOLECULAR MASS OF POLYMER

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

The molecular mass of a polymer is expressed as

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

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

where N_i is the number of molecules of molecular mass M_i

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

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

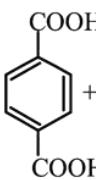
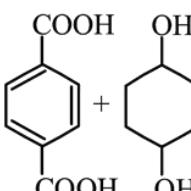
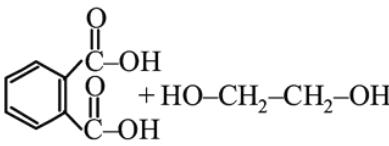
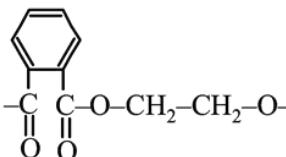
where N_i is the number of molecules of molecular mass M_i . Methods such as light scattering and ultracentrifuge depend on the mass of the individual molecules and yield weight average molecular masses. \bar{M}_n is determined by employing methods which depend upon the number of molecules present in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

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

In synthetic polymers, which are always polydisperse, PDI $>$ 1 because \bar{M}_w is always higher than \bar{M}_n .

**COMMON POLYMERS**

Monomer	Repeating unit	Polymer
1. $\text{CH}_2=\text{CH}_2$ Ethylene	$-\text{CH}_2-\text{CH}_2-$	Polyethylene
2. $\text{CH}_3-\text{CH}=\text{CH}_2$ Propene	$-\text{CH}_2-\underset{\substack{ \\ \text{CH}_3}}{\text{CH}}-$	Polypropene
3. $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$ Styrene	$-\text{CH}_2-\underset{\substack{ \\ \text{C}_6\text{H}_5}}{\text{CH}}-$	Polystyrene
4. $\text{CF}_2=\text{CF}_2$ Tetrafluoroethylene	$-\text{CF}_2-\text{CF}_2-$	Polytetrafluoro ethylene (PTFE), Teflon
5. $\text{CH}_2=\text{CH}-\text{Cl}$ Vinyl chloride	$-\text{CH}_2-\underset{\substack{ \\ \text{Cl}}}{\text{CH}}-$	Polyvinyl Chloride(PVC)
6. $\text{CH}_2=\text{CH}-\text{CN}$ Vinyl cyanide or Acrylonitrile	$-\text{CH}_2-\underset{\substack{ \\ \text{CN}}}{\text{CH}}-$	Polyvinyl cyanide, poly acrylonitrile, Orlon.
7. $\text{CH}_2=\text{C}(\text{H}_3\text{C})\text{O}-\text{CH}_3$ Methyl methacrylate	$-\text{CH}_2-\underset{\substack{ \\ \text{CH}_3}}{\text{C}}(\text{COOCH}_3)-$	Polymethyl metha acrylate, Plexiglas, Lucite
8. $\text{CH}_2=\text{CH}-\text{O}-\text{C}(=\text{O})-\text{CH}_3$ Vinyl acetate	$-\text{CH}_2-\underset{\substack{ \\ \text{OCOCH}_3}}{\text{CH}}-$	Polyvinyl Acetate
9. $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ 1,3-butadiene	$-\text{CH}_2-\text{CH}-\text{CH}=\text{CH}_2-$	Polybutadiene, Buna rubber
10. $\text{CH}_2=\text{CH}-\text{Cl}$ (vinyl chloride) + $\text{CH}_2=\text{CCl}_2$ (Vinylidene chloride)	$-\text{CH}_2-\underset{\substack{ \\ \text{Cl}}}{\text{CH}}-\text{CCl}_2-\text{CH}_2-$	Saran

11. $\text{C}_6\text{H}_5\text{-CH=CH}_2$ (Styrene) + $\text{CH}_2=\text{CH-CN}$ (acrylonitrile)	$\text{--CH}_2\text{-CH}(\text{C}_6\text{H}_5)\text{CN}-\text{CH}_2-$	SAN
12. $\text{CH}_2=\text{CH-CN} + \text{CH}_2=\text{CH-CH=CH}_2$ + $\text{C}_6\text{H}_5\text{-CH=CH}_2$	—	ABS
13. $\text{CH}_2=\text{C}(\text{CH}_3)\text{-CH}_2 + \text{CH}_2=\text{C}(\text{CH}_3)\text{-CH=CH}_2$	—	Butyl rubber
14. $\text{C}_6\text{H}_5\text{-CH=CH}_2 + \text{CH}_2=\text{CH-CH=CH}_2$	—	Buna -S, SBR
15. $\text{CH}_2=\text{CH-CN} + \text{C}_6\text{H}_5\text{-CH=CH}_2$	—	Buna-N, NBR
16. $\text{CH}_2=\text{C(Cl)-CH=CH}_2$ Cloroprene	$\text{--CH}_2\text{-C(Cl)=CH-CH}_2-$	Neoprene
17.  + HO-CH ₂ -CH ₂ -OHb	$\text{--C(=O)-C}_6\text{H}_4\text{-C(=O)-O-CH}_2\text{-CH}_2\text{-O-}$	Poly(ethylene terephthalate, Terylene, Dacron or Mylar)
18. 	$\text{--C(=O)-C}_6\text{H}_4\text{-C(=O)-O-C}_6\text{H}_10\text{-O-}$	Kodel Polyester
19. 		Polyethylene phthataate alkyd resin (Glyptal)

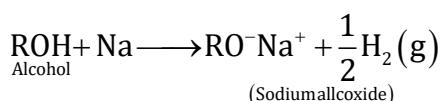
20. Caprolactam	$\text{--NH(CH}_2)_5\text{C=--}$	Nylon-6
21. $\text{NH}_2(\text{CH}_2)_6\text{--NH}_2$ Hexamethylenediamine $\text{HO--C}=\text{--(CH}_2)_4\text{--C--OH}$ Adipic Acid	$\text{--NH--(CH}_2)_6\text{--NH--C}=\text{O--(CH}_2)_4\text{--C}=\text{O--}$	Nylon - 66
22. + HCHO		Bakelite or resol
23. $\text{NH}_2\text{--C}=\text{O--NH}_2$ + HCHO		Urea- formaldehyde resin
24. + HCHO Melamine		Melamine formaldehyde resin

CHEMICAL TESTS FOR FUNCTIONAL GROUPS

- Elemental analysis, physical, spectral and solubility test give a reasonable idea regarding the identity of unknown compound.
- Despite the tremendous importance and ease of spectral analysis, chemical tests are indispensable to complete characterization.

1. Test For Alcohols :

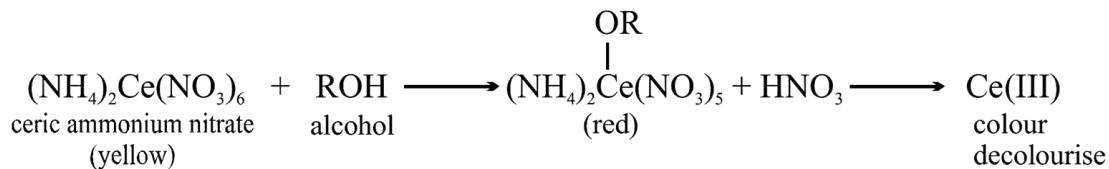
(i) Sodium Metal



- When Na-metal reacted with alcohol H₂(g) evolve
- It occurs in 1°, 2° & 3°

- The rate is highly variable and depends upon the alcohol structure.
 - Other Functional groups that evolve H₂(↑)
R₂NH, RSH, RC ≡ C – H, RCO₂H etc.

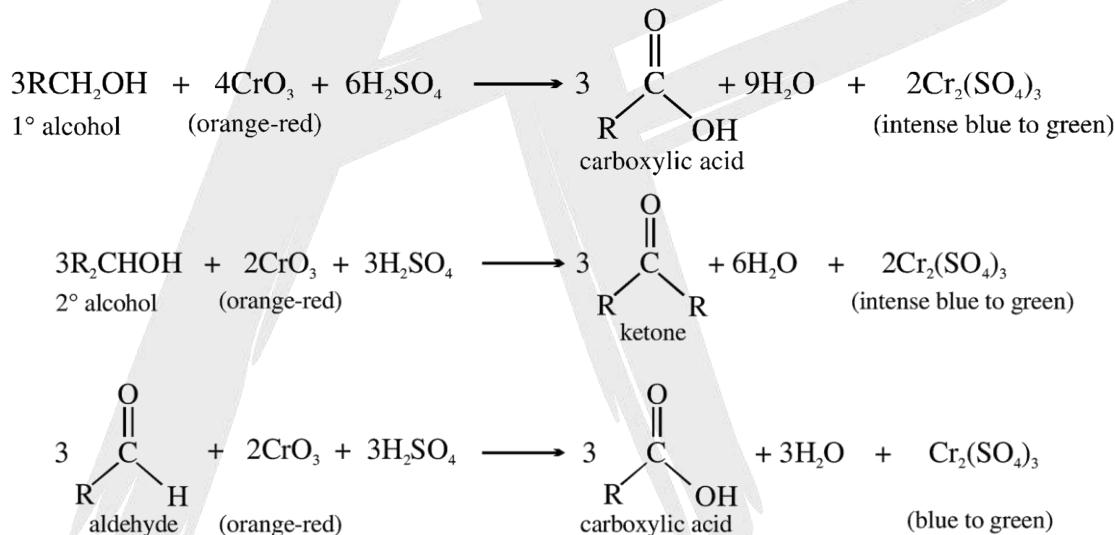
(ii) Ceric Ammonium Nitrate Oxidation (CAN Test)



- Positive Test: Color changes from yellow to red first then to colorless solution. (1 min. to 12hrs)
 - A positive test includes successively the formation, and then the disappearance of the red color.
 - Very good test for 1°, 2° alcohol, but slow for 3° alcohol
 - **Note:** Phenols gives brown or black products.

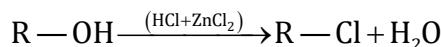
(iii) Jones Oxidation: Chromic anhydride or Chromium Trioxide (CrO_3)

- A positive test for 1°, and 2° alcohols consists in the changes from an orange-red color (Cr^{6+}) to opaque suspension with green to blue color (Cr^{+3}) in 2sec.
 - 3° alcohols give no visible reaction within 2 sec. remaining orange
 - **Note:** Aldehydes give positive result.



(iv) Lucas Test

- This test distinguishes 1°, 2° & 3° alcohol from each other
 - It uses, anhydrous $ZnCl_2$ in conc. HCl (lucas reagent)



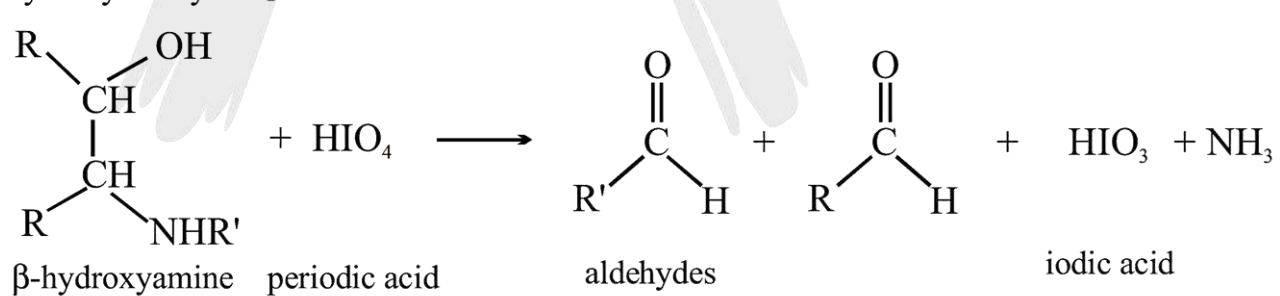
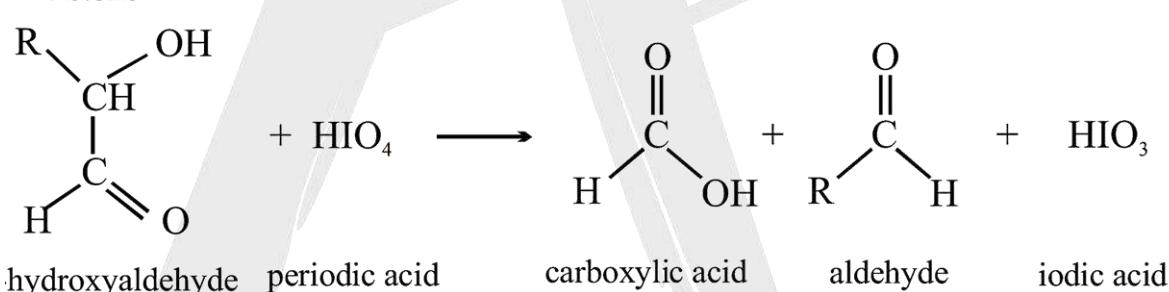
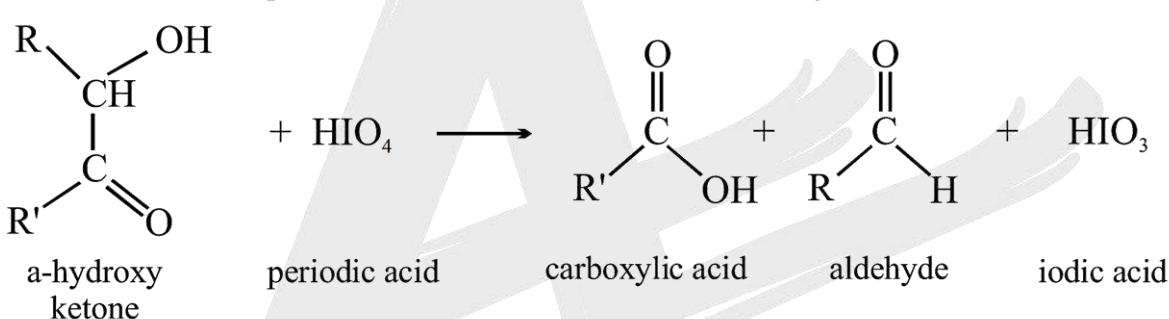
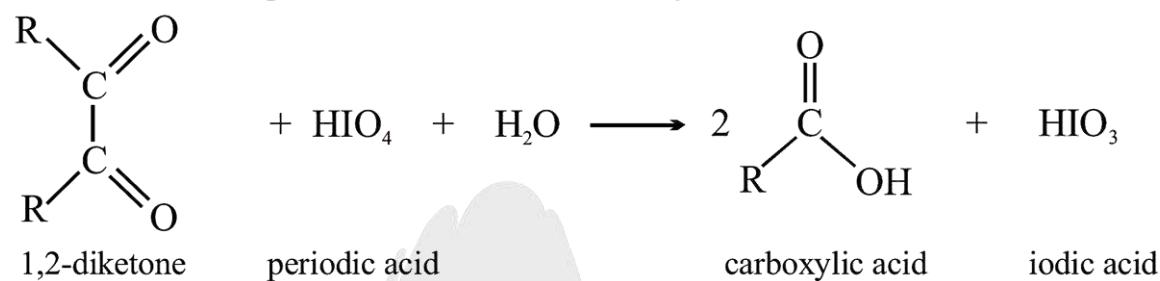
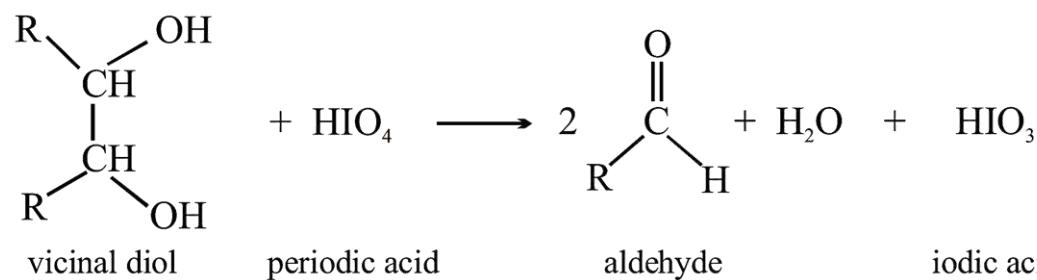
- 3° alcohols give white turbidity solution immediately
 - 2° alcohols give white turbidity solution within 5 to 10 minutes
 - 1° alcohols does not give white turbidity at normal temperature

Note : Benzyl alcohol also react immediately

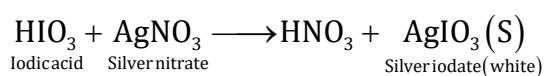
(v) Victor-Mayer Test

- This test also distinguishes 1°, 2° & 3° alcohol

1° - Alcohol	2° - Alcohol	3° - Alcohol
$\begin{array}{c} \text{R}-\text{CH}_2-\text{OH} \\ \downarrow \\ \text{Red P} + \text{I}_2 \\ \text{R}-\text{CH}_2-\text{I} \\ \downarrow \\ \text{AgNO}_2 \\ \text{R}-\text{CH}_2-\text{N}=\text{O} \\ \downarrow \\ \text{HNO}_2 \\ \text{R}-\text{C}(\text{N}-\text{OH})=\text{O} \\ (\text{Nitrolic Acid}) \\ \downarrow \\ \text{NaOH} \\ \text{R}-\text{C}(\text{N}-\text{O}^\ominus \text{Na}^\oplus)=\text{O} \\ (\text{Red colour}) \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{CH}-\text{OH} \\ \downarrow \\ \text{Red P} + \text{I}_2 \\ \text{R} \\ \\ \text{R}-\text{CH}-\text{I} \\ \downarrow \\ \text{AgNO}_2 \\ \text{R}-\text{CH}-\text{NO}_2 \\ \downarrow \\ \text{HNO}_2 \\ \text{R}-\text{C}(\text{N}=\text{O})=\text{O} \\ (\text{Psuedo nitrol}) \\ \downarrow \\ \text{NaOH} \\ (\text{Blue colour}) \end{array}$	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{R} \\ \downarrow \\ \text{Red P} + \text{I}_2 \\ \text{R} \\ \\ \text{R}-\text{C}-\text{I} \\ \downarrow \\ \text{AgNO}_2 \\ \text{R} \\ \\ \text{R}-\text{C}-\text{NO}_2 \\ \\ \text{R} \\ \downarrow \\ \text{HNO}_2 \\ \text{No Reaction} \end{array}$

(vi) Periodic Acid (HIO_4) Test for detection of Vicinal Diols and Related Compounds

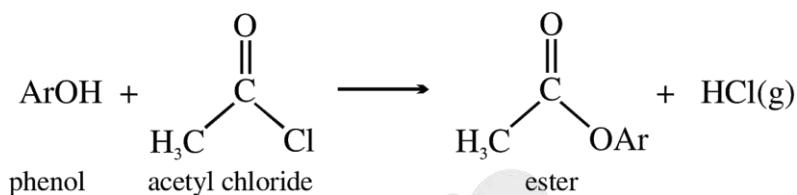
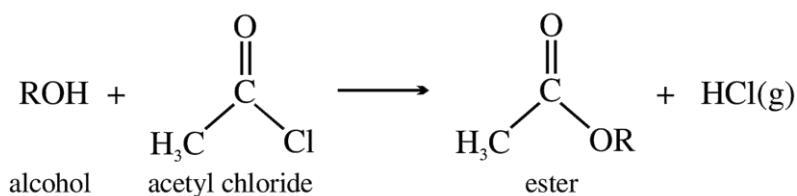
- The iodic acid is detected with 5% AgNO_3 solution -an immediate precipitation of silver iodate occurs.



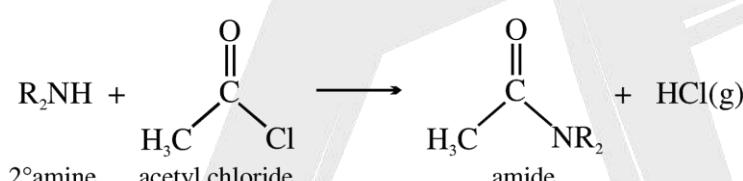
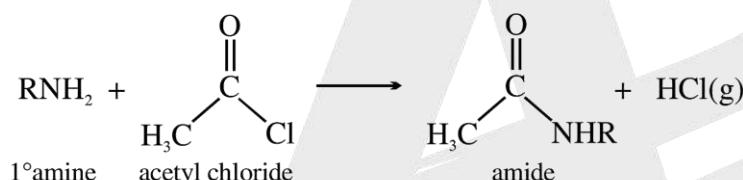
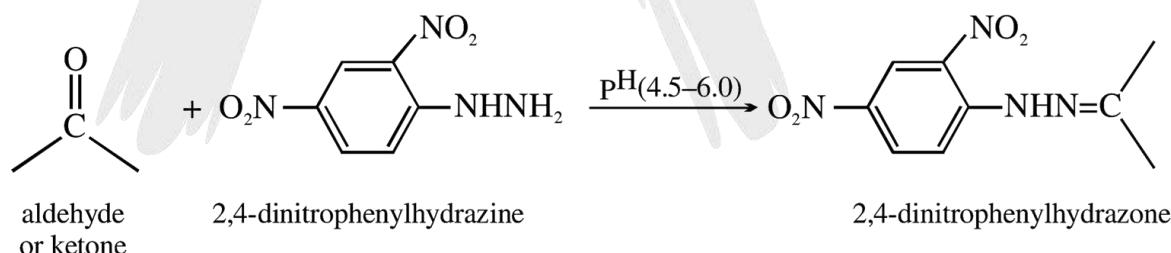
- Olefins, 2° alcohols, 1,3-glycols, ketones and aldehydes are not affected by HIO_4 under the test condition.

(vii) Acetyl Chloride

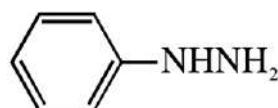
- Positive Test: Evolution of HCl gas and formation of ester as a top layer



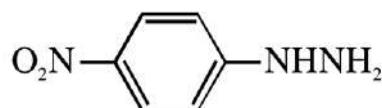
- 3° alcohols form primarily alkyl chloride due to the reaction of the liberated HCl on another molecule of the alcohol.
- Other functional groups that give positive test: 1° and 2° amines

**2. Classification Tests For Aldehydes and Ketone****(i) 2,4-Dinitrophenyl Hydrazine**

- Positive Test:** formation of yellow, orange or red ppt.
- The precipitate may be oily at first and become crystalline on standing.

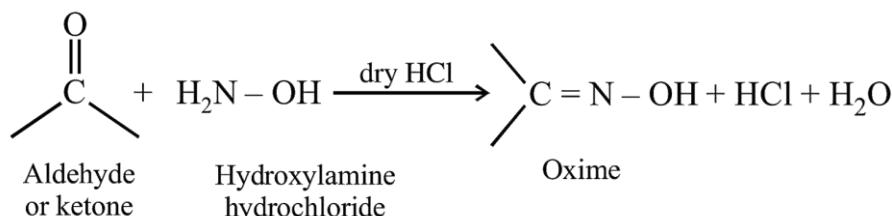
(ii) Phenyl hydrazine and p-Nitrophenyl hydrazine.

phenylhydrazine

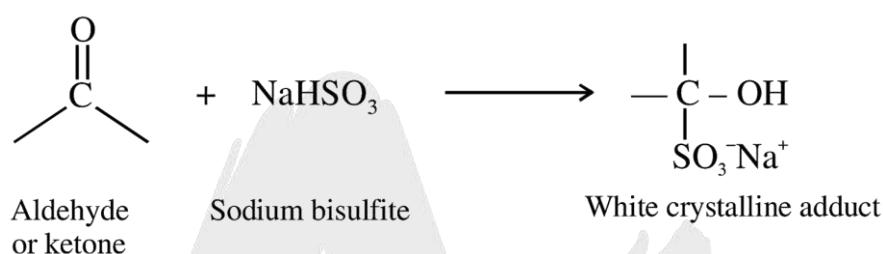


p-nitrophenylhydrazine

(iii) Hydroxylamine Hydrochloride

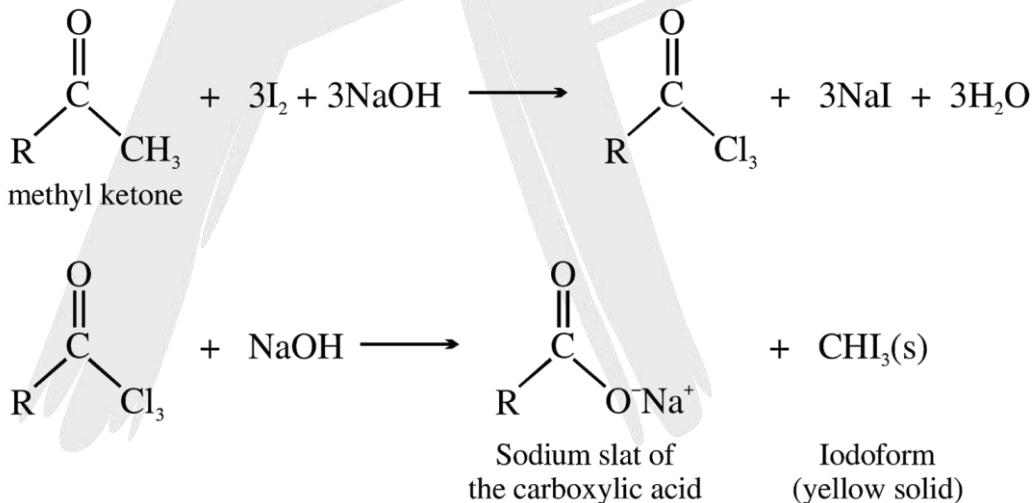


The liberation of hydrogen chloride can be detected by the change in color from orange to red of a pH indicator.

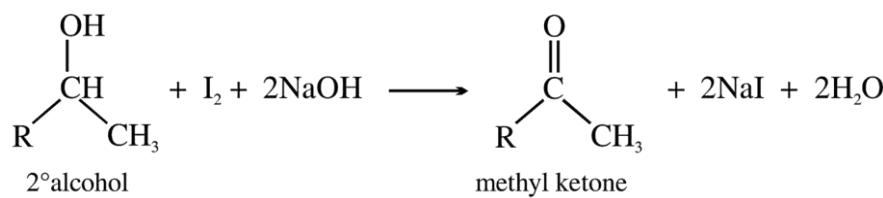
(iv) Sodium Bisulfite (NaHSO_3)

- **Positive Test:** By aldehydes and methyl ketone
- Only some cyclic ketones give positive results (ppt)
- This reaction is greatly inhibited by the steric constraints about the carbonyl group.

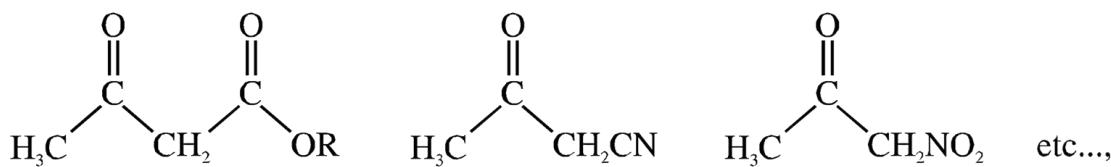
(v) Iodoform Test (For Methyl Ketones)



- **Positive Test:** Yellow ppt for methyl ketones
- **Disadvantages:** Some compounds that can be easily oxidized to methyl ketones give also positive results
- The principal types of compounds that give a positive test:

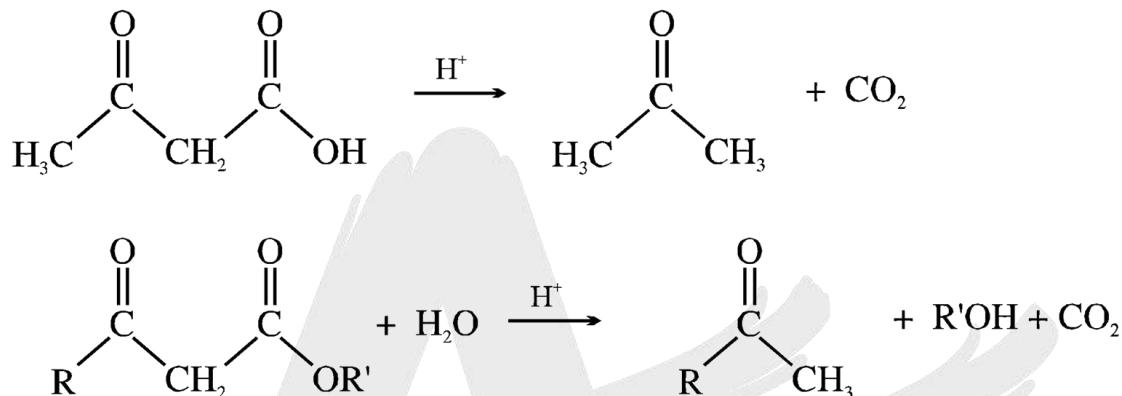


- The test is negative for the following type:



In such compounds the reagent removes the acetyl group and converts it to acetic acid, which resists iodination.

Acetoacetic acid is unstable, acidic aqueous solutions decompose to give CO_2 and acetone.

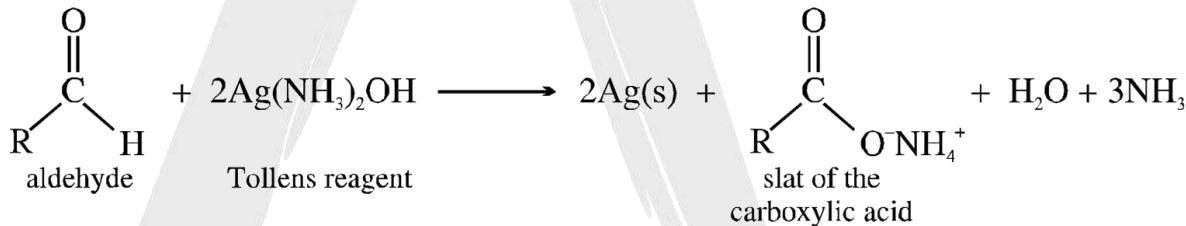


3. Tests that give positive results with aldehydes and negative results with Ketones

(i) Jones Oxidation: Chromic anhydride or Chromium Trioxide (CrO_3)

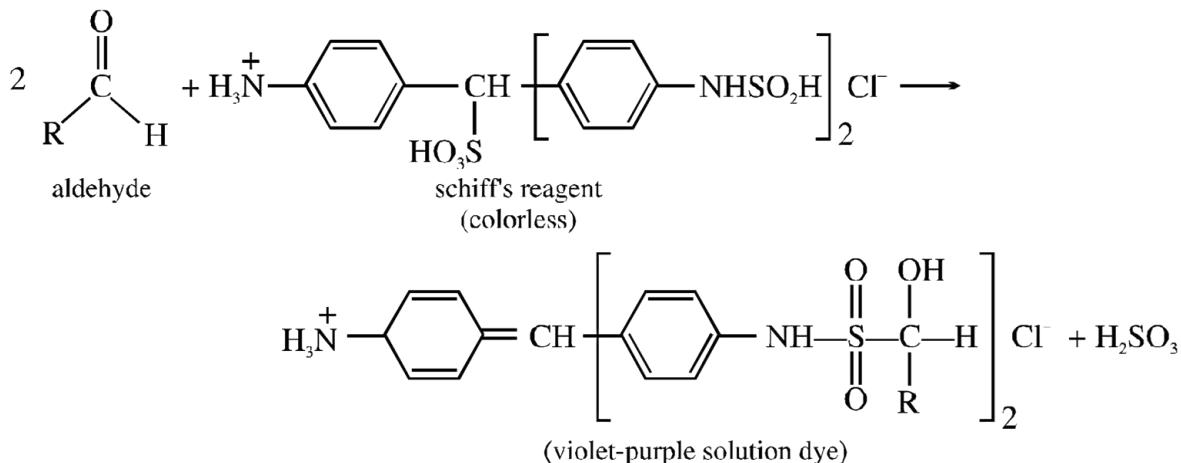
(Refer Jones Oxidation for alcohols at Page No. 22)

(ii) Tollens Reagents $\text{Ag}(\text{NH}_3)_2\text{OH}$



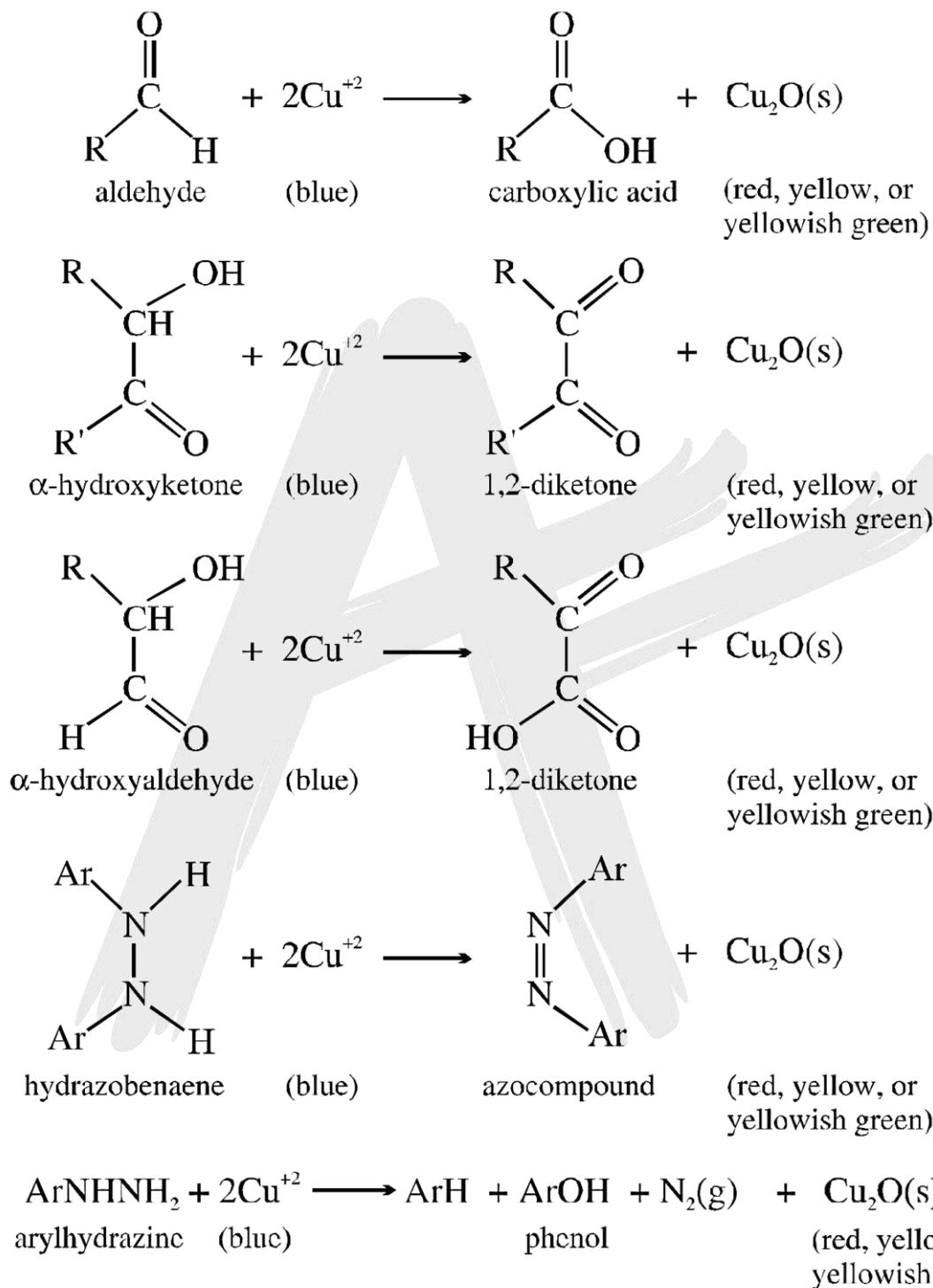
- Positive Test:** Formation of silver mirror (Ag(s)) or colloidal (granular) gray or black Ag precipitate.

(iii) Fuchsin Reagent



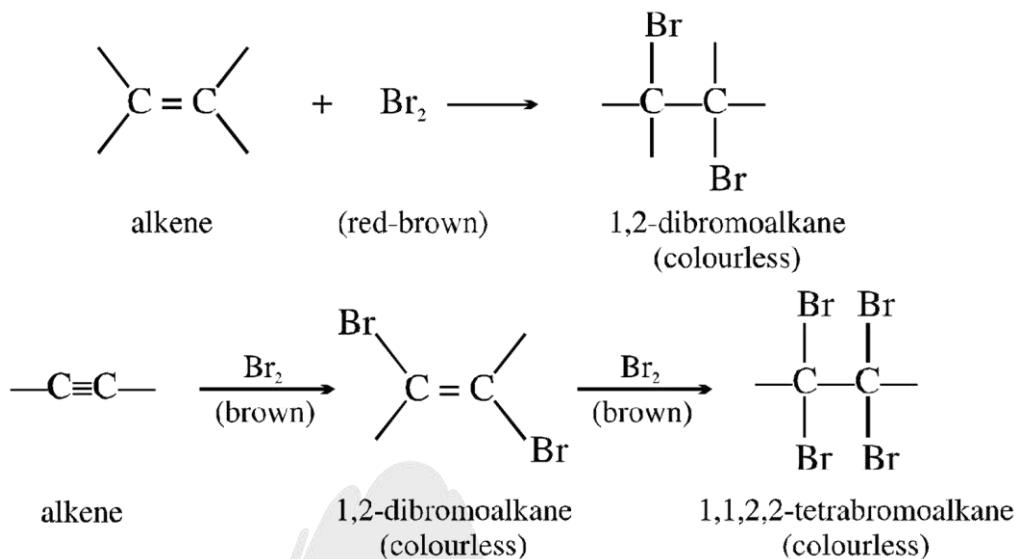
(iv) Benedict's solution and Fehling's Solution

- Positive Test:** yellow or yellowish green ppt.
- All aldehydes give positive result except aromatic aldehydes (negative)

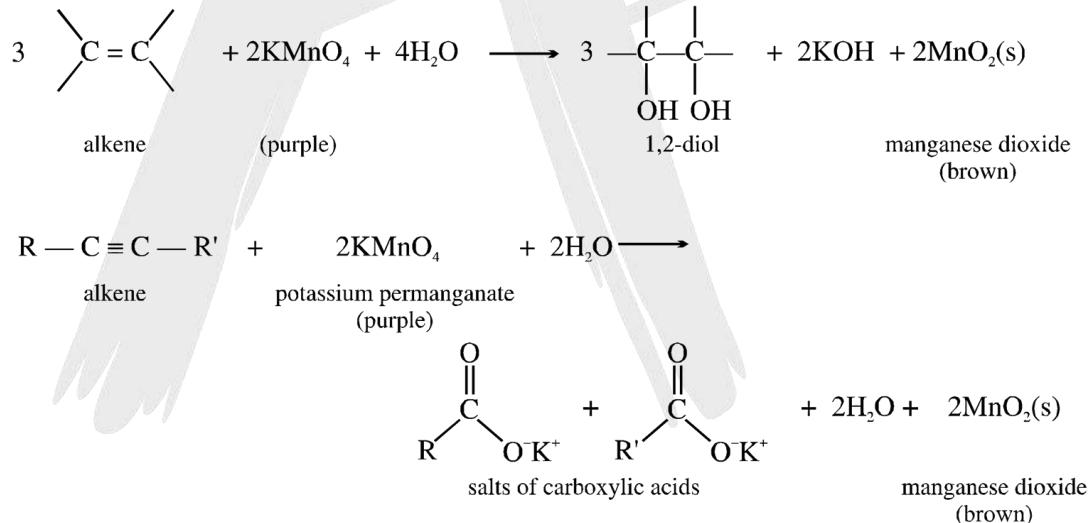


4. Classification Tests for Unsaturation "alkenes & alkynes"

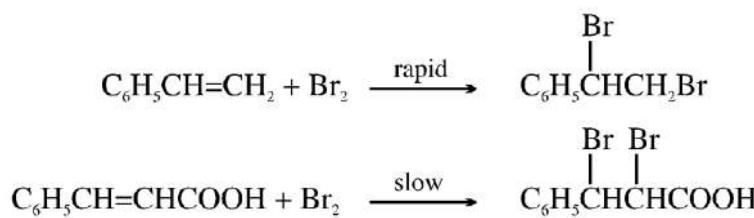
- Alkanes are not usually characterized chemically because they are quite inert to most classification reactions

(i) Bromine in CCl_4 

- Positive Test:** Bromine color discharged without evolution of gas (HBr)
- Alkenes & alkynes give positive results
- If HBr is evolved, it indicates phenols, enols & enolizable compounds ,-,
- Bromine color is discharged by amines to produce a salt, which could be mistaken for addition.

(ii) Baeyer Test (KMnO_4 aqueous)

- Positive Test:** Purple color discharges, and brown color ppt (MnO_2) appears
- Note :** Aldehydes and alcohols also give positive result
- Since the ionic characters of the Br_2 and KMnO_4 reactions are very different, there is some complementary character between the two tests.
- For example, some alkenes bearing electron-withdrawing groups undergo rapid reaction with KMnO_4 but often slow or negligible reaction with Br_2 .



- A few tetrasubstituted olefins such as $\text{C}_6\text{H}_5\text{CBr} = \text{CBrC}_6\text{H}_5$ and $(\text{C}_6\text{H}_5)_2\text{C} = \text{C}(\text{C}_6\text{H}_5)_2$ fail to give positive tests with Br_2 in CCl_4 or KMnO_4 solution.

5. Tests for Alkyl Halides

- Aliphatic halides are often detected initially by qualitative by halogen analysis halogen analysis.

(i) Ethanolic Silver Nitrate & (ii) Sodium Iodide in Acetone

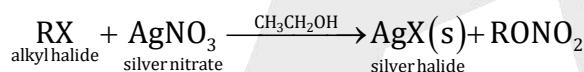
- Both tests involve displacement of halogen:
- AgNO_3 /ethanol test proceeds by a carbocation (S_N1) process & NaI / acetone test proceeds by a direct displacement (S_N2)

AgNO_3 /ethanol test : $\text{R}_3\text{CX} > \text{R}_2\text{CHX} > \text{RCH}_2\text{X}$

NaI / acetone test: $\text{R}_3\text{CX} < \text{R}_2\text{CHX} < \text{RCH}_2\text{X}$

(i) Ethanolic Silver Nitrate Solution

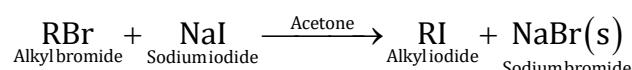
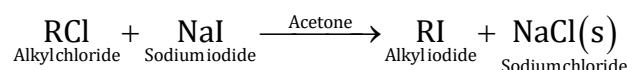
- The reaction of alkyl halide with silver nitrate yields a silver halide precipitate



- Positive Test: formation of ppt. indicates 2° and 3°RX
- 1°RX , Ar-X , and vinyl halides give negative Result.
- Note:** allylic and benzylic RX give positive result
- The identity of the halogen can sometimes be determined from the color of the silver halide: AgCl (white); AgBr (pale yellow); AgI (yellow)

(ii) Sodium Iodide in Acetone Test

- The NaI test can be used to test for the presence of bromine or chlorine.
- Sodium halide (NaX) precipitates from the solution.



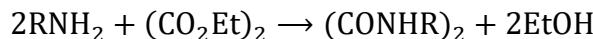
- Positive Test:** precipitate forms
- Indications :** 1° , 2°RX , allylic and benzylic halides. Not good for ArX , vinyl halides , HCCl_3 , and 3°RX .

- Since reactivity toward alcoholic silver nitrate is often very different from reactivity toward sodium iodide in acetone, both tests should be used with any halogen compound.

6. Tests for Amines and Amine Salts

(i) Diethyl oxalate test :

- This method helps in the separation of primary, secondary and tertiary amines.
 - Primary amines on reaction with diethyl oxalate gives solid oxamide, secondary amine gives liquid oxamic ester and tertiary amine remains unreacted in gaseous form.

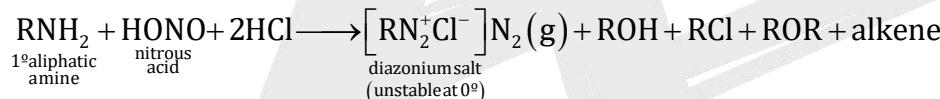


1. The gaseous tertiary amine is separated out.
 2. The solid oxamide is filtered out of the liquid oxamic ester.
 3. These products are added to the alkaline solution of NaOH.

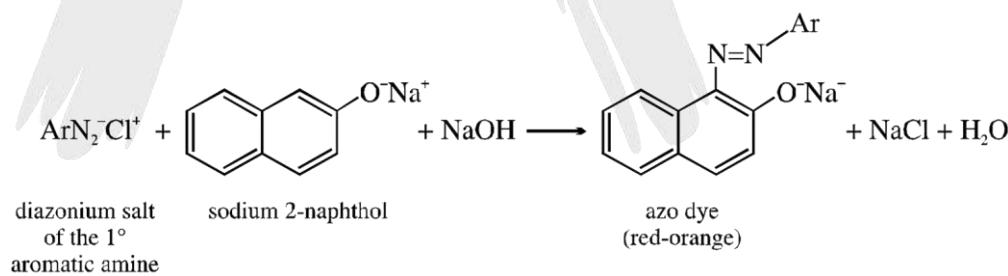
In this way, Primary, secondary and tertiary amines are separated by Hoffmann's Method

(ii) Nitrous Acid

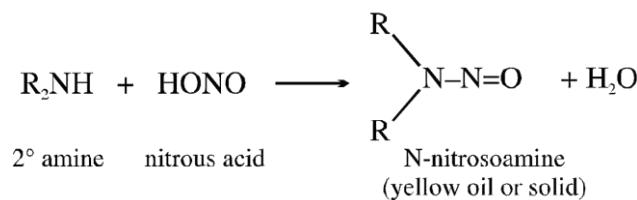
- Reaction of amines with nitrous acid (HONO) classifies the amine not only as 1°, 2°, or 3°, but also as aliphatic or aromatic.



- The diazonium salt of the primary aromatic amine reacts with sodium 2-naphthol to produce a red-orange azo dye.



- 2° amines undergo a reaction with nitrous acid to form N-nitrosoamine, which are usually yellow solids.

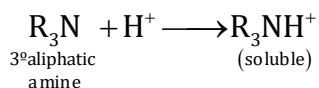




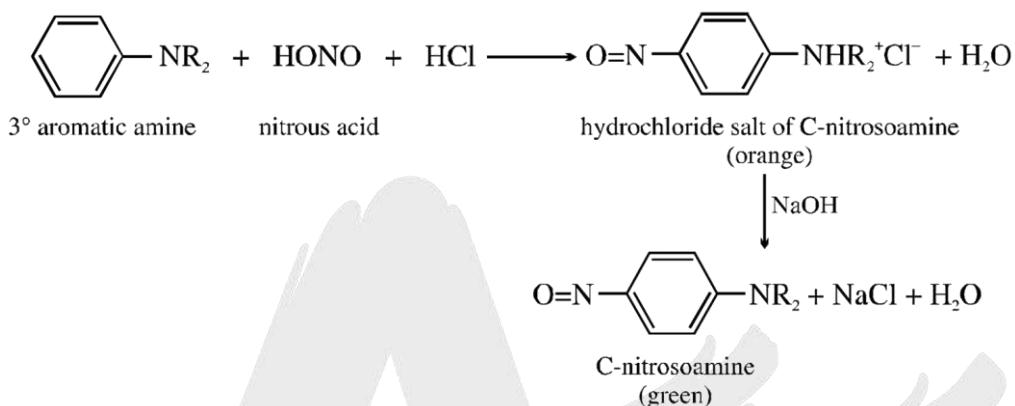
(Organic Chemistry)

POLYMERS & POC

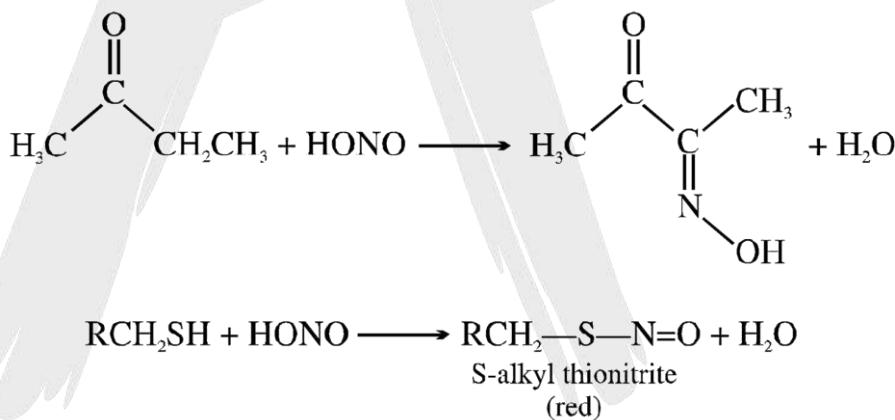
- 3° aliphatic amines do not react with nitrous acid, but they form a soluble salt. The reaction mixture gives an immediate positive test on the starch-iodide paper for nitrous acid.



- 3° aromatic amines react with nitrous acid to form the orange-colored hydrochloride salt of the C-nitrosoamine. Treating the solution with base liberates the blue or green C-nitrosoamine.

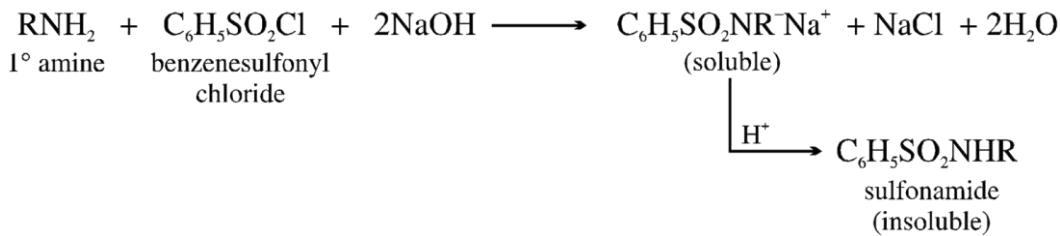


- Although nitrous acid is useful for characterizing amines, other functional groups also react.
- A methylene group adjacent to a keto group is converted to an oximino group and alkyl mercaptans yield red S-alkyl thionitrites.

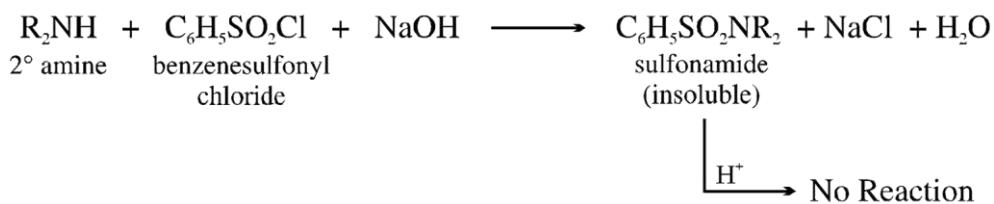


(iii) Hinsberg Test

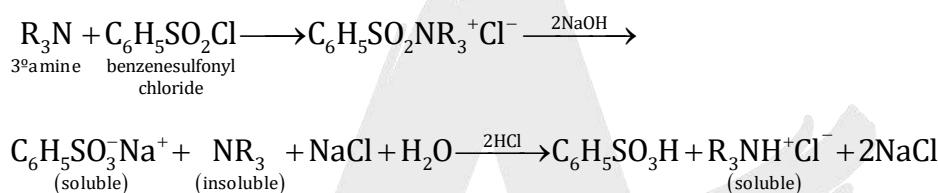
- Based on the reaction of the amine with benzenesulfonyl chloride (Hinsberg reagent), it can be used to separate 1°, 2°, and 3° amines.
- 1° amines: give solution that produce ppt after addition of HCl



2° amines: give ppt - acidification of the solution does not dissolve the sulfonamide (i.e., the PPT is not soluble in NaOH or HCl)



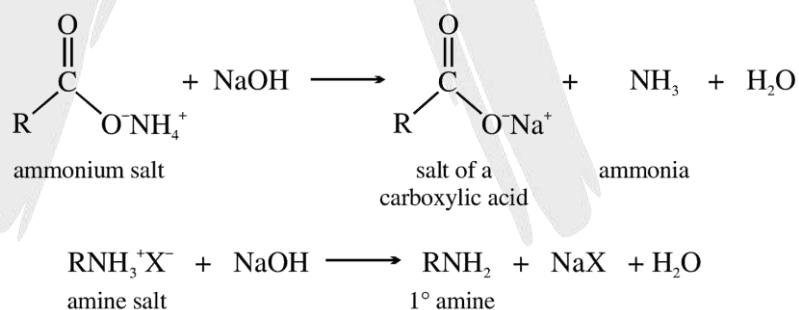
- 3° amines: undergo reaction with benzenesulfonyl chloride to produce quaternary ammonium sulfonate salts, which yield sodium sulfonate and insoluble 3° amines in basic solution.
- Acidification of the reation mixture results in the formation of sulfonic acids and soluble amine salts



- The results of the Hinsberg test must not be used alone in classifying amines. The solubility of the original compounds must also be considered.
- If the original compound is amphoteric, which means that it is soluble in both acids and alkalies, the Hinsberg method fails to distinguish among the types of amines.

(iv) Sodium Hydroxide Treatment of Ammonium Salt and Amine Salts

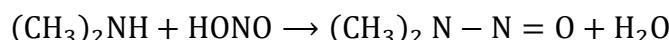
- Amine salts can be detected by treating the salt with NaOH to liberate ammonia or amine.



Moistened pink litmus paper placed in the vapor above the solution will turn blue if ammonia or a volatile amine is present.

(v) Libermann's nitroso test :

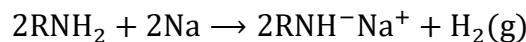
It is used as a test for secondary amines. Secondary amines(aliphatic as well as aromatic) reacts with nitrous acid to form N-nitrosoamines.



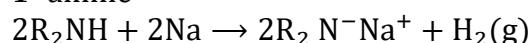
- Nitrosoamines are water soluble yellow oils and when warmed with phenol and few drops of conc. H_2SO_4 produce a green colour solution which turns blue on adding alkali. This reaction is called Libermann's nitroso reaction.
- Tertiary amine do not react with nitrous acid.

Sodium Metal :

- The active hydrogen on 1° and 2° amines undergo reaction with sodium to form salt and liberate hydrogen gas



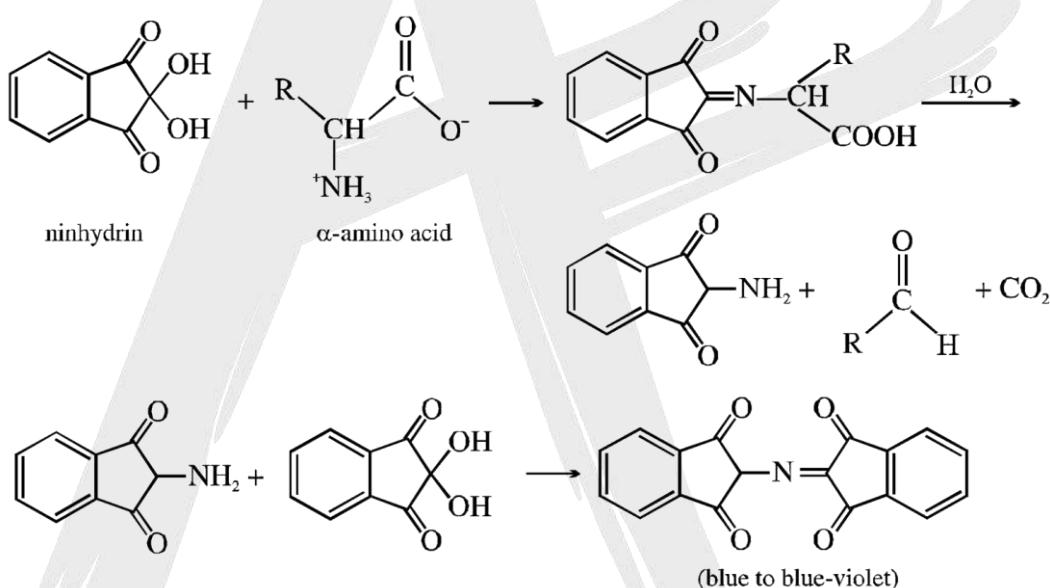
1° amine



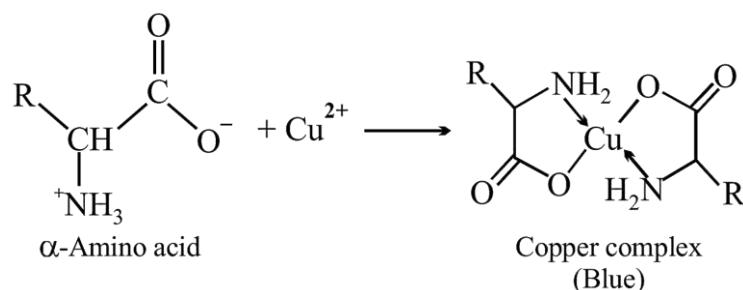
2° amine

7. Tests for Amino Acids**(i) Ninhydrin Test :**

- Amino acids and p-amino acids react with ninhydrin to give a positive test which is blue or blue-violet color.



- Ammonium salts (NH_4^+Cl^-) give a positive test.
- Some amines, such as aniline, yield orange to red colors, which is considered a negative test.
- Proline, hydroxyproline, and 2-, 3-, and 4-aminobenzoic acids fail to give

Blue colour but produce a yellow color instead.**(ii) Copper Complex Formation**



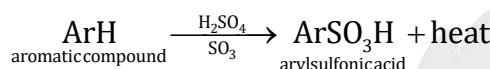
- Reaction with copper(II) sulfate solution yields a moderate-to deep-blue liquid or a dark-blue solid.

8. Tests for Aromatics

- If the molecule already contains reactive chemical substituents (acids, amines, ethers, carbonyl compounds, etc.,) use the corresponding classification test for that particular group.
- New substituents can be added onto the aromatic ring or existing substituents can be modified, such that the new

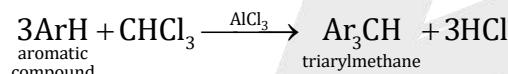
Compound May be More Readily Characterized.

(i) Fuming Sulfuric Acid



- This test is good for aromatics with no other functional groups.
- Positive Test: the aromatic compound dissolves completely in H_2SO_4 with the evolution of heat (Fuming)

(ii) Chloroform and Aluminum Chloride



- Aromatics give colored solution or powder.
- Positive Test: (Orange, red, blue, purple, green)
- Non aromatics give yellow color (Negative result)

(iii) Azoxybenzene and Aluminum Chloride

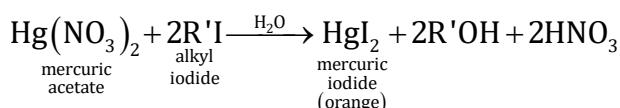
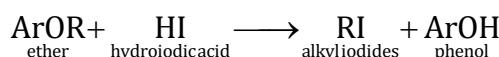
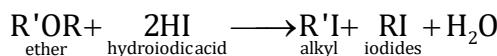
- The color of the solution or precipitate is dependent on the functional groups present on the aryl group.
- Aromatic hydrocarbons and their halogen derivatives produce a deep-orange to dark-red color in solution or give a precipitate.
- Fused aromatic ring (such as naphthalene, anthracene, and phenanthrene) produce brown color.
- Aliphatic hydrocarbons give no color or, at most, a pale yellow.

9. Tests for Ethers

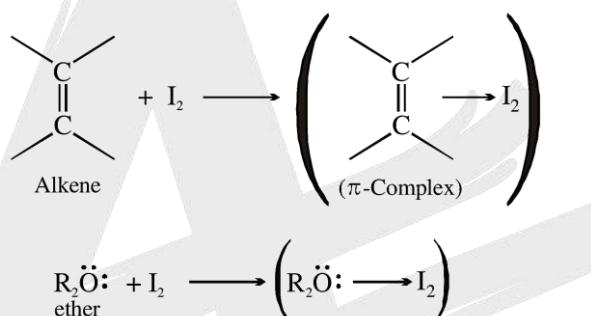
- Ethers are only a little more polar and slightly more reactive than either saturated hydrocarbons or alkyl halides

- Ethers form extremely explosive peroxides upon standing, especially when exposed to air and/or light. Liquid ethers that show solid precipitates should not be handled.

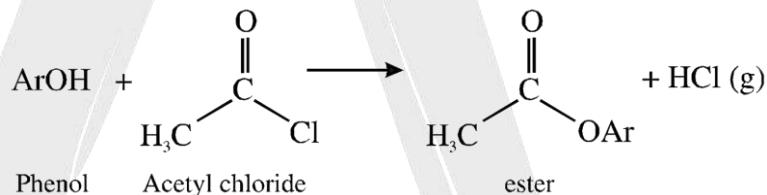
(i) Hydroiodic Acid (Zeisel's, Alkoxy method)



- **Positive Test:** Orange or Orange-red color indicating.
 - **Note:** Ethyl and methyl esters give also positive result.



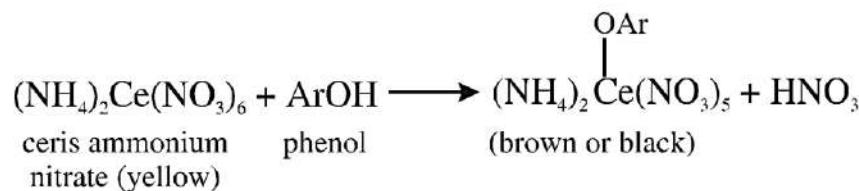
(ii) Iodine Test for Ethers and Unsaturated Hydrocarbons



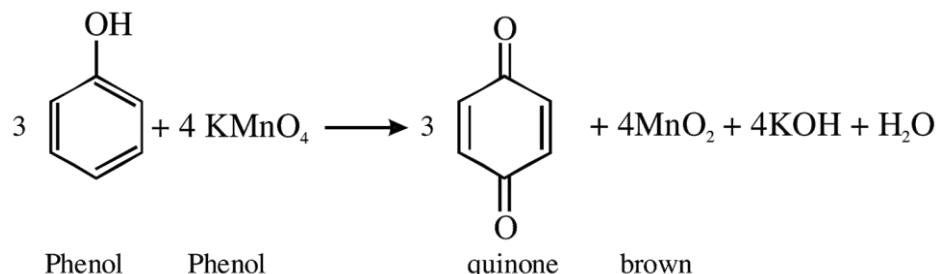
- Positive test: the color of the solution changes from purple to tan.
 - Aromatic hydrocarbons, saturated hydrocarbons, fluorinated hydrocarbons and chlorinated hydrocarbons do not react.
 - Unsaturated hydrocarbons produce a light-tan solid, while retaining the purple color of the iodine solution.

10. Tests for Phenols

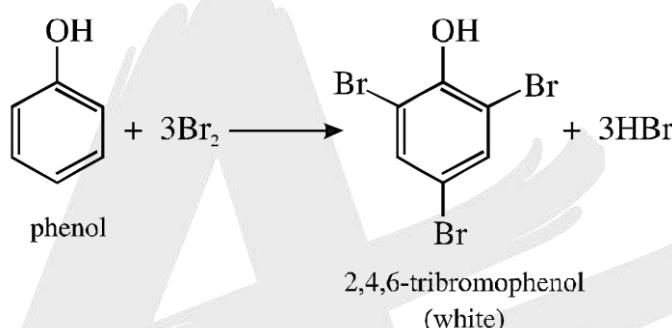
- As with alcohols, the acidic hydrogen in phenol can be detected with sodium (hydrogen gas is evolved) or with acetyl chloride (an ester layer is formed).



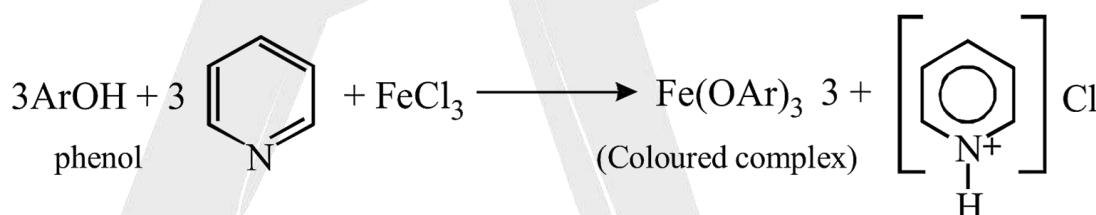
- Phenols undergo reaction with yellow ceric ammonium nitrate to produce brown or black products.



- Phenols reduce potassium permanganate solution and undergo oxidation to quinones.
- The manganese is reduced from +7 which gives a purple solution to +4 which is brown.

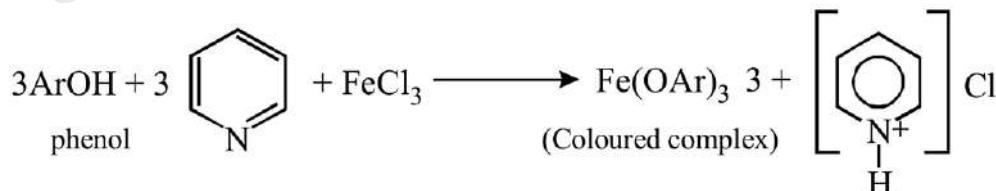


(i) Bromine water



- Positive Test: decolorization of bromine.
- This is good for water soluble phenols

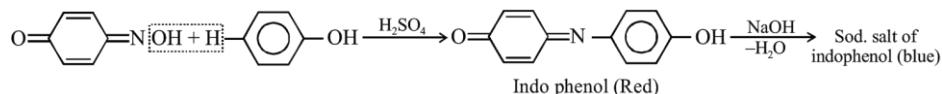
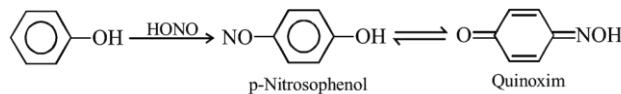
(ii) Ferric Chloride - Pyridene Reagent



- Positive Test:** Production of blue, violet, purple, green, or red-brown colors
- Good for all types of Ar-OH.
- Positive test for enols. $\left(\begin{array}{c} \text{OH} \\ | \\ \text{C}=\text{C}-\text{C}=\text{O} \end{array} \right)$
- Carboxylic acid with FeCl_3 gives red colour only when saturating with NH_3 .

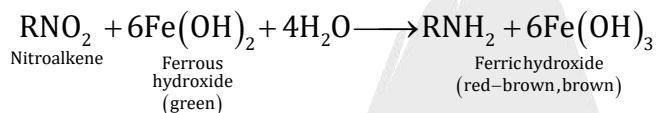
(iii) Libermann's nitroso test :

While phenol is reacted with NaNO_2 and concentrated H_2SO_4 , it provides a deep green colour which changes to red on dilution with water. while generated alkaline along with NaOH , blue colour is restored. This reaction is termed as Liebermann's nitroso reaction and is employed as a test of phenol.



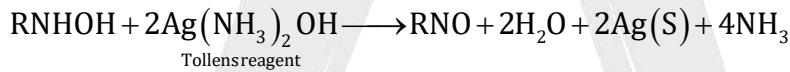
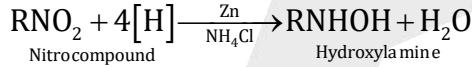
11. Test For Nitro Compounds

(i) Ferrous Hydroxide Reduction



- **Positive Test:** indicated by the change in color from green to red-brown or brown due to the oxidation of iron from +2 to +3 .
 - A negative test is indicated by a greenish precipitate.
 - **Note:** Nitroso compounds, quinones, hydroxylamines alkyl nitrates give also positive results

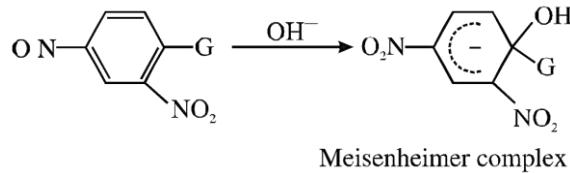
(ii) Zinc and Ammonium Chloride Reduction



- Test the solution with Tollens Reagent
 - Positive Test: formation of metallic silver
 - Only 3° aliphatic nitro compounds and aromatic nitro compounds are reduced by Zn/NH₄Cl to the hydroxylamine.
 - The hydroxylamine is then detected by the formation of metallic silver in the Tollens test (or formation of a black or grey precipitate). This is known as Mulliken-baker test.

(iii) Treatment of Aromatic Compounds with Sodium Hydroxide

- The number of nitro groups on an aromatic ring can be determined by the reaction with NaOH
 - In the reaction with NaOH :
 - Mononitro aromatic compounds yield no color change or a very light yellow
 - Dinitro aromatic compounds produce a bluish-purple color
 - Trinitro aromatic compounds give a red color
 - The color of the solution is due to a Meisenheimer complex



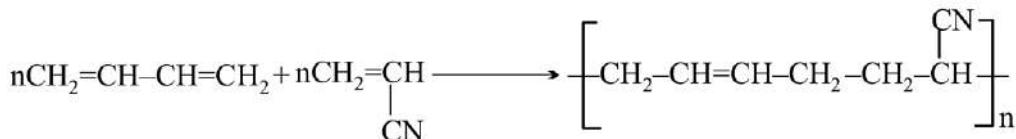
(A) ELEMENTAL ANALYSISLassaigne method (Detection of elements)

Element	Sodium Extract (S.E.)	Confirmed Test	Reactions
Nitrogen	$\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$ (S.E.)	S.E. + FeSO_4 + NaOH , boil and cool, + FeCl_3 + conc. HCl Blue or green colour (i) S.E.+ sodium nitro prusside (A) A deep violet colour. (ii) S.E. + CH_3COOH + $(\text{CH}_3\text{COO})_2\text{Pb}$ A black ppt.	$\text{FeSO}_4 + 2\text{NaOH} \longrightarrow \text{Fe}(\text{OH})_2 + \text{Na}_2\text{SO}_4$ $\text{Fe}(\text{OH})_2 + 6\text{NaCN} \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_6] + 2\text{NaOH}$ $3\text{Na}_4[\text{Fe}(\text{CN})_6] + 4\text{FeCl}_3 \xrightarrow{\text{HCl}} \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 + 12\text{NaCl}$ Prussian blue
Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$ (S.E.)	(i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \xrightarrow{\text{(A)}} \text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ deep violet (ii) $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}} \text{PbS} \downarrow + 2\text{CH}_3\text{COONa}$ black ppt.	
Halog en	$\text{Na} + \text{Cl} \xrightarrow{\Delta} \text{NaCl}$ (S.E.)	(i) White ppt. soluble in aq NH_3 confirms Cl (ii) Yellow ppt partially soluble in aq. NH_3 confirm Br (iii) Yellow ppt insoluble in aq NH_3 confirms I As in test for nitrogen; instead of green or blue colour, blood red coloration confirms presence of N and S both	$\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow$ white ppt $\text{AgCl} + 2\text{NH}_3(\text{aq}) \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$ soluble
Nitrogen and Sulphur together			$\text{NaCNS} + \text{FeCl}_3 \longrightarrow [\text{Fe}(\text{CNS})]\text{Cl}_2 + \text{NaCl}$ blood red colour



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

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



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

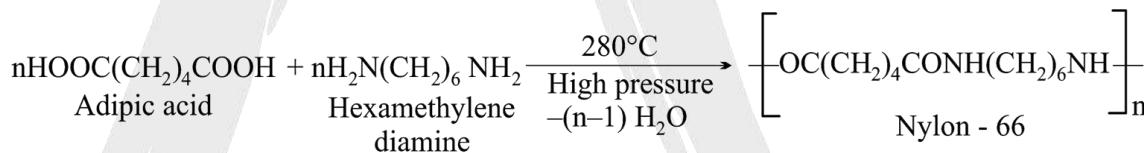
- (d) Cold Rubber :** Cold rubber is obtained by polymerisation of butadiene and styrene at -18° to 5°C temperature in the presence of redox system. Cold rubber has a greater tensile strength and greater resistance of abrasion than SBR.

NYLON

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

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

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



- (2) NYON-610 (Nylon six, ten)**

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

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

- (3) NYON-6 (Perlon L)**

A polyamide closely related to nylon is known as perlon L (Germany) or Nylon - 6 (USA). It is prepared by prolonged heating of caprolactum at $260 - 270^\circ\text{C}$. It is formed by self condensation



of a large number of molecules of amino caproic acid. Since, caprolactum is more easily available, it is used for polymerization, which is carried out in the presence of H_2O that first hydrolyses the lactam to amino acid. Subsequently, the amino acid can react with the lactam and the process goes on and onto form the polyamide polymer.

SEPARATION TECHNIQUES

METHODS OF PURIFICATION OF ORGANIC COMPOUNDS :

Organic compounds obtained either from natural source (or) synthesized in laboratory are contaminated with impurities. Various methods are used for removal of impurities from an organic compound depends on the nature of compound and type of impurities present in it. The following methods are commonly used for purification

- (1) Sublimation
- (2) Crystallisation
- (3) Distillation
- (4) Solvent extraction (differential extraction)
- (5) Chromatography.

Note: Most of the pure compounds contain sharp Melting point & Boiling points.

Sublimation :

The process of conversion of sublimable solid to vapour state directly by heating without passing through liquid state is called sublimation.

Solid vapour

- This method is used for purification of solids
- Sublimation process is used for separation of sublimable volatile compounds from non sublimable impurities.
- Sublimation is generally used for purification of camphor, naphthalene, Anthracene, Benzoic acid, phthalic anhydride, Anthraquinone, Indigo and Iodine $HgCl$, solid SO_3

Crystallisation :

- It is used for purification of solid organic compounds.
- Crystallisation is based on the difference in solubilities of the compound and impurities in a suitable solvent.
- The principle involved in this method is impure compound dissolved in a solvent is sparingly soluble at low temperature, but appreciably soluble at high temperature. Insoluble impurities are separated by filtration. The filtrate on cooling saturated solution, pure compound crystallises out. If a compound is highly soluble in one solvent and too little soluble in another solvent then crystallisation is carried out by using mixture of these solvents.
- Impurities, which impart colour are removed by adsorbing over activated charcoal.



- Repeated crystallisation is required if organic compound contains impurities of comparable solubilities.
- The process of separation of different components of a mixture by repeated crystallisation is called fractional crystallisation.
- Fractional crystallisation is used for separation of two or more soluble substances which have different solubilities in the same solvent.
- Most commonly used solvents for crystallisation are water, alcohol, ether, chloroform, carbontetrachloride, acetone, benzene, petroleum ether. - Sugar having an impurity of common salt can be crystallised from hot ethanol. since sugar dissolves in hot ethanol but common salt does not.
- Fractional crystallisation can be used to separate a mixture of KClO_3 (less soluble) and KCl (more soluble).

DISTILLATION :

Distillation is an important method used to separate

- (i) Volatile liquids from non volatile impurities.
- (ii) Liquids having sufficient difference in boiling points.

Simple Distillation :

- This process is used for purification of liquids which does not undergo decomposition at their boiling points
- The vapourisation of a liquid by heating and subsequent condensation of vapours by cooling is known as distillation.
- Liquid mixture is taken in a round bottom flask and heated carefully, the vapour component with lower boiling point distills first, the vapour formed is condensed by using condenser and the liquid is collected in a receiver. The vapours of component with higher boiling point distills later.
- The liquids that have boiling point difference greater than 40°C can be purified by this method,
- e.g:
 - (i) Chloroform (BP. 334 K) & Aniline (B.P. 457 K)
 - (ii) Ether (B.P. 308 K) & Toluene (B.P. 384 K)
 - (iii) Benzene (B.P. 353 K) & Aniline (B.P. 457 K)

Fractional Distillation :

- Fractional distillation is used if the difference in boiling point of two liquids is less than 40°C .
- Vapours of liquid mixture are passed through fractionating column before condensation, which is fitted over mouth of the round bottom flask.
- Vapours of liquid with higher boiling point condense before the vapours of liquid with lower boiling point the vapours raising up in the fractionating column is richer in more volatile component.

- Fractionating column provides many surfaces for heat exchange between ascending vapours and descending condensed liquid.
- Each successive condensation and vapourisation unit in the fractionating column is called a theoretical plate.
- Liquids forming a constant boiling mixture (azeotropic mixture) can not be separated by this method.
- Fractional distillation is used to separate different fractions of crude oil in petroleum industry.
- This method is used for separation of mixture of acetone(B.P. 330K) and methyl alcohol (B.P. 338K)
- Mixture of benzene and toluene can be separated by fractional distillation.

Ex.1 How is ethyl alcohol purified from methylated spirit.

Sol: Methylated spirit is ethyl alcohol contaminated mainly with methyl alcohol. Ethyl alcohol is purified by fractional distillation since the difference in boiling point is less.

DISTILLATION UNDER REDUCED PRESSURE (Vacuum Distillation)

- This method is used to purify liquids having very high boiling points, which decompose at or below their boiling points.
- These liquids are made to boil at a temperature lower than their normal boiling point by reducing pressure on their surface with the help of vacuum pump.
- Glycerine, H_2O_2 , formaldehyde are purified by vacuum distillation.
- Glycerol can be separated from spent-lye in soap industry by using vacuum distillation.
- Sugar cane juice is concentrated in sugar industry by evaporation under reduced pressure which saves lot of fuel.

Steam Distillation :

- This method is used for separation and purification of organic compounds (solids or liquids) which
 - (i) are steam volatile
 - (ii) are insoluble in water.
 - (iii) Process high vapour pressure (10-15 mm of Hg at 373 K)
 - (iv) Contains non volatile impurities.
 - Steam distillation is based on Dalton's law of partial pressure i.e., $P = P_1 + P_2$. where P = Atmospheric pressure.
- P_1 = Partial pressure of organic liquid
- P_2 = Vapour pressure due to water.
- Compounds which can be purified by steam distillation are aniline, nitrobenzene, bromobenzene, o-nitrophenol, o-hydroxy benzaldehyde (salicylaldehyde), o-hydroxy acetophenone, turpentine oil, essential oils.



Ex.2 Mention about the purification of (a) aniline and (b) naphthalene

Sol. (a) Aniline can be purified by steam distillation because it is immiscible with water and steam volatile.

(b) Naphthalene can be purified by sublimation because it changes on heating directly to vapour state and on cooling, it changes back into solid form.

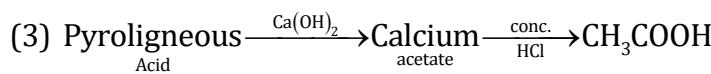
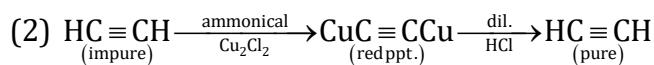
Solvent Extraction (Differential Extraction) :

- Definition: The process of isolating an organic compound from its aqueous solution by shaking with a suitable solvent is called differential extraction. It is also called solvent extraction
- When an organic compound is present in an aqueous medium, then it is separated by shaking it with an organic solvent in which it is more soluble than in water.
- Solvent should be immiscible with water and organic compound to be separated should be highly soluble in it
- Organic solvent and aqueous solution are immiscible with each other, so they can form two distinct layers (which can be separated by separator funnel).
- Organic solvent is distilled or evaporated to get organic compound.
- If organic compound is less soluble in organic solvent then large quantity of solvent is required to extract small quantity of compound, which is said to be continuous extraction. - Benzoic acid can be extracted from its aqueous solution using benzene as solvent.
- Ether is a better solvent in differential extraction due to:
 - (i) its less polarity
 - (ii) less reactivity
 - (iii) Less Boiling Point
 - (iv) higher solubility of organic compounds

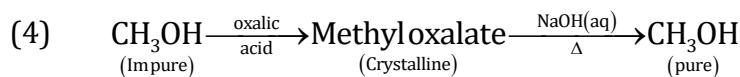
SEPARATION BY CHEMICAL METHODS :

- It is used for mixture of substances which are chemically different.

e.g : (1) Separation of acidic and basic compound of coal-tar.



(from wood distillation industry) $\rightarrow \text{CH}_3\text{COOH} + \text{MeCoMe} + \text{MeOH}$



Chromatography :

- This method is used for separation of mixtures into their components, purification of compounds and also to test the purity of compounds.
- Chromatography is obtained from the Greek word "Chroma" means colour and "graphy" means writing.
- This method was first used for separation of coloured substances found in plants.
- This method was described by Tswett.
- This Technique consists of two phases one is stationary phase of large surface area while the second is moving phase which is allowed to move slowly over the stationary phase.
- Stationary phase is either liquid or solid, while moving phase may be liquid or gas.
- The technique of chromatography is based on the rates at which the components of the mixture moves through a porous medium (called stationary phase) under the influence of some solvent (or) gas (called mobile phase).
- Mixture of substances is applied on a stationary phase which may be solid or liquid A pure solvent, a mixture of solvents or a gas is allowed to move slowly over the stationary phase, the components of the mixture get gradually separated from one another.
- Recovery of separated substances by using suitable solvent is known as elution. The solvent used is known as eluant.

S.No.	Chromatography process	Stationary Phase	Mobile Phase
1.	Column chromatography (Adsorption)	Solid	Liquid
2.	Liquid-liquid partition chromatography	Liquid	Liquid
3.	Paper chromatography	Liquid	Liquid
4.	Thin layer chromatography (TLC)	Liquid (or) solid	Liquid
5.	Gas-liquid chromatography (GLC)	Liquid	Gas
6.	Gas-solid chromatography (GSC)	Solid	Gas
7.	Ionic exchange chromatography	Solid	Liquid

- Based on the principle involved chromatography is classified into
 - (a) Adsorption chromatography and
 - (b) partition chromatography.

**(a) Adsorption Chromatography :**

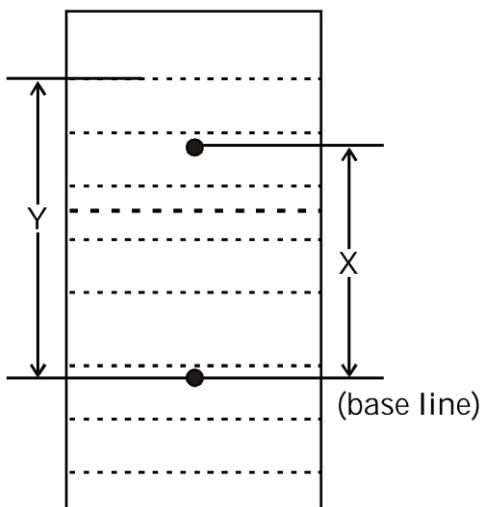
- Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees.
- Commonly used adsorbents are silica gel, alumina, magnesium oxide, cellulose powder, activated animal charcoal.
- When a mobile phase is allowed to move over stationary phase, the components of the mixture move by varying distances over stationary phase.
- There are two main types of chromatographic techniques based on principle of differential adsorption
 - (i) Column chromatography and
 - (ii) Thin layer chromatography (TLC)

(i) Column Chromatography

- It involves separation of a mixture over a column of adsorbent packed in a glass tube, which is fitted with stop cock at its lower end.
- The mixture to be separated on the adsorbent is placed at the top of the stationary phase.
- An appropriate eluant, which is a liquid or a mixture of liquids is allowed to flow down the column slowly.
- The strongly adsorbed substances are retained near the top and others come down to various distances in the column,

(ii) Thin layer chromatography (TLC)

- It involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate.
- The glass plate is coated with adsorbent (ex: silica gel, alumina) as a thin layer (about 0.2 mm thick) is called chromatography plate or chroma plate .
- The solution of mixture to be separated is applied as small spot about 2 cm above from one end of the TLC plate. - The glass plate is placed in a closed jar containing the eluant. As the eluant rises up, the components of the mixture move up along the eluant to different distances depending on their degree of adsorption and separation takes place.
- The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e, R_f value.



$$R_f = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$$

- The spots of coloured compounds are visible on TLC plate due to their original colour.
- The colourless compound which fluoresce are detected with ultraviolet light
- Spots of compounds are even detected by allowing them to adsorb iodine, will show up as brown spots.
- Some times an appropriate reagent is sprayed on the plate.
eg : Amino acids are detected by spraying the plate with ninhydrin solution.

Partition Chromatography :

- Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases.
- Paper chromatography is a type of partition chromatography.
- In paper chromatography a special quality known as chromatography paper is used.
- In Chromatography paper, cellulose helps as support, and water absorbed from air on to hydroxyl groups of cellulose acts as stationary phase.
- The chromatography paper spotted with the solution of mixture at the base is suspended in a suitable solvent or mixture of solvents, this solvent (s) act as mobile phase.
- The solvent rises up the paper by capillary action and flows over the spot.
- The paper selectively retains different component according to their differing partition in the two phases. The paper strip so developed is called chromatogram.
- The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram. - The spots of the separated colourless compound may be observed either under ultraviolet or by the use of appropriate spraying agent

**Additional Information : Applications of Chromatography:**

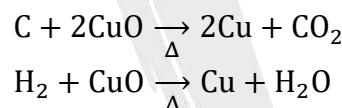
- I. i) In Chemical Industry column chromatography is used for separation of required components obtained after synthesis.
ii) TLC is useful for monitoring large scale column chromatography.
- II. **Pharmaceutical industry :** Chromatography is used for separation of chiral compounds to obtain pharmaceutically active optical isomer.
- III. **Food Industry :** Chromatography techniques are used for quality control in food industry. It is used to determine presence and to separate additives, flavours etc. It is also used to detect presence of contaminants like mould, bacteria in food.
- IV. **Environment-Testing lab :** Presence and quality of pollutants in air and drinking water can be determined by chromatography technique.
- V. **Diagnostic Technique:** Presence of certain drugs and the marker compounds for medical diagnosis in blood and urine are determined.

Qualitative Analysis of Organic Compounds (Detection of Elements):

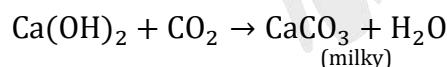
- The qualitative analysis of an organic compound involves detection of all elements present in it

Detection of Carbon and Hydrogen :

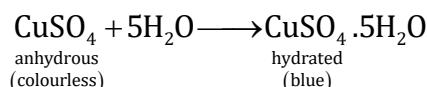
- Carbon and hydrogen are detected by heating the compound with cupric oxide (CuO).
- Carbon present in the compound is oxidised to carbondioxide, which turns lime water milky.
- Hydrogen present in the compound is converted into water, which turns anhydrous copper sulphate into blue.



- Carbondioxide turns lime water milky.



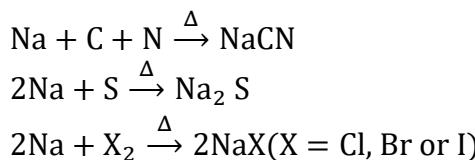
- Water vapours turn anhydrous copper sulphate into blue.

**Detection of Nitrogen, Sulphur Halogens & Phosphorus :**

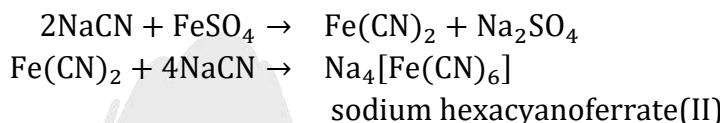
- Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by Lassaigne's test.
- Organic compounds are fused with dry sodium in fusion tube and fused mass after extraction with water is boiled and filtered, the filtrate is called sodium fusion extract



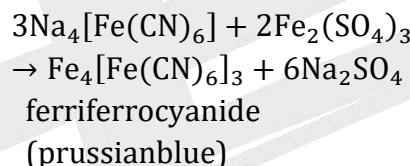
- During preparation of sodium fusion extract covalent compound is converted into ionic compound. - The following reactions takes place

**Test for Nitrogen :**

Sodium fusion extract is boiled with freshly prepared ferrous sulphate (FeSO_4) solution and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen.



On heating with concentrated sulphuric acid some Iron(II) ions are oxidised to Iron(III) ion, which reacts with sodium hexacyanoferrate(II) to produce Iron (III) hexacyanoferrate(II) (ferriferrocyanide) which is Prussian blue in colour.



- This test fails in case of diazo compounds.
- If the amount of nitrogen present is less, then Prussian blue is present in colloidal form and the solution looks green.

Ex.3 Hydrazine does not give Lassaigne's test, Why?

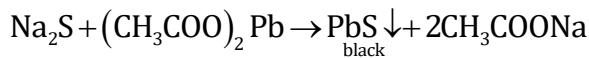
Sol. In the Lassaigne's test, nitrogen is converted to cyanide by combining with carbon of the compound Hydrazine does not contain carbon and hence cyanide cannot form.

Ex.4 Why diazonium salts do not show positive Lassaigne's test for nitrogen ?

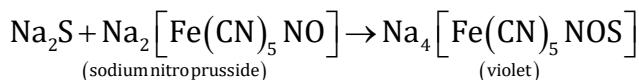
Sol. Diazonium salts are unstable and lose nitrogen as N_2 gas on heating. Hence during fusion, no sodium cyanide is formed in Lassaigne's extract due to the loss of nitrogen.

Test for Sulphur:

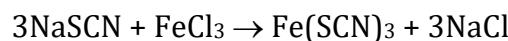
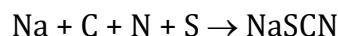
- (a) Sodium fusion extract is acidified with acetic acid and lead acetate is added to it, a black precipitate of lead sulphide is formed, which indicates presence of sulphur.



- (b) Sodium fusion extract is treated with freshly prepared sodium nitroprusside, appearance of violet colour (purple) indicates presence of sulphur.

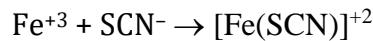


- In case both nitrogen and sulphur are present in an organic compound sodium thiocyanate is formed, which gives blood red colour with neutral FeCl_3 solution.



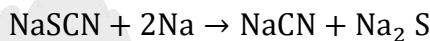
(blood red)

(or)



(blood red)

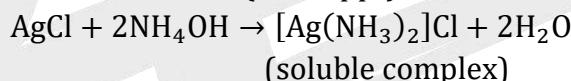
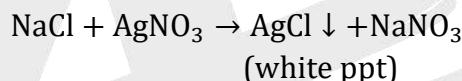
- If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide, these ions gives their usual tests.



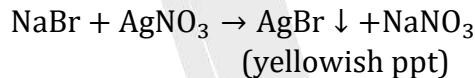
Test for Halogens:

- Sodium fusion extract is acidified with nitric acid and then treated with silver nitrate solution.

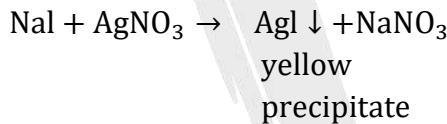
- (i) White precipitate, soluble in ammonium hydroxide indicates presence of chlorine.



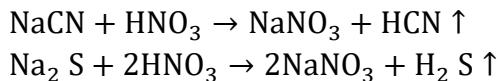
- (ii) Yellowish precipitate, sparingly soluble in ammonium hydroxide indicates presence of bromine.



- (iii) Yellow precipitate, insoluble in ammonium hydroxide indicates presence of Iodine.



- Nitrogen and sulphur are also present in the compound, the sodium fusion extract is boiled with concentrated nitric acid to decompose sodium cyanide & sodium sulphide formed during Lassaigne's test, otherwise they interfere with silver nitrate test for halogens.



- If NaCN and Na_2S are not decomposed, then white and black precipitates of AgCN and Ag_2S are formed respectively with silver nitrate solution.

Beilstein's Test:

A copper wire flattened at one end is heated in an oxidising flame of Bunsen burner. The heating is continued till it does not impart blue colour flame. The hot end of copper wire is now touched with the organic substance and is once again kept in flame, the appearance of green or blue colour indicates the presence of halogens in the organic compound.

**Limitations :**

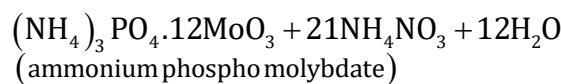
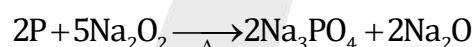
- (a) Substances such as urea, thiourea do not contain halogens but gives this test
- (b) It does not tell which halogen is present in organic compound.

Chlorine Water Test for Bromine and Iodine :

- Both AgBr and AgI are yellow precipitates, it is a little bit difficult to identify given halogen in bromine or iodine, to confirm it chlorine water test is used.
- Sodium fusion extract is acidified with dilute H_2SO_4 (or) HNO_3 , to this 1 (or) 2ml of chloroform (or) Carbon tetrachloride is added and then excess of chlorine water is added with constant shaking.
- (i) If chloroform (or) carbon tetrachloride layer becomes yellow (or) brown indicates presence of bromine. $2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$ Br_2 dissolves in chloroform (or) carbontetrachloride gives yellow (or) brown colour
- (ii) If chloroform (or) carbon tetrachloride layer becomes violet indicates presence of iodine $2NaI + Cl_2 \rightarrow 2NaCl + I_2$ I_2 dissolves in chloroform (or) carbontetrachloride gives violet colour.
- Presence of $NaCN$ (or) Na_2S in sodium fusion extract does not interfere in this test.

Test for Phosphorus :

The compound is heated with oxidising agent (sodium peroxide) or with fusion mixture (sodium carbonate and potassium nitrate) phosphorus present in the compound is oxidised to sodium phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate, a canary yellow (ammonium phospho molybdate) precipitate formation (or) yellow colouration indicates presence of phosphorus.

**Test for Oxygen :**

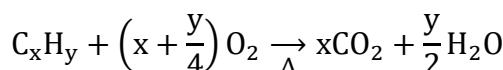
- There is no direct test for oxygen.
 - If organic compound is heated in a dry test tube in nitrogen atmosphere, if water droplets are formed on the walls of the test tube indicates presence of oxygen.
 - Presence of oxygen can be known by testing functional groups containing oxygen.
- eg:** $-OH, -COOH, -CHO, -NO_2$ etc

QUANTITATIVE ANALYSIS

It involves the estimation of percentage composition of various elements by suitable methods.

Estimation of Carbon and Hydrogen

- Carbon and hydrogen are estimated by Liebig's combustion method.
- A known mass of an organic compound is burnt in the presence of excess of oxygen (free from CO_2) and Cupric oxide (CuO) - Carbon and hydrogen present in the compound are oxidised to CO_2 and H_2O respectively



- CO_2 and H_2O produced are weighed by absorbing in concentrated solution of potassium hydroxide and anhydrous calcium chloride (or) magnesium perchlorate respectively

$$\% \text{C} = \frac{12}{44} \times \frac{\text{weight of } \text{CO}_2 \text{ formed}}{\text{weight of organic compound}} \times 100$$

$$\% \text{H} = \frac{2}{18} \times \frac{\text{weight of } \text{CO}_2 \text{ formed}}{\text{weight of organic compound}} \times 100$$

- Ex.5** On complete combustion, 0.246g of an organic compound gave 0.198 g of carbon dioxide and 0.1014 g of water. Determine the percentage composition of carbon and hydrogen in the compound.

Sol. % of carbon = $\frac{12 \times 0.198 \times 100}{44 \times 0.246} = 21.95$

% of hydrogen = $\frac{2 \times 0.1014 \times 100}{18 \times 0.246} = 4.58$

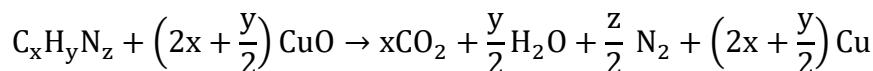
ESTIMATION OF NITROGEN

Nitrogen present in organic compound is estimated by

- (a) Dumas method
- (b) Kjeldahl's method

(a) Dumas method

- In this method nitrogen present in the organic compound is converted into N_2 (molecular nitrogen)
- A weighed amount of organic compound is heated with cupric oxide in an atmosphere of carbondioxide.
- Carbon and hydrogen present in the compound are oxidised to CO_2 and H_2O , while N_2 is at free.
- Some oxides of nitrogen formed are reduced to free nitrogen by passing over heated copper gauze



- Oxides of nitrogen + Cu \rightarrow N_2 + CuO
- The mixture of gases produced is collected over caustic potash solution (KOH solution) which absorbs CO_2 .

- Nitrogen is collected in the upper part of nitro meter.

$$\% \text{ N} = \frac{28}{22400} \times \frac{\text{Volume of nitrogen in ml at STP}}{\text{Weight of organic compound}} \times 100$$

Ex.6. 0.25 g of an organic compound gave 30 cm³ of moist dinitrogen at 288 K and 745 mm pressure.

Calculate the percentage of nitrogen. (Aqueous tension at 288 K = 12.7 mm)

Sol. Mass of the substance = 0.25 g

Volume of moist dinitrogen = 30 cm³

Temperature = 288 K

Pressure = 745 – 12.7 = 732.3 mm

Volume of dinitrogen at STP :

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{732.3 \times 30 \times 273}{288 \times 760} = 27.4 \text{ cm}^3$$

Percentage of nitrogen in organic compound

$$= \frac{28}{22400} \times \frac{\text{vol of N}_2 \text{ at STP}}{\text{wt of organic compound}} \times 100 = \frac{28}{22400} \times \frac{27.4}{0.25} \times 100 = 13.6$$

Ex.7 0.3g of an organic compound gave 50ml nitrogen at 27°C and 715 mm pressure. If the aqueous tension at 27°C is 15 mm, calculate the percentage composition of nitrogen in the compound.

Sol. Mass of the substance = 0.3 g

Volume of the moist dinitrogen = 50ml

Temperature = 27°C = 27 + 273 = 300 K

Pressure = 715 – 15 = 700 mm

Volume of dinitrogen at STP :

$$v_2 = \frac{P_1 V_1}{T_1} = \frac{T_2}{P_2} = \frac{700 \times 50 \times 273}{760 \times 300} = 41.9 \text{ ml}$$

$$\frac{28}{22400} \times \frac{\text{vol of N}_2 \text{ STP}}{\text{wt of organic compound}} \times 100 = \frac{28}{22400} \times \frac{41.9}{0.3} \times 100 = 17.46$$

22400ml of dinitrogen at STP weight = 28 g

$$41.9 \text{ ml dinitrogen at STP weight} = \frac{28 \times 41.9}{22400} \text{ g}$$

$$0.3 \text{ g of organic compound contains} = \frac{28 \times 41.9}{22400} \text{ g of N}_2$$

$$100 \text{ g of organic compound contain} = \frac{28 \times 41.9}{22400} \times \frac{100}{0.3} = 17.46$$

percentage of nitrogen = 17.46

Kjeldahl's Method :

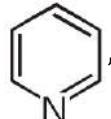
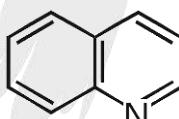
- In this method nitrogen in the organic compound is converted into ammonia (NH_3)
- A known mass of organic compound containing nitrogen is heated with concentrated sulphuric acid in presence of K_2SO_4 and CuSO_4 then nitrogen present in the compound is converted into ammonium sulphate. K_2SO_4 increases boiling point of H_2SO_4 and CuSO_4 acts as catalyst.
- Organic compound + $\text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4$
- The resulting solution is distilled with excess of sodium hydroxide
 $(\text{NH}_4)_2\text{SO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{NH}_3 + 2\text{H}_2\text{O}$
- Ammonia evolved is absorbed in a known but excess volume of standard HCl (or) H_2SO_4 solution.
- The acid left unreacted is estimated by titration against standard solution of sodium hydroxide.

$$\text{Percentage of Nitrogen} = \frac{14}{1000} \times \frac{V \times N}{\text{wt. of organic compound}} \times 100$$

$$\% \text{ N} = \frac{1.4 \times V \times N}{\text{Weight of organic compound}}$$

Where V = volume of acid in ml neutralised by ammonia

N = Normality of acid.

- This method is simpler and more convenient
- It is mainly used to find percentage of nitrogen present in food stuffs, soils, fertilizers and various agricultural products.
- This method is not applicable to compounds containing nitro ($-\text{NO}_2$), Nitroso (NO), azo group ($-\text{N}=\text{N}-$), azoxy compounds $\left[\begin{array}{c} \text{O} \\ | \\ -\text{N}=\text{N}- \end{array} \right]$ and nitrogen present in the ring (pyridine , quinoline ) because nitrogen present in these compounds is not quantitatively

converted in to ammonium sulphate.

- Ex.8** In Kjeldahl's estimation of nitrogen, the ammonia evolved from 0.5 g of an organic compound neutralised 10ml of 1M H_2SO_4 . Calculate the percentage of nitrogen in the compound?

Sol. 10ml of 1M H_2SO_4 = 20ml of 1M NH_3

1000ml of 1M ammonia contains 14 g nitrogen

$$20\text{ml of 1M ammonia contains} = \frac{14 \times 20}{1000} \text{ g N}_2$$

$$\% \text{ of nitrogen} = \frac{14 \times 20 \times 100}{1000 \times 0.5} = 56.0$$

Ex.9 In Kjeldahl's estimation of nitrogen, the ammonia obtained from 0.5 g of an organic substance was passed into 100 cm³ of $\frac{M}{10}$ NaOH for neutralisation. Calculate the percentage of nitrogen in the compound.

Sol. m eq. of H₂SO₄ taken = molarity x basicity x volume (ml)

$$= \frac{1}{10} \times 2 \times 100 = 20$$

$$\text{m. eq of NaOH} = \frac{1}{10} \times 1 \times 154 = 15.4$$

$$\text{m. eq of H}_2\text{SO}_4 \text{ unused} - 20 - 15.4 = 4.6$$

$$\% \text{ of nitrogen} = \frac{1.4 \times \text{meq of H}_2\text{SO}_4 \text{ unused}}{\text{wt of organic compound}} = \frac{1.4 \times 4.6}{0.5} = 12.88\%$$

ESTIMATION OF HALOGENS CARIUS METHOD

- A weighed amount of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as carius tube.
- Carbon and hydrogen present in the compound is converted into CO₂ and H₂O.
- Halogen present in the organic compound is converted into silver halide.
- The perecipitate is washed, dried and weighed

$$\text{Percentage of halogen} = \frac{\text{Atomic weight of halogen}}{\text{Mwt of silver halide}} \times \frac{\text{Weight of silver halide formed}}{\text{Weight of organic compound}} \times 100$$

$$\% \text{Cl} = \frac{35.5}{143.5} \times \frac{\text{wt of AgCl formed}}{\text{wt of organic compound}} \times 100$$

$$\% \text{Br} = \frac{80}{188} \times \frac{\text{wt. of AgBr formed}}{\text{Wt. of organic compound}} \times 100$$

$$\% \text{I} = \frac{127}{235} \times \frac{\text{Wt. of AgI formed}}{\text{Wt. of organic compound}} \times 100$$

Ex.10 In Carius method, 0.1890 g of an organic compound gave 0.2870 g of silver chloride. Calculate the percentage of chlorine in the compound

Sol. Weight of substance = 0.1890 g

Weight of silver chloride = 0.2870 g

$$\% \text{ of chlorine} = \frac{\text{weight of AgCl} \times 35.5 \times 100}{\text{weight of substance} \times 143.5} = \frac{0.2870 \times 35.5 \times 100}{0.1890 \times 143.5} = 37.8$$

Ex.11 One gram of bromoalkane on heating with excess silver nitrate in Carius tube method gave 0.94g of yellow precipitate. What is the percent weight of halogen?

Sol. Weight of substance = 1g Yellow precipitate is AgBr; Weight of AgBr = 0.94 g

$$\% \text{ of bromine} = \frac{0.94 \times 80 \times 100}{1 \times 188} = 40$$

Ex.12 In carius method of estimation of halogen 0.15 g of an organic compound gave 0.12 g of AgBr.

Find out the percentage of bromine in the compound

Sol. % of bromine

$$= \frac{80 \times 0.12 \times 100}{188 \times 0.15} = 34.04$$

Estimation of Sulphur Carius method:

- A weighed amount of organic compound is heated in a carius tube with sodium peroxide or fuming nitric acid.
- Sulphur present in the compound is oxidised into sulphuric acid, which is treated with BaCl_2 solution gives precipitate of BaSO_4 .
- It is filtered, the precipitate is washed, dried and weighed.

$$\% \text{ S} = \frac{\text{Atomic wt of sulphur}}{\text{Mol.wt of } \text{BaSO}_4} \times \frac{\text{wt of } \text{BaSO}_4 \text{ formed}}{\text{wt of organic compound}} \times 100$$

$$\% \text{ S} = \frac{32}{233} \times \frac{\text{wt of } \text{BaSO}_4 \text{ formed}}{\text{wt. of organic compound}} \times 100$$

Ex.13 In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound?

Sol. 233 g BaSO_4 contain 32 g sulphur

$$0.4813 \text{ g } \text{BaSO}_4 \text{ contain} = \frac{32 \times 0.4813}{233} \text{ g sulphur}$$

$$\% \text{ of sulphur} = \frac{32 \times 0.4813 \times 100}{233 \times 0.157} = 42.10$$

Ex.14 On heating 0.2g of an organic compound with a mixture of barium chloride and nitric acid, 0.466 g of barium sulphate was obtained. Calculate the percentage of sulphur.

Sol. Weight of substance = 0.2 g

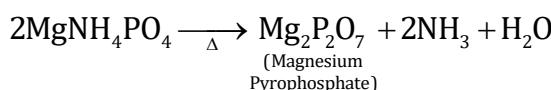
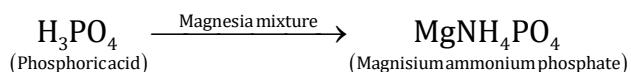
Weight of barium sulphate = 0.466 g

$$\text{Weight percentage of sulphur} = \frac{0.466 \times 32 \times 100}{0.2 \times 233} = 32$$

Estimation of Phosphorus Carius Method :

A weighed amount of organic compound is heated with fuming nitric acid, then phosphorus present in the compound is oxidised to phosphoric acid. Phosphoric acid is precipitated as magnesium ammonium phosphate (MgNH_4PO_4), by addition of magnesia mixture ($\text{MgCl}_2 + \text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$)

- Magnesium ammonium phosphate is washed, dried and it is heated strongly to get magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$).



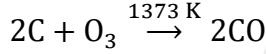
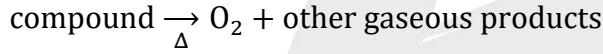
$$\% \text{P} = \frac{62}{222} \times \frac{\text{wt. of Mg}_2\text{P}_2\text{O}_7 \text{ formed}}{\text{wt. of organic compound}} \times 100$$

- Phosphoric acid is precipitated as ammonium phospho molybdate $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ by adding ammonia and ammonium molybdate. (Molecular mass of $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 = 1877$)

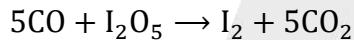
$$\% \text{P} = \frac{31}{1877} \times \frac{\text{wt of } (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \text{ formed}}{\text{wt of organic compound}} \times 100$$

Estimation of oxygen

- Usually percentage of oxygen in organic compound is determined by method of difference % of oxygen = $100 - (\text{sum of the percentages of all other elements})$
- Oxygen present in the organic compound is estimated by Aluise's method.
- A known amount of organic compound is subjected to pyrolysis in a stream of nitrogen.
- The mixture of gaseous products containing oxygen is passed over red-hot coke, then all the oxygen is converted into carbon monoxide.



- CO formed is quantitatively converted into CO_2 by passing over warm Iodine pentoxide (I_2O_5)



The resulting gaseous mixture (CO_2 and I_2) is passed through potassium iodide solution, which absorbs iodine, and then passed over KOH to absorb CO_2 .

$$\% \text{ of oxygen} = \frac{16}{44} \times \frac{\text{wt. of CO}_2 \text{ formed}}{\text{wt. of organic compound}} \times 100$$

Ex.15 0.2g of an organic compound on analysis gave 0.147 g of carbondioxide, 0.12 g of water and 74.6c.c of nitrogen at S.T.P. Calculate the weight percentages of constituents.

Sol. Weight of compound = W = 0.2 g

Weight of CO_2 = $W_1 = 0.147 \text{ g}$

Weight of $\text{H}_2\text{O} = W_2 = 0.12 \text{ g}$ Volume of N_2 at STP = 74.6 c.c.

$$\% \text{ of carbon} = \frac{W_1 \times 12 \times 100}{W \times 44} = \frac{0.147 \times 12 \times 100}{0.2 \times 44} = 20.04\%$$

$$\% \text{ of Hydrogen} = \frac{W_2 \times 2 \times 100}{W \times 18} = \frac{0.12 \times 2 \times 100}{0.2 \times 18} = 6.66\%$$

$$\% \text{ of Nitrogen} = \frac{W_2 \times 28 \times 100}{W \times 22400} = \frac{74.6}{8 \times 0.2} = 46.63\%$$

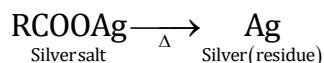
Remaining is oxygen.

$$\% \text{ of Oxygen} = 100 - (\% \text{C} + \% \text{H} + \% \text{ N}) = 100 - 73.33 = 26.67\%$$

Note : Presently estimation of elements (C, H and N) in organic compound is estimated by using CHN elemental analyser by taking very small amount of substance (1-3 mg), results are displayed on screen with in short time.

Chemical Methods used to Find Molecular Mass Silver Salt Method for Acids :

Organic acid form insoluble silver salts, which on heating undergoes decomposition to leave a residue of metallic silver.



$$\frac{\text{Equivalent of silver salt}}{\text{Equivalent wt. of silver}} = \frac{\text{mass of silver salt}}{\text{Mass of silver}}$$

$$\frac{E + 108 - 1}{108} = \frac{\text{Mass of silver salt}}{\text{Mass of silver}}$$

$$E = \left[\frac{\text{Mass of silver salt}}{\text{Mass of silver}} \times 108 \right] - 107$$

Molecular weight of acid = Equivalent weight of acid (E) \times basicity .

Platinic Chloride Method for Base

- Organic bases combine with chloroplatinic acid (H_2PtCl_6) to form insoluble platinichloride, which on ignition gives metallic platinum.
- If 'B' is mono acidic base then formula of salt will be $\text{B}_2\text{H}_2\text{PtCl}_6$.



$$\frac{\text{Molecular mass of platinum salt}}{\text{Atomic mass of platinum}} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$$

$$\text{If E is equivalent weight of base then } \frac{2E+410}{195} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$$

$$E = \frac{1}{2} \left[\frac{\text{Mass of platinum salt}}{\text{Mass of platinum}} \times 195 - 410 \right]$$

Molecular mass of base = Equivalent mass of base \times acidity

Emperical formula

- The simplest whole number ratio between the atoms of various elements present in one molecule of a substance is called emperical formula.

Calculation of Emperical Formula

The steps involved are

- Divide mass percentage of each element by its atomic mass, gives relative number of atoms.
- Simplest ratio is obtained when the figures obtained is divided by lowest number.
- If the simplest ratio obtained is not a whole number ratio, then multiply all the figures with suitable integer to get simplest whole number ratio.
- Write symbols of various elements side by side with above numbers at the lower right corner of each, which is emperical formula of compound.

Molecular formula

The actual number of atoms present in one molecule of a substance is called molecular formula.

Molecular formula = (Empirical formula)_n

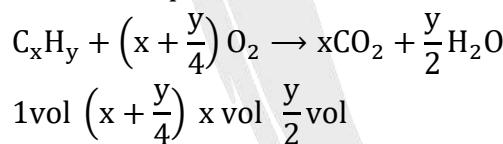
where

$$n = \frac{\text{Molecular wt of the compound}}{\text{Empirical formula weight of the compound}}$$

- If vapour density is given then molecular weight = $2 \times$ vapour density.

Determination of molecular formula of Gaseous Hydrocarbons (Eudiometry) :

- Eudiometry is a direct method used to find molecular formula of gaseous hydrocarbon without finding percentage composition of elements and its molecular weight.
- A known volume of gaseous hydrocarbon is mixed with excess of pure and dry oxygen in eudiometer tube placed inverted in a trough of mercury.
- The mixture is exploded by passing an electric spark between platinum electrodes. As a result carbon and hydrogen of hydrocarbon are oxidised to CO_2 and H_2O vapour respectively.
- The tube is allowed to cool to room temperature, then water vapour is condensed in to liquid water, whose volume occupied is almost negligible. Thus the gaseous mixture left in eudiometer tube is CO_2 and O_2 .
- Caustic potash solution is then introduced in to eudiometer tube which absorbs CO_2 completely. The gas left is unused O_2 -
 $2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ - Decrease in volume on introducing KOH solution gives volume of CO_2 used.
- Some times volume of O_2 left unused is found by introducing pyrogallol and noting the decrease in volume.
- Let molecular formula of gaseous hydrocarbon is C_xH_y . On combustion one volume of it forms x' volumes of CO_2 & ' $y/2$ ' volumes of water vapour.



- For 1 volume of hydrocarbon

$$\text{Volume of O}_2 \text{ used} = \left(x + \frac{y}{4}\right) \text{ vol}$$

$$\text{Volume of CO}_2 \text{ produced} = x \text{ vol.}$$

$$\text{Contraction on explosion and cooling} = 1 + \frac{y}{4} \text{ (volume of liquid water is neglected)}$$

Determination of Molecular mass by Victor Meyer's Method

- A known mass of the volatile substance is vapourised in victor meyer's method.
- The vapours obtained displaces an equal volume of air in to graduated tube.
- The volume of air displaced is calculated at STP condition by using

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\text{Mol. mass of volatile substance} = \frac{\text{Mass of substance taken}}{\text{Volume of air displaced in ml at STP}} \times 22400$$



EXERCISE # O-I

1. Which of the following is monomer unit of polystyrene :-

(A) $\text{CH}_2 = \text{C}(\text{CN})\text{H}$ (B) $\text{CF}_2 = \text{CF}_2$ (C) $\text{CH}_2 = \text{C}(\text{Cl})\text{H}$ (D) $\text{CH} = \text{C}(\text{C}_6\text{H}_5)\text{H}_2$
2. Weakest intermolecular forces are present in :-

(A) Neoprene (B) Terylene (C) Polystyrene (D) Bakelite
3. Thermosetting polymer, Bakelite is formed by the reaction of phenol with :-

(A) $\text{CH}_3\text{CH}_2\text{CHO}$ (B) CH_3CHO (C) HCHO (D) HCOOH
4. Which one is classified as a condensation polymer?

(A) Teflon (B) Acrylonitrile (C) Dacron (D) Neoprene
5. Novolac is a :

(A) linear polymer of urea and formaldehyde
 (B) crosslink polymer of urea and formaldehyde
 (C) linear polymer of phenol and formaldehyde
 (D) crosslink polymer of phenol and formaldehyde
6. Which of the following is not a semisynthetic polymer.

(A) cis-polyisoprene (B) cellulose nitrate (C) cellulose acetate (D) vulcanised rubber
7. Which one of the following polymers is prepared by condensation polymerization

(A) Styrene (B) Nylon-6,6 (C) Teflon (D) Rubber
8. Which of the following statement is not true :

(A) Natural rubber has the trans-configuration at every double bond.
 (B) Buna-S is a copolymer of butadiene and styrene.
 (C) Natural rubber is a 1, 4-polymer of isoprene.
 (D) In vulcanization, the formation of sulphur bridges between different chains make rubber harder and stronger.
9. Structures of some common polymers are given. Which one is not correctly presented ?

(A) Nylon 66 $\left\{ \text{NH}(\text{CH}_2)_6 \text{NHCO}(\text{CH}_2)_4 - \text{CO} \right\}_n$
 (B) Teflon $\left\{ \text{CF}_2 - \text{CF}_2 \right\}_n$
 (C) Neoprene $\left(-\text{CH}_2 - \underset{\text{Cl}}{\overset{|}{\text{C}}} = \text{CH} - \text{CH}_2 - \text{CH}_2 - \right)_n$
 (D) Terylene $\left(\text{OC} \begin{array}{c} \text{O} \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{COOCH}_2\text{CH}_2\text{O} \right)_n$
10. Of the following which one is classified as polyester polymer ?

(A) Terylene (B) Bakelite
 (C) Malamine formaldehyde (D) Nylon-66



11. Which one of the following is not a condensation polymer?
- (A) Dacron (B) Neoprene (C) Melamineformaldehyde (D) Glyptal
12. Which of the following statements is false?
- (A) The repeat unit in natural rubber is isoprene
(B) Both starch and cellulose are polymers of glucose
(C) Artificial silk is derived from cellulose
(D) Nylon-66 is an example of elastomer
13. Which one of the following sets forms the biodegradable polymer ?
- (A) HO – CH₂ – CH₂ – OH & HOOC––COOH
(B) –CH = CH₂ and CH₂ = CH – CH = CH₂
(C) CH₂ = CH – CN and CH₂ = CH – CH = CH₂
(D) H₂N – CH₂ – COOH and H₂N – (CH₂)₅ – COOH
14. Nylon is an example of :-
- (A) Polythene (B) Polyester (C) Polysaccharide (D) Polyamide

**EXERCISE # O-II**

1. For the Separation of two immiscible liquids which method (or apparatus) is used?
 - (1) Chromatography
 - (2) Fractionating column
 - (3) Fractional distillation
 - (4) Separating funnel / Decantation
2. A mixture of benzene and chloroform is separated by
 - (1) Sublimation
 - (2) Separating funnel
 - (3) Crystallization
 - (4) Distillation
3. Which of the following has molecular weight of 92 ?
 - (1) Toluene
 - (2) Benzene
 - (3) Methanol
 - (4) Propene
4. Aniline is usually purified by
 - (1) Chromatographic technique
 - (2) Steam distillation
 - (3) By addition of oxalic acid
 - (4) Fractional crystallization
5. The most suitable method for separation of 1:1 mixture of ortho- and para- nitrophenols is
 - (1) Sublimation
 - (2) Chromatography
 - (3) Crystallization
 - (4) Steam distillation
6. Distillation under reduced pressure is employed for
 - (1) Benzene
 - (2) Petrol
 - (3) Glycerol
 - (4) Organic compounds used in medicine
7. Impure glycerine is purified by
 - (1) Steam distillation
 - (2) Simple distillation
 - (3) Vacuum distillation
 - (4) None of the above
8. Absolute alcohol is prepared by
 - (1) Fractional distillation
 - (2) Kolbe's method
 - (3) Azeotropic distillation
 - (4) Vacuum distillation
9. The latest technique used for purification for organic compounds is
 - (1) Chromatography
 - (2) Vacuum distillation
 - (3) Fractional distillation
 - (4) Crystallisation
10. In paper chromatography
 - (1) Moving phase is liquid and stationary phase is solid
 - (2) Moving phase is liquid and stationary phase is liquid
 - (3) Moving phase is solid and stationary phase is solid
 - (4) Moving phase is solid and stationary phase is liquid
11. A is a lighter phenol and B is an aromatic carboxylic acid. Separation of mixtue A and B can be carried out easily by using a solution of
 - (1) Sodium hydroxide
 - (2) Sodium sulphate
 - (3) Calcium chloride
 - (4) Sodium bicarbonate

- 12.** In sodium fusion test of organic compounds the nitrogen of the organic compound is converted into
(1) Sodamide (2) Sodium cyanide (3) Sodium nitrite (4) Sodium nitrate

13. The Lassaigne's extract is boiled with dil. HNO_3 before testing for halogens because
(1) Silver halides are soluble in HNO_3 (2) Na_2S and NaCN are decomposed by HNO_3
(3) Ag_2S is soluble in HNO_3 (4) AgCN is soluble in HNO_3

14. In a Lessaigne's test for nitrogen, the blue colour is due to the formation of
(1) Potassium ferricyanide (2) Sodium cyanide
(3) Sodium ferrocyanide (4) Ferri-ferro cyanide

15. Which of the following compounds does not show Lassaigne test for nitrogen?
(1) Urea (2) Hydrazine (3) Phenyl hydrazine (4) Azo benzene

16. When piece of human hair are heated strongly with soda lime smell of ammonia can be detected. which one of the following conclusion can be drawn from this observation.
(1) Ammonia is present in human hair (2) Ammonium salt is present in hair
(3) Hair contains amino acids (4) None of the above

17. The Beilstein test for organic compounds is used to detect
(1) Nitrogen (2) Sulphur (3) Carbon (4) Halogen

18. Which of the following is the best scientific method to test presence of water in liquid?
(1) Smell (2) Taste
(3) Use of litmus paper (4) Use of anhydrous copper sulphate

19. Liebig's method is used for the estimation of
(1) Nitrogen (2) Sulphur
(3) Carbon and hydrogen (4) Halogens

20. 0.765 gm of an acid gives 0.535 gm of CO_2 and 0.138gm of H_2O . Then the ratio of percentage of carbon and hydrogen is
(1) 19: 2 (2) 18: 11 (3) 20: 17 (4) 1: 7

21. Nitrogen in an organic compound can be estimated by
(1) Kjeldahl's method only (2) Duma's method only
(3) Both the methods (4) none of these methods

22. Dumas method involves the determination of nitrogen content in the organic compound in form of
(1) NH_3 (2) N_2 (3) NaCN (4) $(\text{NH}_4)_2\text{SO}_4$

23. In Kjeldahl's method, nitrogen present is estimated as
(1) N_2 (2) NO (3) NH_3 (4) NO_2

24. The percentage of sulphur in an organic compound whose 0.32 g produces 0.233 g of BaSO_4 [At.wt.Ba = 137, S = 32] is
(1) 1.0 (2) 10.0 (3) 23.5 (4) 32.1

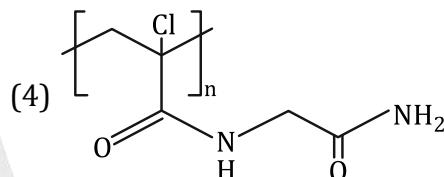
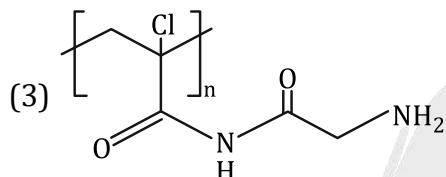
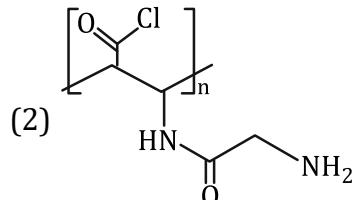
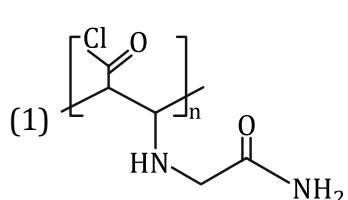
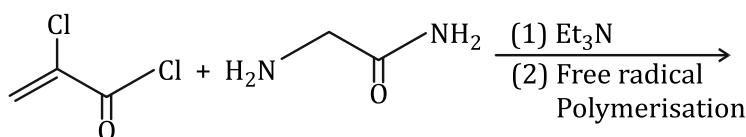
25. If 0.2 gram of an organic compound containing carbon, hydrogen and oxygen on combustion, yielded 0.147 gram carbon dioxide and 0.12 gram water. What will be the content of oxygen in the substance?
 (1) 73.29% (2) 78.45% (3) 83.23% (4) 89.50%
26. If a compound on analysis was found to contain C = 18.5%, H = 1.55%, Cl = 55.04% and Oxygen = 24.81%, Then the empirical formula is
 (1) CHClO (2) CH₂ClO (3) C₂H₂OCl (4) ClCH₂O
27. An organic compound contains C = 40%, H = 13.33% and N = 46.6%. Its empirical formula would be
 (1) CHN (2) C₂H₂N (3) CH₄N (4) C₃H₇N
28. Two elements X (atomic weight = 75) and Y (atomic weight=16) combine to give a compound having 75.8%X. The formula of the compound is
 (1) XY (2) X₂Y (3) X₂Y₂ (4) X₂Y₃
29. On analysis a saturated hydrocarbon is found to contain 83.70% carbon and 16.30% hydrogen. The empirical formula will be (at wt. of C = 12, at. wt. of H = 1)
 (1) C₃H₆ (2) C₃H₈ (3) C₃H₄ (4) C₆H₁₂
30. Empirical formula of a hydrocarbon containing 80% carbon and 20% hydrogen is
 (1) CH (2) CH₂ (3) CH₃ (4) CH₄
31. An organic compound with C = 40% and H = 6.7% will have the empirical formula
 (1) CH₄ (2) CH₂O (3) C₃H₆O₃ (4) C₂H₄O₂
32. In a hydrocarbon, mass ratio of hydrogen and carbon 1: 3, the empirical formula of hydrocarbon is
 (1) CH₄ (2) CH₂ (3) C₂H (4) CH₃
33. 8.24 g of a volatile liquid on vaporization gives 45ml of vapours at NTP. What will be the vapour density of the substance? (Density of H₂ = 0.089 g L⁻¹)
 (1) 95.39 (2) 39.95 (3) 99.53 (4) 59.93
34. 0.1914 g of an organic acid is dissolved in about 20ml of water. 25ml of 0.12 N. NaOH is required for the complete neutralization of the acid solution. The equivalent weight of the acid is
 (1) 65.0 (2) 64.0 (3) 63.8 (4) 62.5
35. The equivalent weight of an acid is equal to
 (1) Molecular weight x acidity (2) Molecular weight x basicity
 (3) Molecular weight/basicity (4) Molecular weight /acidity
36. Simple distillation can be used to separate liquids which differ in their boiling points at least by
 (1) 5°C (2) 10°C (3) 35 – 50°C (4) 100°C
37. Empirical formula of a compound is CH₂O. If its vapour density is 90, then the molecular formula of the compound is
 (1) C₅H₁₀O₅ (2) C₃H₆O₃ (3) C₆H₁₂O₆ (4) C₄H₈O₄

- 38.** The empirical formula of an acid is CH_2O_2 , the probable molecular formula of the simplest acid may be
 (1) CH_2O (2) CH_2O_2 (3) $\text{C}_2\text{H}_4\text{O}_4$ (4) $\text{C}_3\text{H}_6\text{O}_6$
- 39.** A gaseous hydrocarbon has 85% carbon and vapour density of 28. The possible formula of the hydrocarbon will be
 (1) C_3H_6 (2) C_2H_4 (3) C_2H_2 (4) C_4H_8
- 40.** a hydrocarbon has C = 85.72% and remaining H. The hydrocarbon is
 (1) C_2H_4 (2) C_2H_6 (3) C_2H_2 (4) CH_4
- 41.** An organic compound containing carbon, hydrogen and oxygen contains 52.2% carbon 13.04% hydrogen. Vapour density of the compound is 23. Its molecular formula will be
 (1) $\text{C}_2\text{H}_6\text{O}$ (2) $\text{C}_3\text{H}_8\text{O}$ (3) $\text{C}_4\text{H}_8\text{O}$ (4) $\text{C}_5\text{H}_{10}\text{O}$
- 42.** percentage of Se(at.wt 78.4) in peroxidase anhydrase enzyme is 0.5% by weight, then minimum molecular weight of peroxidase anhydrase enzyme is
 (1) 1.568×10^4 (2) 1.568×10^3 (3) 15.68 (4) 2.136×10^4
- 43.** The empirical formula of a compound is CH_2 . One of the compound has a mass of 42 g. its molecular formula is
 (1) CH_2 (2) C_2H_2 (3) C_3H_6 (4) C_3H_8
- 44.** In a compound C, H and N atoms are present in 9:1:3.5 by weight. If molecular weight of the compound is 108, then the molecular formula of the compound is
 (1) $\text{C}_2\text{H}_6\text{N}_2$ (2) $\text{C}_3\text{H}_4\text{N}$ (3) $\text{C}_6\text{H}_8\text{N}_2$ (4) $\text{C}_9\text{H}_{12}\text{N}_3$
- 45.** The following is the percentage composition of a compound. Na = 16.08%, C = 4.19%, O = 16.78%, and $\text{H}_2\text{O} = 62.95\%$. Its molecular formula is
 (1) Na_2CO_3 (2) $\text{Na}_2\text{CO}_3\text{H}_2\text{O}$ (3) $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ (4) $\text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$
- 46.** An organic compound contains 49.3% carbon, 6.84% hydrogen and its vapour density is 73. Empirical Formula of the compound is
 (1) $\text{C}_3\text{H}_5\text{O}_2$ (2) CH_{10}O_4 (3) $\text{C}_3\text{H}_{10}\text{O}_2$ (4) $\text{C}_4\text{H}_{10}\text{O}_4$
- 47.** Molecular mass of a volatile substance may be obtained by
 (1) Kjeldahl's method (2) Duma's method
 (3) Victor meyer's method (4) Liebig's method
- 48.** The most suitable method of separation of 1: 1 mixture of ortho and para nitro phenol is
 (1) Distillation (2) Crystallization (3) Sublimation (4) Chromatography]
- 49.** Kjeldahl's method can not be used for the estimation of Nitrogen in
 (1) Pyridine (2) Nitro compounds (3) Azo compounds (4) All
- 50.** In Kjeldahl's method nitrogen present is estimated as
 (1) N_2 (2) NH_3 (3) NO_2 (4) None

EXERCISE # JEE-MAINS & ADVANCED

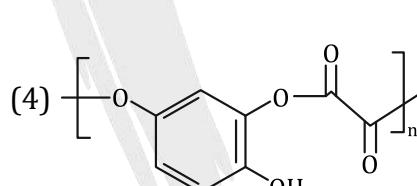
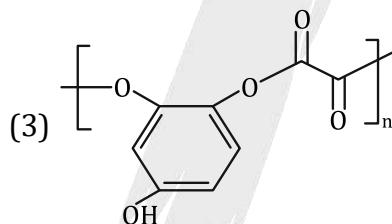
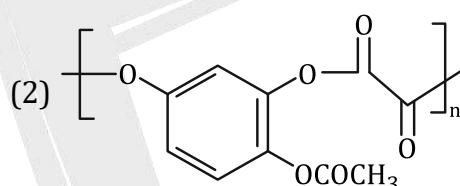
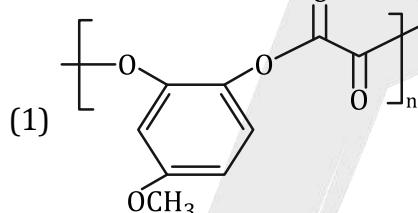
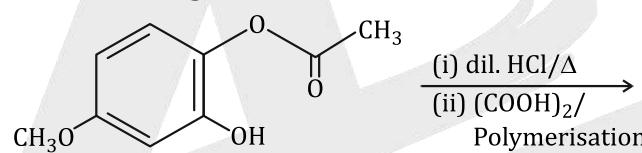
Q.1 Major product of the following reaction is:

[JEE-MAINS 2019]



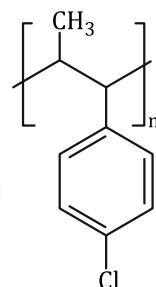
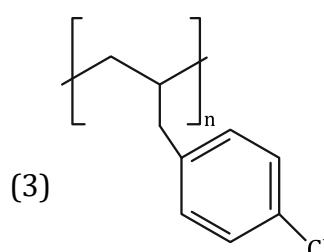
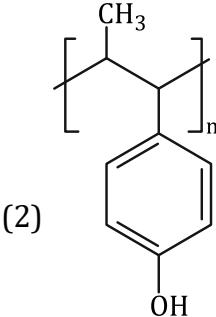
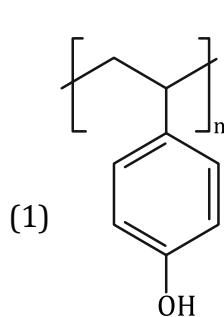
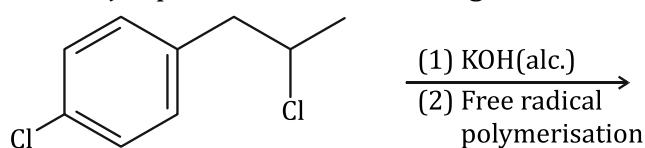
Q.2 The major product of the following reaction is:

[JEE-MAINS 2019]



Q.3 The major product of the following reaction is:

[JEE-MAINS 2019]



Q.4 The correct match between Item - I and Item- II is:

[JEE-MAINS 2019]

Item-I		Item-II	
(a)	High density polythene	(I)	Peroxide catalyst
(b)	Polyacrylonitrile	(II)	Condensation at high temperature/ & pressure
(c)	Novolac	(III)	Ziegler-Natta catalyst
(d)	Nylon 6	(IV)	Acid or base catalyst

(1) (a) → (IV), (b) → (II), (c) → (I), (d) → (III)

(2) (a) → (II), (b) → (IV), (c) → (I), (d) → (III)

(3) (a) → (III), (b) → (I), (c) → (II), (d) → (IV)

(4) (a) → (III), (b) → (I), (c) → (IV), (d) → (II)

Q.5 Which one of the following polymers is not obtained by condensation polymerisation?

[JEE-MAINS 2020]

(A) Buna-N

(B) Nylon 6

(C) Bakelite

(D) Nylon 6,6

Q.6 Consider the Assertion and Reason given below.

[JEE-MAINS 2020]

Assertion (A): Ethene polymerized in the presence of Ziegler Natta Catalyst at high temperature and pressure is used to make buckets and dustbins.

Reason (R) : High density polymers are closely packed and are chemically inert.

Choose the correct answer from the following:

(A) Both (A) and (R) are correct and (R) is the correct explanation of (A).

(B) Both (A) and (R) are correct but (R) is not the correct explanation of (A).

(C) (A) is correct but (R) is wrong

(D) (A) and (R) both are wrong

Q.7 The correct match between Item-I and Item-II is

[JEE-MAINS 2020]

Item - I

Item - II

(a) Natural rubber

(I) 1, 3-butadiene + styrene

(b) Neoprene

(II) 1, 3-butadiene + acrylonitrile

(c) Buna- N

(III) Chloroprene

(d) Buna-S

(IV) Isoprene

(A) (a) -(111), (b) - (IV), (c) - (1), (d) - (11)

(B) (a) - (IV), (b) - (III), (c) - (II), (d) - (1)

(C) (a) - (III), (b) - (IV), (c) - (II), (d) - (1)

(D) (a) - (IV), (b) - (III), (c) - (I), (d) - (II)



Q.8 Preparation of Bakelite proceeds via reactions:

[JEE-MAINS 2020]

- (A) Electrophilic substitution followed by condensation.
- (B) Nucleophilic addition followed by dehydration.
- (C) Electrophilic addition followed by dehydration.
- (D) Hydration followed by condensation.

Q.9 Match List I with List II

[JEE-MAINS 2023]

	List-I (Name of polymer)		List II (Uses)
A.	Glyptal	I.	Flexible pipes
B.	Neoprene	II.	Synthetic wool
C.	Acrilan	III.	Paints and Lacquers
D.	LDP	IV.	Gaskets

Choose the correct answer from the options given below :-

- (1) A-III, B-II, C-IV, D-I
- (2) A-III, B-IV, C-II, D-I
- (3) A-III, B-IV, C-I, D-II
- (4) A-III, B-I, C-IV, D-II

Q.10 Match List-I and List-II.

[JEE-MAINS 2023]

List-I	List-II
A. Elastomeric polymer	I. Urea formaldehyde resin
B. Fibre polymer	II. Polystyrene
C. Thermosetting polymer	III. Polyester
D. Thermoplastic polymer	IV. Neoprene

Choose the correct answer from the options given below:

- (1) A-II, B-III, C-I, D-IV
- (2) A-II, B-I, C-IV, D-III
- (3) A-IV, B-III, C-I, D-II
- (4) A-IV, B-I, C-III, D-II

Q.11 Caprolactam when heated at high temperature in presence of water, gives

[JEE-MAINS 2023]

- (1) Teflon
- (2) Dacron
- (3) Nylon 6,6
- (4) Nylon 6



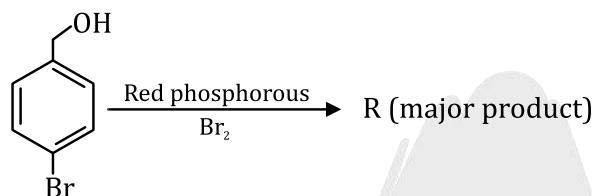
Q.12 Among the following, the correct statement(s) about polymers is(are)

[JEE-Adv. 2022]

- (A) The polymerization of chloroprene gives natural rubber.
- (B) Teflon is prepared from tetrafluoroethene by heating it with persulphate catalyst at high pressure.
- (C) PVC are thermoplastic polymers.
- (D) Ethene at 350-570 K temperature and 1000 - 2000 atm pressure in the presence of a peroxide initiator yields high density polythene.

Q.13 Consider the following reaction.

[JEE-Adv. 2022]



On estimation of bromine in 1.00 g of **R** using Carius method, the amount of AgBr formed (in g) is [Given: Atomic mass of H = 1, C = 12, O = 16, P = 31, Br = 80, Ag = 108]

Q.14 The reaction of 4-methyloct-1-ene (**P**, 2.52 g) with HBr in the presence of $(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$ gives two isomeric bromides in a 9:1 ratio, with a combined yield of 50%. Of these, the entire amount of the primary alkyl bromide was reacted with an appropriate amount of diethylamine followed by treatment with aq. K_2CO_3 to give a non-ionic product **S** in 100% yield. The mass (in mg) of **S** obtained is_____.

[Use molar mass (in gmol⁻¹) : H = 1, C = 12, N = 14, Br = 80]

[JEE-Adv. 2023]

**ANSWER KEY****EXERCISE # O-I**

- | | | | | | | | | | | | | | |
|-----------|---|-----------|---|------------|---|------------|---|------------|---|------------|---|------------|---|
| 1. | D | 2. | A | 3. | C | 4. | C | 5. | C | 6. | A | 7. | B |
| 8. | A | 9. | C | 10. | A | 11. | B | 12. | D | 13. | D | 14. | D |

EXERCISE # O-II

- | | | | | | | | | | | | | | |
|------------|---|------------|---|------------|---|------------|---|------------|---|------------|---|------------|---|
| 1. | 4 | 2. | 4 | 3. | 1 | 4. | 2 | 5. | 4 | 6. | 3 | 7. | 3 |
| 8. | 3 | 9. | 1 | 10. | 2 | 11. | 4 | 12. | 2 | 13. | 2 | 14. | 4 |
| 15. | 2 | 16. | 3 | 17. | 4 | 18. | 4 | 19. | 3 | 20. | 1 | 21. | 3 |
| 22. | 2 | 23. | 3 | 24. | 2 | 25. | 1 | 26. | 1 | 27. | 3 | 28. | 4 |
| 29. | 2 | 30. | 3 | 31. | 2 | 32. | 1 | 33. | 4 | 34. | 3 | 35. | 3 |
| 36. | 3 | 37. | 3 | 38. | 2 | 39. | 4 | 40. | 1 | 41. | 1 | 42. | 1 |
| 43. | 3 | 44. | 3 | 45. | 3 | 46. | 1 | 47. | 3 | 48. | 1 | 49. | 4 |
| 50. | 2 | | | | | | | | | | | | |

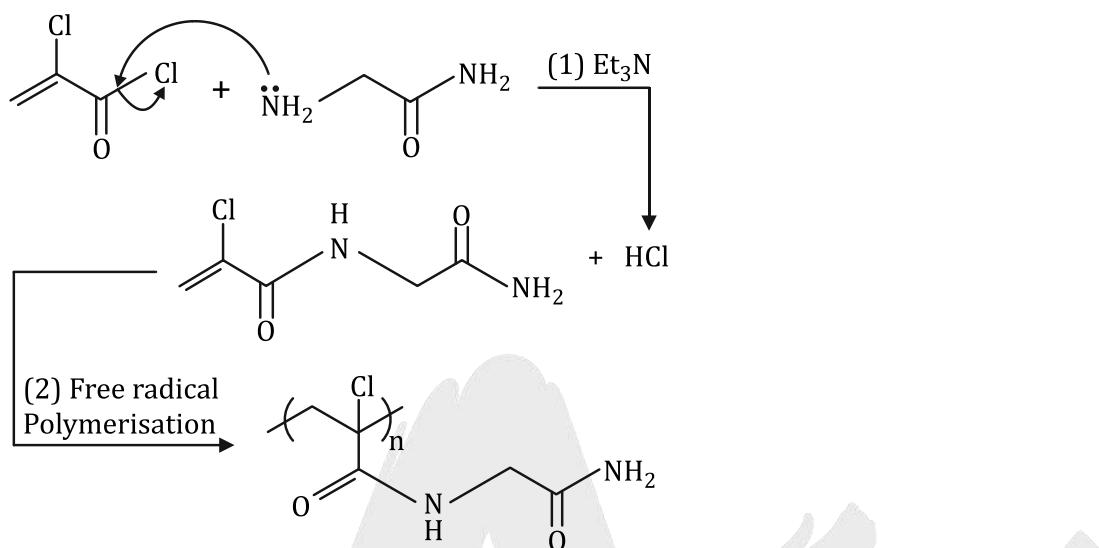
EXERCISE # JEE-MAINS & ADVANCED

- | | | | | | | | | | | | |
|------------|--------|------------|--------|-----------|-----|------------|-----|------------|-----|------------|-------|
| 1. | (4) | 2. | (1) | 3. | (4) | 4. | (4) | 5. | (A) | 6. | (A) |
| 7. | (B) | 8. | (A) | 9. | (2) | 10. | (3) | 11. | (4) | 12. | (B,C) |
| 13. | (1.50) | 14. | (1791) | | | | | | | | |

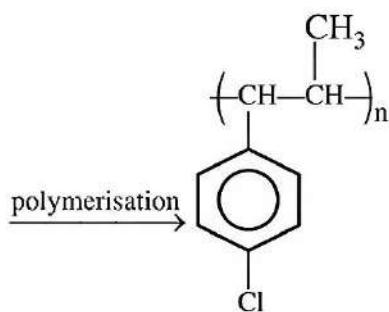
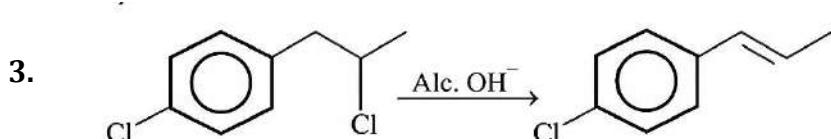
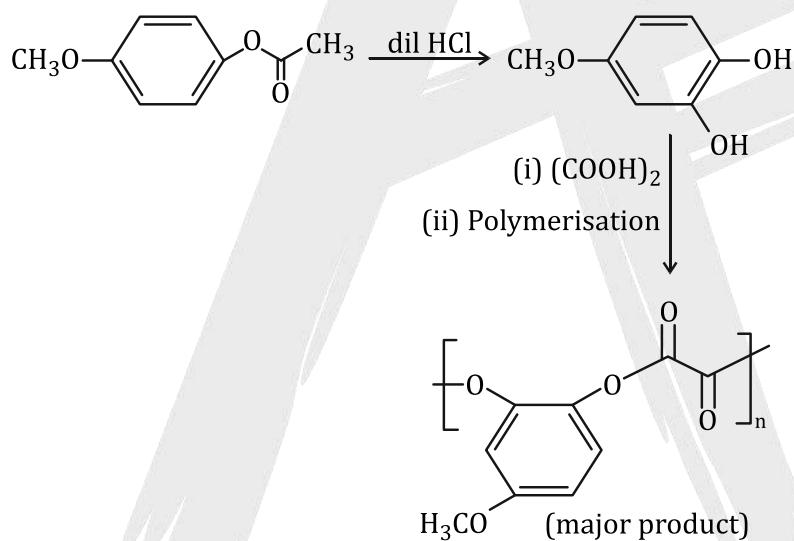
SOLUTION

EXERCISE # JEE-MAINS & ADVANCED

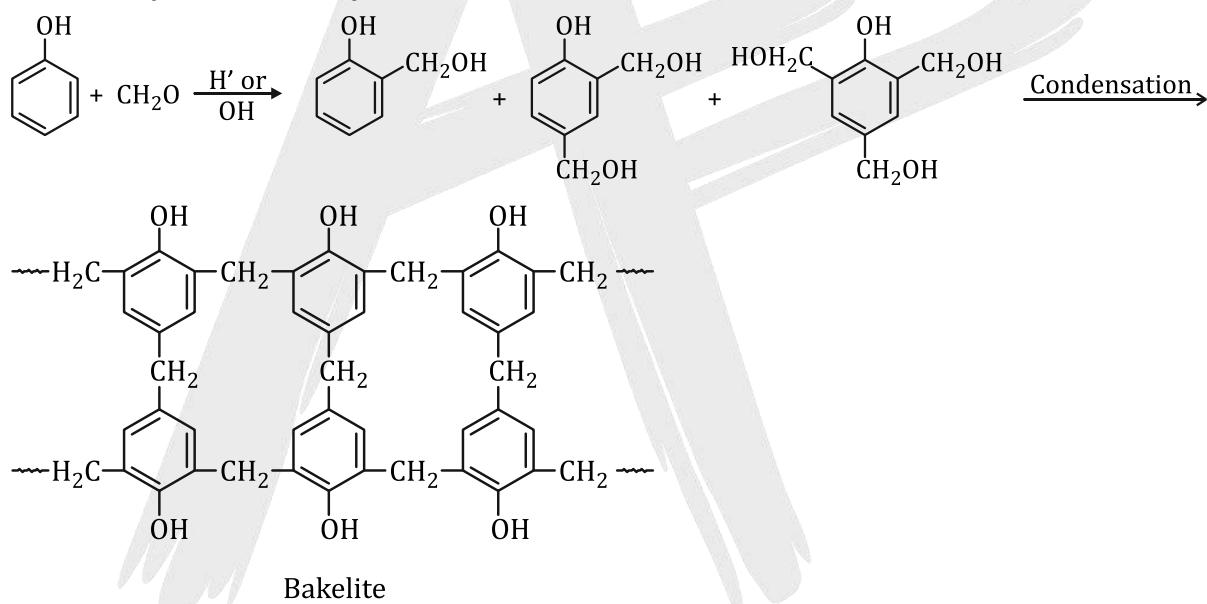
1. Mechanism for the formation of major product is as follows:



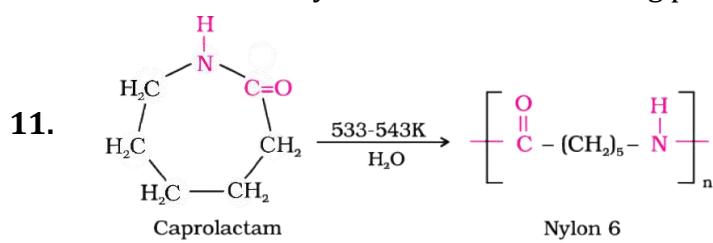
2. Reaction involved:



4. a. HDPE - Ziegler-Natta catalyst
 b. Polyacrylonitrile - Peroxide catalyst
 c. Novolac - Catalysed by acid or base
 d. Nylon-6 - Condensation at high T and P
5. Buna- N : Obtained by addition polymerisation Nylon 6 , Bakelite, Nylon 6,6 :
 Obtained by condensation polymerisation.
6. High density polyethene is hard and chemically inert that's why used to make buckets and dustbins.
7. Natural rubber - Polymer of isoprene Neoprene
 Polymer of chloroprene Buna N
 Polymer of 1,3 -Butadiene and acrylonitrile
 Buna S
 Polymer of 1,3 -Butadiene and styrene
8. Formation of Bakelite follows electrophilic substitution reaction of phenol with formaldehyde followed by condensation.

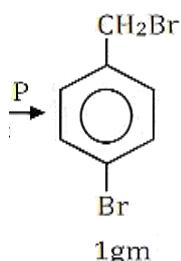


9. Fact based
10. Neoprene : Elastomer
 Polyester : Fibre
 Polystyrene : Thermoplastic
 Urea-Formaldehyde Resin: Thermosetting polymer

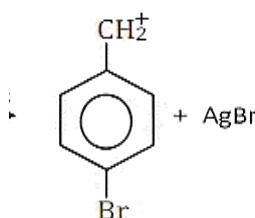


12. Polymerization of chloroprene gives synthetic rubbers not natural rubbers. Teflon is prepared from tetrafluoroethene by heating it with persulphate catalyst at high pressure. PVC are thermoplastic polymers. High density polythene is formed when addition polymerization of ethene takes place in a hydrocarbon solvent in the presence of a catalyst such as triethylaluminium and titanium tetrachloride (Ziegler-Natta catalyst) at a temperature of 333 K to 343 K and under a pressure of 6 – 7 atmospheres.

13.

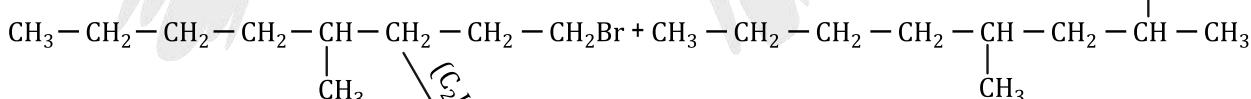
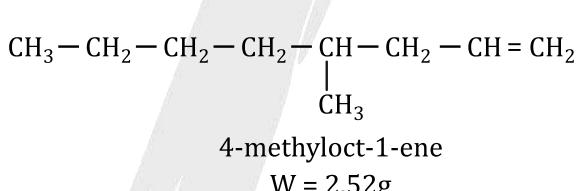
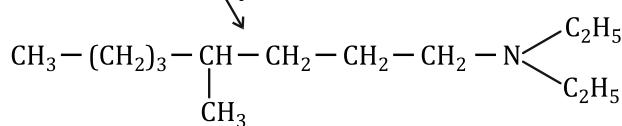


moles



$$= \frac{1}{125} \\ < 188 = 1.50 \text{ gm}$$

14.

(Minor)
9(Minor)
1

(S)