DRUGS AND POLYMER CHEMISTRY

(DSCHE32)

(BSC CHEMISTRY-IV)

ACHARYA NAGARJUNA UNIVERSITY

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Unit – I

DRUGS AND DRUG INTERMEDIATES

LESSON - 1

DEFINITION OF DRUG - REQUIREMENT OF DRUG

Drugs cure disease. A majority of diseases in man are caused by the entry of micro-organisms into the body. Depending on the cause of diseases, different chemicals are used to relieve pain, suffering and the stress associated with the disease. Such chemicals used for the cure of disease are called as drugs. The word drug is derived from the French word ' drogue' which means a dry herb. A drug may be defined as a substance used in the prevention, diagnosis and cure of a disease in man or in other animals. According to WHO (World Health Organisation), drug is a susbstance that is used or intended to be used to modify or explore physiological systems or pathological states for the benefit of the patient. Drugs have to be applied correctly in a proper dosage, for a specific period of time. William Withering wrote in 1787, poisons in small doses are the best medicines and useful medicines in too large doses are poisonons. i.e. drugs are useful poisons.

Historical Evolution of Drugs :

The world's oldest knnown Pharmacological or Therapeutic writings came from India and china. The earliest Indian records are the Vedas. The medicinal properties of plants are described in the Rigveda and Atharvaveda from which Ayurveda, knowledge of life or the science of life was developed. Through out history many people have contributed to the improvement of the health sciences. Charaka, ancient indian physician, later sushruta and Vagbhatta described various medicinal preparations in Ayurveda. The Charakasamhita, mostly dealing with plants and sushrutsamhita dealing with surgery are the best known ancient treatises in Ayurveda. The importance of Amla Fruit as a tonic, the use of Rau Wolfia serpentina as a tranquiliser, the dried roots and stems of Withania Somnifera (Aswagandha) as a sedative were known to ancient indians. The antipyretic effects of chang shang which has now been shown to contain antimalarial alkaloids and the drug ' Ma Huang ' for its diaphoretic and stimulatory effect were discovered by chinese emperor Scholar Shen Nung.

The Greek physian Hipocrates (450 B.C.) laid the foundation of modern medicine. According to him, a disease is a pathological process and its treatment with a drug is a scientific process. Upto the 19th century, diseases were treated using the extracts of herbs and animals.

Francois Magendie laid the foundation of modern pharmacology. However, it was Paul Ehrlich who did outstanding work in medicinal chemistry and therefore called " Father of Chemdtherapy".

Terminology and description of Terms :

1. Pharmacy :

Pharmacy deals with the collection, preparation and standardisation of drugs. It includes the cultivation of medicinal plants and the synthesis of the compounds of medicinal value, chemical analysis and testing of the compounds so synthesised.

2. Pharmacology :

It deals with the effect of drugs on living animals, organs or tissues. The word pharmacology is derived from Greek words – Pharmacon – drug and logos – treatise. Pharmacology includes pharmacy, Chemotherapy, posology, toxicology etc. Clinical pharmacology applies pharmacological priniciples to the study of the effects and action of drugs on human beings.

3. Pharmaco Dynamics :

It is concerned with the response of living organism to chemical stumuli in the absence of disease. It explains about the use of a particular therapeutic agent in the treatment of a disease in human beings.

4. Pharmacophore :

Pharmcaophore is a functional group responsible for the medicinal activity of a drug. By introducing the pharmacophores it is possible to make the compounds biologically active. The common pharmacophoric groups are –R, – OH, – OR, – CHO, >CO, X etc.

5. Pharmaco Dynamic Agents :

Pharmaco dynamic agents are those drugs which stimulate or depress various functions of the body so as to provide relief without curing the disease. Analgesics, sedatives and anaesthetics are examples of pharmacodynamic agents.

6. Metabolites and Antimetabolites :

Metabolites are the substances that take part in cellular metabolic reactions while antimetabolites are the chemical agents that block the metabolism due to its structural similarity with that of metabolite. An antimetabolite acts either by preventing the combination of the metabolite with its specific enzyme or by combining itself with the enzyme to form a metaboically inactive compound. Sulphonamides are examples of antimetabolites. These are antimetabolities to P-amimo benzoic acid which is an essential metabolite.

7. Bacteria :

Bacteria are group of Micro - Organisms which are unicellular and surrounded by rigid, complex, protein cell wall. Bacteria may be useful as well as harmful to man, animals and plants. Bacteria are classified into two types namely gram-positive and gram-negative depending on their staining characteristics. Bacteria that retain the violet stain of Gram's reagent (crystal violet + iodine) are known as gram-positive bacteria while those which donot retain the violet stain of Gram's reagent are known as gram-negative bacteria.

8. Virus :

Virus is a very small micro - organism which have one kind of nucleic acids either DNA or RNA and do not reproduce by binary fission. Virus can multiply in living tissues and it is reponsible for many diseases in man.

9. Fungi :

It is a low form of vegetable life including many microscopic organisms. It doesnot contain chlorophyll and grows on organic matter and causes many diseases.

10. Actinomycetes :

Actinomycetes is a class of organisms used for the isolation of the first antibiotic i.e streptomycin. Actinomycetes grow as branching rods and form filaments which are smaller than that of pencillium.

11. Mutation :

The sudden change of a gene in an organism is known as mutation. It may be spontaneous or induced and is inherited by the subsequent generation.

12. Chemotherapy :

The treatment of infectuous disease by using chemical agents is called chemotherapy. These chemical agents are called as Chemotherpeutic agents.

13. Therapeutic index :

The medicinal value of the drug is generally represented by therapentic is generally represented by therapeutic index. It is the ratio of the amount of the drug necessary to kill the patient (MTD) to that required for a maximum curatic dose (MCD). resistant to the drug after its use for some time.

$$\text{Therapeutic index} = \frac{\text{Maximum tolerated dose (MTD)}}{\text{Maximum Curated dose (MCD)}}$$

However, in actual practice these qualities are for away from reality for a majority of commonly used drugs.

The requirements of an ideal drug :

An ideal drug should satisfy the following requirements -

1. The action of the drug should be localized at the site where it is desired to act.
2. It should be non toxic.
3. It should exhibit minimum side effects.
4. It should be available everyewhere.
5. It should be pharmacentically elegant, and physically and chemically stable under various conditions of use and storage.

6. It should eliminate the disease from the body efficiently and completely.
7. It should not damage the host tissues in the body.
8. It should not make the host cells.

14. Different types of diseases and types of drugs :

Drugs are classified into two groups basing on their (i) chemical structure and (ii) Therapeutic action. Drugs based on their chemical structure has similarity in their chemical structure.

Drugs based on their therapenutic action are classified into -

a) Chemotherpeutic agents (b) Pharmacodynamic agents and (c) Vitamins and hormones.

15. Chemotherapy and Chemotherapentic agents :

The word chemotherapy was introduced by Paul Ehlrich and may be defined as the use of chemical agents in the treatment of infectious diseases. The diseases caused by infection with micro-organisms like bacteria, fungi, protozoa, Virus etc. are called as infectious diseases. The chemotherapeutic agents, destroy the disease causing parasites or organisms without damaging the tissues of the patient. Depending on the disease caused by parasite, these drugs are further divided into the following types.

CLASS OF DRUG	DISEASE	DRUGS USED
Antimalarials	Malaria	Chloroquine, Quinine
Antibacterials (Sulpha drugs)	Bacterial infection	Sulphanila mide, Sulphadiazine
Antibiotics	Bacterial infection	Pencillin G, Gentamycin
Antifungals	Fungal	Flucanozole, Micanozole
Antiprotozoals	Trypanosomiasis	Suramin, Metronidazole
Antihelmentics	Helminths	Niclosamide, Quinacrine
Antiseptics	Micro-organisms	2-propanol, Ethanol, Phenol, Cresol, resorcinol
Antileprosy drugs	Leprosy	Dapsone, Thiazolsulphone
Antitubercular drugs	Tuberculosis	Streptomycin, Isoniazid, Rifampin

16. Phamacodynamic agents :

Drugs which act on any system of the body like the central nervous system (CNS); peripheral nervous system (PNS); Cardiovascular system; hematopoietic system; renal system etc are termed as pharmacodynamic agents. These are not specific remedies for particular diseases.

S.NO	TYPE OF DRUGS	SITE OF DISEASE	DRUGS USED
Drugs acting on the central nervous systems (CNS) :			
1.	CNS depressants - non selective	CNS	Morphine, Codeine
2.	CNS depressants - selective	CNS	L- dopa, diazepam, gabapentin.
3.	CNS - stimulants	CNS	Caffeine, Strychnine
4.	Anaesthetics	CNS	Thiopenntal Sodium, Chloroform, Cyclopropane.
5.	Antipyretics and analgesics	CNS	Aspirin, Analgin, paracetamol.
Drugs acting on the Peripheral nervous system :			
6.	Antihistamines	PNS	Benadryl, Linadryl
7.	Antipasmodics	PNS	Atropine, Papaverine
Drugs acting on the cardiovascular system:			
8.	Cardiovascular agents	Heart or Blood vessels	Digitalis, Lidocaine, Reserpine
Drugs acting on the hematopoietic system:			
9.	Anticoagulants	Blood	Heparin, Dicoumarol, Aspirin etc.
10.	Antia- anemic	Blood	Ferrous sulphate, Vitamin B_{12}.
Drugs acting on therenal system:			
11.	Diuretics	Kidney	Bumetanide, Chlorothiazide

LESSON - 2

SOURCES OF DRUGS

Drugs from plants, bacteria, and synthetic drugs :

Drugs are discovered from several kinds of natural sources or prepared synthetically in the laboratory.

Alkaloids, glycosides, vitamins, hormones and antibiotics are some of the drugs obtained from natural sources. Some of these drugs can also be prepared synthetically. The sources of drugs include (a) Plant origin drugs (b) animal origin drugs (c) Synthetic drugs (d) biotechnology and (e) human gene therapy.

a) Plant origin drugs :

In history, plant materials have served as a reservoir of new drugs. After the isolation and identification of structure, of plant constituents, these natural chemicals are used as the starting material in preparing semisynthetic drugs which have slightly different chemical structures.

Examples :

1. Reserpene, a tranquillizer and hypotensive agent is an example, isolated from the plant ' Rauwolfia Serpentina'.
2. Two alkaloids, vincristine and Vinblastine used as anticancer drugs have been isolated from a plant.
3. The various species of Dioscorea are rich in steroids from which hormonal drugs such as cortisone and estrogens are semi synthetically prepared.
4. Morphine, Quinine and Atropine are some examples of drugs isolated from plants.

Drugs from animals :

1. Hormonal substances such as thyroid extract, insulin and the pituitary hormone are drugs, obtained form the endocrine glands of cattle, sheep and pig.
2. The urine of pregnant mares is a source of estrogens.
3. Vaccine for mumps and influenza are prepared from fluids of chick embryos.
4. Vaccine for rubella (German measles) is prepared from duck embryos.

Drugs from bacteria :

Bacteria are the simplest microscopic, unicellular organisms. Bacteria act as both friend and enemy to mankind as they show some useful activities as well as harmful activities.

1. Bacteria produce many industrial chemicals, organic acids and enzymes.

2. Useful in the production of antibiotics eg - Streptomycin, terramycin, Chloromycin, erythromycin, neomycin etc.

3. Bacteria are now used in recombinant DNA technology.

Synthetic Drugs :

Today, laboratory is the most common source of potentical drugs. A synthesized drug should have a simpler structure and more useful properties than that of a natural drug. For example, Novocain, a synthetic anaesthetic, has a simpler structure with no side effects when compared to cocaine, having complex structure and many side effects.

Majority of drugs used now are of synthetic origin. The following are some examples of synthetic drugs.

1. Anaesthetic drugs : eg - Thiopental sodium ; Methohexital.

2. Sedative drugs : eg- Benzodiazepenes ; Phenobarbital.

3. Antipyretic drugs : eg - Aspirin & phenyl butazone.

4. Analgesic drugs : eg - Paracetamol & Analgin.

5. Anti - inflammatory drugs : eg - Ibuprofen.

6. Anti convulsants : eg - Diazepam & Gabapentin.

7. Bromchodilators : eg - Salbutamol

8. Antihypertensive drugs : eg - Captopril & Guanethidine.

9. Cardiovascular drugs : eg - Diltiazem & Cardene.

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LESSON - 3

PAIN KILLERS

Analgesics and Antipyretics - Pain killers :

Pains will arise due to parasitic infections, disturbances in metabolic activities, surgical operations, nutritional deficiencies, tissue degeneration etc.

The central nervous system is depressed by the use of many therapeutics, generally known as narcotics. Depending upon their degree of physiological action, the narcotics are classified into analgesics ; hypnotics and anaesthetics. An analgesic lowers sensitivity to pain without causing unconsiciousness.

A hypnotic known as sleep producing drug leads to unconsciousness akin to sleep. An anaesthetic produces insensibility to pain either through out the body or only a part of the body.

Analgesics :

Drugs which relieve pain by depressing the central nervous system without producing general anaesthesia are called analgesics. They are classified into two types namely narcotic and non - narcotic analgesics.

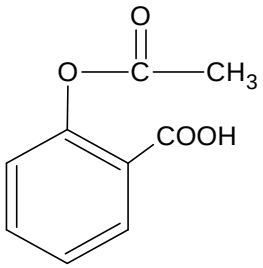
The term narcotic is applied to drugs which are sedatives as well as pain killers. Narcotic analgesics act on central nervous system of the patient and relieve severe pains. Over dosage of these drugs may lead to excess sweating; increased heart beat, drowsiness, respiratory depression etc.

Eg : Morphine and Cocaine.

Non - narcotic analgesics are mild analgesics relieve minor pains such as head ache, body pain etc. Non - narcotic analgesics do not produce addiction or respiratory depression like narcotics. The non - narcotic analgesics can be classified on the basis of their chemical structure into three groups namely salicylic acid and its derivatives, P - aminophenol derivatives and pyrazolone derivatives (eg : amino pyrine , Aspirin, paracetamol) These drugs even cure mild fevers and muscular inflammations eg: Aspirin, paracetamol etc. Antipyretics are the drugs used to reduce the body temperature in fever. Antipyretics have no effect on body temperature. The antipyretic compounds synthesised in the earlier days were also found to possess the analgesic properties. But, now some compounds are known which possess only the antipyretic property.

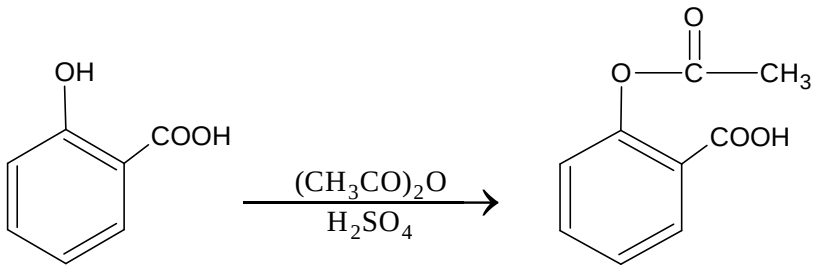
Eg : Aspirin, Paracetamol etc.

1) Aspirin (Acetyl Salicylic Acid) :



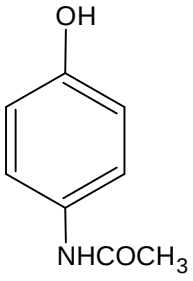
It is the most widely used drug in the world for pain relief. It is a product of salicylic acid. It can cure even slight fever. Hence aspirin is both analgesic and antipyretic.

Aspirin is synthesized by reacting salicylic acid with a mixture of acetic acid and acetic anhydride in the presence of sulphuric acid or by acetic anhydride in the presence of pyridine.



Aspirin is a white crystalline compound with bitter taste. It reduces fever and also removes minor pains such as head ache, muscular pain, knee pains, Rheumatic pains etc. Aspirin is hydrolysed into salicylic acid and absorbed into the blood stream. It inhibits the transmission of pain impulses to the brain. Excess dosage damages Kidneys and Lungs and may lead to coma or even to death.

2) Paracetamol (N - acetyl P - amino phenol) :

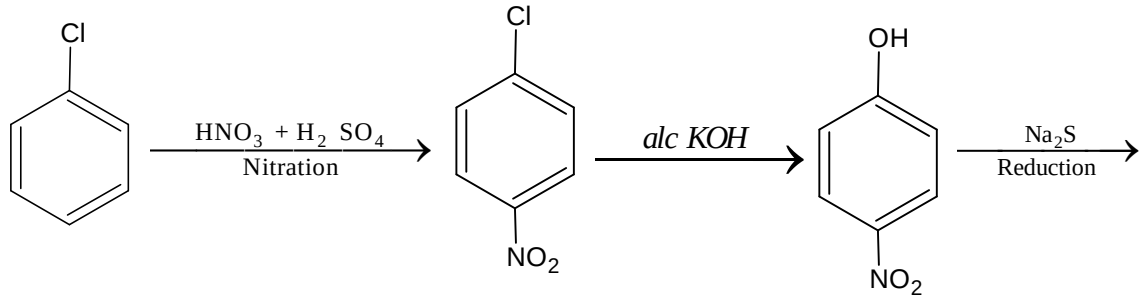


Trade name : Crocin ; metacin and colpol.

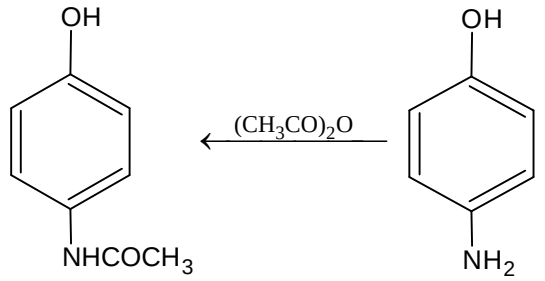
It is a product of P- amino phenol. It is used for relief from pain and fever. It is a good substitute for aspirin. It is available as tablets and syrup.

Synthesis of paracetamol :

Chlorobenzene on nitration forms P- Chloronitro benzene which is converted into P- nitrophenol by heating with alcoholic KOH. P - nitrophenol is then reduced to P- amino phenol with Na_2 S. P - amino phenol on acetylation with acetic anhydride gives paracetamol.



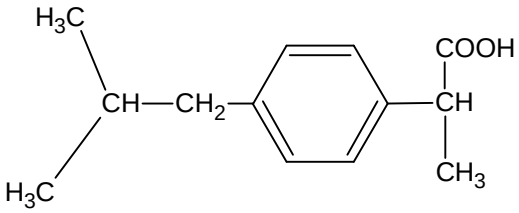
Chlorobenzene P- Chloro nitrobenzene P- Nitrophenol



Paracetamol P - aminophenol

Paracetamol is a white crystalline compound with bitter taste. It is analgesic and antipyretic with low inflammatory activity. Prolonged use of the drug may lead to skin allergy, anaemia etc. Over dosage of the drug may damage Liver and Kidney leading to death.

Ibuprofen (Brufen) :

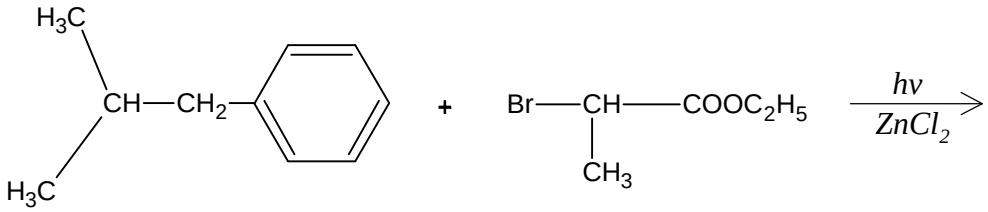


It is a product of propanoic acid. Its chemical name is 2- (4- isobutyl Phenyl) acid. It is analgesic and antipyretic with anti - inflammatory action.

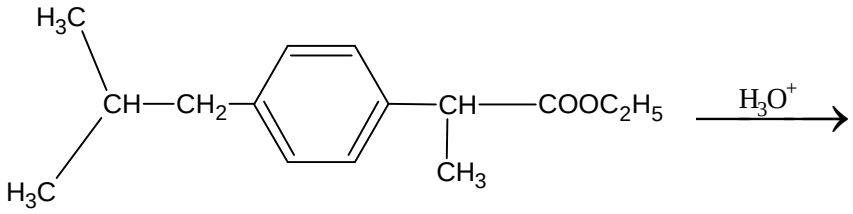
Synthesis :

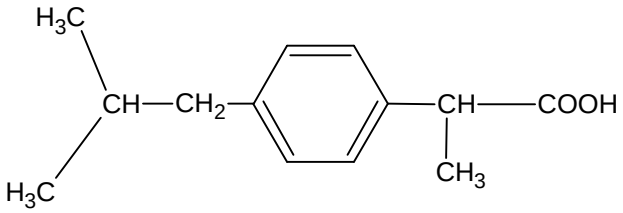
I Method :

Isobutyl benzene is subjected to a photochemical reaction with α - bromo ethyl propionate in presence of anhydrous $ZnCl_2$. The ester formed by this reaction on hydrolysis gives Ibuprofen.



Isobutyl benzene 2- Bromo ethyl propionate

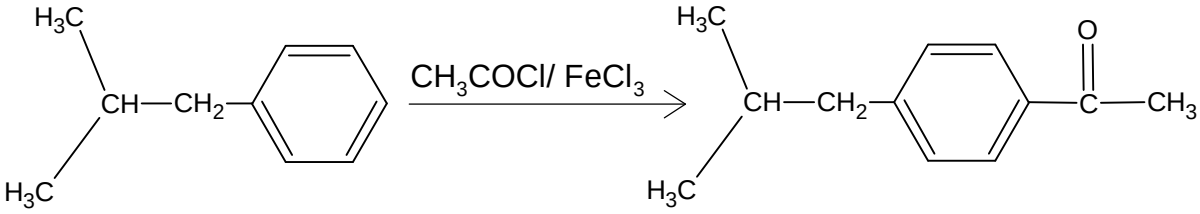




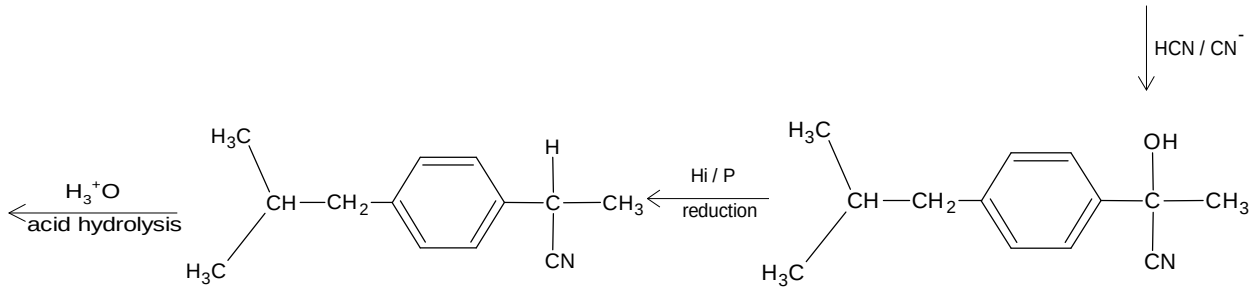
Ibuprofen

II Method :

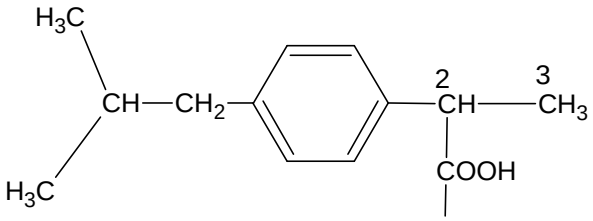
4 - Isobutyl benzene on Friedal - craft's acetylation gives 4 - isobutyl acetophenone which on reaction with HCN forms cyanohydrin. The cyanohydrin on reduction followed by hydrolysis gives Iboprofen.



4 - isobutyl aceto phenone



2 - (4 - isobutyl phenyl)
2 - Hydroxy - propane nitrite



Ibuprofen

Ibuprofen is a white powder, insoluble in water. It is a non - steroidal anti-inflammatory drug. In small doses it is as effective as Aspirin. Over dosage of the drug may cause gastric pain, ulcer formation and damage to the liver.

Anaesthetics :

The term anaesthetic is derived from the Greek word, anaesthesia means insensibility. Hence anaesthetics may be defined as drugs which produce insensibility to the vital functions of all types of cells especially those of the nervous system. An anaesthetic produces temporary insensibility to pain or unconsciousness all over the body or in a particular organ which has to undergo surgical operation. Anaesthetics are classified into two types namely General anaesthetics and local anaesthetics basing on their application.

General Anaesthetics :

General anaesthetics depress the central nervous system. They produce total loss of sense of pain. They produce unconsciousness all over the body. General anaesthetics have been further sub- divided into volatile or gaseous and non- volatile or fixed anaesthetics depending upon their mode of administration. Volatile or gaseous anaesthetics are administered by inhalation while non volalile anaisthetics are by injection.

Volatile general anaesthetics :

a) Nitrous Oxide, N_2O :

Nitrous oxide was the first anaesthetic. It is prepared by heating ammonium nitrate upto 200°c.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

It is used only in dental operations and in a few minor surgical operations.

Ether ($CH_3\ CH_2O\ CH_2\ CH_3$) :

Systhesis :

1. Diethyl ether is prepared by heating ethyl alcohol with Conc H_2SO_4 at 140°c.

$$C_2H_5OH + HO\ H_5C_2 \xrightarrow[140^0C]{Conc.H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

2. Williamson's Synthesis : Diethyl ether is prepared by treating ethyl chloride with sodium ethoxide.

$$C_2H_5Cl + NaO\ H_5C_2 \rightarrow C_2H_5OC_2H_5 + NaCl$$

It is a colourless, volalile, highly inflammable liquid with a characteristic smell. It brings quick anaesthesia by directly attacking the central nervous system.

Sir James Simpson popularised the use of ether in surgical operations. But due to its easy formation of explosive and dangerous peroxide on exposure to light and its high inflammability it was not used for a long time as an anaesthetic.

b) Chloroform, ($CHCl_3$) :

Chloroform is among the most widely used general anaesthetics.

1. Chloroform is prepared by heating ethyl alcohol with bleaching powder and water.

$$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

$$C_2H_5OH + Cl_2 \rightarrow CH_3CHO + 2HCl$$

$$CH_3CHO + 3Cl_2 \rightarrow CCl_3\ CHO + 3HCl$$

$$2CCl_3\ CHO + Ca\ (OH)_2 \rightarrow CHCl_3 + (HCOO)_2\ Ca$$

2. It is also obtained by heating acetone with bleaching powder and water.

$$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

$$CH_3 . CO. CH_3 + 3Cl_2 \rightarrow CCl_3 . CO. CH_3 + 3HCl$$

$$CCl_3 . CO. CH_3 + Ca(OH)_2 \rightarrow CHCl_3 + (CH_3COO)_2 Ca$$

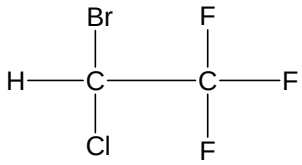
Chloroform is a colourless, Volatile liquid with a characteristic sweet smell. Chloroform is non-inflammable and only small quantity is sufficient to produce surgical anaesthesia. For anaesthetic purposes, it must be kept protected from light and air, otherwise it undergoes oxidation in air in the presence of light forming toxic substance carbonyl chloride or phosgene.

$$CHCl_3 + \frac{1}{2}O_2 \rightarrow COCl_2 + HCl$$

So purity of chloroform should be checked before its use as anaesthetic. Pure chloroform does not give white precipitate with $AgNO_3$. Due to its decomposition it should be stored in amber-coloured bottles. Due to the oxidation of chloroform other safer agents are preferred.

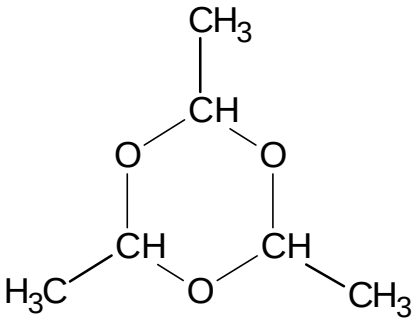
c) Halothane : Fluothane, (CF_3CH Br Cl) :

It is a substituted product of ethane. Chemically it is 2 - bromo - 2 - chloro- 1,1,1, trifluoro ethane.



It is a colourless liquid. It is the most widely used anaesthetic agent at present. It has been introduced recently in hospitals as a general volatile anaesthetic. It is nearly four times more active than ether with a therapeutic index twice that of ether. It is not inflammable. It is quick in action. Patient becomes normal after the effect of the drug.

d) Paraldehyde, [$(CH_3CHO)_3$] :



2,4,6, - trimethyl trioxane

It is a trimer of acetldehyde. Paraldehyde is prepared by the reaction of acetaldehyde with conc. H_2SO_4 at room temperature.

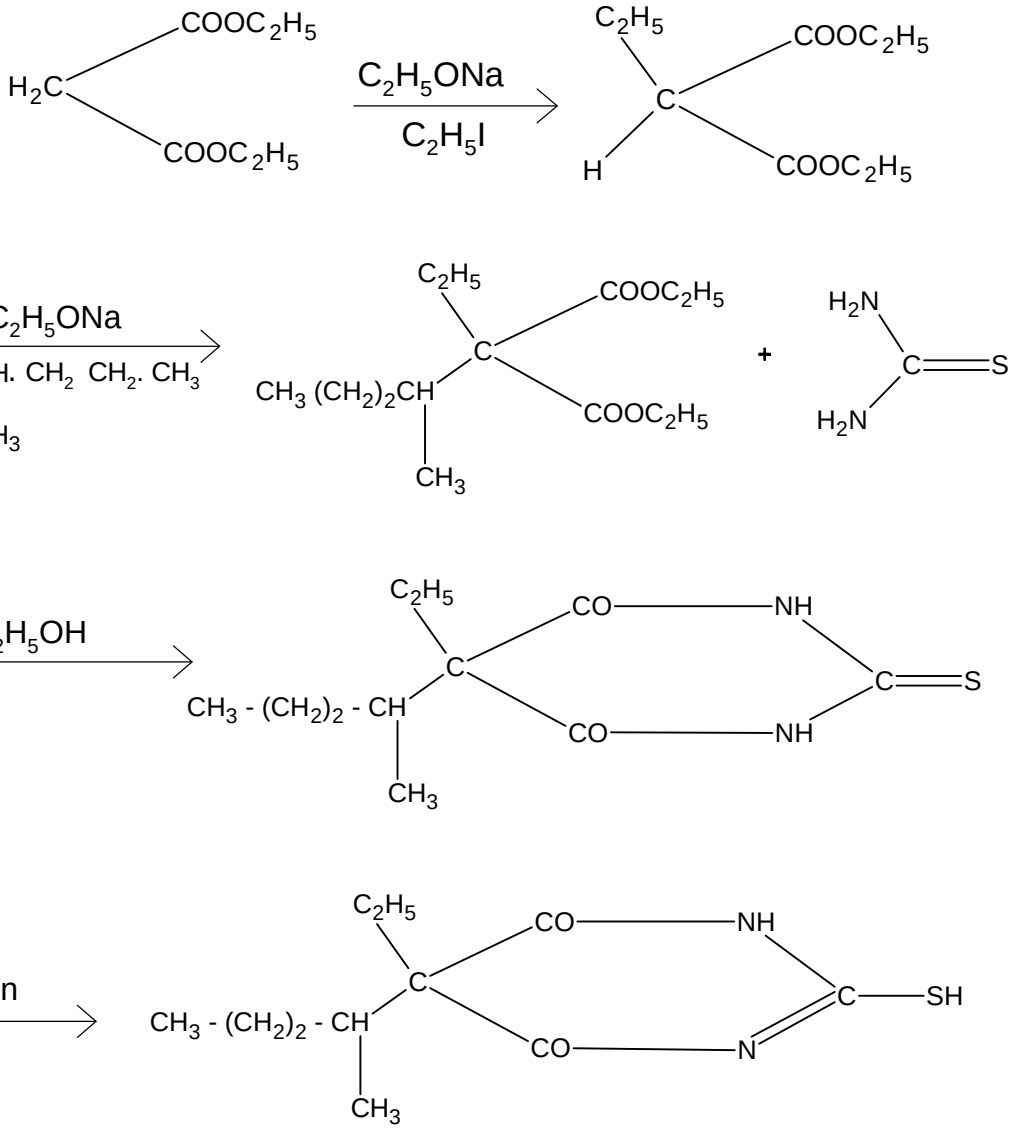
It is a colourless liquid, freely soluble in water. It acts as anaesthetic and also as a hypnotic. It produces sound sleep. It is also used in delivery times as pain reliever.

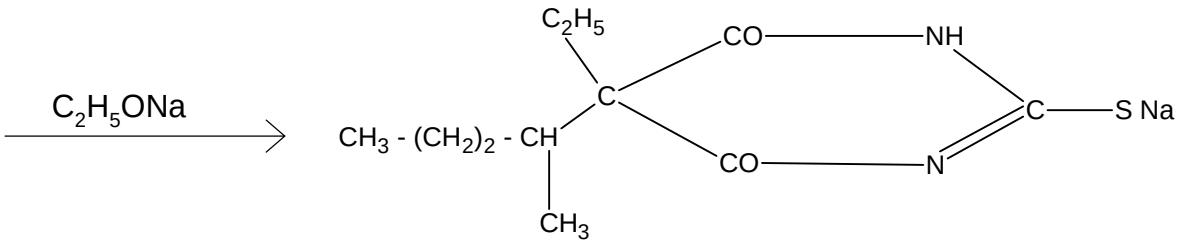
e) Thiopental Sodium :

It is also known as pentothal sodium. It is one of the most widely used non- volatile general anaesthetic. It is administered mainly intravenously.

Synthesis :

Thiopental Sodium is synthesised from malonic ester. Malonic ester is converted into ethyl malonic ester by treating with sodium ethoxide and ethyl iodide. It is then treated with sodium ethoxide and 2- iodopentane to form ethyl 1- methyl butyl malonic ester which is then heated in presence of sodium ethoxide with thiourea to produce thiopental sodium.





Thiopental Sodium

Thiopental Sodium is available as White powder or Yellowish White powder. It is unstable in solution. The drug is stored in the drystate in sealed ampules. During utilization the drug is mixed with distilled water and is then injected into the body. It is used in orthopedic operations. It is also used to produce muscular relaxation in the shock treatment of mentally depressed patients. It is also used to control the convulsions, in tetanus and in dental surgery for the extraction of teeth.

This drug is not recommended for operations requiring long anaesthesia.

It is prohibited for patients with asthma and heart diseases. The drug is not used in case of patients having haemorrhage (Bleeding due to breaking of capillary walls).

Model Questions :

1. What are analgesics ? How are they classified? Give the structure of one narcotic and non-narcotic analgesics and explain its physiological activity.
2. What are antipyretics ? Describe the preparation of paracetamol and give its uses.
3. Give the systhesis and uses of the following compounds.
   (a) Aspirin
   (b) Ibuprofen
   (c) Thiopental Sodium
4. What are general anaesthetics ? How do you classify them ? Give suitable examples.
5. Write notes on the following anaesthetics -
   (a) Chloroform
   (b) Paraldehyde
   (c) Ether
6. Give an account of Halothane and Thiopental sodium.

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LESSON - 4

HYPNOTICS, SEDATIVES AND TRANQUILISERS

The central nervous system consists of the brain and the spinal card and is able to control the thought processes, emotions, senses and motor functions. Hypnotics, sedatives and tranquilizers are used for relieving anxiety and tension. Sedatives and hypnotics are used in sleep disorders. Hypnotics and sedatives give relief by acting on nervous system.

Hypnotics are central nervous system depressants that produce sleep and reduce resstlesseness and emotional tension.

A hypnotic compels the patient to sleep and induces a stronger form of depression.

Sedatives are central nervous system depressants that reduce nervous tensions and give relaxation and rest without producing sleep. A sedative produces mild depression and calms anxiety without causing drowsiness. A sedative is used to induce mild relaxation.

There is no clearcut difference between a sedative and a hypnotic. They differ only in their degree of action.

Some of these drugs when administered cause sedation, larger doses cause hypnotic sleep and still larger doses produces anaesthesia and even death in some cases.

Patient $\rightleftharpoons$ Sedation $\rightleftharpoons$ Hypnosis $\rightleftharpoons$ Anaesthesia $\rightleftharpoons$ Coma $\rightarrow$ Death

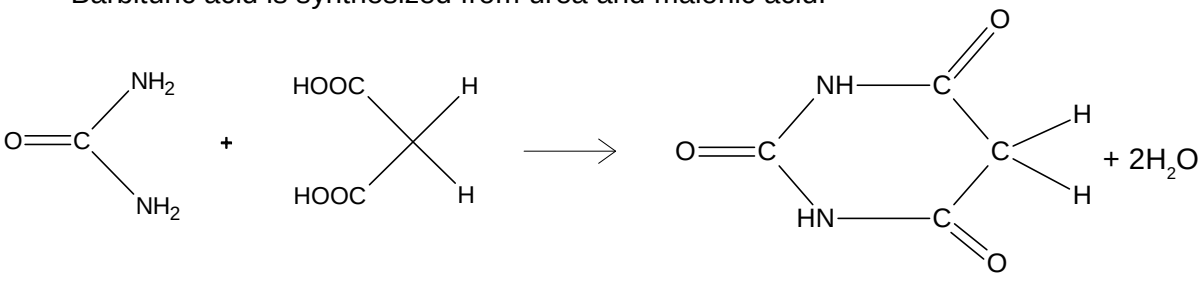
But in some cases a compound will have only one effect. eg : Simple bromides are good sedatives and possess little or no hypnotic action. Similarly, certain powerful hypnotics, eg : Thiopentone cannot be used as sedatives.

Barbiturates :

Barbiturates are the most frequently used drugs for sedation of the central nervous system. They have the capacity of producing depressive action of the central nervous system ranging from mild sedation through production of sleep, to deep anaesthesia and finally to death, depending on the dose.

The first hypnotic barbiturate was introduced by Fischer in 1903 under the trade name of Veronal. Barbiturates are derivatives of barbituric acid (malonyl urea).

Barbituric acid is synthesized from urea and malonic acid.



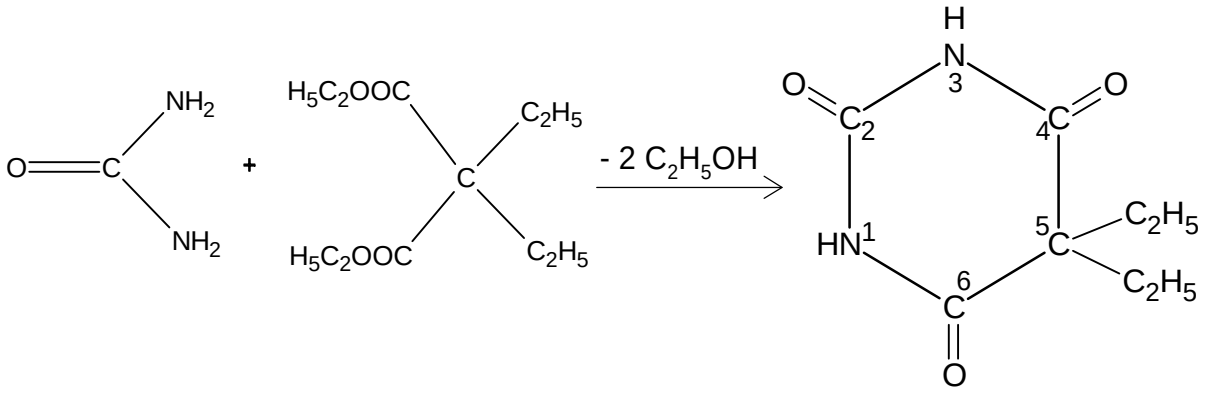
Urea Malonic acid Barbituric acid

Barbituric acid, itself is not a CNS depresant and does not possess hypnotic properties. But the derivatives of barbituric acid obtained by the replacement of the two hydrogen atom on the carbon atom in position ' 5' by alkyl or aryl groups are called barbiturates and get hypnotic property.

1) Barbitone or Barbitol:

5, 5 - diethyl barbituric acid.

It is also a long action hypnotic. It is prepared by the condensation of diethyl malonic ester with urea.



Barbitol is a colourless substance, slightly soluble in water and highly soluble in alcohol and ether.

The drug is available in the form of tablets.

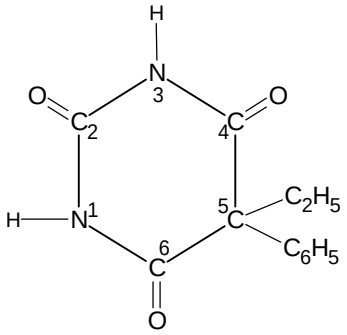
Its aqueous solution is acidic in nature.

It is a powerful hypnotic and produces natural and dreamless sleep within 15 - 30 minutes.

Barbitol has a drawback of having low therapeutic index (about 2) so, a slight over dosage of the drug may lead to death of the patient.

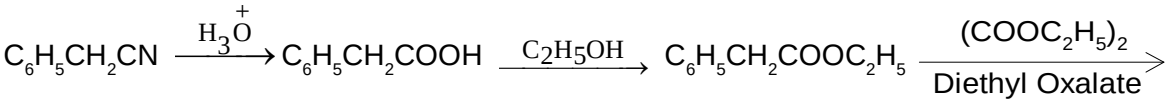
2) Phinobarbitone or Phenobarbitol :

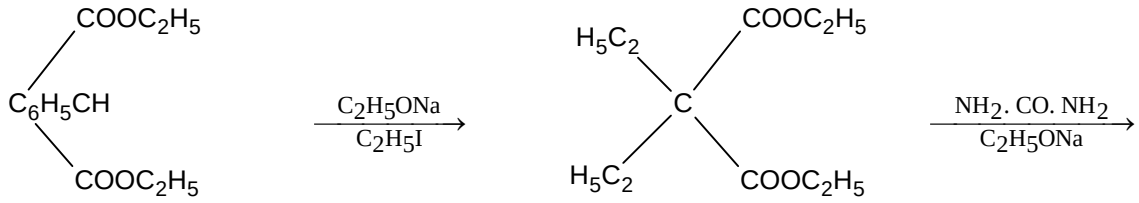
5 - ethyl - 5- phenyl barbituric acid is known as phenobarbitol. It is commonly known as Gardinol.



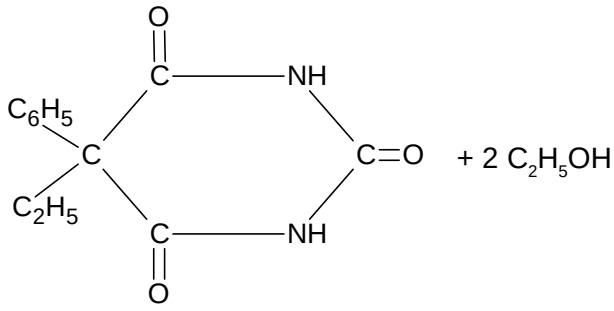
Synthesis :

It is prepared from benzyl cyanide in the following way.





Phenyl, ethyl malonic ester



Phenobarbitol

It is a white crystalline compound with slight bitter taste.

It is slightly soluble in water. It is an important sleeping tablet and works as a sedative and hypnotic. The drug provides relief in hyper tension, sleeplessness, and restlessness.

It causes illusion and hence people become addicted to the drug.

It is used in the treatment of Epilepsy.

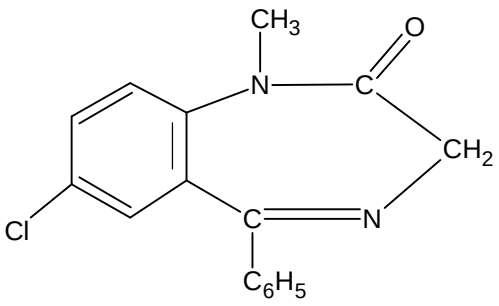
It should not be prescribed to drunkards and asthma patients.

Tranquilizers :

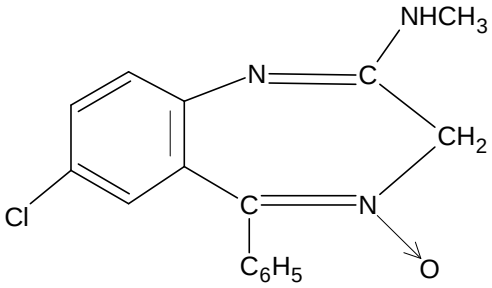
Tranquilizers are the drugs used in the treatment of mental disorders. They make the mind free and calm from disturbences and give relaxation and rest without producing sleep.

Eg :

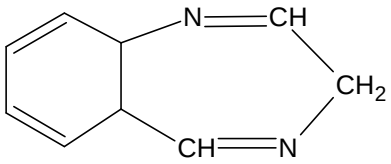
i) Diazepan :



ii) Chlordiazepoxide :



iii) Benzodiazepoxide :



Action of these drugs is almost similar to barbiturate hypnotics but they produce less sedation. Drunkards when suddenly stop drinking alcohol, they undergo severe mental tension. In such cases diazepam is used for relieving tension and anxiety in them. Their prolonged use cause side effects such as drowsiness, nausea, weakness etc.

Model Questions :

1.What are hypnotics, sedatives and tranquilizers ? Explain each with one example.

2. Write an account on barbiturates.

3. Give the preparation and uses of phenobarbitol and barbitol.

4. What are tranquilizers ? Give examples and represent their structures.

5. Write a note on hypnotics and sedatives.

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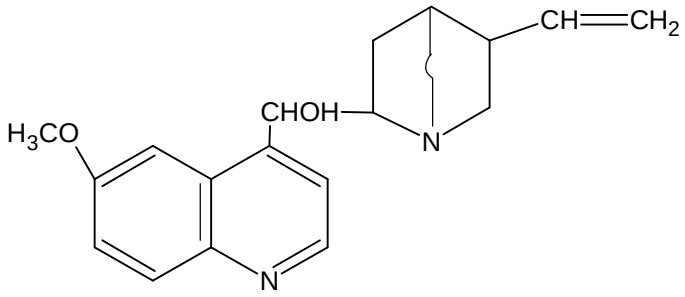
LESSON - 5

ANTIMALARIALS

Malaria is the most wide spread of all human diseases. The symptoms of malaria are periodic fever, anaemia and enlargement of liver and spleen. It is caused when female anopheles infected by few species of plasmodium bites the human being. Due to the co-operation of all the countries and WHO, this disease has been controlled to certain extent in the last 20 years. The four species i.e. Plasmodium Vivax; Plasmodium malariae ; Plasmodium Ovale and Plasmodium falciparum are responsible for malaria in man. The medicines used for the treatment of malaria fever are called antimalarials. They are divided into two types namely Natural antimalarials and synthetic antimalarials.

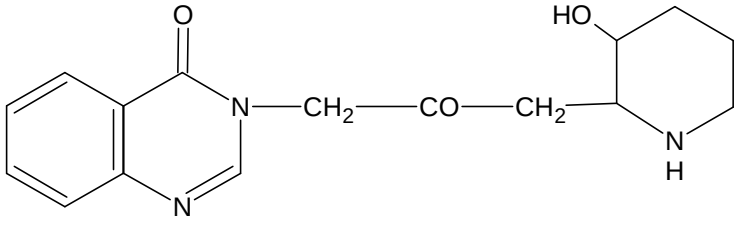
Natural antimalarials :

The antimalarials isolated from natural sources (plants) are called natural antimalarials. In the early days, cinchona bark was used as a remedy for malaria. The medicinal value of cinchona bark was found to be due to the presence of certain alkaloids i.e. Quinine ; Cinchonine ; Quinidine and Cinchonidine out of which Quinine is the most important one.



Quinine

The root of the chinese plant chiang shan has also been used as an antimalarial. The antimalarial activity of the root is due to the presence of two alkaloids namely febrifugine and isofebrifugine.



Febrifugine

Synthetic antimalarials :

The demand for synthetic antimalarials is increasing day by day. So efforts were made to find synthetic substitute for quinine and a number of compounds were prepared and tested against malarial parasites.

The synthetic antimalarials can be classified as follows -

i) 8 - Amino quinoline derivatives

ii) 4- Amino quinoline derivatives

iii) Acridine derivatives

iv) Pyrimidine derivatives

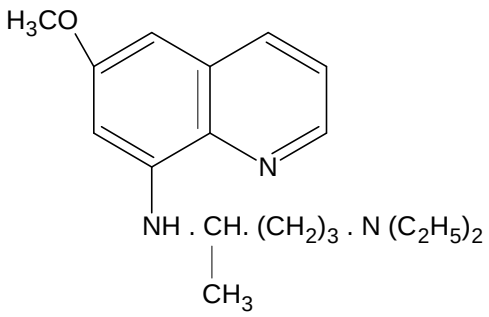
v) Biguanide derivatives

vi) Sulphones

vii) Miscellaneous antimalarials.

8 - Amino quinoline derivatives :

Pamaquine or Plasmaquine or Plasmochin :

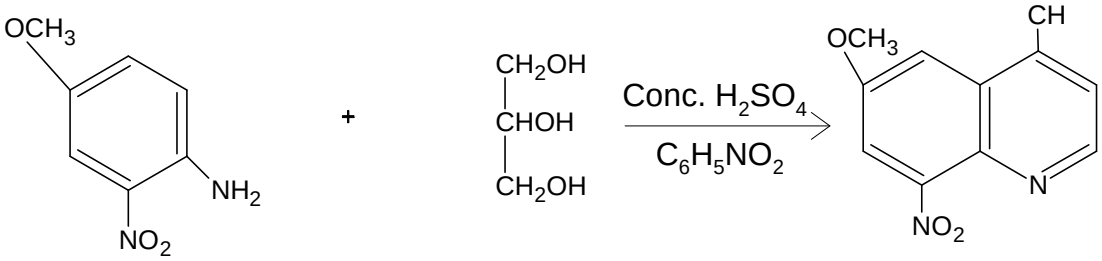


Pamaquine

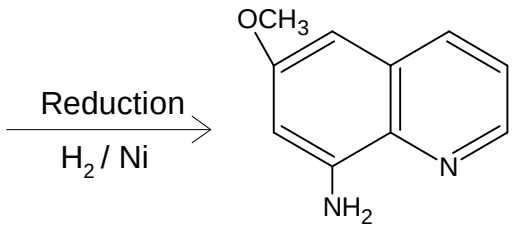
Synthesis :

Pamaquine is prepared by the condensation of 6 - methoxy- 8- amino quinoline with 1-diethyl amino - 4- bromopentane.

i) Synthesis of 6 - methoxy - 8 - amino quinoline.

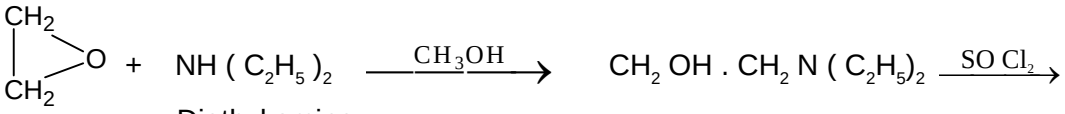


3 - nitro - P- anisidine Glycerol



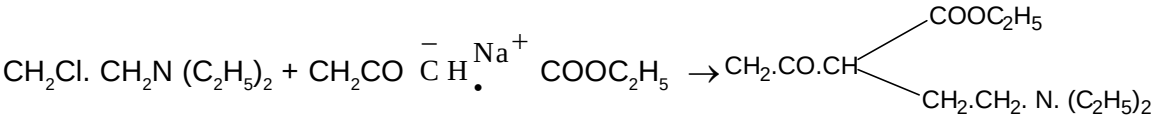
6- methoxy - 8 - aminoquinoline

ii) Synthesis of 1-diethyl amino - 4- bromopentane.



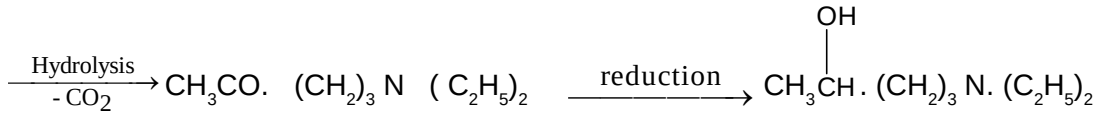
Diethyl amine

Ethylene Oxide

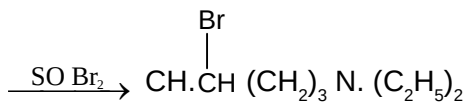


Choloroethyl diethyl amine

Monosodio aceto acetic ester

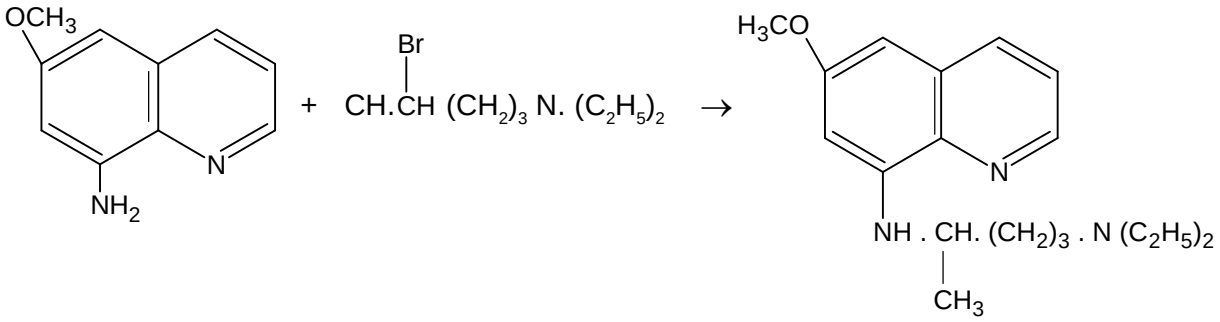


Amino alcohol



1-diethyl amino - 4- bromopentane.

iii) Codensation of 6- methoxy - 8 - aminoquinoline with 1-diethyl amino - 4- bromopentane gives pamaquine.



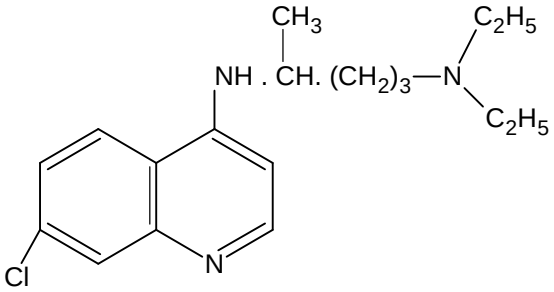
Pamaquine

Pamaquine is a gametocidal agent. In combination wiht quinine it has been used to reduce the relapse rate in vivax malaria. However, it is fairly toxic.

Side effects. Loss of appetite, nausea, abdominal pain, muscle cramps are some of the ill effects observed on the prolonged use of the drug. Hence it is not popularised.

4 - Amino quinoline derivatives :

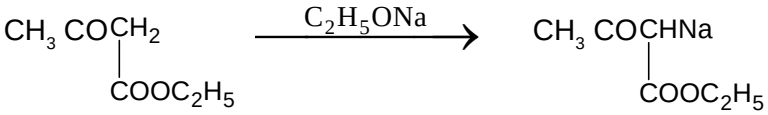
Eg : Chloroquine



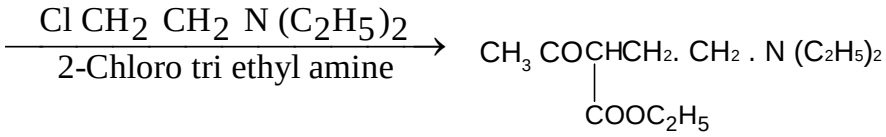
Synthesis :

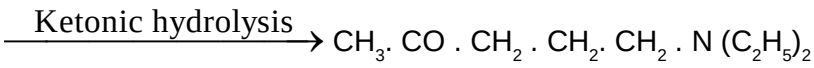
Chloroquine is prepared by condensing 4,7 - dichloro quinoline with 1- diethyl amino - 4- amino pentane.

i) Synthesis of 1-diethyl amino - 4- amino pentane.

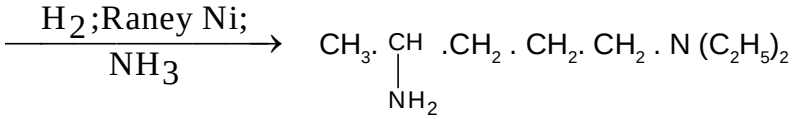


Aceto acetic ester





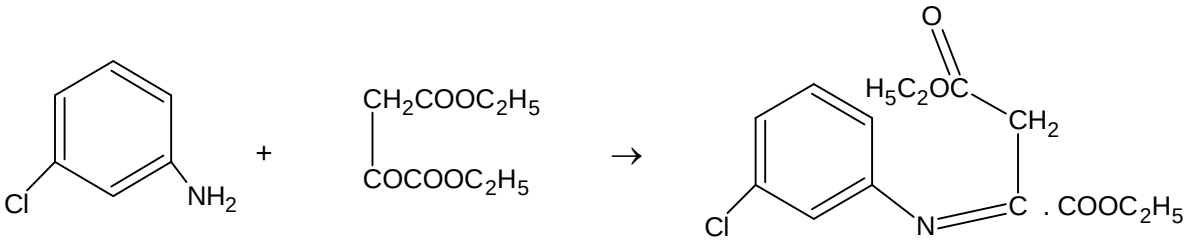
5-diethyl amino - 2- amino pentane.

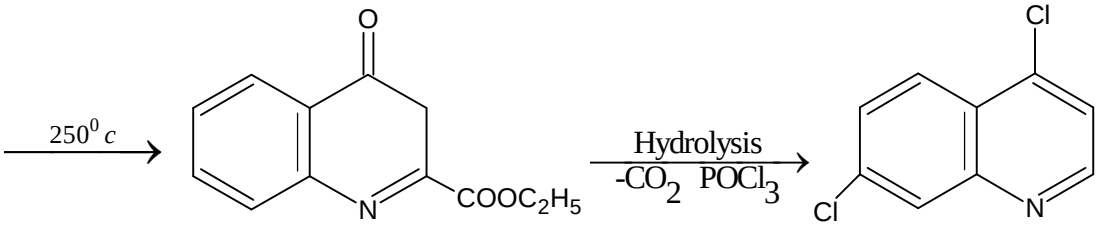


1-diethyl amino - 4- amino pentane.

ii) Synthesis of 4,7 - dichloro quinoline.

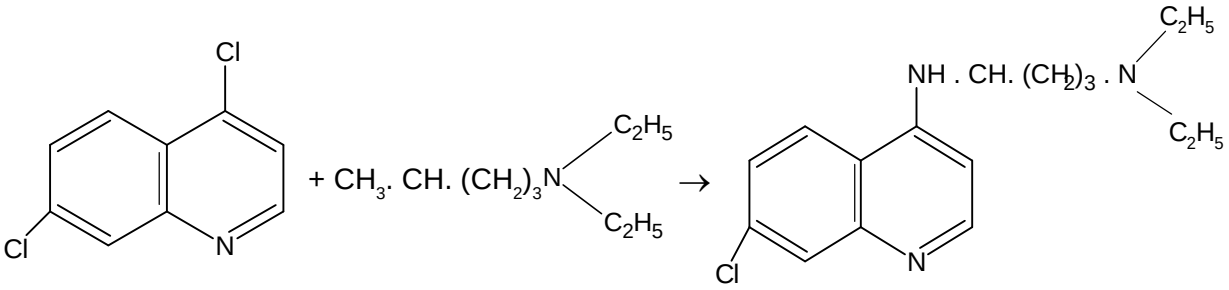
The oxalyl acetic ester on condensation with m- chloro aniline forms a product which on heating to about 250°c undergoes Cyclisation to form ethyl ester of 7 - chloro- 4- hydroxy quinoline-2- carboxylic acid which on heating undergoes decarboxylation and the product formed when treated with phosphorus oxytrichloride gives 4,7 - dichloroquinoline.





4, 7 - dichloro quinoline

iii) Condensation of 4, 7 - dichloro quinoline with 1 - diethyl amino - 4 - aminopentane gives chloroquine.



chloroquine.

It is a white or slightly yellowish crystalline powder, slightly soluble in water. Its hydrochloride is used for injuctions.

Its sulphate (Nivaquine) and phosphate are used as tablets.

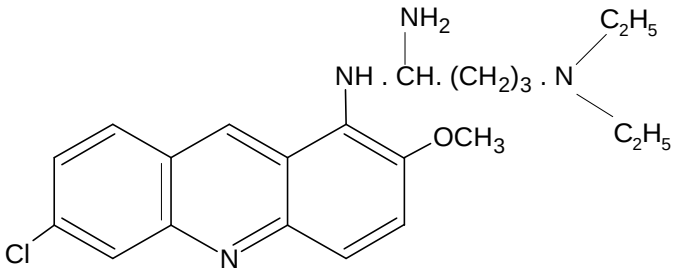
It is active against plasmodium Vivax and Plasmodium falciparum and it is four times powerful than normal quinine.

It does not completely cure malaria and relapse occurs after one to three months.

It has side effects such as general uneasiness in epigastrium, loss of appetite, Vomiting, diarrhoea and occasional insomnia. But all of these symptoms disappear as soon as the use of the drug is stopped.

Acridine derivatives :

Eg : Mepacrine (atabrin ; atebrin ; Quinacrine or Chinacrine)

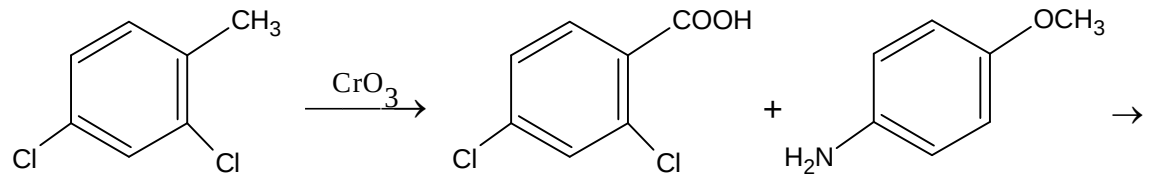


Mepacrine

Synthesis :

It is prepared by the condensation of 2 - methoxy - 6, 9-dichloroacridine with 1- diethyl amino-4-amino pentane.

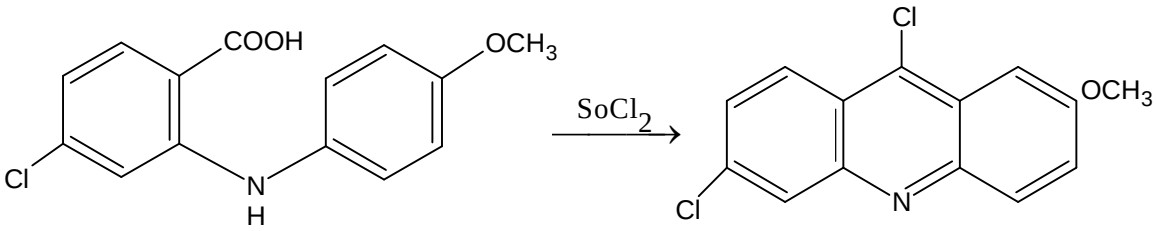
i) Synthesis of 2- methoxy - 6, 9 - dichloro acridine :



2,4-dichloro acridine

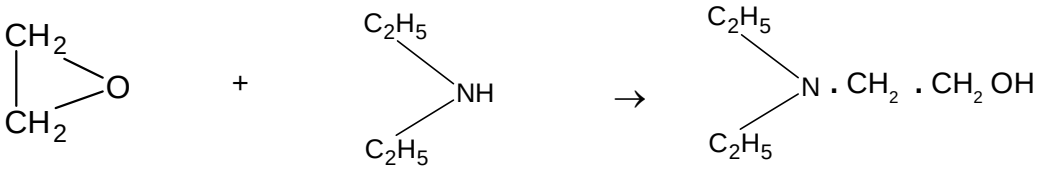
2,4-dichloro benzoic acid

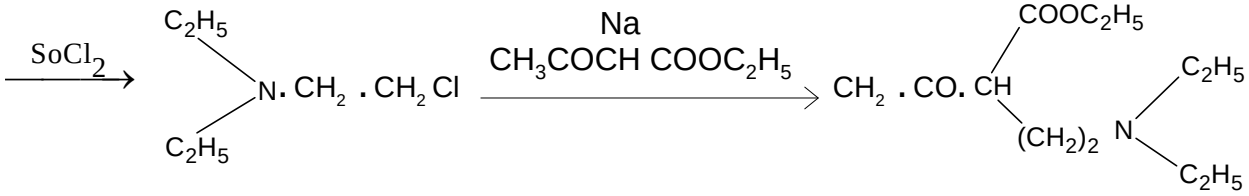
P- anisidine

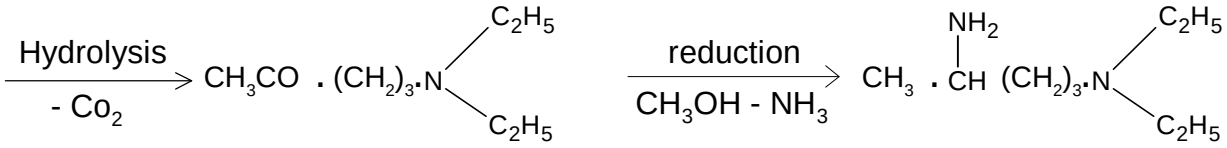


2- methoxy - 6, 9 - dichloro acridine

ii) Synthesis of 1- diethyl amino - 4- amino pentane :

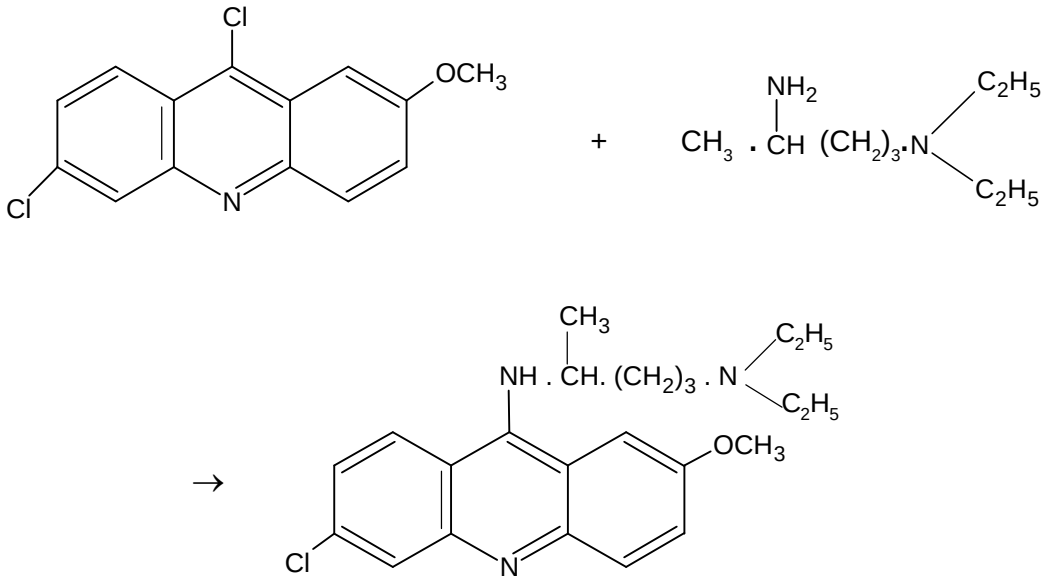






1-diethyl amino - 4- amino pentane.

iii) Condensation of 2 - methoxy-6,9-dichloroacridine with 1- diethyl amino 4-aminopentane gives Mepacrine.



Mepacrine

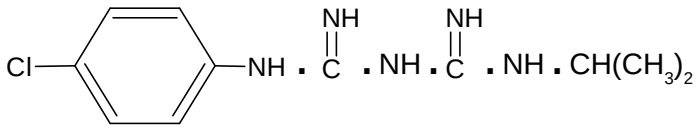
Mepacrine is an acridine derivative. It can eliminate plasmodium vivax and plasmodium malariae. It is used in the treatment of black water fever.

Side Effects :

Its prolonged use may cause change in skin colour (yellow). It is bitter in taste. Hence it is replaced by chloroquine.

Biguanide derivatives :

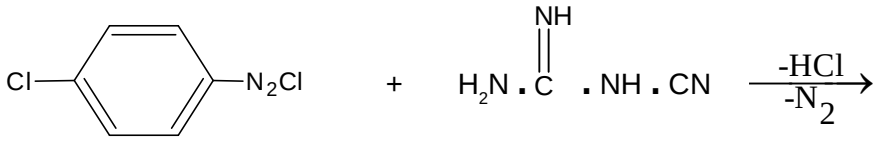
Eg : Paludrine (Proguanil ; Chlorognanide)



Paludrine

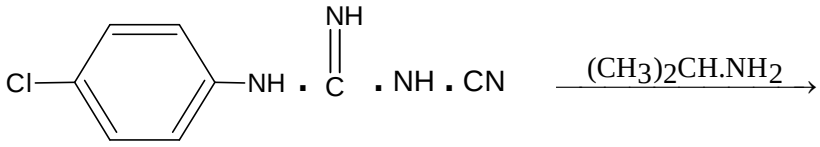
Synthesis :

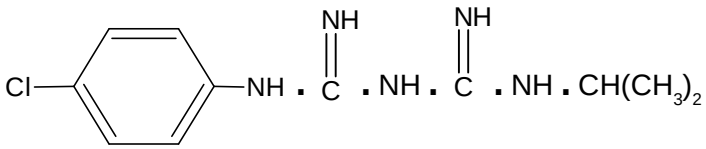
It is prepared by coupling P- chloro benzene diazonium chloride with cyanoguanidine and then treating the product with isopropyl amine in the presence of $CuSO_4$.



P- Chloro benzene diazonium Chloride

Cyanoguanidine





Paludrine

Paludirine is colourless, tasteless, least toxic antimalarical and hence it is widely used. It inhibits folic acid synthesis. It is used in the treatment of malaria fever caused by plasmodium falciparum. It has least side effects.

MODEL QUESTIONS :

1. What are antimalarials ? How are they classified ? Explain the synthesis of pamaquine.
2. Discuss the synthesis of chloroquine and mention its bad effects.
3. Give the synthesis of mepacrine . Discuss its side effects ?

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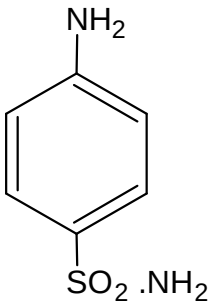
Lesson - 6

SUPHONAMIDES, SULPHA DRUGS OR ANTIBACTERIALS

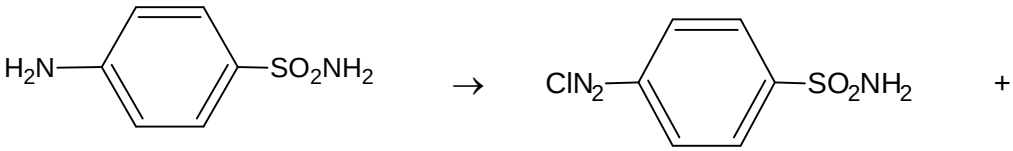
Sulpha drugs are the derivatives of Sulphanilamide.



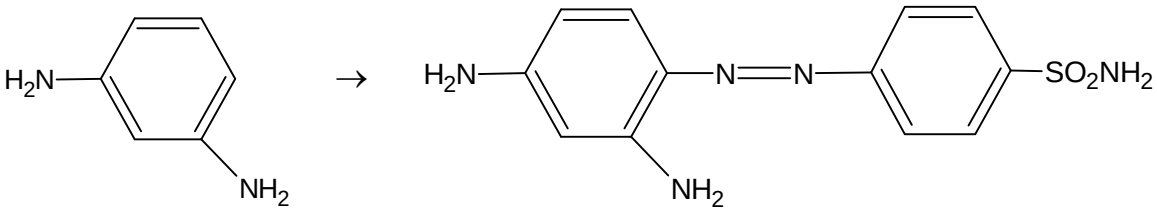
These drugs are widely used for the cure of bacterial infection in humans.

They are not only cheap and safe antibacterials but efforts made to determine their mechanism of action have given chance to investigate other antimetabolites of therapeutic interest. At present sulphanilamides have been largely replaced by antibiotics in the treatment of bacterial infections. yet they are still used either alone or in combination with an antibiotic.

while preparing some synthetic dyes Glemo succeded in preparing sulphanilamide in 1908. Paul Ehrlich's idea on dye stuffs and their staining properties to the bacterial cell stimulated Gerhard Domagk in 1930 for testing the effect of certain dyes on germs in mice. Gerhard Domagk's daughter got an infection in her finger which could not be stopped by any means. At that moment, Domagk gave his daughter oral doses of an azodye called prontosil by which the girl recovered completely. Prontosil dye was found to be active against homolytic streptococci. The dye was prepared by diazotising sulphanilamide followed by coupling with m- phenylene diamine.

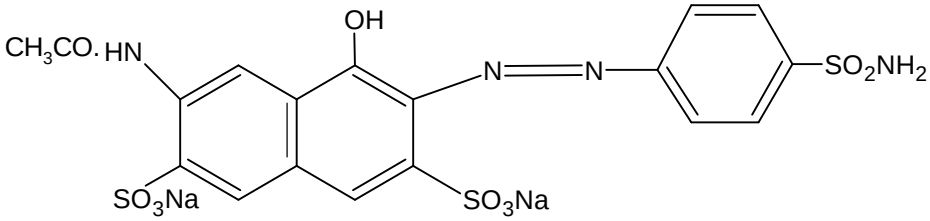


Sulphanilamide Diazotised Sulphanilamide

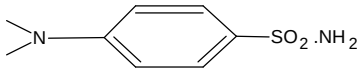


m- Phenylene diamine Prontosil

In short period of time the drug became very popular. It was used in the treatment of streptococcal sore throat, acute endo carditis etc. Due to its low solubility, it was generally used as its hydrochloride as a soluble prontosil. Later on it was replaced by prontosil soluble which has greater solubility and superior bactericidal activity.



Prontosil Soluble

Later on , prontosils are degraded in Vivo to sulphanilamide which led to the fact that the activity of prontosils as drug is due to the presence  grouping. Finally, it was confirmed that sulphanilamide part was the real active group in prontosils. Since that time, thousands of substituted Sulphanilamides have been prepared and tested for their antibacterial activity. For many years, Sulphonamides were the chief medical weapons against many gram positive bacterial diseases but now - a - days these have been superceeded by the much toxic more effective drugs called antibiotics.

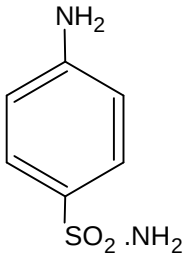
The sulphlanilamides were found to be active against several types of bacteria and hence they are used in the treatment of various diseases like pneumonia, gonorrhea, blood poisoning, sinus infections, some types of meningitis etc. The sulpha drugs are more effective with less toxicity.

Bacteria synthesize folic acid which is necessary for their growth. The compound required for the synthesis of folic acid is P- amino benzoic acid (PABA). But the Sulpha drugs prevent the synthesis of folic acid from P-amino benzoic acid. In the absence of folic acid bacterial cells disintegrate and become functionless.

Thus sulphanilamide inhibits the growth of bacteria. Hence sulpha drugs act as antibacterials.

Examples :

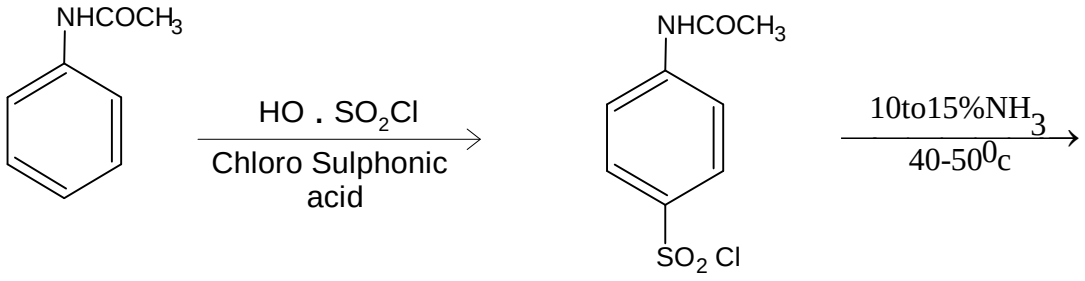
i) Sulphanilamide (Sulphonamide or P- aminobenzene Sulphonamide) :



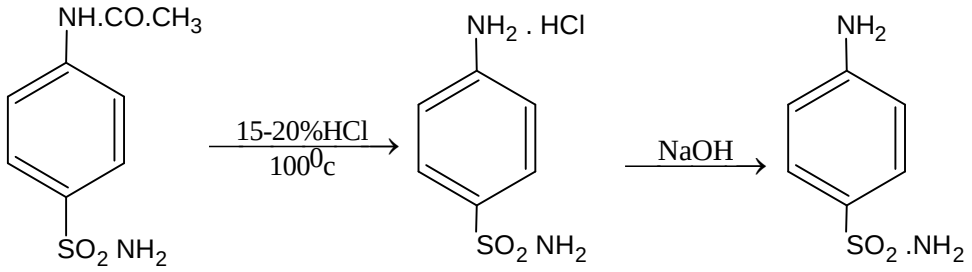
It is the parent compound of Sulpha drugs.

It can be prepared by the following methods.

a) From acetanilide :

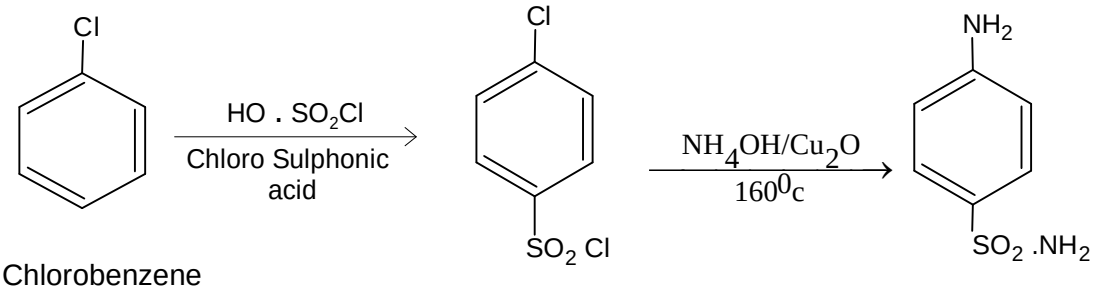


Acetanilide P- N- acetyl Sulphanilyl Chloride



P- N- acetyl Sulphanilylamide Sulphanilylamide

a) From Chlorobenzene :

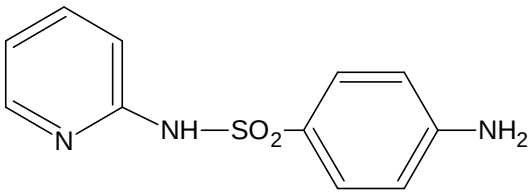


Chlorobenzene

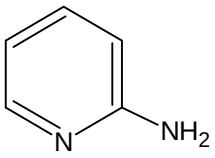
Sulphanilamide is widely used in the control of cocci infections such as pneumococci ; streptococci, gonococci and meningococci.

Now - a - days, sulphanilamide is replaced by its various derivatives which are less toxic, more effective and more specific. All the important substituted sulphonamides are either 1-or 4-substituted sulphanilamides.

ii) Sulphapyridine (N^1-2-pyridyl Sulphanilamide) :



It is obtained by the condensation of P-N-acetyl sulphanilyl chloride with 2-amino pyridine in presence of pyridine as a solvent followed by alkaline hydrolysis of the product.



2 - aminopyridine

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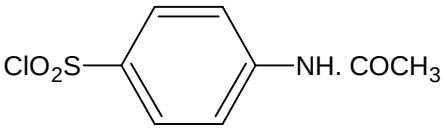
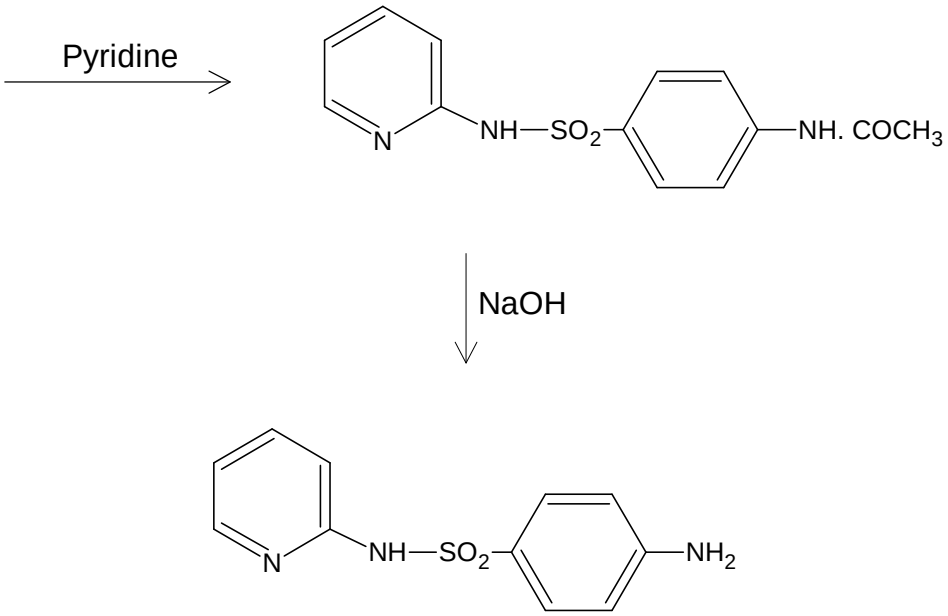


P- N- acetyl sulphanilyl chloride

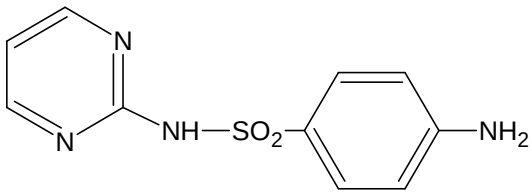


Sulphapyridine is used in the treatment of streptococcai and meningocOccai infections. It is used in curing pnenmonia.

It causes severe nausea.

It is readily acetylated and the acetyl sulpha pyridine crystals deposited in the kidneys ultimately damage kidneys.

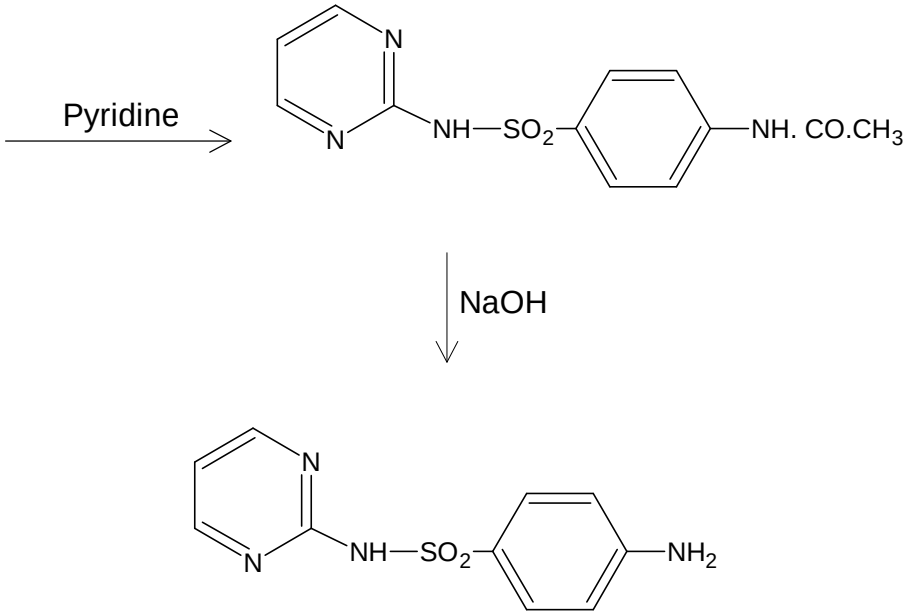
iii) Sulpha diazine or Sulphapyrimidine (N^1-2-Pyrimidinyl Sulphanilamide) :



Sulphadiazine

It is prepared by the condensation of 2-aminopyrimidine with P-acetyl sulphanilyl chloride in presence of pyridine and then hydrolysing the product with alkali.

2 - amino Pyrimidine + P- acetyl sulphanilyl Chloride



Sulphadiazine

it is about 8 times as active as sulphanilamide.

it is used against all the coccus infections.

It is less toxic than most of the other Sulphonamides. Hence it is the most widely used sulpha drug.

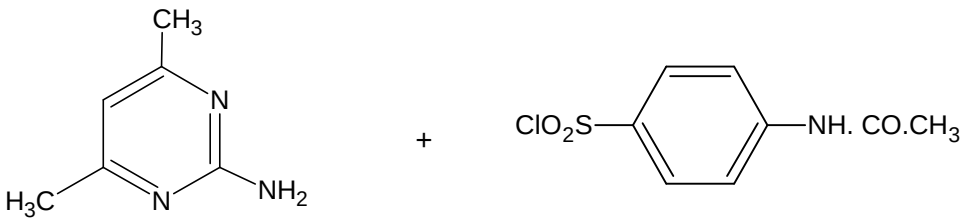
It is absorbed slowly and also excreted slowly.

iv) Sulphamethazine Or Sulphamezathine :

Its Chemical name is N^1–2– (4,6- dimethyl Pyrimidinyl Sulphanilamide

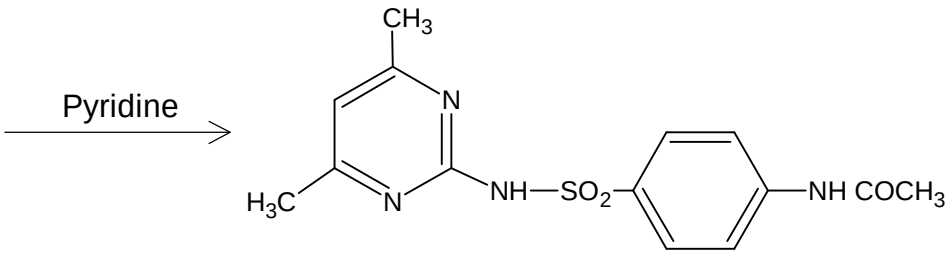
Synthesis :

It is prepared by hte condensation of P-N-acetyl Sulphanilyl Chloride and 2- amino - 4,6-dimethyl pyrimidine and then hydrolysing the product with alkali.

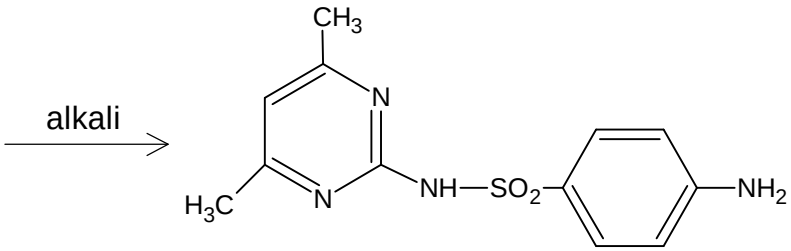


2 - amino- 4, 6 - dimethyl Pyrimidine

P- acetyl sulphanilyl Chloride



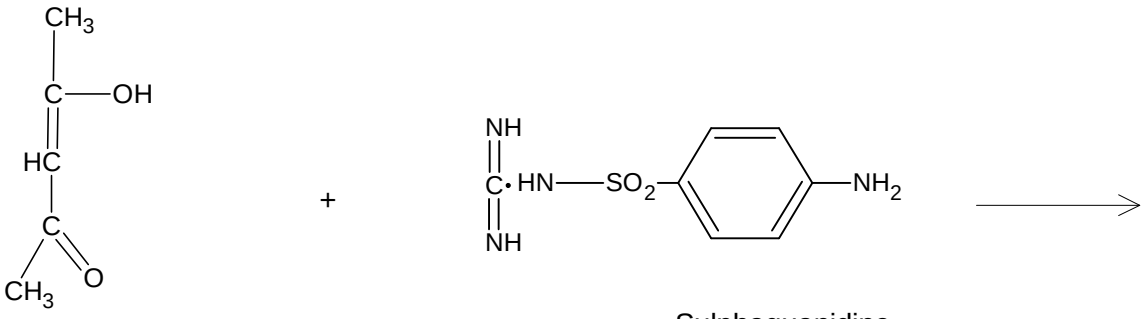
Sulphamezathine



Sulphamethazine

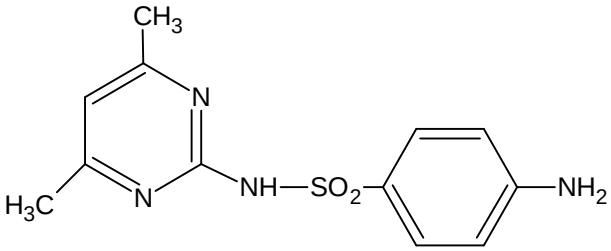
III Method :

Sulphamethazine can also be prepared by condensing sulphaguanidine with acetylacetone.



Acetyl acetone

Sulphaguanidine

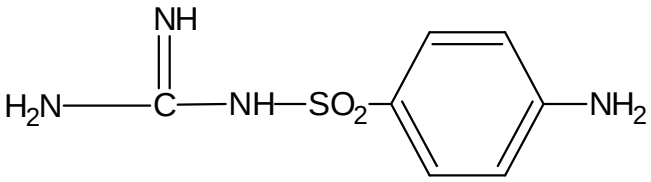


Sulphamethazine

Sulphamethazine is used against all the coccus infections. Its solubility in acidic urine prevents the formation of its crystals in kidney.

It is absorbed more rapidly but excreted very slowly.

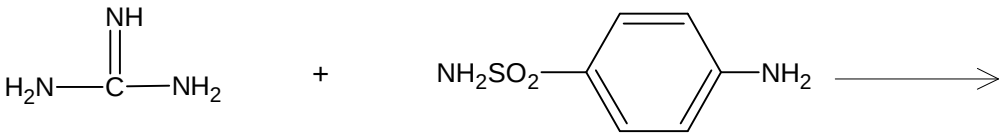
Sulphaguanidine :



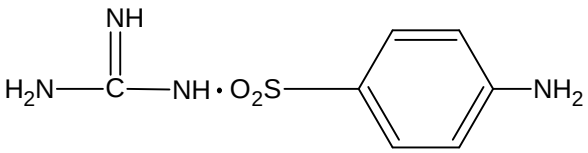
Synthesis :

I Method :

It is prepared by the condensation of guanidine with sulphanilamide.



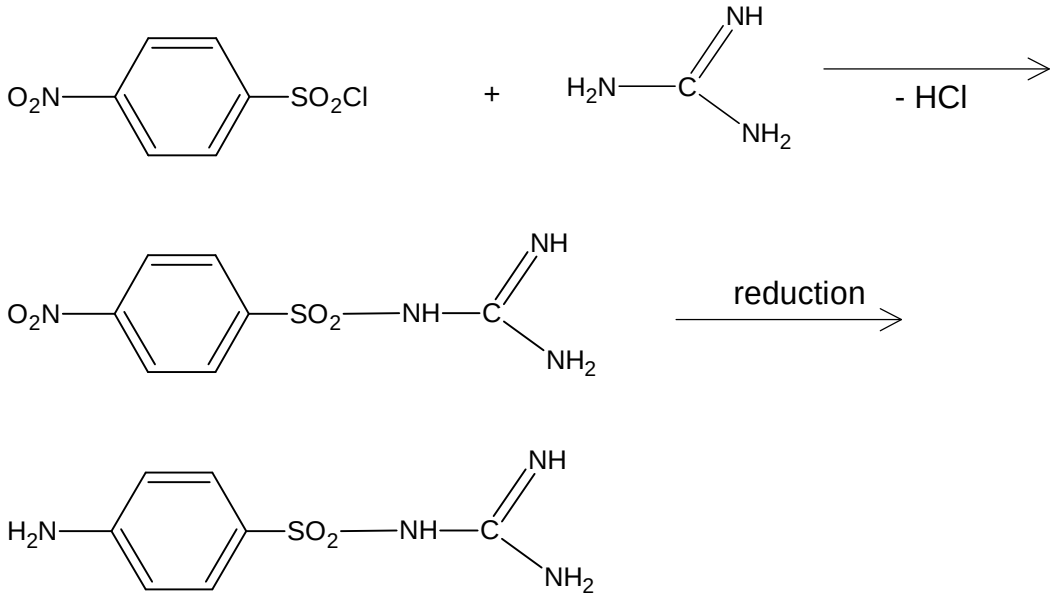
Guanidine Sulphanilamide



Sulphaguanidine

II Method :

It can also be prepared by condensing guanidine with P- nitrobenzene sulphonyl chloride and reduction of the nitro group.

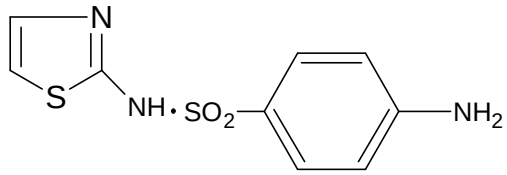


Sulphaguanidine

Sulphaguanidine is only slightly absorbed in the intestinal tract and posses no toxic after effects and hence it is considered as one of the best drugs against bacillary dysentery. Slight toxic effects such as rashes and haematuria are observed.

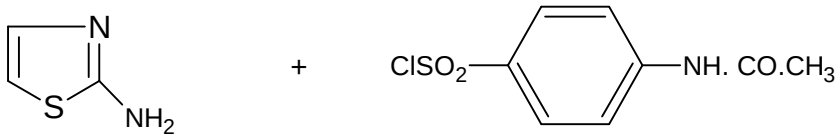
Sulphathiazole or Cibazole :

Chemical name : N^1-2-thiazolyl sulphanilamide

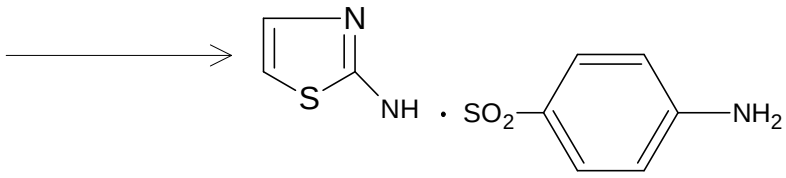


Synthesis :

Sulphathiazole is prepared by condensing 2-aminothiazole with P-N- acetyl sulphanilyl chloride.



2- aminothiazole P-N- acetyl Sulphanilyl Chloride



Sulphathiazole

Sulphathiazole is about 50 times more powerful than sulphanilamide. It is less toxic in nature.

It is particularly against stephylococci infections and in bubonic plague.

MODEL QUESTIONS :

1. Give the preparation and uses of sulphanilamide.
2. Write the preparation and uses of sulpha piperidine and sulphathiazole.
3. How are sulpha drugs discovered ? Give the synthesis of sulphanilamide.
4. Write notes on the following sulpha drugs -
   a) Sulpha diazine
   b) Sulpha guanidine and
   c) Sulpha methoxazole.

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Lesson - 7

ANTIBIOTICS

The term ' antibiotic ' has been derived from the word ' antibiosis ' which means the process by which one organism may destroy another to preserve itself. The term ' antibiotic ' was first introduced by Vuillemin in 1889.

Antibiotics are the chemicals produced by various species of micro- organisms, which in low concentration destory or inhibit the growth or reproduction of other micro-organisms.

Antibiotics have a magical touch, damaging the cell walls of susceptible organisms and causing their disintegration without damaging the host tissues.

Since antibiotics are required only in low concentrations, these are also known as chemotherapeutic agents. The action of antibiotic is very specific. Antibiotictherapy is a case of setting one thief against another because the antibiotics themselves are the products of microbial growth. They are not the main products but are by products of the growth and multiplication of various types of micro - organisms. Thus, they are produced from moulds, **eg :** Pencillin ; from bacteria ; **eg :** Gramicidin and from actinomycetes ; **eg :** streptomycin.

All chemical substances derived from living cells can not be antibiotics.

An antibiotic must have been a product of metabolism.

It should be effective at low concentrations.

If the antibiotic is a synthetic product, then it should be a structural analogue of naturally occuring antibiotic.

The antibiotic should be stable.

The antibiotic should be completely eliminated from the system soon after its administration has stopped.

History of antibiotics :

Instances of micro - organisms fighting against other micro-organisms have been known to man for centuries. The modern history of antibiotics goes back to 1899 when Emmerich and Low used " Pyocyanase " isolated from B. Pyocyaneous culture for the treatment of infected areas. Later on , pyocyanase was found to contain atleast two active substance Pyocyanine and one of its degradation products 1- hydroxy phenazine. However the preparation was found to be toxic and hence its use is stopped.

The accidental discovery of pencillin by Alexander Fleming in 1929 was a landmark in the history of antibiotic therapy. Waksman in 1940 discribed the antibiotic actinomycin but its toxic nature restricted its use. In 1940, Florey and his co - workers at Oxford Univeristy demoonstrated successful results using pencillin in the treatment of septic conditions. After Florey's observation, techiniques were developed for pencillin production by fermentation. Many hundreds of new

antibiotics have been isolated, but of these only a small number are safe to be used on human beings. The rest of the antibiotics were not in use because of high toxicity, low stability and lack of effectiveness. The demand for antibiotics is increasing day by day. The antibiotics isolated from natural sources are not sufficient and hence antibiotics are now prepared in the laboratory which are known as synthetic antibiotics.

Classification of Antibiotics :

The full range of micro-organisms attacked by an antibiotic is called its Spectrum.

Basing on their range of activity, against different organisms, antibiotics are classified into two types namely broad spectrum antibiotics and narrow spectrum antibiotics.

Broad Spectrum Antibiotics :

These are effective in the treatment of gram - positive as well as gram - negative bacterial infections. Pencillin is active against gram- positive infections.

Streptomycin and dihydrostreptomycin are active against gram - negative infections.

Other important broad spectrum antibiotic drugs are chloramphenicol ; chlorotetracycline, Oxytetracycline and tetracycline.

Broad spectrum antibiotics are useful in the treatment of rickettsial diseases like typhus fever.

ii) Narrow Spectrum Antibiotics :

These are highly specific in their action. Eg : Bacitracin ; Nystatin etc.

2) Classification on the basis of type of bacteria attacked :

This classification was given by Christian Gram and is called Gram - staining method. This classification depends on the type of bacteria destroyed by an antibiotic.

In this method the fixed bacteria smear is treated with a solution of a dye, crystal violet and then with iodine solution. The smear is then washed with alcohol. The bacteria which retain the colour of the crystal violet and appear deep violet in colour are known as gram- positive bacteria.

Eg : Pencillins ; erythromycin ; bacitracin etc.

The bacteria which lose the violet colour and get counter strained by safranin and appear red in colour are called gram negative bacteria.

Eg : Streptomycin, Gentamycin.

The following are some of the examples of gram - positive bacteria and gram - negative bacteria –

Gram Positive bacteria	Gram - Negative bacteria
Diphtheria bacillus	Coli and typhoid bacillus
Leprocy bacillus	Gonococcus
Pneumococcus	Meningococcus
Staphylococcus	Plague bacillus
Streptococcus	Vibrios
Tuberclecoccus	

3) Classification based on Chemical Structure :

i) Pencillins :

Derived from amino acids

eg : Pencillins , Cephalosporins etc.

ii) Aminoglucosides :

Contain a sugar molecule glycosidically linked to an amino compound.

eg : Streptomycin, Neomycin etc.

iii) Tetracyclines :

These have four six- membered fused ring systems.

eg : Tetracycline ; Aureomycin, terramycin etc.

iv) Macrolides :

Contain a large lactone ring.

eg : Erythromycin ; Oleandomycin etc.

v) Polyenes :

Have a conjugated polyene system.

eg : Mystatin ; amphotericin etc.

vi) Polypeptides :

These contain a polypeptide chain.

eg : Bacitracin ; Tyrothyricin etc.

vii) Lincomycins :

These are sulphur containing antibiotics in which sulphur atom is not present in the ring.

eg : Lincomycin ; Clindamycin etc.

viii) Antitubercular antibiotics :

Include antibiotics having antitubercular action.

eg : Cycloserine ; Viomycin sulphate etc.

ix) Antineoplastic antibiotics :

Include antibiotics used for controlling cancer.

eg : Dactinomycin ; Mitomycin etc.

x) Chloramphenicol and Synthetic analogues :

xi) Unclassified antibiotics :

Antibiotics not covered under any of the above classes.

eg : Fulvicin ; vanomycin etc.

Importance of antibiotics :

A number of antibiotics have become important therapentic agents. Many antibiotics have been found to be clinically effective in prottozoan and fungal infections. Several antitumor antibiotics have been discovered and are used in the control of malignant disease. Antibiotics have become useful tools for the study of biochemical cellular mechanisms. The antibiotics has been used to study messenger RNA and virus multiplication.

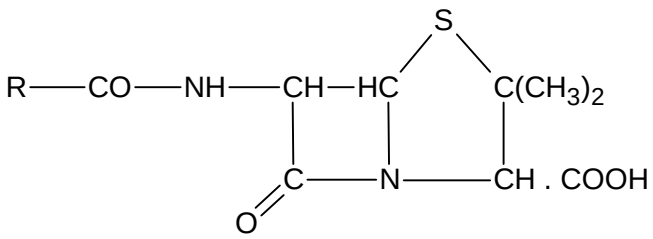
Antibiotics are also used in agriculture. They are used to suppress the pathogenic micro-organisms which could not be recognisable but decreases the animals rate of growth.

Antibiotics are used by the geneticists to produce mutations in moulds. Antibiotics are used as animal feed supplements and in the preservation of poultry and freshly caught sea food.

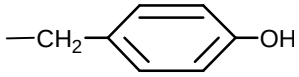
In plants, antibiotics are directly absorbed into the vascular system from the leaves and stems and thus help the plant to fight diseases and also accelerate plant's metabolism.

Pencillins :

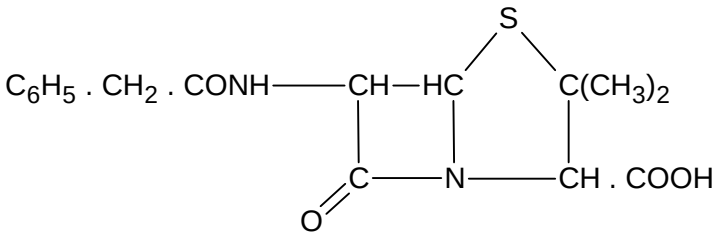
Pencillins can be represented by the general formula $C_9H_{11}N_2O_4SR$ produced by Various Stains of pencillium notatum. All the pencillins have the same nucleus but differ only in the nature of side chain 'R'.



They are named by using prefixes indicating the nature of side Chain 'R'. Some of the common pencillins are listed below -

			Side Chain ' R '	
S.No	**Chemical Name**	**Other name**	**Name**	**Structural Formula**
1.	Pent -2-enyl Penicillin	Penicillin F	Pent - 2- enyl group	$-CH_2-CH=CH-CH_2-CH_3$
2.	N- Amyl Penicillin	Dihydro - F- Penicllin	Amyl group	$-CH_2-(CH_2)_3 \cdot CH_3$
3.	Benzyl Penicillin	Penicillin -G	Benzyl group	$-CH_2-C_6H_5$
4.	n-heptyl penicillin	Penicillin - K	n- heptyl group	$-CH_2-(CH_2)_5-CH_3$
5.	P-hydroxy benzyl pencillin	Penicillin - X	P- hydroxy benzyl group	
6.	phenoxy methyl penicillin	Penicillin - V	Phenoxy methyl group	$-CH_2-OC_6H_5$

All the Penicillins are mono carboxylic acids. Of all the penicillins, benzyl penicillin is the most important one and has been studied in detail.



Benzyl Penicillin

Production of Penicillins :

Various culture methods are developed for the production of penicillin on a large scale. Out of which three methods are given below –

i) Surface Culture method :

This was the first method used for the production of penicillin on commercial scale but now it was used for laboratory studies.

In this method, an aqueous solution of molasses is used as a medium at P^H 7-8, for the micro orgranisms because it contain sucrose, mineral salts and nitrogenous materials which is suited for mould growth. The growth of micro organisms starts and after 6-7 days the concentration of penicillin becomes 0.3 to 0.4 mg per^{ml-}

ii) Bran method :

Moist bran is a good substrate for mould growth and the resultant penicillin may be extracted in a liquid or the penicillin containing may be used directly.

But bran is a bad conductor of heat and hence it is difficult to sterilise it due to the long time taken to attain the desired temperature. And also the developing mould produces heat which partly destroys the penicillin.

iii) Submerged culture method :

In this method the pencillium chrysogenum is used for the culture. The culture medium of 1000 parts contain 20 parts of lactose ; 20 parts of corn steep solid, 3 parts of sodium nitrate ; 0.05 parts of dipotassium phosphate ; 0.125 part of magnesium phosphate ; 1.8 parts of calcium carbonate ; 0.5 part of phenyl acetic acid.

The culture and culture medium are taken in large tanks and the medium is agitated by a stream of sterile air and the temperature is maintained at about 24°c for 2 to 3 days. Under these conditions of aeration and agitation, the mould grows through out the bulk of the liquid as globular pellices consisting mainly of mycelium.

Isolation of Penicillin :

The next step is the extraction of penicillin from the dilute solution in the froth, involved many problems. Some of the problems are listed below.

Penicillin is readily decomposed by too acidic or too alkaline solution and also by heavy metal ions.

Penicillin is destroyed by an elevated temperature.

The yield of penicillin from the culture filtrate is also affected by bacterial contamination. Bacteria ; Escherichia coli secrete enzyme, penicillinase which in turn attacks the basic penicillin structure. Hence, complete aseptic conditions should be maintained during penicillin production.

The contents of the vessels are rapidly cooled, after fermentation and then the mycelium is filtered on a sterile rotatory filter.

Next, P^H of the filtrate is adjusted, the magnitude of which depends up on the nature of the solvent used. If amyl alcohol is used as an extracting solvent, the P^H is adjusted 2.3 while if butyl alcohol is used, the P^H is adjusted to 6-7 by adding ammonium sulphate. After solvent extraction, petroleum ether is added to the cold solvent extract and then shaken well with sodium bicarbonate solution. The P^H is adjusted to 6-7 and is then rapidly freeze - evaporated to yield the sodium salt. The sodium salt of penicillin is then dried in a high vaccum. The penicillin is generally administered by injection. In order to get the sample which is non-toxic, sterilised and free from pyrogens the concentrated solution is allowed to pass through asbestos which absorbs micro - organisms and poisonous pyrogens. Finally the drug is standardised and preserved.

Properties :

i) The purified penicillins are white or slightly yellowish white crystalline powders.

ii) They are dextrorotatory.

iii) They are not soluble in water but their sodium and potassium salts are soluble in water.

iv) They absorb moisture from atmosphere and hence they are stored in closed containers.

v) Pencillins undergo hydrolysis readily and the product formed depends on the nature of the hydrolysing agent.

Uses :

Penicillins are very effective against gram positive bacteria. Hence penicillins are narrow spectrum antibiotics. Penicillin G is a bacterial drug, active aganist the pneumococcus, streptococcus, gonococcus, treponema, anthrax and actinomycosis fungus. The clinical use of penicillin G has been restricted due to its allergic reactions.

Procaine penicillin with aluminium stearate is used in treating siphilis. Benzathin penicillin is used against streptococcal infections in patients having rheumatic fever.

Penicillin V is useful in the prophylaxis of rheumatic fever and acute nephritis in children Methicillin sodium is used for treating infections caused by staphylococci which are resistant to benzyl penicillin.

Streptomycin :

Streptomycin is an antibiotic isolated from the actinomycete, streptomyces griseus, an organism of the soil by Waksman in 1944. When injected into the body, streptomycin is effective against gram positive as well as gram negative organisms.

Production of Streptomycin :

Streptomycin has a more complex structure than penicillin. Like penicillin, streptomycin was prepared by surface culture method but now - a - days it is produced by submerged cultures. The yield of streptomycin depends on the medium used. The culture medium must contain protein materials such as soya bean meal and cotton seed meal ; in addition to glucose, peptone, meat extract, corn steep liquor and sodium chloride in water. The culture solution is kept in large vats, growth of the micro - organisms starts at 24 - 28°c the maximum yield is obtained after three to five days. The yield of streptomycin can be increased by irradiating culture solution by X- rays or Ultraviolet light.

Isolation of Streptomycin :

After separating the mycelium and waste materials, the streptomycin is obtained from the filtrate either by adsorption on charcoal or on base exchange resins. It is then eluted from the adsorbent by means of dilute aqueous or alcoholic mineral acids and then the acidic eluate is purified by passing it through an ion exchange resin. In pure form, streptomycin has been isolated as sulphate or Crystalline double salt of calcium chloride. Aseptic conditions must be maintained through out the production and isolation of Streptomycin.

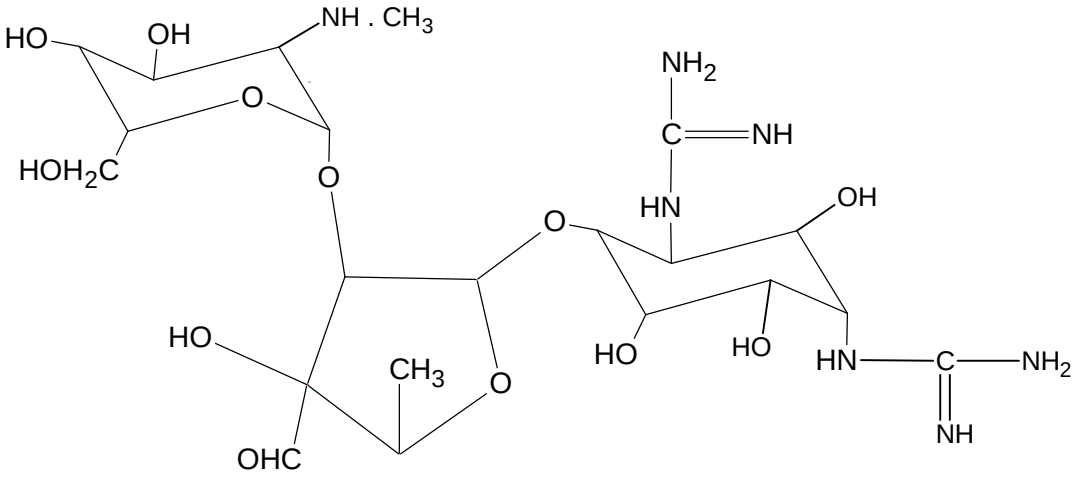
For getting completely sterile drug, the crystalline streptomycin so obtained is redissolved to give 25% solution, freed from undesirable impurities such as heavy metals, colour etc., by passing through seitz filter and then freeze dried. The freeze dried powder is then transferred aseptically to small vials.

Properties :

Streptomycin is a colourless solid, soluble in water.

It is laevorotatory.

It is an aminobase and forms salts that are very soluble in water. Streptomycin molecule contains two strongly basic guanido groups and a weakly basic methyl amino group.



Streptomycin

Uses of Streptomycin :

Streptomycin is a bactericidal drug. It is effective against gram positive as well as gram-negative organisms.

It is useful in the treatment of tuberculosis ; plague, pheumonia and bacterial dysentery.

It is used in infections produced by E. coli, influenzal meningitis caused by Haemophilus influenza etc. In the treatment of tuberculosis, streptomycin is used alone or in combination with P-amino salicylic acid (PAS) and isoniazid (Isonicotinic acid hydrazide) since tubercle bacilli have developed some strains resistant to the drug.

The after effects of streptomycin injections are temporary or permanent deafness ; nansea, giddiness, head - ache, skin eruptions, pain and irritation at the site of injections.

Tetracyclines :

Tetracyclines are all broad spectrum antibiotics prepared from soil inhibiting actinomycetes. Tetracyclines are safety in use, highly stable and have a high degree of efficiency against several bacteria as wll as rickettsial, large viruses and even the protozoa responsible for amoebic dysentery. They can be administered orally and they are also retained by the body for sufficient time and not rapidly excreted like penicillin.

The three most important members which are produced by actinomycetes are chlorotetra cycline also known as aureomycin, oxytetrachlorine or terramycin and tetracycline.

i) Chlorotetra cycline is also known as aureomycin. It was discovered by Duggar in 1948.

It was isolated from the micro - organisms streptomyces aureofaciens.

Aureomycin is a golden yellow amphoteric compound usually obtained in the form of its hydrochloride.

ii) Oxytetracycline or terramycin was discovered and isolated from soil by A.C. Finley in 1950. It was produced by Streptomyces rimosus.

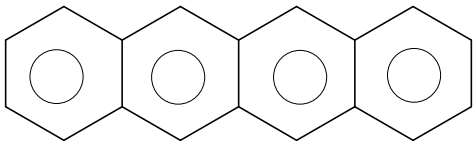
It is an yellow, crystalline, amphoteric substance, sparingly soluble in water.

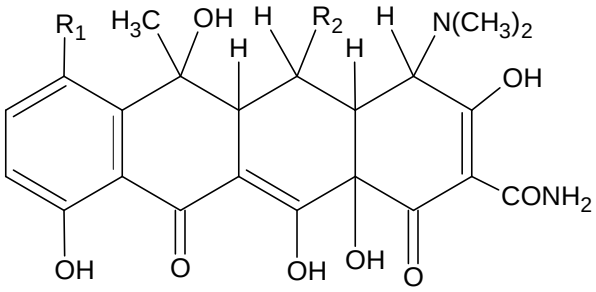
iii) Tetracycline is prepared by dechlorinating chlorotetracycline by replacing the halogen with hydrogen by catalytic hydrogenation.

Structure :

All the tetracycline antibiotics contain hydronapthacene skeleton as a structural unit.

They have four ringed system in common, the differences between them being confined to the groups R_1 -, R_2 -





Chlorotetra cycline	R_1 = Cl ; R_2 = H
Oxytetra cycline	R_1 = H ; R_2 = OH
Tetra cycline	R_1 = H ; R_2 = H

Uses :

The tetracyclines have a broad spectrum of activity. They are active against gram - postive as well as gram - negative bacteria.

These are orally effective and non toxic.

These are used in the treatment of pneumonia, rickettsial diseases such as typhus and Q-fever ; whooping coughs.

Aureomycin is used in the treatment of chicken pox, small pox; measles and hepatitis. Tereamycin is effective against bacterial and viral pneumonia, urinary tract infections, streptococcal infections, acute gonorrheal Urethritis.

Polypeptides :

This group of antibiotics are all prepared from bacteria and not from any other forms of micro - organisms.

Polypeptides are one of the most powerful bactericidal antibiotics and have polypeptide structure. The only antibioitcs of this class suitable for internal use are the polymyxins - B and E. The rest are all toxic and at the most can external applications for wounds and burns.

Five polymyxins - A, B, C, D and E are obtained as a mixture from Bacillus polymyxa. They are basic polypeptides differing in their amino acid content. They are used against gram- negative bacteria. Since polymyxin - B and E are least toxic, they are used in combating resistant strains of bacteria responsible strains for meningitis and gastrointestinal infections. Colistin sulphate has been used for the treatment of Urinary tract infections caused by gram - negative bacteria.

Model Questions :

1. What are antibiotics ? Give the classification of antibiotics.
2. What do you mean by broad spectrum antibiotics and narrow spectrum antibiotics Explain with examples.
3. Explain the isolation of penicillin and give its applications.
4. Give the structural formula of streptomycin. Mention its applications.
5. Give the structural formula of penicillin. Discuss the different types of penicillins.
6. Give an account of production and isolation of streptomycin.
7. Write notes on tetracyclines.

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Lesson - 8

ANTI - DIABETICS

More than one half of the food in the normal diet of human beings consists of carbohydrates. Carbohydrates undergo digestion mainly in the small intestine and there, they are attacked by pancreatic amylase and other enzymes and are converted to galactose, fructose and glucose which are transported to the liver. In the liver galactose and fructose are converted to glucose by the appropriate isomerases. In the body, glucose is used as a fuel for production of energy. Glucose is either converted to liver glycogen and stored or it is directly passed into the circulatory system and transported to the cells.

The glucose sugar that circulates in the blood is known as blood sugar. Abnormally low and high concentrations of glucose in the blood when compared to the normal value are known as hypoglycemia and hyperglycemia. The concentration of glucose in the blood is mainly controlled by the synthesis and degradation of glycogen.

Pancreas is one of the important part of gastrointestinal tract. Diabetes is caused due to the deficiency of insulin, a hormone secreted by the beta cells of the pancreas. Insulin controls the carbohydrate metabolism and lipid and protein metabolisms. Substances like amino acids, free fatty acids, ketone bodies, glucagon causes the release of insulin. The over all effect of insulin is to lower the blood sugar.

When the concentration of glucose in blood exceeds the normal level (180 mg / 100 ml of blood) or the condition in which excess glucose is present in the blood is called " Hyperglycemia". When glucose level in the blood exceeds a certain point, the glucose is excreted through urine. The amount glucose excreted through urine depends upon the condition of the disease. Hyperglycemia is popularly known as Diabetes Mellitus. It means hyperglycemia due to lack of insulin. This disease may also occur due to over production of hormones which are antagonists to insulin and also due to increased production of insulinase which inactivates insulin.

In severe diabeles mellitus, nearly 100gms of glucose can be excreted daily in the urine. Due to the loss of such large amount of glucose, the patient is thirsty inspite of drinking large amounts of fluid (Polydipsia) other symptoms include increased urine output (Polyuria), presence of glucose in the urine (glycosuria) and presence of ketone bodies in the blood and urine (Ketonemia and Ketonuria) which are accompanied by weight loss and muscular weakness. So, patients become weak and thin, Vulnerable for infections and also healing of wounds is delayed.

Permanent cure of hyperglycemia is not possible. Mild diabetes may be cured by dietary treatment alone. Carbohydrates and fats are limited in the diet. The patient has to continue on a low sugar diet in order to maintain a normal blood sugar value. The severe cases of diabetes require insulin. The disease can be controlled by giving insulin at regular intervals in specified doses.

Hypoglycemia :

Release of large quantities of insulin, administraion of large dosage of insulin and antidibetic drugs to the diabetic patients ; poor consumption of food, heavy drinking of alcohol are the reasons for the decrease of glucose level in blood. Such a condition with a low glucose level is called hypoglycemia.

Increased heart beat, increased pulse rate, anemia, oversweating are common symptoms of this disease. The patients are advised to carry a pack of glucose or sucrose with them. The patients can be given glucose or sucrose solution immediately to restore the normal condition and then they are to be taken to doctor for further treatment.

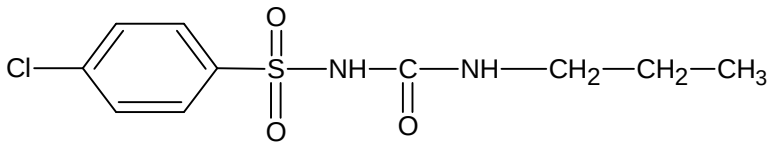
Oral hypoglycemic agents :

The chemical substances which reduce blood sugar concentration are called hypoglycemic agents. Insulin is the natural hypoglycemic agent and it can't be administered orally because of its degradation by enzymes present in gastrointestinal tract. The compounds that are effective orally are called oral hypoglycemic agents. They reduce blood sugar concentration when taken by mouth. These drugs belong to the sulphonyl ureas and biguanides.

Sulphonyl Ureas :

They are derivatives of urea. The sulphonyl ureas stimulate the secretion of insulin from the pancreas. The sulphonyl ureas can work only when the liver is in the functional state.

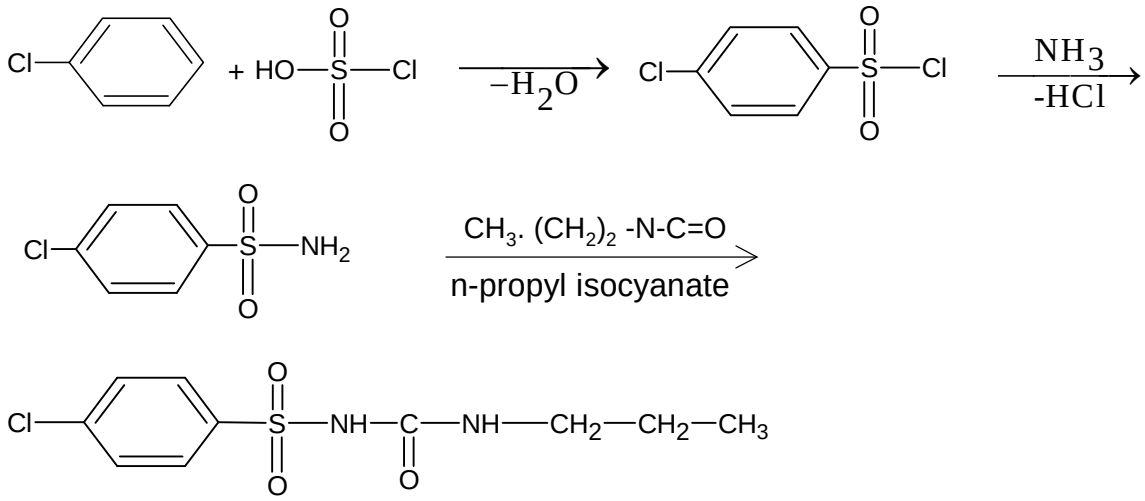
1) 4 - Chlor propamide :



Chemical name : 1 - (4 chlorobenzene sulphonyl) 3 - n- propyl urea.

Synthesis :

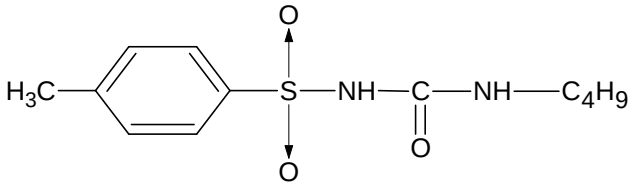
Chlorobenzene on treatment with chlorosulphuric acid forms 4 - chlorobenzene sulphonyl chloride which on treatment with ammonia gives 4 - chloro benzene sulphonamide which on reaction with n - propyl isocyanate gives 4 - chlor propamide.



4 - Chlor propamide

It is a white crystalline powder, insoluble in water but soluble in organic solvents like chloroform. It stimulates the secreation of insulin. It is used for the treatment of diabetes in mild conditon.

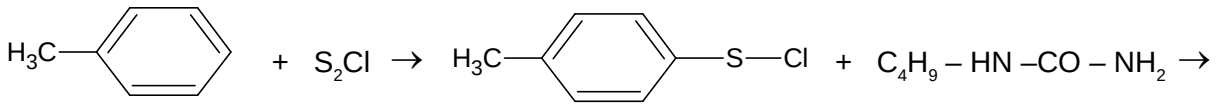
2) Tolbutamide :



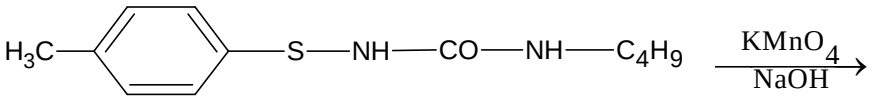
Chemical name of Tolbulamide is 1– (4 – methyl benzene sulphonyl) 3 – n-butyl urea.

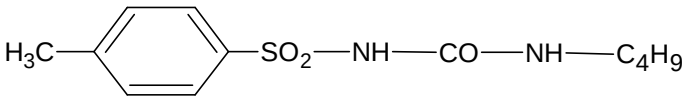
Synthesis :

P- toluene sulphonyl chloride is obtained by treatment of P - toluene with sulphonyl chloride. Then the P - toluene sulphonyl chloride on treatment with n - butyl urea and the product obtained on further treatment with alkaline $KMnO_4$ gives tolbutamide.



P- toluene | Sulphonyl Chloride | P-toluene sulphonyl chloride | n - butyl urea



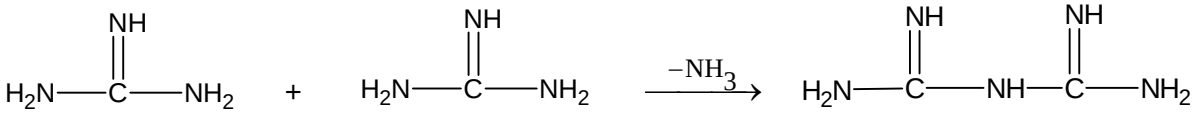


Tolbutamide

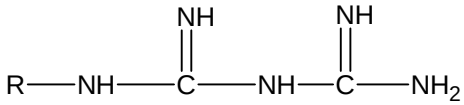
It is a hypoglycemic agent, gets metabolised by oxidation of its P - methyl group to –COOH group. It is a white crystalline powder, insoluble in water but soluble in alcohol and chloroform. It is a safe drug for elderly patients.

Biguanides :

A structure where two guanidine moleules are combined together through a common –NH linkage is called biguanidine.

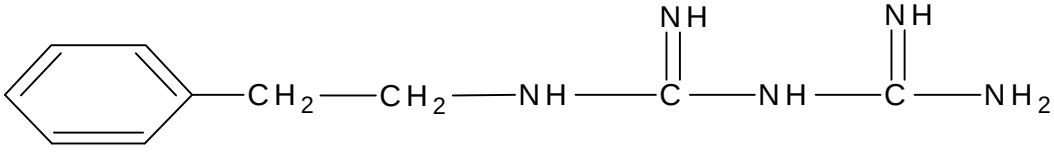


Alkyl or aralkyl derivatives of biguanidine are called biguanides. They are active oral hypoglycemic agents.



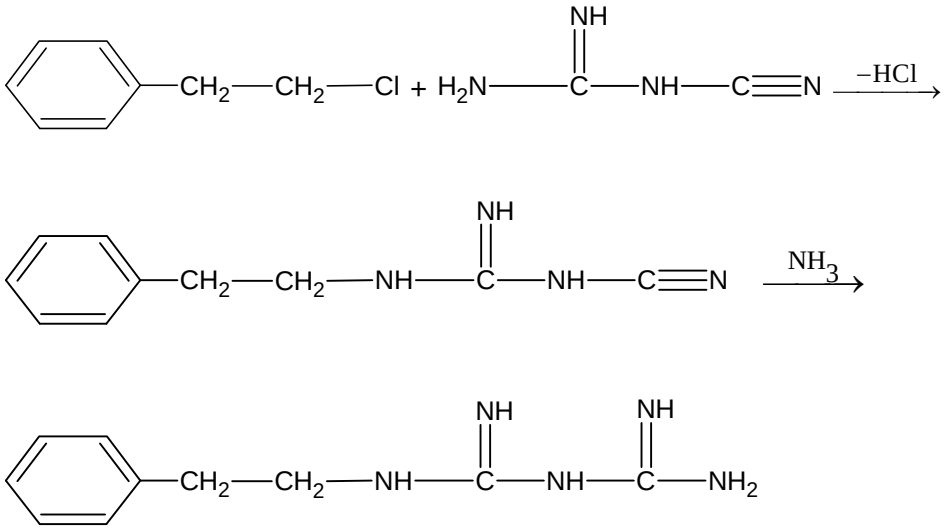
Where R = alkyl or aralkyl group

3) Phenformin :



Phenformin

Its chemical name is phenyl ethyl biguanidine. It is used in the form of its hydro chloride



Phenformin

It is a white crystalline powder with bitter taste. It stimulates pancreas and promotes the secretion of insulin. It works only when the liver is in good functional state.

Model Questions :

1. What is diabetes mellitns ? Discuss the sources of insulin and its administration.
2. Write an account on hyperglycemia and hypoglycemia and glycosuria.
3. Discuss with examples antidiabetic drugs or oral hypoglycemic agents.
4. Give the synthesis of tolbutamide. Mention its uses.
5. How is Phenformin synthesised ? Give its uses.

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Lesson -9

VITAMINS

A balanced diet is required for several biological processes taking place in the human body which includes carbohydrates; proteins,fats, minerals and water.

Carbohydrates ;rovide energy for the body.

Proteins are essential for building up the structural units of the body called cells.

Fats serve as'reservoirs ' of food,.Fatty cells store food mostly in the form of triglycerides.

Minerals are nutrient elements such as calcium, phosphous, magnesium , iron,iodine etc., which are the constituents of enzymes, Co-enzymes, transport molocules etc., water is the medium for most of the biochemical processses in the body.

In addition to the above classes of nutrients, the body requires other class of nutrients called vitamins. The term 'vitmine' is derived from the word vital (means life) and mine. As the first discovered compounds contain amino group, they were named as vitamines. Later, it was found that all of them do not have amino group, the letter ' e' was deleted from vitamine. So, vitamins are defined as the chemically unrelated compounds necessary for the normal functioning of the human body. They are not produced in the body (except D) and hence they must be supplied from outside through food. The human body needs vitamins in balanced proportions and in small quantities. In general, fresh and natural foods contain all the necessary vitamins in appropriate amounts. But as the human beings take food which is prepared by some processes result in the loss or deficeincy of some vitamins in the food. The deficiency of a particular vitamin may lead to metabolic disorder and causes a specific disease which can be cured by sufficient intake of that vitamin.

Classification of Vitamins :

Vitamins are classified into two types -

a) Fat soluble vitamins which includes vitamins A,D,E and K.

b) Water soluble vitamins includes vitamins of B group and Vitamin ' e' .

Vitamin ' H' is an exception. It is insoluble both in fat and in water.

Provitamins or Precursors :

These are some biologically inactive compounds which are quite similar to the vitamins in structure and are converted easily into active vitamins in ViVo.

For example, β - Carotene is the provitamin for vitamin A and ergosterol is the provitamin for Vitamin D_2.

Vitamin ' A ' :

a) Sources :

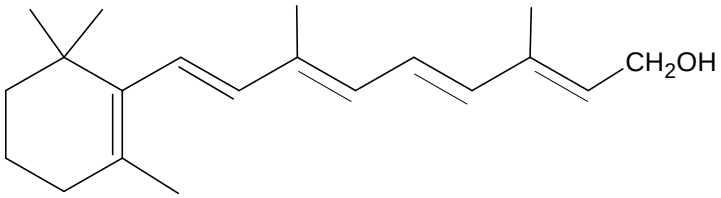
The chief source of vitamin ' A ' is fish liver oils, Halibut - liver, Shark - liver and Cod - liver oils other sources are eggs, butter, blood, milk, sweet potatoes, tomatoes, carrots, cabbage etc.,

Vitamin ' A_1 ' is found mainly in the liver of salt water fish while vitamin A_2 is found in the liver of fresh - water fish.

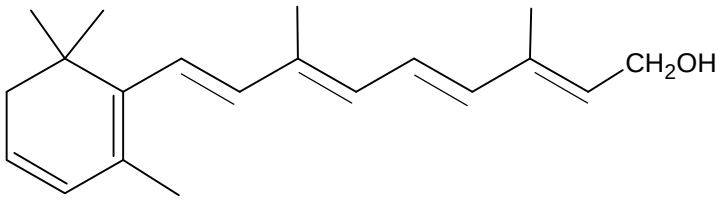
Structure :

Vitamin A is also known as retinol.

It exists in two forms namely vitamin A or A_1 (Retinol$_1$) and Vitamin A_2 (Retionol $_2$)



vitamin A_1



vitamin A_2

vitamin A_2 is similar to vitamin A or A_1 but possess more conjugated doubled bond in its structure.

Diseases due to deficiency :

i) The deficiency of Vitamin A causes night blindness i.e inability of the eye to see at night. In the process of vision, the photoreceptors transmit stimulus of light to the optic nerve. Two types of photoreceptors are located in the retina of the eye

a) The rods responsible for dim light vision and

b) **The cones responsible for bright light colour vision :**

The rods and cones contain a pigment which is bleached by light. In retinal pigment, the rods contain rhodospin while cones contain idopsin as pigment. Vitamin A is required for the synthesis of rhodospin. When vitamin A is deficient, rhodospin cannot be synthesised which leads to the failure of vision in dim light.

ii) Its prolonged deficiency lead to the hardening of the conjunctive, softening of cornea known as Xerophthalmia and may lead to complete blindness.

iii) The deficiency of A_1 produces dryness of skin hair.

iv) In children, deficiency of A_1 retards growth and leads to weight loss.

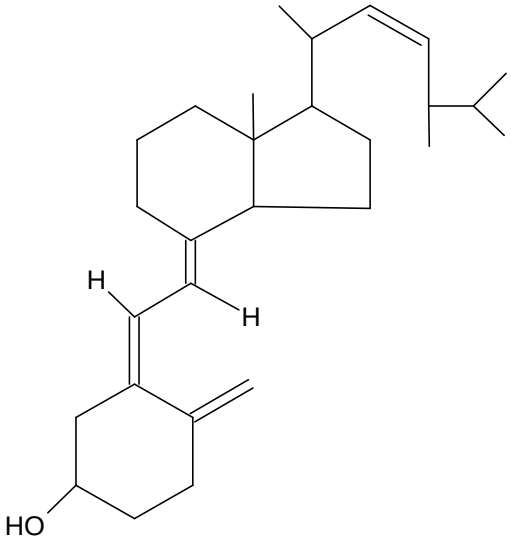
Vitamin D :

Vitamin D is fat soluble. So far, five vitamins of this group have been isolated, Viz D_1, D_2,D_3, D_4 and D_5. Vitamin D_1 or D is found to be a molecular compound of D_2 and lumisterol. All these vitamins are formed by the irradiation of sterols. Vitamin D_2 is also called as ergo calciferol. Vitamin D3 is called as cholecalciferol. The various ' D ' vitamins differ from each other in the nature of the side chain.

Sources :

Vitamin D_2 is formed in nature by the irradiation of sterols. Other sources are cod - liver oil and other fish liver oils ; Egg yolk ; milk etc.

Structure :



Vitamin D_2 = Ergocalciferol

Diseases due to deficiency :

The deficiency of vitamin D causes rickets and other bone diseases.

Excessive doses of vitamin D are toxic and cause calcification of other tissues besides bones. For example walls of blood vessels will become calcified producing hardening of arteries.

Vitamin K :

There are two Vitamins K namely K_1 and K_2. Vitamin K was discovered by Dam in 1939.

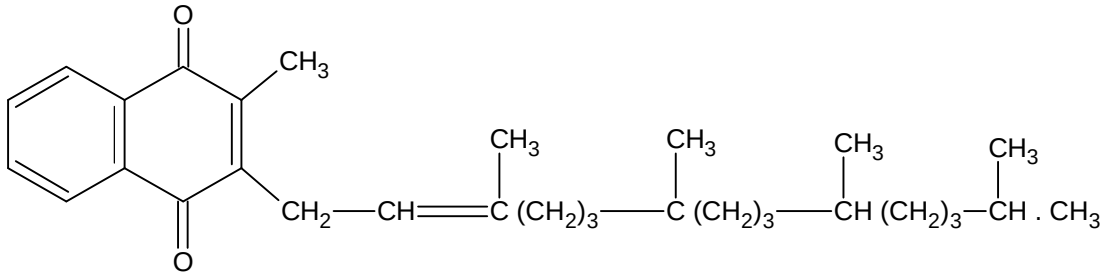
Sources :

Vitamin K_1 occurs in all green, leaves and vegetables.

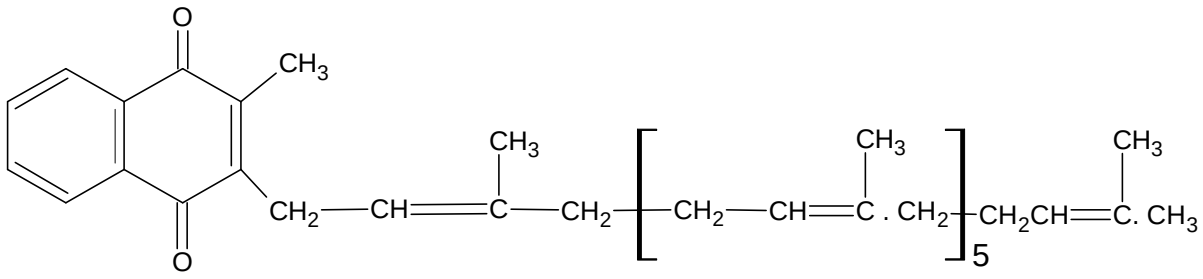
Eg : alfalfa ; carrot tops ; Cabbage ; Cauliflower ; Spinach etc.

Vitamin K_2 occurs in bacteria and in purified fish and meat.

Structure :



Vitamin K_1



Vitamin K_2

Diseases due to deficiency :

The Vitamins K are necessary for coagulation of blood. Prothrombin is essential for the coagulation of blood. Vitamin K help in coagulation of blood by activating prothrombin the precursor of thrombin, for the formation of blood clotting enzyme. When an injury occurs, generally bleeding stops with in 5 to 10 minutes which is due to coagulation of blood on the surface of the wound. When Vitamin K is deficient, coagulation can't occur which leads to continuous bleeding from the wound. Thus the deficiency of vitamins K_1 and K_2 increases the time of blood clotting and hence they are called antihaemorrhagic vitamins.

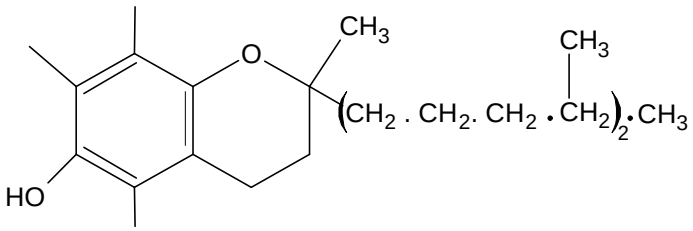
Vitamin E :

Vitamin E represents a group of compounds, collectively called as tocopherols. Out of these, α - tocopherol is biologically very active.

Sources :

Wheat germ oil, cotton seed oil, soyabean oil, palm oil, green vegetables, egg yolk, meat, nuts, liver of horses and catlles are some of the sources of Vitamin E.

Structure :



Vitamin E (α - Tocopherol)

Diseases due to deficiency :

i) It causes oedema and anuemia in infants.

ii) Causes antisterility. Vitamin E is often called antisterility vitamin , as it is responsible for normal reproductive function.

iii) It canses increase in the number of leucocytes i.e., W.B.C. of the blood leading to blood anaemia .

iv) It canses increased excretion of sugar ribose in wine due to degeneration of muscles.

v) It increases concentration of RNA and DNA in the bone marrow.

Watter soluble Vitamins :-

Vitamin B complex:-

This is not one vitamin but includes a group of water soluble vitamins which are found in yeast, liver ,rice polishings etc., . The group includes thiamine (B_1) , riboflavin (B_2) ; Pontothenic acid (B_3) ; nicotinic acid (B_5); Pyridoxin(B_6); folic acid (Bc) ; biotin (B_7) ; cynocobalamine (B_{12}) ; myoionositol.

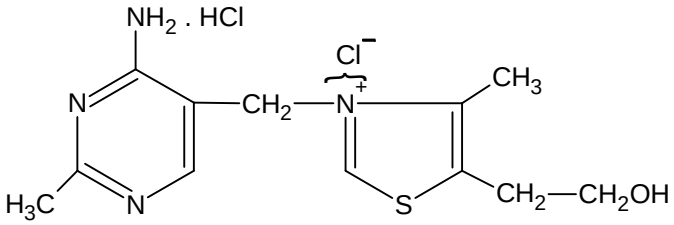
Vitamin-B_1 (Thiamine or Aneurin) :

Sources :

It is present in the cereal grains like rice, wheat etc. Other sources are yeast, milk, ground nuts, green vegetables, eggs, fruits and diary products except butter.

Structure :

The molecule contains a pyrimidine ring and a thiazole ring linked by methylene bridge. The nitrogen of the thiazole ring is cationic and is associated with chloride ions.



Diseases due to deficiency :

i) Deficiency of vitamin B1 causes loss of appetite, gastrointestinal disturbances, muscular weakness, pain in arms.

ii) The entire nervous system is effected in case of severe deficiency results in a type of paralysis and leads to beri - beri. Lesser deficiency of thiamine leads to dry beri - beri and severe deficiency leads to wet beri - beri.

iii) Causes weight loss and stunted growth.

iv) Reduced eye sight, unconditional movement of eye lids i.e., parkinsonism is effected.

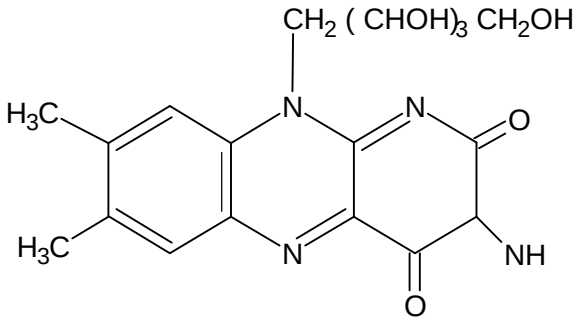
The deficinecy can be rectified by using hand powdered rice or par - boiled rice.

Vitamin-B_2 (Riboflavin or Lactoflavin) :

Sources :

It is widely distributed in plants and animals. Yeast, vegetables, milk, egg white, liver, kidney, meat, fish are sources of Vitamin - B_2.

Structure :



Diseases due to deficiency :

Deficiency of vitamin B_2 causes -

i) Inflammation of the tongue.

ii) Cheilosis (cracking of lips and corners of the mouth).

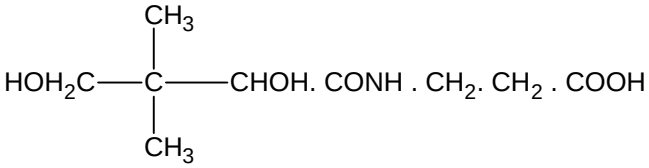
iii) Stunted growth.

Vitamin-B_3 (Pantothenic acid) :

Sources :

Sources of Vitamin - B_3 are liver, kidney heart spleen, brain, pancreas etc. Some moulds and green plants are some other sources. The name pantothenic is derived from a greek word meaning " from every where ". This vitamin is almost of universal occurence.

Structure :



Diseases due to deficiency :

The symptoms of pantothenic acid deficiency in man is unknown. However, it is believed, that its deficiency in man may cause burning sensation, muscle weakness, abdominal disorder and general depression.

Deficiency of vitamin B_3 in chicks causes a specific dermatitis, retardation and toughnesS of feathers where as in rats, it causes retardation of growth, depigmentation of the fur.

It is also capable of promoting the growth of yeast and bacteria.

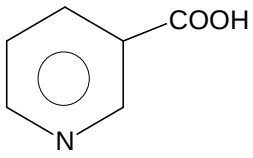
Vitamin-B_5 (Nicotinic acid Or Niacin) :

Niacin is the official name of the vitamin nicotinic acid. The bio chemically active part of the vitamin is nicotinamide.

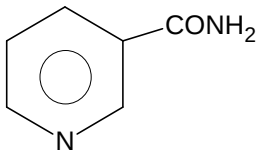
Sources :

It occurs in all living cells in small amounts. Liver, meat, kidney, yeast, grain cereals, pulses, ground nuts, peanut, potatoes are the sources of Vitamin B_5.

Structure :



Nicotinic acid



Nicotinamide

Diseases due to deficiency :

Deficiency causes pellagra.

Severe deficiency of nicotinic acid and nicotinamide causes disturbances in digestive and nervous systems.

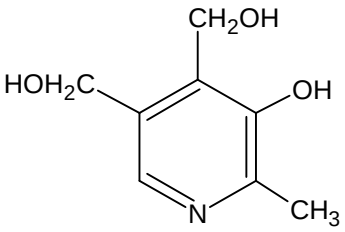
Vitamin-B_6 (Pyridoxine Or Adermine) :

Vitamin B_6 is a group of three vitamins namely Pyridoxine, Pyridoxal and pyridoxamine. These are derivatives of Pyridine and are inter convertible in the form of their phosphates. Pyroxine, alone is also known as Vitamin B_6.

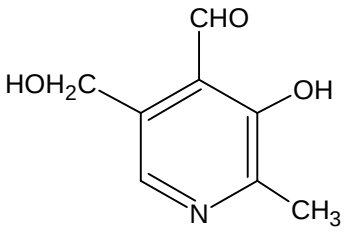
Sources :

Vitamin B_6 is widely distributed in plants, animals, molasses, yeast, liver, meat, milk, eggs, rice polishings seeds, cereals and fresh vegetables.

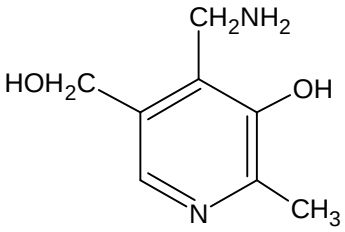
Structure :



Pyridoxine



Pyridoxal



Pyridoxamine

Diseases due to deficiency :

Deficiency of Vitamin B_6 causes nervousness, irritability, stomatitis and general weakness.

Vitamin-B_{12} (Pyridoxine Or Adermine) :

Vitamin B_{12} is the first natural product that contains Cobalt.

Sources :

Liver, meat, kidneys, milk, eggs, cheese marine fish and fresh vegatables are the sources of Vitamin B_{12}.

Diseases due to deficiency :

i) Deficiency of B_{12} causes anaemia which is followed by degradation of spinal card.

ii) Causes hyperglycemia.

iii) Effects the synthesis of lipids from carbohydrates.

β - Biotin (Vitamin H) :

Sources :

Egg yolk, liver, kidney, milk are sources of β - Biotin. In animals and in yeast it is present in the combined form but in plants it occurs in free state.

eg : Vegetables, grains, nuts etc.

Diseases due to deficiency :

The deficiency of the Vitamin H causes dermatitis, loss of hair and Paralysis.

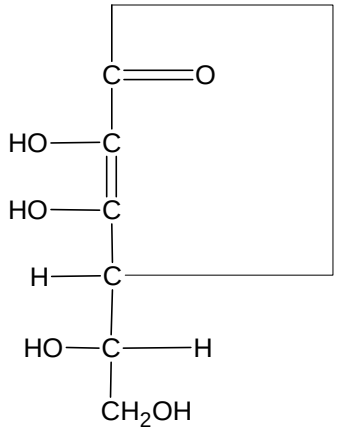
Vitamin C (Ascorbic acid) :

Sources :

Vitamin C is widely distributed in both plants and animals. It occurs in fresh vegetables like cabbage ; califlower ; beans and tomatoes. It is mainly found in citrous fruits like lemons, oranges, pine apple etc. In small quantities it occurs in milk and blood.

Structure :

It is a derivative of carbohydrate. i.e. L - glucose. It has L - configuration.



Vitamin C or L - Ascorbic acid

Diseases due to deficiency :

i) The deficiency of vitamin - C causes the disease scurvy. In severe deficiency, occurs swelling and bleeding of gums and teeth become lose.

ii) Coagulation of blood is delayed.

iii) Healing of wounds is delayed.

iv) Resistance power decreases and hence the person is easily attacked by infections.

Model Questions :

1. What are vitamins ? How are they classified ? write the structures of Vitamin - A and Vitamin - C. Give their sources and diseases caused due to their deficiency.
2. What are fat soluble vitamins ? Mention the sources and diseases due to deficiency for any two fat soluble vitamins.
3. What is vitamin - K ? What are its sources. Mention the diseases caused by its deficiency.
4. What is Vitamin - B complex ? Give the sources and diseases due to deficiency of B_1, B_2, B_6 and B_{12}.
5. Mention the structure and chemical names of any five vitamins.

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Lessons - 10

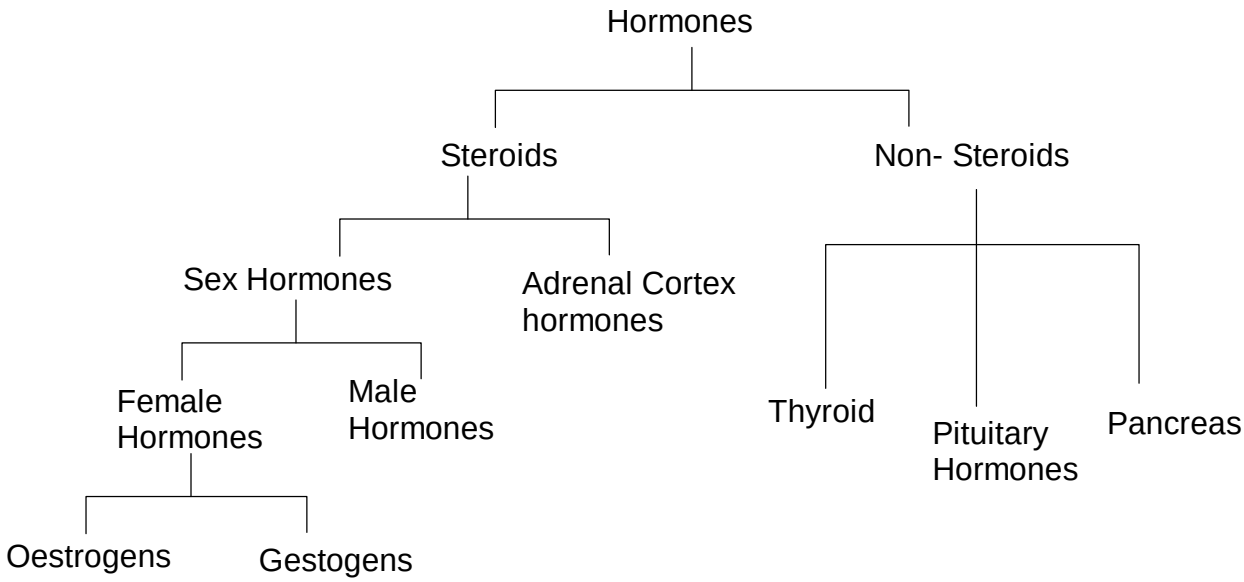
HORMONES

Many of the Physiological functions in the body are performed by chemical compounds which are secreted in small quantities by ductless glands called the endocrine glands. The term hormone is derived from the Greek word ' hormaein ' means " to set in motion ". Hormones are chemical messengers. Hormones are produced in the body and have diverse structures just like vitamins. Hormones are brought to different organs of the body by means of blood stream. The deficiency of a hormone causes a particular disease which can be cured by the administration of that hormone.

The exact mechanisms by which hormones exert their effects are not known.

Classification of hormones :

More than 80 hormones are known out of which 50% are steroids while the rest are non steroidal in nature.



Important glands in our body are -

1. Pituitary gland
2. Thyroid gland
3. Adrenal gland
4. Pancreas and
5. Reproductive glands.

1. Pituitary gland :

Pituitary gland posseses two lobes namely the anterior pituitary lobe and the posterior pituitary lobe. The pituitary gland releases several hormones, which are polypeptide in nature. The names and the Physiological functions of the hormones are given below -

i) Growth Hormone :

It is a single chain poly peptide.

It is made up of 188 aminoacids.

It promotes the synthesis of protein in liver and peripheral tissues.

It increases body growth.

It effects several aspects of carbohydrate, fat metabolisms.

It increases the secretion of milk during lactation.

ii) Prolactin :

It initiates lactation on child birth.

iii) Oxytocin :

It is a cyclic peptide consisting of nine amino - acids.

It stimulates the secretion of milk and contraction of smooth muscles of the uterus. Oxytocin means quick child birth.

iv) Adrino Corticotrophic hormone (ACTH) :

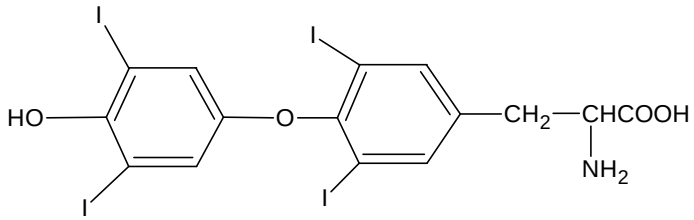
It is a protein hormone made up of 39 amino acids.

It mainly acts on the adrinal cortex.

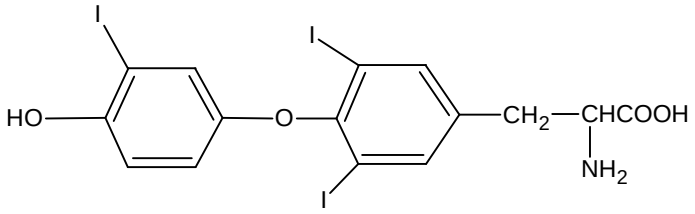
It promotes the synthesis of pregnanolone from cholesterol.

2. Thyroid gland :

Thyroxine is secreted by thyroid gland in the form of a protein thyroglobulin. Thyroid gland secrets another enzyme called 3,3^1,5- tri iodothyronine which is four to ten times more active than thyroxine.



Thyroxine



3,3^1,5- tri iodothyronine

i) Thyroxine regulates the rate of oxygen consumption.

ii) It regulates the metabolism of carbohydrates, lipids and proteins.

iii) Lowers the cholesterol level in serum and increase coenzyme and vitamin requirements.

i) The deficiency of thyroxine causes disturbance in metabolism of carbohydrates, lipids, proteins, electrolytes etc.

ii) The deficiency of thyroxine in childhood causes critinism which is characterised by retarded growth etc. In adults it leads to myxedema.

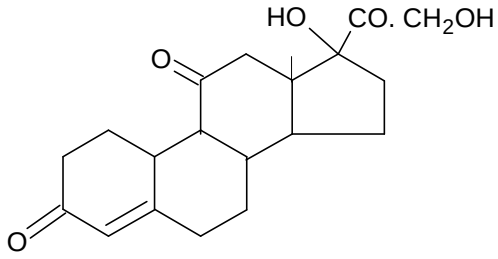
iii) Enlargement of thyroid gland is known as goitre. It is observed as a swelling on the neck which is caused by iodine deficiency.

iv) Over production of thyroxine causes the rapid heart beat and nervous irritability.

3. Adrenal gland :

Adrenal gland is situated above the kidneys. It is dividded into two zones in which outer zone is called Cortex and inner zone is called medulla.

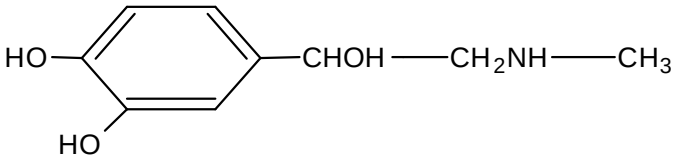
The cortex produces several hormones known as cortical hormones that are steroidal in nature. Out of these, corticoids are the characteristic adrenal cortical hormones. Important hormone is cortisone, stimulates the conversion of proteins into carbohydrates.



Cortisone

Deficiency of this hormone produces Addison's disease - its symptoms are colouration (Yellow) of skin, muscular weakness, increase in blood urea level etc.

Medulla produces adrenaline.



It is very important hormone.

It can be considered as the hormone acting during emergency. During accidental conditions, When there is need for sensory organs to act immediately hormone enters the blood stream.

Its secretion makes the individual ready to fight.

It raises, oxygen consumption.

It increases heart beat, raises blood pressure.

Rate of respiration increases

It produces a sense of restlessness and anxiety.

4. Pancreas :

Pancreas is an endocrine gland which is situated behind the stomach. It is one of the most important parts of gastro intestinal tract. Pancreas secretes two hormones namely insulin and glucagon.

There is a region in the pancreas consisting of some special cell called islets of Langerhans. It has two types of cells called as α & β cells. α - cells secrete glucagon which converts glycogen into glucose. It also decreases the synthesis of proteins and fat, causes increase in metabolic rate.

β - cells secrete hormone insulin which is used formaintaining glucose level in body fluids.

Insulin :

It is a polypeptide hormone. It is made up of 48 amino acids, which are arranged in two straight chains A and B, linked by two sulphide bridges. The sequence of amino acids in insulin was discovered by " Sanger ". He was awarded Noble prize for the remarkable work on insulin.

Insulin regulates the carbohydrate metabolism in the body.

The deficiency of insulin causes a disease called diabetes mellitus which has the following symptoms.

i) Hypergdycemea – increase in blood sugar level.

ii) Glucose urea – Appearence of sugar in urea.

iii) Polyurea – Production of large volumes of sugar.

iv) Frequent urination.

v) Healing of wounds is delayed.

The diabetes can be controlled by the administration of insulin.

The physiological activity of insulin is largely lost in the body on acetylation and partially restored on deacetylation.

Glucagon :

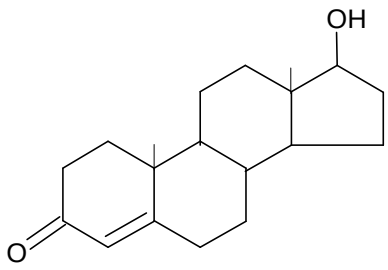
It is a pancreatic hormone and is a protein consisting of 29 aminoacids arranged in a straight chain. It maintains the blood sugar level by breaking down glucose and glycogen in the liver.

5. Reproductive glands :

Sex hormones are produced in testes in male and in ovaries in female. The production of these hormones is stimulated by another group of hormones secreted by the anterior lobe of the pituitary gland and carried to the gonads (testes and ovaries) through the blood stream. Hence the sex hormones are sometimes called the secondary sex hormones and the sex hormones of the anterior lobe of the pituitary gland are called Primary sex hormones.

Male Sex Hormones :

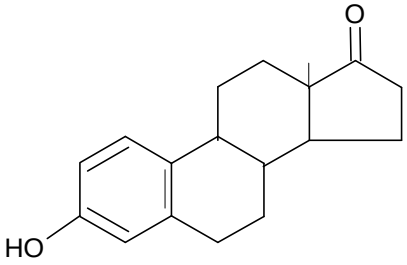
Testosterone is the male sex hormone, produced by testes. It promotes the development of the secondary male sex characteristics.



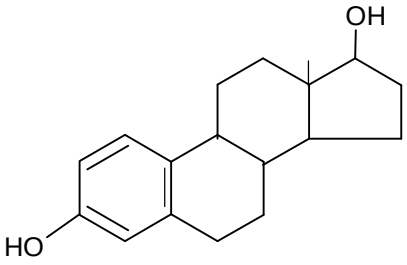
Testosterone

Female Sex Hormones :

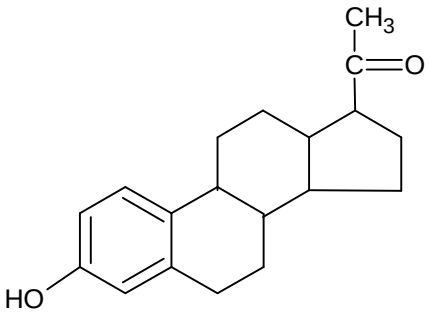
The oestrogens and progesterone are female sex hormones secreted by the ovaries. The oestrogens include oestrodiol, oesterone, oestriol out of which oestrodiol is the most important hormone . Oestrodiol stimulates female sex characteristics and regulates the menstrual cycle. Progesterone, another hormone regulates the menstrual cycle and supports pregnancy. If pregnancy does not occur, its secretion ceases after few days.



Oestrone



Oestradiol



Progesterone

Model Questions :

1. What are hormones ? Mention the important endocrine glands present in the body. Give the hormones secreted by them. Mention the functions of each hormone.
2. Name the hormones secreted by thyroid gland. Discuss the bad effects caused by their deficiency.
3. Give the hormones secreted by adrinaline gland. What are the diseases caused by their deficiency.
4. Write notes on hormones secreted by reproductive glands.
5. Mention the name of gland that secretes insulin. Discuss the role of insulin in the body.

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UNIT – II

POLYMER - CHEMISTRY

Lesson – I

INTRODUCTION TO POLYMERS

2.1.1 Concepts, classification of polymers - condensation, addition polymers. polymerisation of cyclic compounds- examples, inorganic polymess.

2.1.2 Concepts :

a) Polymer

b) Monomer

c) Polymerisation

d) Degree of polymerisation

e) Difference between polymer molecules, simple molecules and macro molecules.

a) Polymer :

The word polymer is derived from Greek (poly = many, mer = part)

A polymer molecule is defined as a number of respecting chemical units held together by covalent bonds.

Ex : Rubber, plastic, cellulose, starch

b) Monomer :

The strating material from which polymer formed is called monomer. When polymerisation involves splitting of small molecules like H_2o, the repeating unit is not equivalent to the monomer.

Ex : 1) polymer is polyethylene $(CH_2 – CH_2)_n$. The Monomer is ethylene $CH_2=CH_2$

Repeating unit is $–CH_2\,CH_2–$

2) Polymer is Polyvinyl Chloride($CH_2=CHCl)_n$. Monomer is vinylchloride $CH_2=CHCl$

Repeating unit is $–CH_2CHCl–$

c) Polymerisation :

The process of small molecules joining together forming a large molecule is called polymerisation. The large molecule is called polymer. The small molecule is called monomer.

Ex : $n\ CH_2 = CH_2 \rightarrow -(CH_2CH_2)-_n$

Monomer Polymer

d) Degree of Polymerisation :

The length of polymer chain is specified by the number of repeating units. This number is called degree of polymerisation (DP) and denoted by 'n'. It is used to calculated Mol.Wt.of a polymer.

Molecular weight of a polymer = n x Mol.Wt of the repeating Unit.

Ex : Mol.Wt of polyvinyl choloride of DP. 1000 is 1000 x 63 = 63000 because Mol.Wt. of the repeating unit (CH_2CHCl) is 63.

e) Characters of polymers (or) Difference between polymer molecules, simple molecules and Macro molecules :

Polymers	Simple molecules
1. They are complex and gaint moleucles. **Ex:** Rubber	They are simple and small molecules **Ex:** Common salt
2. They are molecules of high Mol.Wt. Mol.Wt.of a polymer can be several hundred thousands. **Ex:** Mol.Wt of rubber is 10,000 to 1,000,000.	They are molecules of low Mol. Wt. **Ex.** Mol.Wt. of Common Salt is 58.5
3. They does not melt sharply	They have sharp melting points
4. **Solubility :** They take longtime for dissolution.	**Solubility :** They take short time for dissolution.
5. No saturated solution is formed	Saturated solution is formed
6. Viscosity increases	Viscosity is not much different.

Difference between polymers and macro molecules :

Polymers are composed of repeating units where as macro molecules may not be composed of repeating units.

In Greek, macro = large where as poly = many.

2.1.3 Classification of Polymers :

1. Natural and synthetic polymers.
2. Organic and Inorganic polymers.
3. Thermoplastic and Thermosetting polymers

4. Plastics, elastomers and Fibre forming materials.

5. Addition and condensation polymers.

1. Natural and synthetic polymers :

Based on the origin, polymers are grouped as Natural and synthetic polymers.

Natural polymers : Polymers isolated from natural materials are natural polymers. These are also known as biological polymers

Ex : Ruber, wool, cellulose, starch

Synthetic Polymers : Polymers synthesized from low molecular weight compounds are synthetic polymers.

Ex : polyethylene, PVC, nylon and terylene.

2. Organic and Inorganic polymers :

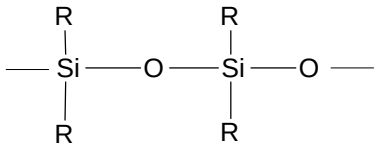
Depending on the nature of backbone chain, polymers are classified as organic and Inorganic polymers.

Organic polymers : Polymers whose backbone chain is essentially made of carbon atoms are organic polymers. Majority of the synthetic polymers are organic polymers.

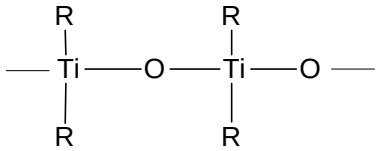
Ex : Polyethylene, PVC,nylon and terylene.

Inorganic polymers : Polymers whose backbone chain does not contain carbon atoms are inorganic polymers.

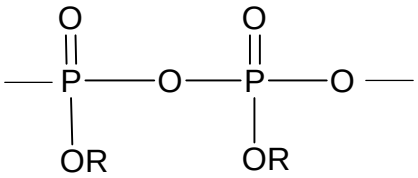
Ex: 1. Polysiloxanes



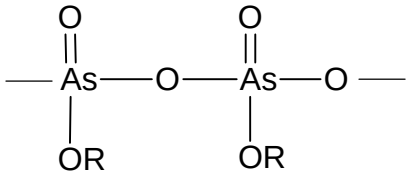
2.Polytitanoxanes



3.Polyphosphates



4.Polyarsenates



3.Thermoplastic and Thermosetting polymers :

Based on the thermal property polymers are classified as thermoplastic and thermosetting polymers.

Thermoplastic Polymers : Polymers which soften on heating and stiffen on cooling are thermoplastic polymers.

Ex : Polyethylene, PVC, and sealing Wax.

Thermosetting Polymers : Polymers which undergo chemical change on heating and convert into infusible mass are thermosetting polymers.

Ex : Bakelite, yolk of the egg.

4. Plastics, elastomers and fibre forming materials :

Depending on the ultimate form and use, polymers are classified as plastics,elastomers and fibre forming materials.

Plastics : Polymers which can be shaped into hard and tough utility articles by heat and pressure are called plastics.

Ex : Polystyrene, PVC and polymethyl methacrylate.

Elastomers : Polymers which have rubber like elastic properties are elastomers. They are popularly known as rubbers.

Ex: Natural rubber, synthetic rubber, silicon rubber.

Volcanized rubber is more elastic than natural rubber.

Fibre forming materials : Polymers drawn into long filaments whose length is at least 100 times its diameter are called fibres.

Ex: Nylon and terylene Cotton and wool are natural fibres.

Fibre forming materials possess rigidity and stiffness.

5. Addition and condensation polymers :

Based on the mode of synthesis, polymers are classified as addition and condensation polymers.

Addition polymers :

Polymers formed when monomers are added without the elimination of molecules are addition polymers.

This process is called addition polymerisation.

Ex : polyethene, polyvinyl chloride.

These polymers are obtained by addition polymerisation. It is also known as chain polymerisation.

In these polymers the monomer retains its structural identity. For example in polyethylene the structural identity of ethylene is retained.

Molecular weight of the addition polymer is equal to that of all molecules which combine to form the polymer. The reason is that there is no elimination of any small molecules during addition process.

Ex: $n\ CH_2 = CH_2 \xrightarrow[\text{Polymerisation}]{\text{addition}} (-CH_2-CH_2-)_n$

polyethene

Condensation polymers :

Polymers formed when monomers react together with the elimination of simple molecules are condensation polymers.This process is called condensation polymerisation.

Ex: Nylon-66, polyester.

These polymers are obtained by condensation polymerisation. It is also known as step polymerisation.

In these polymers the monomer does not retain its structural identity.

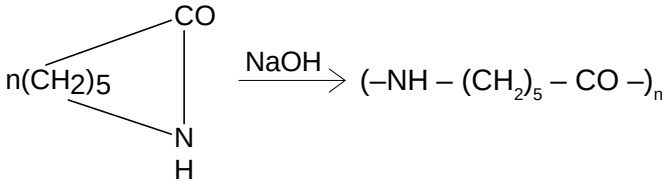
Molecular weight of the condensation polymer is less to that of all molecules which combine to form the polymer. The reason is that there is elimination of small molecules during condensation process.

Ex: $n\ HO-R-COOH \xrightarrow[\text{Polymerisation}]{\text{condensation}} HO\ (-R-COO-)_n\ H + (n-1)\ H_2O$

2.1.4 Polymerisation of cyclic compounds :

Cyclic compounds having strained configuration are opend up under favourable conditions and undergo polymerisation. It is called ring opening polymerisation

Ex: lactams and oxiranes are opend up in the presence of strong alkali or acid and undergo polymerisation



Caporlactam

1) Strained molecules are easy to polymerise. For example 4- and 8- membered ring lactones are easy to polymerise because they are strained molecules.

2) Strain free molecules are difficult to polymerise. For example 5- membered ring lactones are difficult to polymerise because they are strain free molecules.

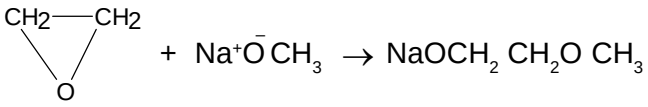
3) It resembles addition or condensation polymerisation

Mechanism :

Mechanism of ring opening polymerisation of Ethylene Oxide

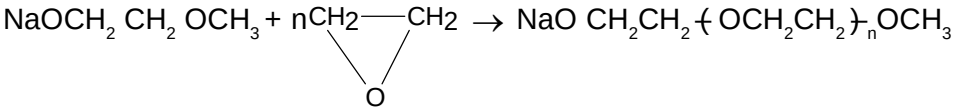
Ethyleneoxide is a hetrocyclic ring oxirane compound.

Initiation :

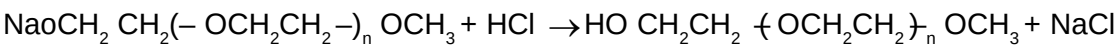


ethylene oxide — Sodium methoxide

Propagation :



Termination :



2.1.5 Model Questions :

1. define and explain polymer and polymerisation.
2. Explain classification of polymers.
3. What is addition and condensation polymerisation? Give examples.
4. Define and explain degree of polymerisation.
5. Explain polymerisation of cyclic compounds with mechanism.
6. Distinguish polymer molecules and simple molecules.

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Lesson – 2

STRUCTURE OF POLYMER MOLECULES

2.2.1 Structure of polymer molecules - micro structures based on chemical structure, micro structures based on Geometrical structures, effect of crystallinity on the properties of polymers.

2.2.2 Structure of Polymers :

Two polymers having same chemical structure and similar molecular weight distribution may have different properties. One sample may be amorphous while the other is crystalline. One soft and flexible, the other hard and rigid one melting on heating, the other only charring. One dissolves in a perticular solvent, the other not. All such properties depend on intermolecular and intramolecular interactions of polymer chains. The nature and the magnitude of such interactions depend on the manner in which monomers are linked in the polymer apart from their number and chemical nature.

The number and chemical nature of monomers gives overall picture of the polymer chain known as macrostructure. The manner in which monomers are linked gives finer aspects of the polymerchain know as microstructure. So the mode of interlinking of monomers indicates microstructure of the polymer. Microstructure of polymers are mainly two types

1) Microsturctures based on the chemical structure

2) Microstructures based on the geometrical structure.

2.2.3 Microstructures based on the chemical structure :

Chemical structure of a macromolecule depends on the chemical linkages of the monomeric units.

Based on chemical structure polymers are classfied as

i) Organic and Inorganic polymers

ii) Homochain and Hetero chain polymers

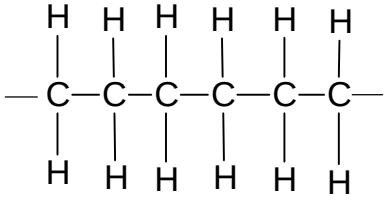
iii) Homo and Co-Polymers.

i) Organic and Inorganic polymers :

Based on the nature of the backbone chain polymers are classified as organic and inorganic polymers.

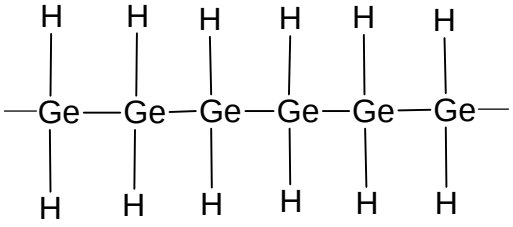
In organic polymers backbone chain is essentially made of carbon carbon (C – C) linkages. Where as Inorganic polymers made of other linkages.

Ex : Polyethylene



Organic polymer made of carbon-carbon linkages

Polygermane



InOrganic polymer made of germanium - germanium linkages

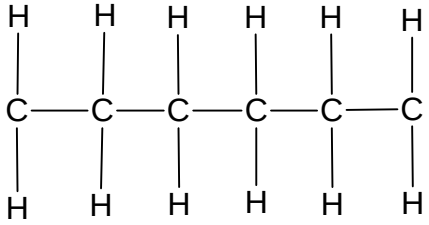
ii) Homochain and Heterochain polymers :

Based on the composition of back bone chain polymers are classified as Homochain polymers and Heterochain polymers.

Homochain polymers :

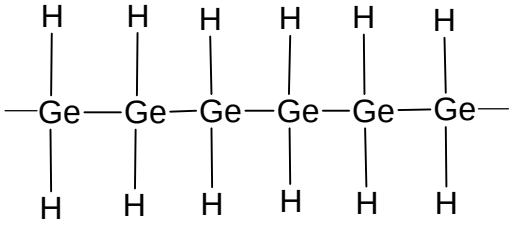
Polymers with backbone chain entirely made of same type of atoms are homochain polymers.

Ex : Polythene



It is Homochain polymer. The backbone chain is made of carbon atoms only.

polygermane

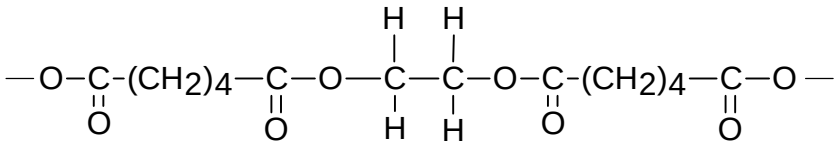


It is Homochain polymer. The backbone chain is made of Germanium atoms only.

Heterochain polymers :

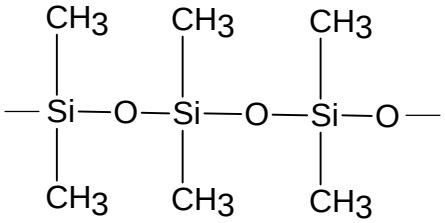
Polymers with backbone chain made of different types of atoms are heterochain polymers.

Ex : Polyethyleneadipate



It is Heterochain polymer. The backbone chain is made of Carbon and oxygen atoms.

Polydimethylsiloxane.



It is Heterochain polymer. the backbone chain is made of silicon and oxygenatoms.

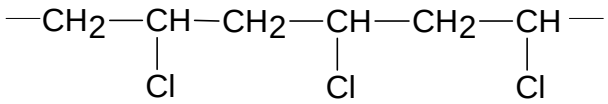
iii) Homopolymers and copolymers:

Based on the repeating units present in a polymerchian,polymers are classified as homopolymers and co-polymers.

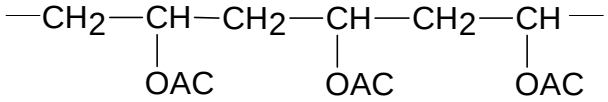
Homopolymers :

Polymers with polymerchain entirely made of same type of repeating units are called homopolymers.

Ex: Polyvinyl Chloride (PVC)



Polyvinylacetate (PVAC)



In general if A represents the repeating unit, the structure of homopolymer can be represented as.

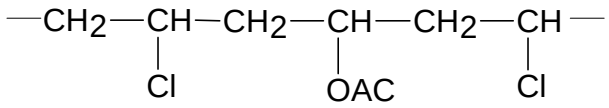
–A–A–A–A–A–A–A–A–

Homopolymers

Co- polymers :

Polymers with polymer chain made of different types of repeating units are called co-polymers.

Ex : Poly (Vinylchloride - Vinylacetate) It is formed when two monomers vinyl chloride and vinylacetate are mixed and then polymerised.



If A and B represent the two different repeating units, the structure of Co-polymer can be represented as.

–A–A–B–B–B–A–A–B–A–A–A–

2.2.4. Micro structures based on geometrical Structure :

The geometrical structure of a macromolecule depends on the spacial arrangement of the monomeric units. Polymers having same chemical structure can have different geometrical structures.

Configuration :

A configuration is anarrangement fixed by chemical bonding between adjacent monomeric units and between atoms of individual monomeric units.

A polymeric chain can not shift from one configuration to another with out breaking or reforming the chemical bonds.

Conformation : A conformation is an arrangement resulting from the rotation of single bonds between adjacent monomeric units.

A polymeric chain can shift from one conformation to another with out breaking or reforming the chemical bonds. Over a period of time, a polymeric chain can assume innumerable conformations.

Flexible chain and rigid chain polymers :

Based on the freedom of rotation polymers are classified as flexible chain polymers and rigid chain polymers.

Flexible chain polymers :

Polymers in which the chain segments can rotate with respect to each other are called flexible chian polymers.

Ex :Polyethylene, polystyrene, rubber.

Random coil, folded chain and helical chain polymers :

Random coil, folded chanin and helical chain are the conformations of Polymers under different situations :

In solid state, amorphous polymers have random coil conformation. Crystalline polymers have folded chain conformation. Biological polymers such as proteins have spiral or helical chain conformation.

Interpenetrated
random coils
Amorphus

orderly folded chains
Crystalline Polymers

Spiral or helical chains
biological polymers
(polypeptides or proteins)

In dilute solutions flexible chain polymers exist as isolated random coils. Rigid chain polymers exist as rigid rods.

In concentrated solutions polymers form interconnected network structure.

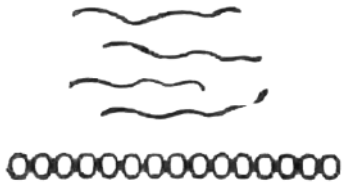
Rigid chain polymers : Polymers is which the rotation of the chain segments is hindered are called Rigid chain polymers. This is due to steric factors or due to strong forces of attraction.

Ex : Polyamides, aromatic polyesters, cellulose esters.

Linear, branched and cross - linked polymers :

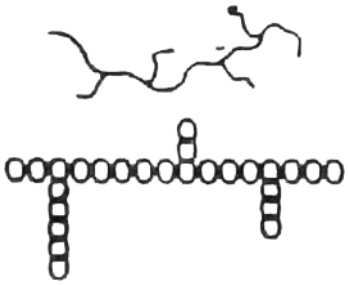
Homopolymers and copolymers exist in three different types of chain configuration. They are linear, branched and cross - linked.

1. In linear polymer monomeric units are added forming a long chain. It can be represented by a single line.



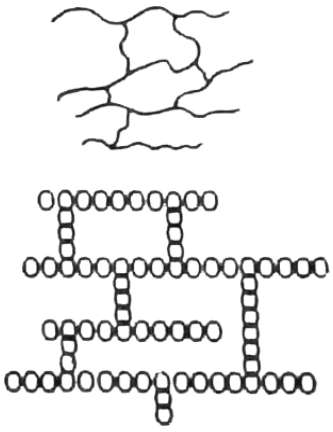
Linear

2. In branched polymer the linear chain is attached to few branches at random points.



Branched

3. In cross linked polymer, the neighbouring branched polymers are inter united forming a single molecule. It has criss- cross three dimensional network.



cross - linked

Random, Alternating, Block and Graft copolymers :

Copolymers exist us random, alternating, block and graft configurations.

1. In Random Co-Polymer the two different repeating units are distributed at random through the chian. In certain polymers a more ordered requence of repeat unit is seen. These are termed as alternating, block or graft copolymers.

Random Co - Polymer.

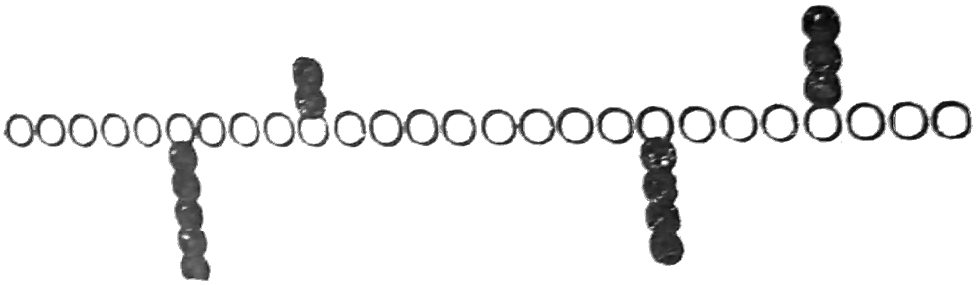
2. In alternating Co-Polymer the two different repeating units are distributed alternatively through out the chain.

Alternating Co-Polymer

3. In block copolymer a block of one repeating units, which inturn by a block of first repeating unit is followed by a block of repeating unit and soon.

Block Co-Polymer

4. In Graft Co- Polymer the main chain is made of one type of repeating units while the branched chains are made of another type of repeating units.



Graft Co-Polymer

2.2.5. CRYSTALLINITY :

Effect of crystallinity on the properties of polymers.

Crystallinity : Crystallinity of a polymer is expressed as fraction of the polymer which is crystalline.

Explanation : X - ray diffraction of most of the polymers contain both sharp as well as broad and diffuse bands. The sharp bands correspond to crystalline regions. The broad and diffuse bands correspond to amorphous regions. So, the crystalline and non - crystalline components of a polymer can coexist. The overall property (Q) of a partially crystalline polymer is given by

Q = Qc + Qa

Where,Qc = Crystalline component of the polymer.

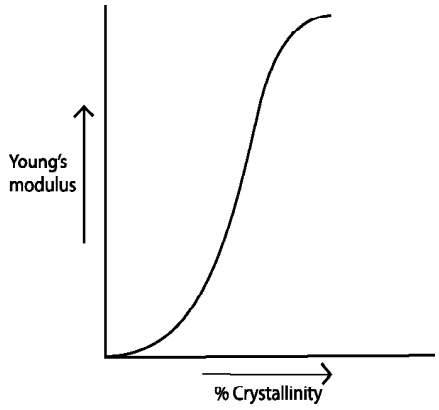
Qa = amorphous component of the polymer.

Effect of crystallinity on the properties of polymers :

The properties of a polymer such as density, youngs modulus, hardness, tensile strength and permeability are largely effected by its crystallinity.

Density : Density of crystalline regions is higher than that of the amorphous regions.

Young's modulus :



dependence of young's modulus on crystallinity in natural rubber.

The initial low value of young's modulus is the characteristic of amorphous polymer. As crystallinity increases, young's modulus increases sharply.

Hardness and tensile strength : Hardness and tensile strength increases as crystallinity increases.

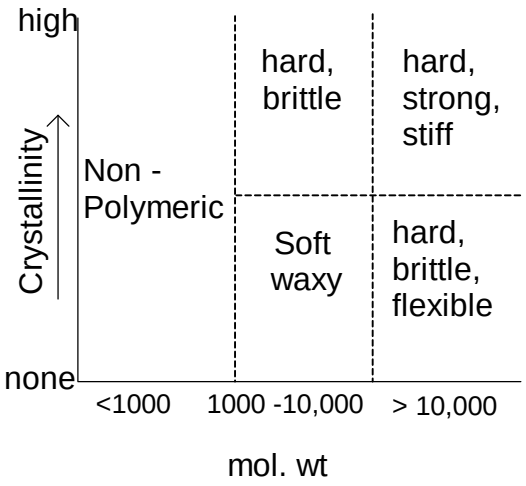
Ex :	**Property**	**Less Crystalline**	**Highly Crystalline**
	Hardness	44 - 50	66 - 73
	Tensile strength	83 - 214	221 - 310

Permeability : Crystallinity has effect on permeability and hence on the chemical degradation of the polymer.

Ex : Acid hydrolysis of cellulose takes place easily at amorphous regions than at crystalline regions.

Crystallinity and Mol. Wt :

A Combined effect of crystallinity and Mol. wt. on the physical properties of a polymer is shown below.

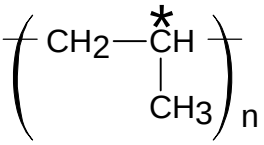


2.2.6. Stereo - regular polymers :

In stereo regular polymers, each monomeric segment has a regular configuraion. This gives a definite structural regularity to the polymer molecule as a whole. As a result optical and geometrical isomerism arise due to the main chain atoms or substituents in the polymer.

i) Optical Isomerism :

Optical Isomerism arises from different configurations of the substituents on an asymmetic carbon atom in a polymer molecule.

Ex : Propylene Polymerisation 

Each C^* site can be either d- or l- depending on whether R group is above or below the carbon chain. It gives rise to three types of configurations. They are

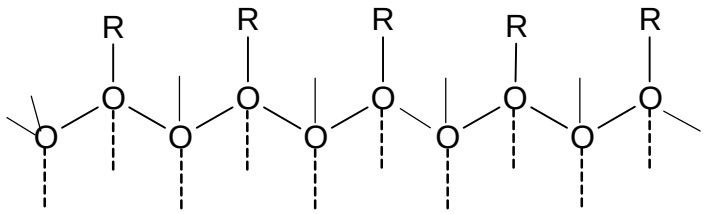
a) Isotactic (Cis arrangement)

b) Syndiotactic (trans or alternating arrangement)

c) Atactic (In Greek atactic = without order) or Heterotactic.

a) Isotactic Configuration :

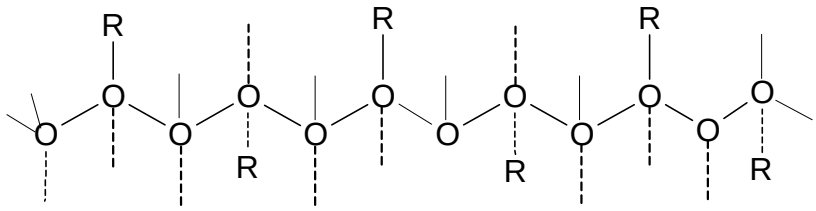
In Isotactic configuration all the alkyl groups (R) are present on one side of the carbon chain.



– d – d – d – d– d – d – (or) – l – l – l – l – l – l –
Isotactic

b) Syndiotactic Configuration :

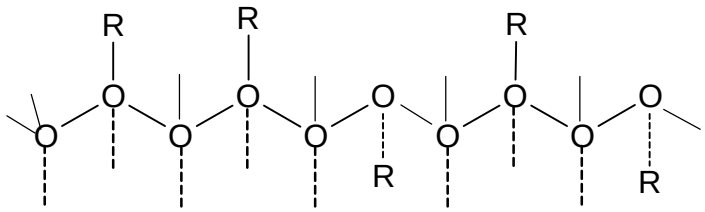
In syndiotactic configuration the alkyl groups are present alternatively above and below the carbon chain.



– d – l –d – l – d – l – d –l (or) – l – d – l – d – l – d –
Syndiotactic

Atactic Configurations :

In atactic configuration the alkyl groups are present randomly above and below the Carbon chain.



– d – d – l – d – l – (or) – l – l – d – l – d –
Atactic

Atactic polymers have low melting points. They are easily soluble Isotactic and syndiotactic polymers have high melting points. They are less soluble.

ii) Geometric Isomerism :

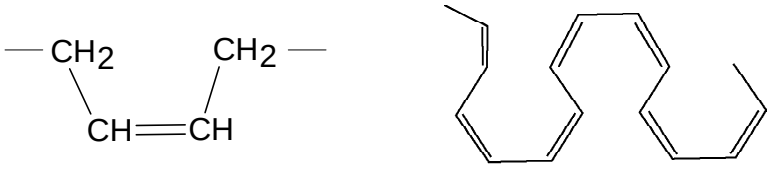
Geometric isomerism arises from different configurations of the substituents on a Carbon–Carbon double bond in a Polymer molecule.

Ex : 1,3 - butadiene polymerisation

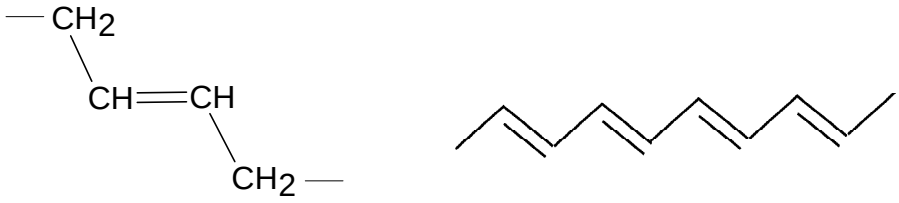
$$(- CH_2 - CH = CH - CH_2 -)_n$$

It gives rise to three types of configurations

a) Cis - polybutadiene



b) Trans polybutadiene



c) 1,2 - polybutadiene

depending on the ratio of Cis to trans segments, the polymer exhibits either high or low elongation.

2.2.7. Model Questions :

1. Explain the following - a) Isotactic polymer b) Syndiotactic Polymer c) Atactic Poylmer.
2. Explain microstructure of polymers based on chemical structure.
3. What is crystallinity ? Write the effect of crystallinity on the properties of molecules.
4. Explain microstructure of polymers based on geometrical structure.
5. What are stereo- regular polymers ? Discuss Geometric isomerism present in stereoregular polymers.

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Lesson – 3

CHEMISTRY OF POLYMERISATION

2.3.1 Chemistry of polymerisation - chain polymerisation, step polymerisation, Co - ordination polymerisation, uses of Ziegler - Natta catalysis, miscellaneous polymerisation reactions, polymerisation techniques.

2.3.2 Chain Polymerisation :

It is addition polymerisation. Chain polymerisation is self addition of monomers very rapidly through a chain reaction.

Ex : Compounds containing reactive double bonds undergo chain polymerisation.

Olefines	$CH_2 = CHR$
Vinyl compounds	$CH_2 = CHX$
Allyl compounds	$CH_2 = CH - CH_2 X$
dienes	$CH_2 = CH - CH = CH_2$

Chain polymerisation has Three major steps. They are -

1. Initiation.
2. Propagation.
3. Termination.

This Process is brought out by three mechanisms -

1. Free radical mechanism.
2. Ionic mechanism.
3. Co - ordination mechanism.

Depending on the mechanism chain polymerisation is three types -

1. Free radical polymerisation.
2. Ionic polymerisation.
3. Co - ordination polymerisation.

Free radical polymerisation :

In free radical polymerisation, initiation of the polymer chain growth takes place through free radicals. Free radicals are produced by the decomposition of initiators.

Chain growth :

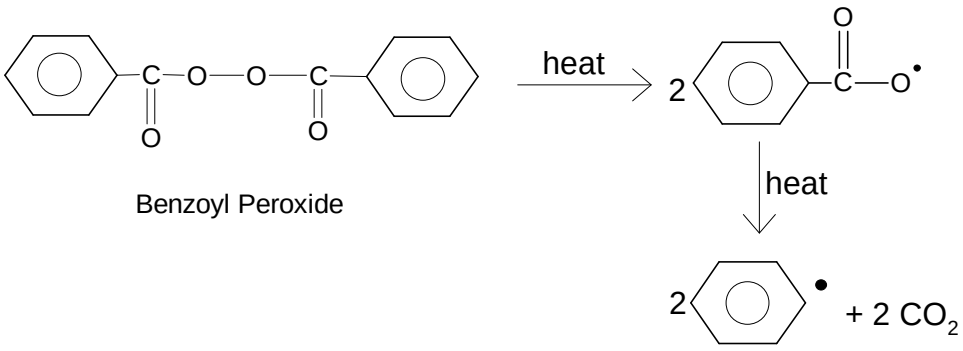
Chain growth is a process involving continuous and rapid addition of the monomeric units forming polymer chain.

Initiators :

Initiators are thermally unstable compounds. They decompose into free radicals. Heat or ultraviolet light produce free radicals.

$$\underset{\text{initiator}}{R:R} \xrightarrow{h\nu} \underset{\text{freeradical}}{2R^{\bullet}}$$

Ex : Peroxides, hydroperoxides, peracids and peresters.



Benzoyl Peroxide

Redox Initiators :

Initiators can be decomposed into free radicals by suitable catalyst involving redox reaction.These initiators are called redoxinitiators and such polymerisation is called redox polymerisation.

Ex : $H—O—OH + Fe^{+2} \longrightarrow HO^{\bullet} + \bar{O}H + Fe^{+3}$

$R—O—OH + Co^{+2} \longrightarrow RO^{\bullet} + \bar{O}H + Co^{+3}$

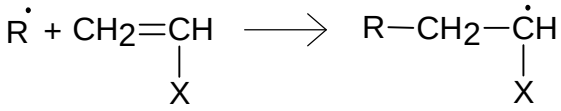
Initiation :

Initiation of a chain reaction involves two steps -

1. The formation of free radicals from an initiator.

2. Addition of free radical to the monomer generating monomeric free radical.

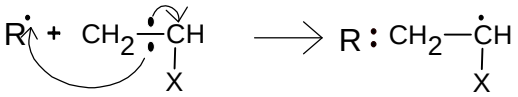
$$\text{Initiator} \longrightarrow R^{\bullet}$$



monomeric free radical

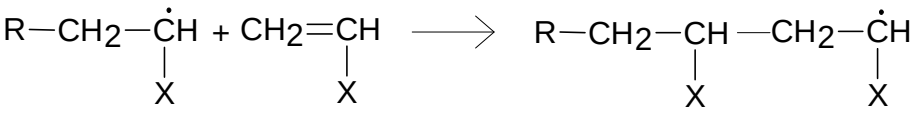
The free radical interferes with one of the π electrons froming normal bond. The other π electron is transferred to the other end of the molecule.

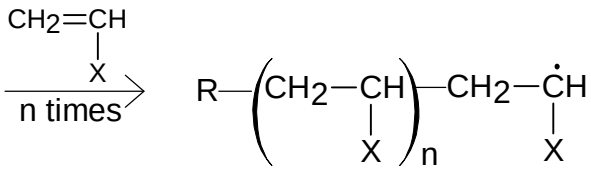
It can be shown as



Propagation :

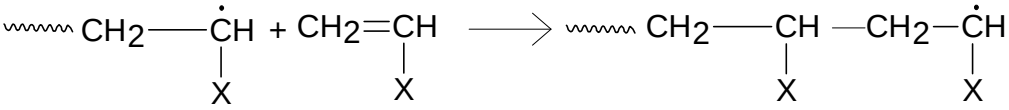
After initiation comes propagation. In propagation the monomeric radical formed is added to the second monomer which in turn added to the third monomer and soon resulting in chain growth.



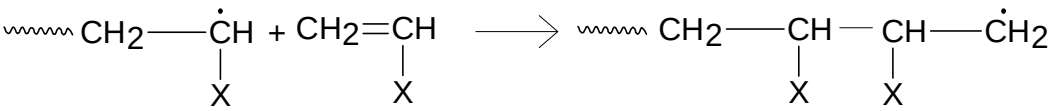


There are four modes of addition -

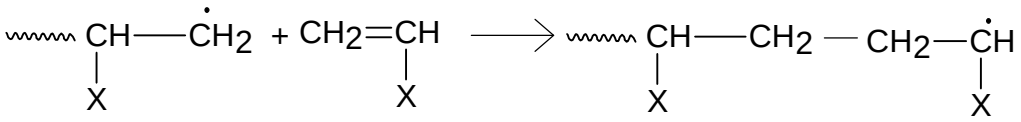
1. Tail to Head



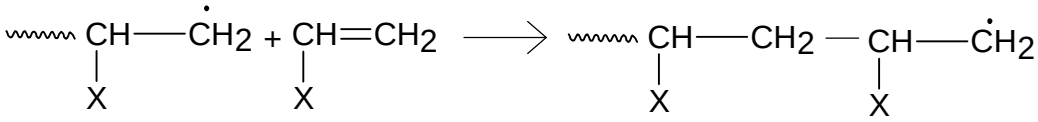
2. Tail to Tail



3. Head to Head



4. Head to Tail



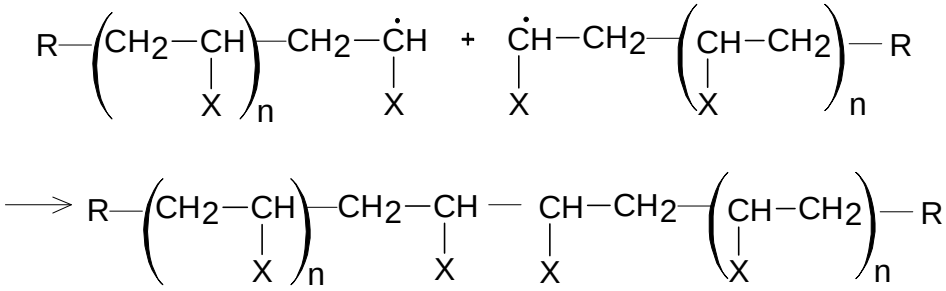
Termination :

After propagation comes termination. In termination the polymer chain growth is stopped. It is brought out by -

1. Coupling termination.
2. Dis proportionation termination.
3. Chain transfer.
4. Inhibitors.

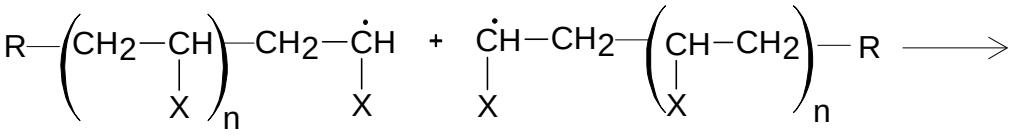
Coupling Termination :

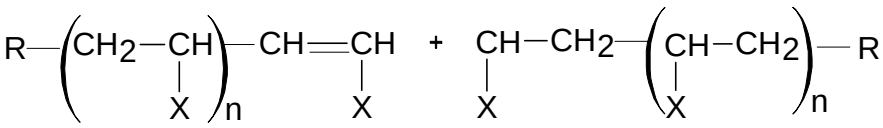
In coupling termination two free radical chains are combined forming a single molecule.



Dis Proportionation termination :

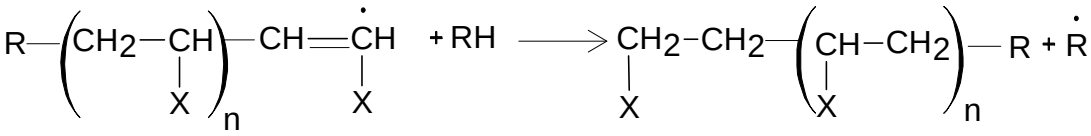
Indisproportionation termination deactivation of the growing chain is due to transfer of H atom from one growing chain to another growing chain. The deactivated polymer chains so formed are called dead polymers.

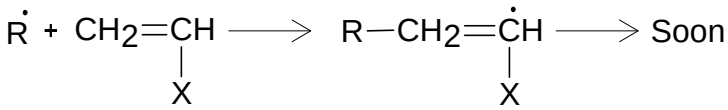




Chain transfer :

In chain transfer termination a chain growth is stopped forming a dead polymer chain. But a new free radical is generated simultaneously by which is a fresh chain growth takes place.





Inhibitors :

Inhibitors are chemical substances capable of inhibiting chain growth by combining with the active free radical chains.

Ex : Hydroquinone, Nitrobenzene, dinitrobenzene.

Ionic Polymerisation :

In ionic polymerisation initiation of polymer chain growth takes place through ions. Ions are produced from the initiators. Ionic polymerisation forms high molecular weight polymers. It can be easily carried out at room temperature.

Based on the nature of ions used for initiation Ionic polymerisation is two types.

1. Cationic Polymerisation.

2. Anionic Polymerisation.

Cationic Polymerisation :

In cationic polymerisation positive ion is used for initiation. The initiators used are BF_3, $AlCl_3$, $SnCl_4$ and $TiCl_4$. attack.

Ex : Isobutylene, Styrene, Vinylethers.

Initiation :

Initiation of chain reaction involves 2 steps

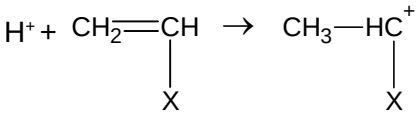
1. formation of +ve ions from initiators.

2. attacking of +ve ion on the π electron pair of the monomer forming carbonium ion.

1. $BF_3 + HOH \rightarrow H^+ + [BF_3OH]^-$

here H^+ is the +ve ion while $[BF_3OH]^-$ is the counterion.

2.



Propagation :

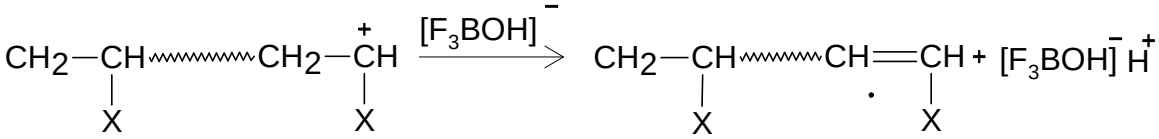
The carbonium ion formed attacks π electron pair of the second monomer which in turn attacks that of the third monomer so on resulting in chain growth.

As more and more monomeric units are added, C^+ ion keeps on moving in the direction of the chain growth. The counter ion also moves along with the C^+ ion like a watch dog.

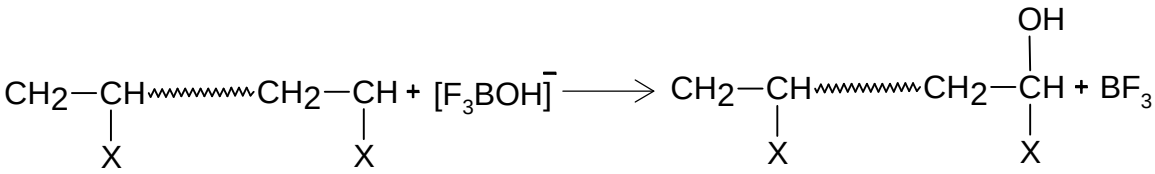
Termination :

Fermination involues the following two factors.

1. Donation of proton to the counter ion.



2. Formation of covalent bond between the carbonium ion and the counter ion.



Anionic Polymerisation :

In anionic polymerisation a negative ion is used for initiation. The initiators used are BuLi, n-BuMgBr where Bu represents (C_4H_9) butyl group.

Ex : Butadiene, Isoprene, acrylonitrile, styrene

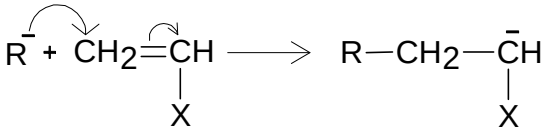
Initiation:

Initiation of chain reaction involves 2 steps.

1. Formation of the negative ion from initiators.

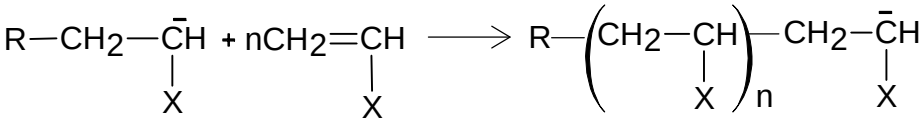
$$RLi \rightarrow R^- + L^+i$$

2. The attack of negative ion on the monomer forming carbanion.



Propagation :

In Propagation, carbanion formed attacks the second monomer which inturn attacks third monomer and so on resulting in chain growth.



Termination :

In anionic polymerisation termination is not spontaneous unless some impurities are present. Thus if polymerisation is carried out under controlled conditions and impurities are avoided, reaction proceeds till the monomer is consumed. It a fresh quantity of monomer is added even after weeks, polymerisation goes again until fresh monomer is consumed. Thus the polymer is a living entity and is called ' Living Polymer'. This living polymerisation technique is useful for many applications. For example block copolymers are prepared by this technique.

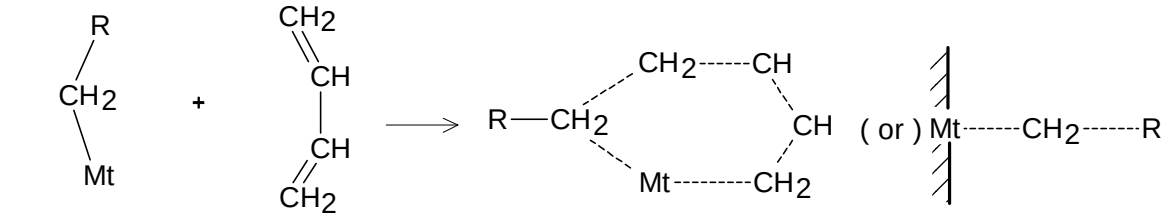
2.3.3 CO- Ordination Polymerisation (or) Ziegler - Natta Polymerisation :

The polymerisation of olefines and dienes catalysed by organometallic compounds is called coordination polymerisation. K. Ziegler and G. Natta discovered this method.

Ex : Formation of High density linear polyethylene.

Initiation :

The first step is the formation of monomer - catalyst complex between the monomer and the organometallic compound. It is a heterogeneous system.



organometallic compound (Catalyst)

Diene (monomer)

Monomer - catalyst complex

Where Mt represents a transition metal such as Ti, Cr, Mo, Ni.

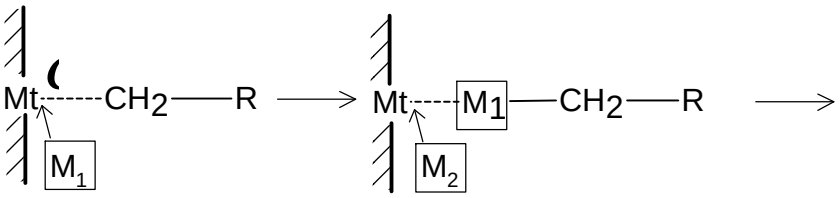
In the formation of monomer - catalyst complex, a coordination bond is involved between carbon atom of the monomer and metal atom of the catalyst. Hence the polymerisation is called 'Co - ordination Polymerisation ' .

Propagation :

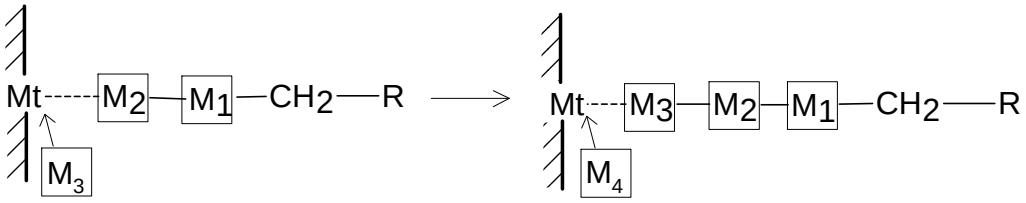
The coordinated carbon- metal bond formed in the monomer - catalyst complex acts as active centre and starts propagation.

Three phases are present in coordination polymerisation :

The monomer - catalyst complex is a heterogeneous system. The metal ion is in the solid phase and carbanion is in the solvent phase. The monomer is in the third phase. The monomer is a inserted between the metal ion and the carbanion. As a result the polymer chain formed is pushed out from the solid surface of the catalyst. Coordination polymerisation is also known as insertion polymerisation.



Solid Phase of the adduct



Here M_1, M_2, M_3 etc are the monomer units added to the growing chain.

Termination :

Termination occurs with an active hydrogen compound.

Importance :

The most important feture is that depending on the polarity of the carbon metal bond and on the solvent medium, the counter ion is placed in a particular special arrangement w.r.t the anion. It effects the spacial orientation of the incoming monomer and its insertion into the growing polymer. Thus, a stereoregular polymer is formed.

Ziegler - Natta catalysts :

Ziegler - Natta catalysts are a special type of coordination catalysts made of two components.

1. Catalyst component.

2. Co- Catalyst component.

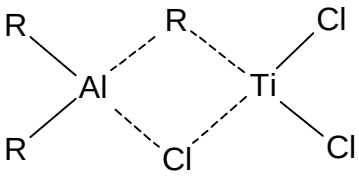
The catalyst component consists of halides of IVB - VIIIB group having transition valency.

The co - catalyst component consists of organometallic compounds like alkyls, aryls and hydrides of I - IV group metals.

Ex : Triethyl aluminium ($Al\ Et_3$)or diethyl aluminium chloride ($Al\ Et_2\ Cl$) in combination with titanium trichloride or titanium tetrachloride.

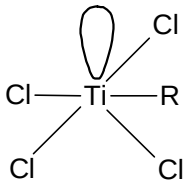
Structure :

Aluminium alkyls act as electron acceptors and titanium halides act as electron donors. They readily form coordination complexes. These complexes are insoluble in the solvent and are heterogeneous in nature.

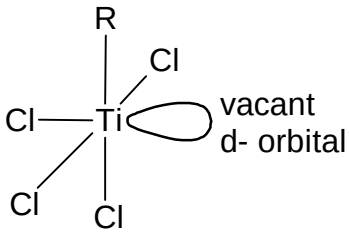


bimetallic active catalyst
bridge complex

Vacant
d- orbital



monometallic active catalyst centre
(or)



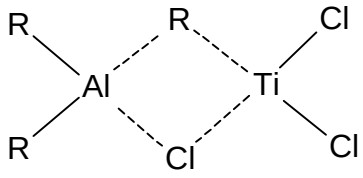
Five Coordinated Ti ion
with octahedral structure

Mechanism :

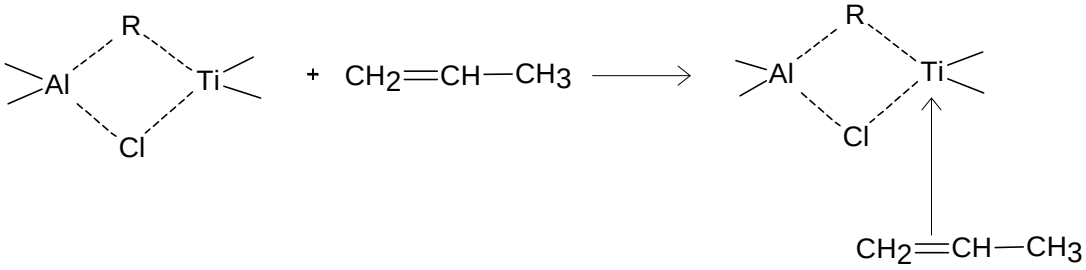
Among several mechanisms proposed the bimetallic mechanism of Natta and mono metallic mechanism of Cossee have received much attention. Cossee mechanism is widely accepted at present.

Bimetallic mechanism :

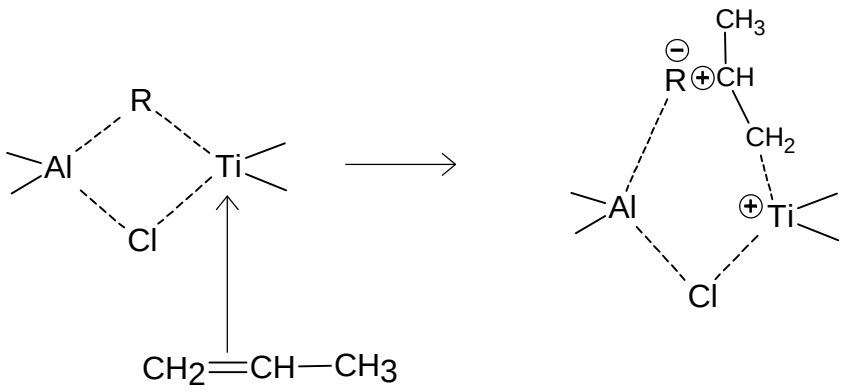
1. **Formation of electron defficient bridge complex :** According to Natta's bimetallic mechanism when the catalyst and co - catalyst components are mixed, the chemisorption of aluminium alkyl occurs on the titanium chloride. As a result an electron defficient bridge complex is formed.



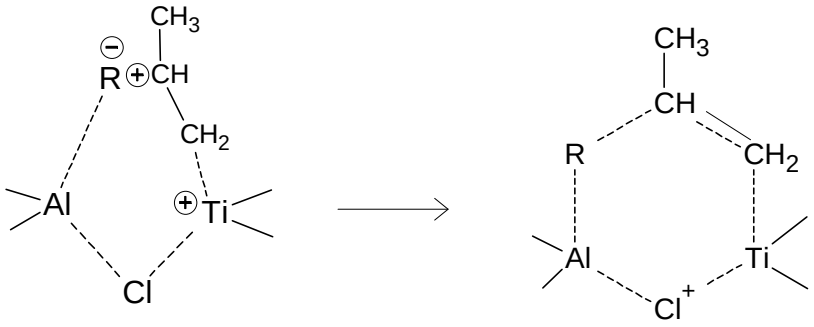
2. **Formation of π complex :** This complex acts as active centre. The monomer is attarcted towards Ti - C bond in active centre forming a – complex.



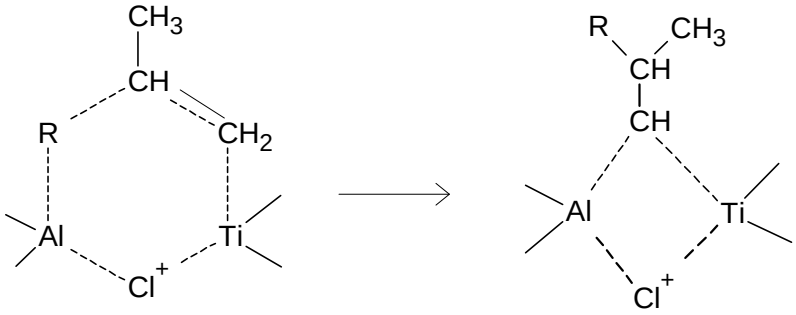
3. Formation of electron deficient Ti and carbanion at R :



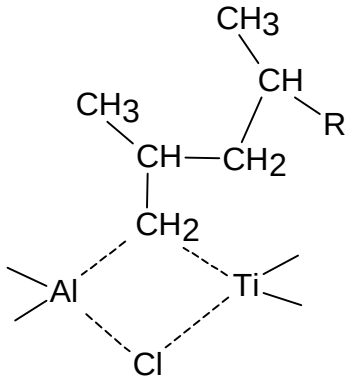
4. Insertion of the monomer into the transition state.



5. Regeneration of active centre.



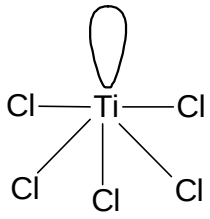
6. Chain growth.



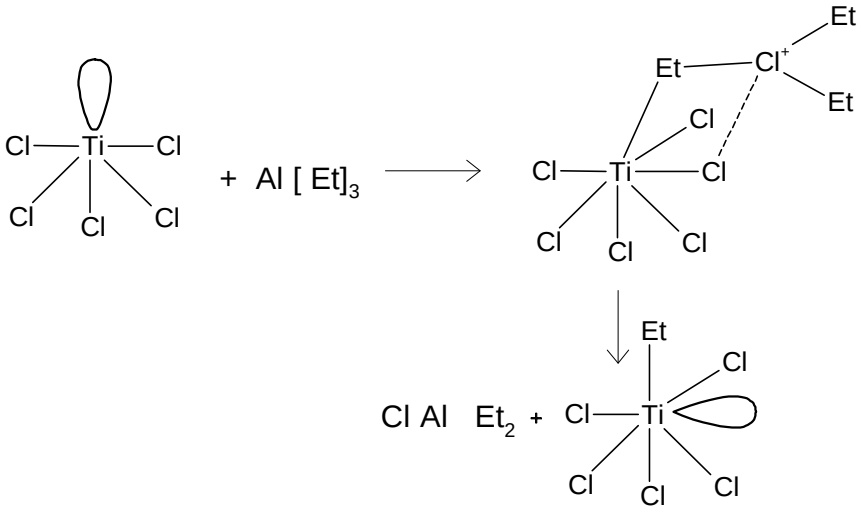
Monometallic mechanism :

According to mono metallic mechanism proposed by Cossee, the active centre is at the Ti–R part of the catalyst while aluminium alkyl acts as alkylating agent only.

1. **Five Co - ordinated titaniumion :**The five coordinated titanium ion having a vacant d - orbital is shown below.

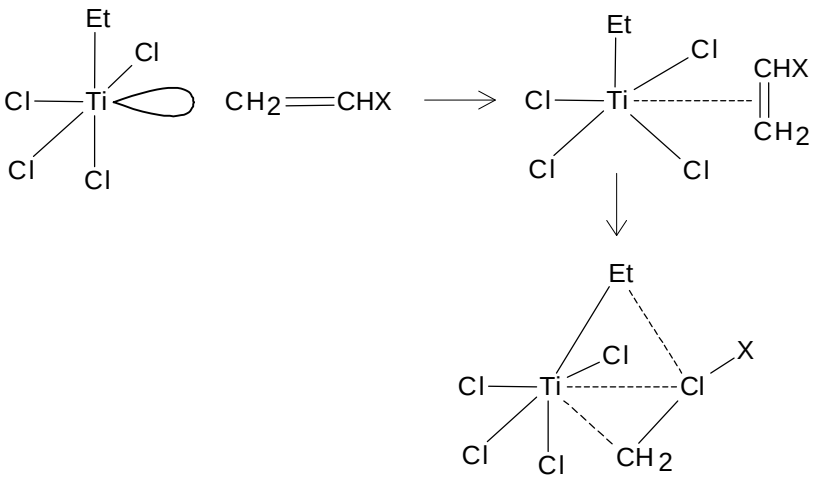


2. **Alkylation of Ti^{+3} :** When the catalyst and Co - catalyst are mixed aluminium is chemisorbed on the solid $TiCl_3$ here soon after Ti^{+3} gets alkylated.



active catalyst octahedral structure

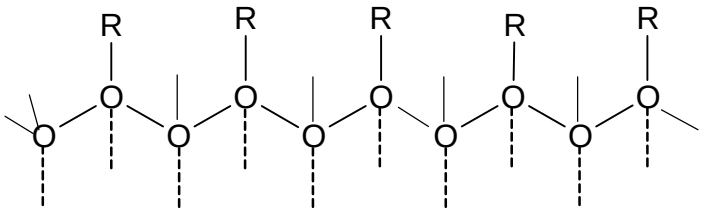
3. **Formation of a π transition complex :** The monomer is attracted towards the vacant d-orbital forming a transition π - complex with Ti.



4. Growth of polymer chain : The transition state quickly gives rise to the growth of the polymer chain by the insertion of the monomer at Ti - Et bond.

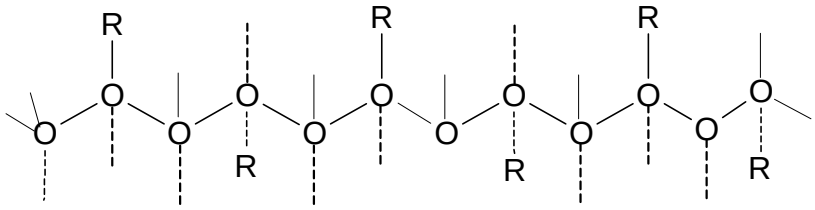
Uses : Formation of Stereo regular polymers :

1) When the vacant d - orbital is generated at the same position all the time, the incoming monomeric units are inserted with the same spacial arrangement. This gives isotactic polymer.



Isotactic

2) When the vacant d- orbital is migrated from one position to other position alternatively, the incoming monomeric units are inserted with the alternating spacial arrangement. This gives syndiotactic polymer.



Syndiotactic

Thus always a stereo regular polymer is obtained.

2.3.4 Condensation (or) Stepgrowth polymerisation :

Step growth polymerisation involves the reaction between bi - functional or multifunctional monomers. The polymer is built up in a step wise manner and chain growth is slow. At each step generally a small molecule is eliminated. In step growth polymerisation condensation, addition, ringopening, amination and ester inter change reactions are most commonly used.

Polycondensation : Polycondensation takes place in monomers containing two or more functional groups condensing with each other.

Types of Polymers : These Polymers are classified into two types.

1. **Linear polymers :** These are obtained from monomers of functiona lity two (bi functional).
2. **Non - Linear polymers (Three dimensional polymers) :** These are obtained from monomers of functionality greater than two.

Important Generalisations :

The important generalisations are made regarding polycondensation or any step polymerisation.

1. The monomer should have two reactive functional groups for polymerisation to proceed.
2. The polymerisation proceeds in a step wise manner.
3. In polymer formation only one type of reaction is involved between the two functional groups.

Ex : Only condensation reaction is involved in poly condensation.

4. The polymer formed contains both the reactive functional groups as end groups. Hence it is active and not dead.

$nHOCH_2\ CH_2OH + n\ HOOC\ (CH_2)_4\ COOH \rightarrow HO\ –[CH_2\ CH_2OOC\ (CH_2)_4\ COO]_n – H + 2n – l\ H_2O$

Types of Polycondensation reactions :

1) AA – BB type

2) A- B type

1. AA – BB type polycondensation :

The two reactive functional groups [– OH and – COOH] are present on the two different bifunctional polymers. This is generally described as AA - BB type polycondensation. The reaction can be shown as.

$n\ A – A + n\ B – B \rightarrow A – [AB]_{2n+1} – B$ + by product.

Polcondensation of aminoenanthic acid.

$nH_2N – (CH_2)_6 – COOH \rightarrow H – [HN – (CH_2)_6 – CO]_n – OH + n – l\ H_2O$

2. A – B type polycondensation :

The both reactive functional groups [– NH2 and – COOH] are present on a single bifunctional monomer. This is generally described as A–B type polycondensation. The reaction can be shown as.

$n\ A – B \rightarrow B – [AB]_{n–1} – A$ + by product.

EX : some generic polycondensation reactions are -

1. Dihydric alcohols undergo polycondensation forming polyethers.

$$nHO – R – OH \rightarrow HO – [R]_n – H + n – l\ H_2O$$

2. Dihydric alcohols and dicarboxylic acids undergo polycondensation forming polyesters.

$nHO – R – OH + nHOOC – R^l – COOH \rightarrow HO – [–R –OOC– R^l – COO]_n – H + 2n – l\ H_2O$

3. Amino acids under go polycondensation forming polyamides (nylons).

$$nH_2N - R - COOH \rightarrow H - [\ HN - R - CO]_n - OH + n - l\ H_2O$$

2.3.5 Model Questions :

1. Write an essay on step polymerisation.
2. Explain mechanism involved in free radical polymerisation with suitable examples.
3. Discuss chain polymerisation.
4. Explain cationic and anionic polymerisations with mechanism.
5. Explain coordination polymerisation with suitable examples.
6. What are Ziegler – Natta catalysts ? Explain their importance.
7. Explain the term living polymer

Dr. S. Siva Ram Babu, M.Sc., Ph.D.
Reader & H.O.D.
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J.K.C.College, Guntur -

Lesson – 4

MISCELLANEOUS REACTIONS AND POLYMERISATION TECHNIQUES

2.4.1. Miscellaneous Polymerisation reactions Electrochemical polymerisation, Metathetical polymerisation, group transfer polymerisation.

Polymerisation techniques :

Bulkpolymerisation, solution polymerisation, suspension polymerisation, Emulsion polymerisation, Melt poly condensation, Solution polycondensation, Inter facial condensation, Solid and Gas phase polymerisation.

2.4.2. Miscellaneous Polymerisation reactions :

These are polymerisation reactions in which the initiating species are produced under special conditions or form specific catalyst systems. They are -

1. Electronchemical Polymerisation.

2. Metathetical Polymerisation.

3. Group transfer polymerisation.

1. Electrochemical polymerisation :

In electrochemical polymerisation the initiating species are produced in an electrolytic cell containing monomer and suitable solvents or additives. The initiating species can be a free radical, a cation or an anion produced at the anode or at the cathode.

i) Anion produced at the cathode.

$$M + \bar{e} \rightarrow M^{-}$$

ii) Cation produced at the anode.

$$M \rightarrow M^{+} + \bar{e}$$

e = electron M = Monomer

iii) Free radical produced at the anode.

$$RCO\bar{O} \rightarrow RCOO^{\circ} + e$$

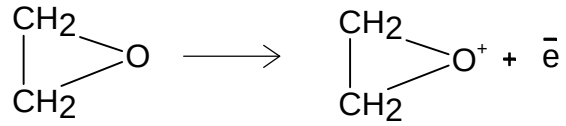
iv) Free radical produced at the cathode.

$$R^{+} + e \rightarrow R^{\bullet}$$

Once the initiating species is formed at the electrode, the initiation and propagation are similar to those of free radical, anionic or cationic polymerisation.

Ex : A typical example of electro chemical polymerisation is cationic initiation of ethylene oxide polymerisation at anode.

i)



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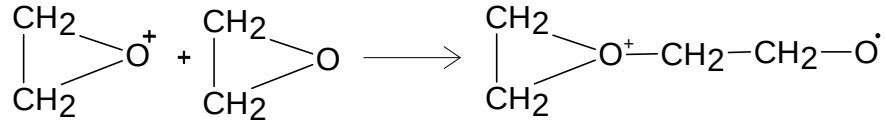

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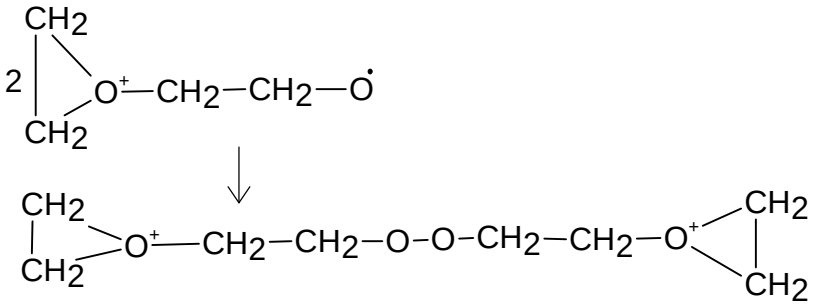

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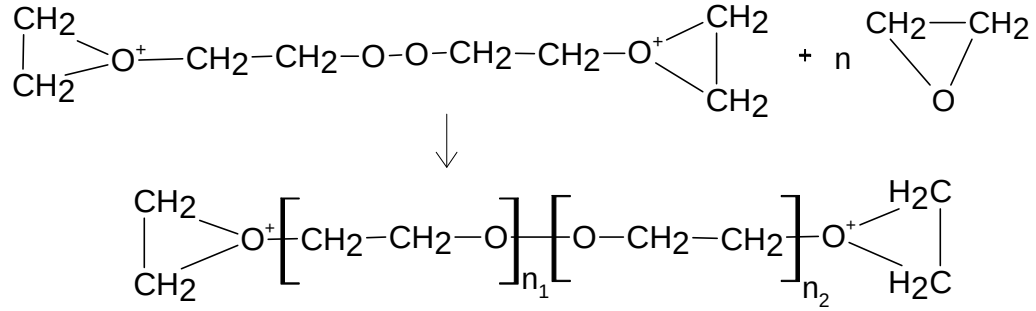


Where $n_1 + n_2 = n$

2. Metathetical Polymerisation :

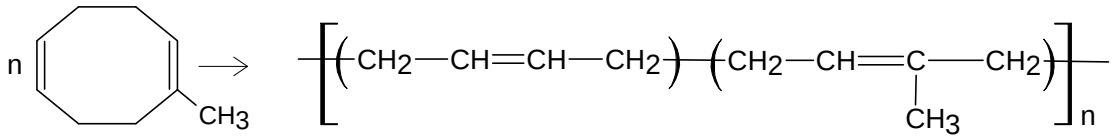
Methathesis is basically an exchange reaction where the reactant molecules are redistributed through the cleavage and reformation of olefinic double bonds.

Ex : By metathesis reaction propylene is converted into ethylene and 2 - butene in the presence of a special catalyst $Mo(CO)_6$.

$$2CH_3 - CH = CH_2 \rightleftharpoons CH_2 = CH_2 + CH_3 - CH = CH - CH_3$$

The equilibrium mixture contains ethylene, propylene and butene in the mole ratio 1:2:1. The olefine methathesis reaction can be used for the synthesis of a polymer.

Ex : Cyclooctadiene undergo metathetical polymerisation It is a Co- Polymer containing butadiene and isoprene repeating units alternatively.

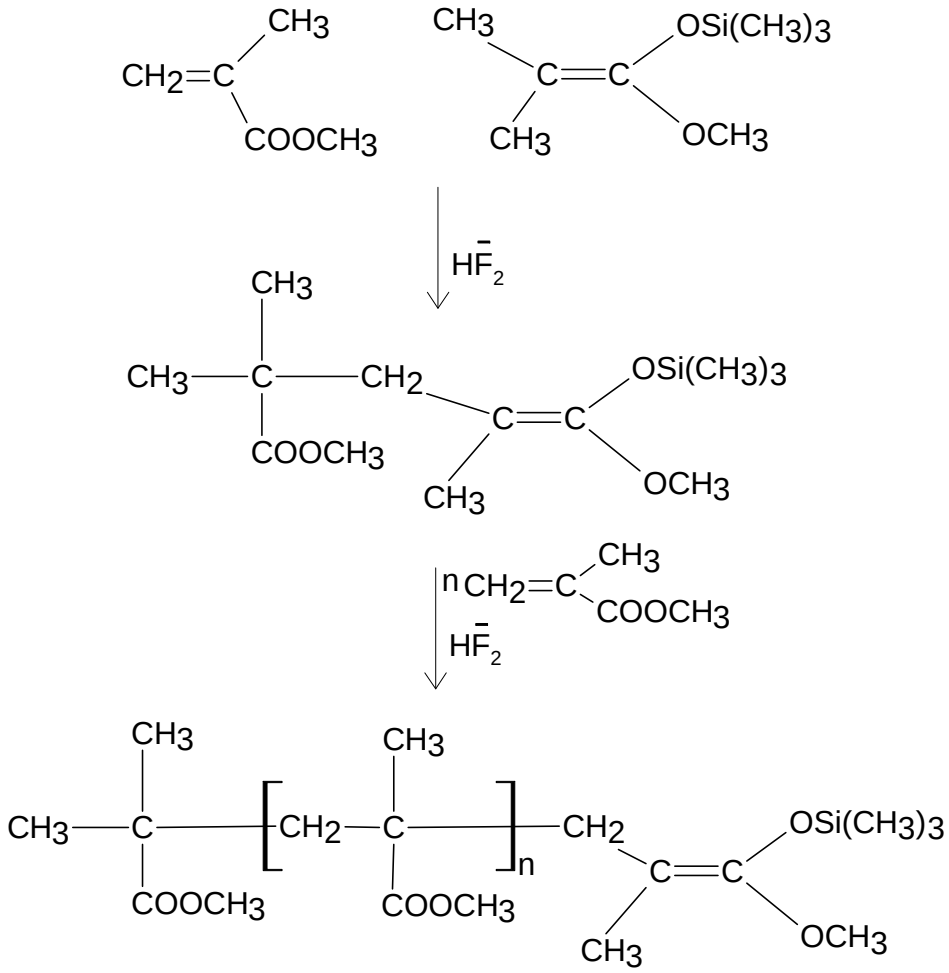


3. Group transfer polymerisation : (GTP)

Group transfer polymerisation is relatively a new process. In this unsaturted esters, Ketones and nitriles are polymerised using an organosilicon initiator and a bifluoride catalyst

Ex : methylmethacrylate undergo group transfer polymerisation.

The polymerisation takes place as follows.



Polymethyl methacrylate

Advantages :

1. The GTP polymer yields are excellant. It is a living polymer. So, it can be isolated and block Co- polymers can be prepared.
2. Unlike anionic polymerisation, GTP does not require a very low temperature.
3. Many of the GT polymerisations can be carried out at room temperature.
4. The major advantage is the perfect control that is achieved in the generation of polymer ends.

2.4.3 Polymerisation Techniques :

The factors dictating physical conditions under which polymerisation is to be carried out are - 1) nature of the monomer, 2) The type of polymerisation mechanism chosen, 3) The required physical form of the polymer and 4) Viability of the process for industrial production. This leads to different polymerisation techniques. They are -

1. Bulk Polymerisation
2. Solution Polymerisation
3. Suspension Polymerisation
4. Emulsion Polymerisation
5. Melt polycondensation
6. Solution Poly condensation
7. Interfacial condensation
8. solid and gas phase Polymerisation

1. Bulk Polymerisation :

In bulk polymerisation the monomer is in the liquid state. The chain transfer agent to control the molecular weight is dissolved in the monomer. The initiator is also dissolved in the monomer. The whole system is in a homogeneous phase. It is heated to suitable temperature.

Ex : PVC, Polystyrene,

Drawbacks :

1. As polymer formation proceeds the medium becomes viscous and it may lead to explosion. In bulk polymerisation heat transfer is poor because medium becomes viscous.
3. Because of the localised over heating degradation and decolourisation of polymer occurs.
4. It requires longer duration for high conversion.

Advantages :

1. Bulk polymerisation is the simplest process.
2. The product obtained has a high purity because it is minimum contaminated.
3. It is used in the free radical polymerisation of methylmethacrylate or poly styrene to get transperant moulding powders and cast sheetings.
4. It is used in the polymerisation of Vinyl chloride to get
   a) PVC resin.
   b) poly methyl methacrylate
   c) Poly styrene
5) it is suitable for free radical polycondensation and Polyaddition polymerisation.
6) It is used for producing medium to high mol. wt products.

2. Solution polymerisation :

In solution polymerisation, the monomer is dissolved in a suitable inert solvent. The chain transfer agent is dissolved in the solvent. The free radical initiator is also dissolved in the solvent itself. The ionic or coordination catalyst is dissolved or supended in the medium helps in promoting heat transfer. It is heated to suitable temperature.

Ex : Poly acrylo nitrite, Poly isobutylene.

Drawbacks :

1. The product is contaminated with solvent.
2. The polymer formed is to be isolated from the solution and removal of final traces is very difficult.
3. It requires longer duration for high conversion.

Advatnges :

1. The presence of inert solvent medium helps to control viscocity increase and promote proper heat transfer.
2. This technique is advantageous when the polymer is to be used in its solution form
   Ex: Certain adhesives and coatings.
3. It is advantageous when the polymer is insoluble in its monomer or solvent because the polymer can be easily isolated.
4. It is used for preparing
   a) polyacrylonitrile by free radical polymerisation and
   b) polyisobutylene by cationic polymerisation.

5. Block Co- polymers are prepared exclusively by this technique.

6. It is used for producing low mol.wt. products.

7. It is suitable for free radical, and polyaddition polymerisations.

3. Suspension polymerisation :

In Suspension polymerisation, the monomer is suspended in water in the form of fine droplets. These are stabilised by using suitable protective colloids, (Surface active agents) and by stirring. The product is obtained as spherical beads or pearls. So, it is also known as bead or pearl polymerisation.

Ex : Polystyrene beads, Polyvinyl acetate beads.

Drawbacks :

1. Only water insoluble monomers can be polymerised.

2. The product is contaminated with the stabiliser

3. It requires longer duration for high conversion.

Advantages :

1. Polymerisation proceeds to 100% conversion.

2. The droplets have large surface area and it can readily transfer heat to water.

3. By using free radical initiators expandable polystyrene beads for making foams, Styrene-divinyl benzene co- polymer beads for preparation of ion exchange resins can be produced.

4. It is used for producing medium to high mol.wt products.

5. It is suitable for free radical and polycondensation polymerisation.

4. Emulsion polymerisation :

In emulsion polymerisation the monomer is dispersed in water as uniform emulsion. It is stabilised by protective colloids (surfactants) and by buffers. Beyond a particular concentration, the surfactants form molecular aggregates known as " micelles ". The concentration beyond which micelle formation is possible is known as " critical micelle concentration " (CMC).

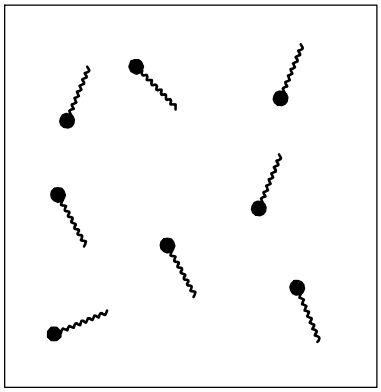
CMC values of some surfactants -

Surfactant	**CMC g/l**	**Temp.°c**
Anionic $CH_3(CH_2)_6COONa$	6.5×10^1	20
Non - ionic $CH_3(CH_2)_7C_6H_{11}O_6$	7.3	25
Cationic $CH_3(CH_2)_9NH_2HCl$	8.5	25

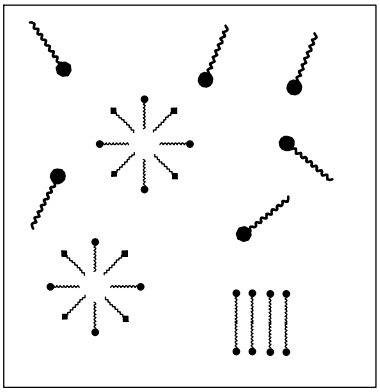
Ex : When soap is dissolved in water, micelles are formed. In micelles hydrophobic hydrocarbon ends facing inwards and hydrophilic carboxyl ends facing outwards. So, the interior of micelle acts as a hydrocarbon phase, where the monomer is stabilised.

The initiator diffuses into the micelle and polymerisation proceeds forming latex.

Ex : emulsion paints, vinylmonomers.



Individual
surfactant molecules



Micelles
aggregated surfactant molecules

At end of the polymerisation, fine particles of the polymers, stabilised by the emulsifier are formed in aqueous phase. It is called ' latex '

Drawbacks :

1. Latex has to be coagulated, filtered and dried to get solid polymer.
2. The product is contaminated with the emulsifier.

Advantages :

1. This is the preferred method for producing high molecular weight products.
2. By this method emulsion paints are also obtained.
3. This technique is extremely used for the free radical polymerisation of vinyl monomers containing water soluble initiators.
2. 100 % conversion is achieved in shorter duration.
3. It is suitable for free radical and polycondersation polymerisation.

5.Melt Poly condensation :

This technique is used for monomers which do not decompose around their melting points. It is carried out in an inert atmosphere of N_2 or CO_2 to avoid oxidation. decarboxylation and degradation. Sometimes it is carried under reduced pressure to fecilitate removal of byproduct. To avoid solidification the hot melt inside the reactor is directly passed to the processing equipments for extension casting or spinning.

Draw backs :

1. Freeing from monomers and by product is difficult. It requires longer duration for high conversion.

Uses :

1. It is used to produce polyethylene terephthalate from dimethyl terephthalate.

2. Nylon -66 is prepared using this technique.

3. The product is minimum contaminated.

4. It is suitable for producing medium to high mol. wt products.

5. It is suitable for polycondensation polymerisation.

6. Solution polycondensation :

In solution polycondensation, the reactants are taken in solution form. The reaction is carried at comparatively low temperature. The solvent serve as an entraping agent for the byproduct.

Draw backs :

1. The product is usually contaminated with solvent.

2. Due to solvent phase, chain growth is low leading to low degree of polymerisation.

3. It requires longer duration for high conversion.

Advantages :

1. The heat and mass transfer are easier than in melt technique.

2. Removal of by product is easy.

3. Many of the liquid polyester resins are prepared by this technique.

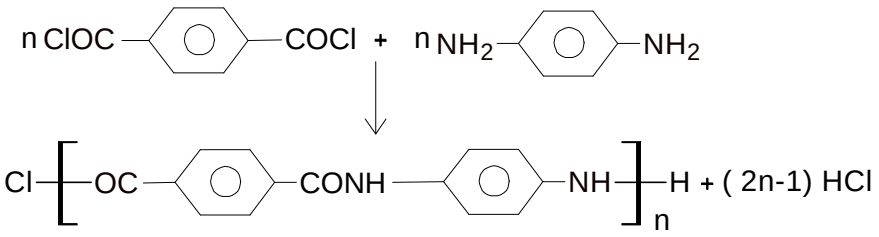
4. It is suitable for producing medium to high mol.wt products.

5. It is sutiable for polycondensation polymerisation.

7. Interfacial condensation :

In this technique polymerisation proceeds at the interface between an aqueous and organic medium. This technique is suitable for reactants having highly reactive functional groups.

A typical example is preparation of fully aromatic polyamides from terephtholoyl chloride and paraphenylene diamine.



The diamine is dissolved in water and acid chloride in an organic solvent. When the two solutions are mixed, diamine molecules diffuse into the organic phase and react with acid chloride to form the polymer.

The polymer formed precipitates out immediately and the byproduct HCl diffuses back into the aqueous phase.

Advantages :

1. It is used to prepare fully aromatic polyamides

2. The process is diffusion controlled. So, high mol.wt product can be obtained.

8. Solid and gas Phase polymerisation :

In all the above mentioned techniques, polymerisation is carried out in a liquid phase. The same can be carried out in solid and gas phases.

a) Solide Phase polymerisation :

In solid phase polymerisation the monomer is in solid phase.

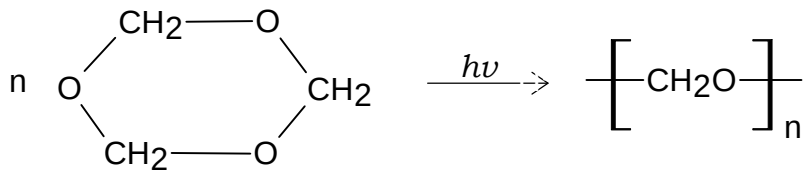
It is used to chain polymerisation as It can be carried out at low temperature.

Draw backs :

1. Thermal activation is difficult. So, radiation activation technique is used.

2. The process is very slow.

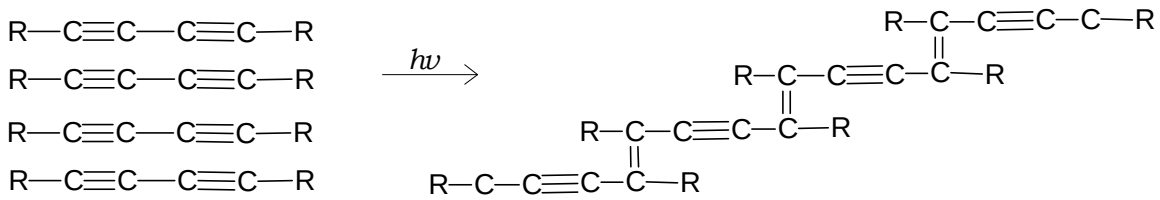
Ex: 1. Preparation of polyformaldehyde by the radiation polymerisation of solid trioxane.



trioxane

Ex : 2. Polymerisation of diacetylene derivatives.

2. Polymerisation of diacetylene derivatives. The polymer formed is highly crystalline and conducts electricity.



Advantages :

1. It is suitable for chain polymerisation.
2. It can be carried out at low temp.
3. The product formed is highly crystalline.

b) Gas phase polymerisation :

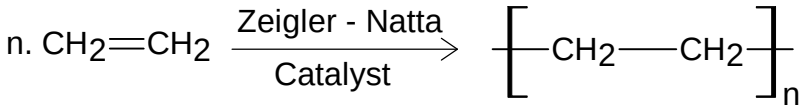
In gas phase polymerisation the monomer is in gaseous phase. Gas phas polymerisation is known in case of very few olefinic polymers. The methods used in gas phase polymerisation are

i) Spraying the catalyst : zeigler - Natta catalyst is generally sprayed into the gasesous monomer.

ii) Feeding the gaseous monomer into a fluidised bed made of catalyst particles.

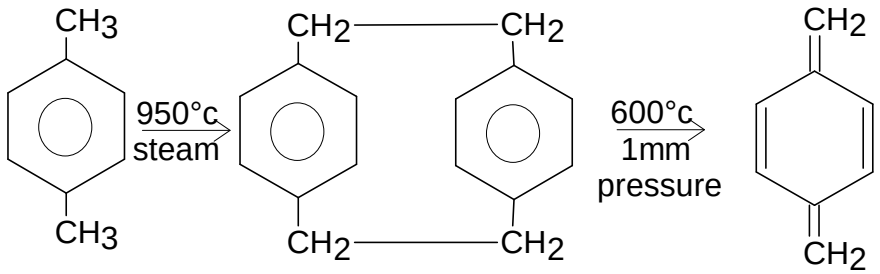
Ex : 1. Gas Phase polymerisation of ethylene forming PVC :

In this process ethylene gas is passed through a bed made of Zeigler - Natta catalyst which is a mixture of titanium chloride and alkyl aluminium in pentane medium. The temperature is maintained at room temperature and pressure at 4-5 atms. The polymer formed is a free flowing powder.

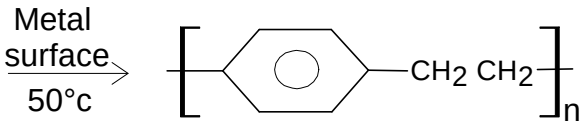


2. Gas Phase polymerisation of P-xylene :

In this process a linear poly - p- xylene is formed as shown below.



P - Xylene dimer



Poly - P - xylene

Draw backs : In gas phase polymerisation heat transfer is very poor.

Advantages :

1. It can be carried out at room temperature.
2. It is suitable for chain polymerisation.
3. The product formed is a free powder.

2.4.4 Model Questions :

1. Explain a) Electro chemical polymerisation b) Metathetical polymerisation .
2. Write about group transfer polymerisation.
3. Write an essay on miscellaneous polymerisation reactions.
4. Explain different polymerisation techniques.
5. Write notes on a) Bulk polymerisation b) Solution Polymerisation c) Emulsion Polymerisation d) Suspension Polymerisation.
6. Explain solid and gas phase polymerisation.
7. What are micelles ? What is critical micelle concentration?

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Lesson – 5

CHEMISTRY OF POLYMERS

2.5.1 Chemistry of Polymers - Polyethylene, Polypropylene, Polystyrene, Polyurethanes, Poly vinyl chlorides, Polyisoprenes, Urea formaldehyde resin, Sliconeresins, Cellulose and its derivatives.

2.5.2 Poly ethylene :

Structure : Polyethylene is the simplest hydrocarbon polymer. It has the following structure.

$$[-CH_2-CH_2-]_n$$

The monomer is ethylene. It is prepared either by the hydrogenation of acetylene or by the dehydration of ethanol.

$$C_2H_5OH \xrightarrow{-H_2O} CH_2=CH_2$$

$$CH \equiv CH \xrightarrow{+H_2} CH_2=CH_2$$

There are two types of Polyethylenes.

1. Low density Polyethylene (LDPE)
2. High density Polyethylene (HDPE)

Low density Polyethylene :

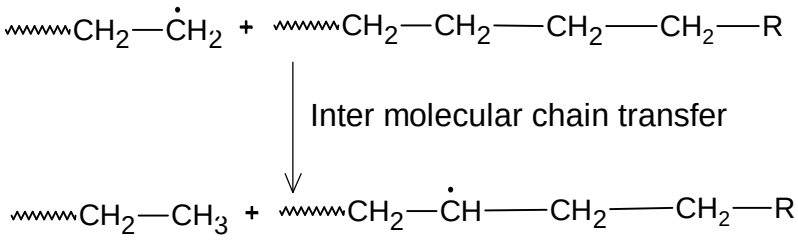
Low density polyethylene consists of branched molecules.

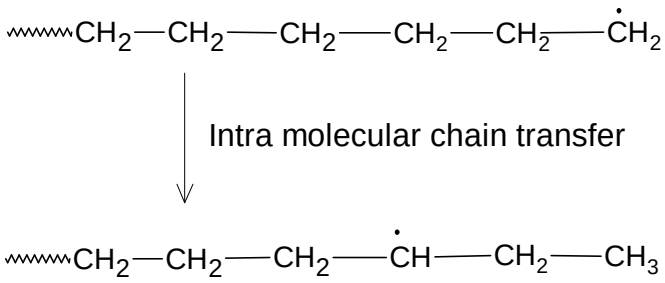
Preparation :

It is produced from ehtylene by solution or bulk polymerisation technique using oxygen as initiator. The reaction occurs at 1500 atmospheres pressure and at 180 - 250°c temperature. Even 0.1% oxygen is sufficient to initiate polymerisation. Other initiators are peroxides, hydroperoxides, and azo compounds.

Branching :

During polymerisation branching occurs either by intermolecular or by intramolecular chain transfer reactions.

1. 

2. 

Properties :

It is a high molecular weight paraffin.

1. It is partially crystalline.
2. Density is 0.91 - 0.92 g/cc.
3. At room temperature it is insoluble in many solvents but at high temperature it is soluble in a no.of solvents.
4. It has good toughness over a wide range of temp.
5. It is having good electrical properties.
6. It is not effected by acids, alkalies and aqueous solution.
7. Strong oxidising agents like H_2O_2, $KMnO_4$, U.V.light oxidise the polymer.

Uses :

1. It is used for cable insulation.
2. Pipes made of LDPE are used for water connections in irrigation and domestic needs.
3. It is used for the manufacture of Squeeze bottles.

High density Polyethylene : (HDPE)

High density polyethylene consists of linear molecules.

Preparation :

It is prepared by two methods.

1. Co-ordiantion polymerisation of Ethylene by using trialkyl aluminium and titanium tetrachloride catatyst.
2. Polymerisation of Ethylene by using metal oxide catalyst such as chromium or molybdenium oxide. The reaction occurs at low pressure of 2-4 atmospheres and 50-75°c temperature.

$$nCH_2= CH_2 \xrightarrow{\text{Catalyst}} (-CH_2-CH_2-)_n$$

Properties :

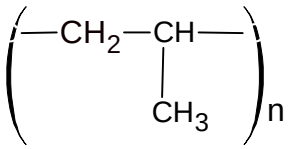
1. At room temperature it is insoluble in all solvents and at high temperature it dissolves in hydrocarbons.
2. It has greater tensile strength and hardness.
3. It is not effected by acids, alkalies and aqueous solution.
4. It is highly crystalline.
5. Strong oxidising agents like HNO_3, H_2O_2 cause decolourisation and deterioration of the polymer.

Uses :

1. It is used for cable insulation.
2. Tubes made of HDPE are used for water connections in irrigation and chemical plants.
3. It is used for the manufacture of house hold articles.

2.5.3 Poly Propylene :

Structure : Poly propylene polymer has the following structure.



The monomer is propylene. It is obtained as a byproduct from gasoline refineries.

Preparation :

Polypropylene is produced commercially by ziegler - Natta process. The typical polymerisation catalyst is trialkyl aluminium and $TiCl_3$.

Isotactic Index :

Poly propylene exists in isotactic, syndiotactic or atactic forms. It is characterised by isotactic index. It is the percentage of the polymer which is not dissolving in boiling heptane.

Ex : Isotactic index of commerical polypropylene is 90 - 98%.

Properties :

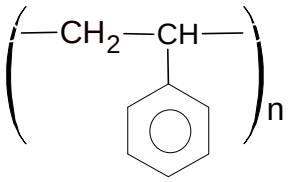
1. The isotactic polymer is linear and highly crystalline.
2. It has greater tensile strength and hardness.
3. It is chemically inert.
4. It is less resistant to oxidation as compared to polyethylene.

Uses :

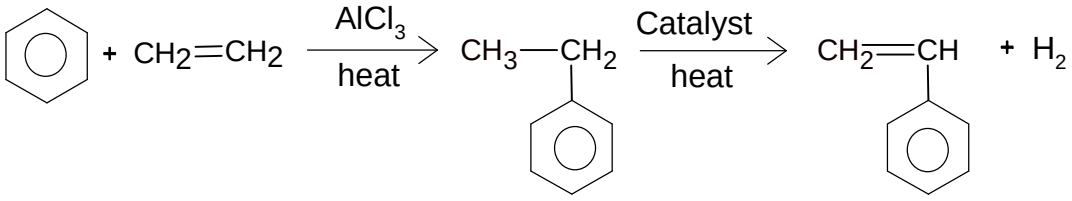
1. It is used for the manufacture of Pipes and Ropes.
2. Poly propylene is used for making Radio and Television components.
3. It is used for book coverings and washable wallpapers.

2.5.4 Poly Styrene :

Structure : Polystyrene is polyvinyl benzene. It has the following structure.



The monomer is styrene. It is produced form Benzene and ethylene.



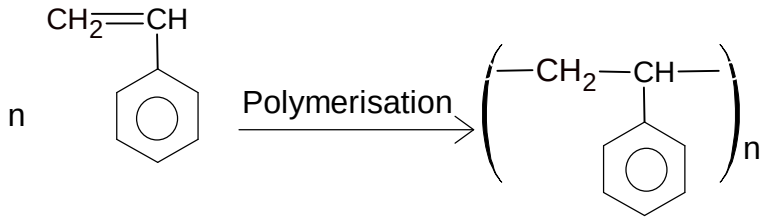
styrene

Preparation :

Polystyrene is prepared from styrene by

1. Coordination, 2. Cationic, and 3. anionic Polymerisation.

Here Bulk or Suspension polymerisation techniques can be used.



Properties :

1. The linear polymer is hard, rigid and brittle.
2. It is highly transperant.
3. It is chemically inert.
4. It has good electrical insulation property.

Disadvantages :

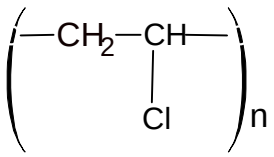
1. It has low heat distortion temperature of 85°c.So, Thermal decomposition is possible.
2. Out door exposure causes yellowing and cracking of the polymer.

Uses :

1. It is used for the manufacture of house hold articles.
2. It is used for making radio and television cabinets.
3. Styrene - acrylonitrile (SAN) copolymer is a transperant plastic used for crockery items.

2.5.5 Polyvinyl Chloride (PVC) :

Structure : Polyvinyl chloride is a the widely used plastic in india. It has the following structure.



The monomer is Vinyl chloride.

It is prepared by the cracking of ethylene dichloride at 500°c temperature.

$$CH_2Cl - CH_2Cl \xrightarrow[\text{Pressure}]{500°c} CH_2 = CHCl + HCl$$

Preparation :

Polyvinyl chloride is prepared by three methods.

1. Bulk polymerisation.
2. Suspension polymerisation.
3. Emulsion polymerisation.

$$nCH_2{=}CHCl \xrightarrow{\text{Polymerisation}} \left(-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}-\right)_n$$

The emulsion polymerisation has the advantage that the polymerisation can be carried out at low temperature of 20°c.

Properties :

1. It has low crystallinity.
2. It is a regid material.
3. It is insoluble in alcohol, water and hydrocarbons.
4. It is not affected by acids and alkalies.

Disadvantages :

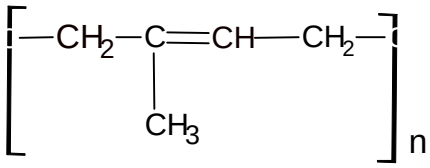
It is thermally unstable. It degrades beyond 200°c.

Uses :

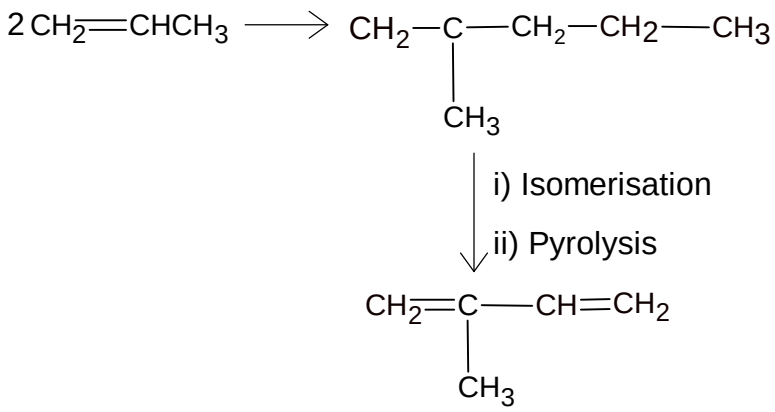
1. PVC is the cheapest and Widely used plastic globally.
2. It is used for the manufacture of pipes and laminated materials.
3. It is used for cable insulation.
4. It finds extensive use in plastisols and organosols.

2.5.6 Poly Isoprenes :

Structure : Both Cis - as well as trans forms occur in nature as natural rubber and gutta percha respectively. It has the following structure.



The monomer is Isoprene. It is produced form propylene as follows.



Preparation :

Natural rubber is obtained in the form of latex from rubber trees. The latex contains 30-60% rubber. It can be used as such. The solid rubber can be coagulated from latex using 1% acetic acid solution.

Rubber trees

(Hevea broseliensis)

↓

Latex

(30 - 60% rubber)

↓ coagulation

1% acetic acid

Solid rubber

↓ rollers

rubber sheets.

Properties :

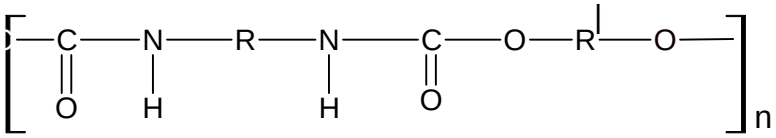
1. Natural rubber is highly soft and elastic.
2. It is soluble in carbon disulphide and petrol.
3. Gutta - Percha is hard and Thermoplastic.
4. It dissolves in petrol only.

Uses :

1. It finds extensive use in rubber based industries.
2. It is used for the manufacture of rubber bands, balloons, shoes, tyres, tubes, gloves etc.

2.5.7 Poly Urethanes :

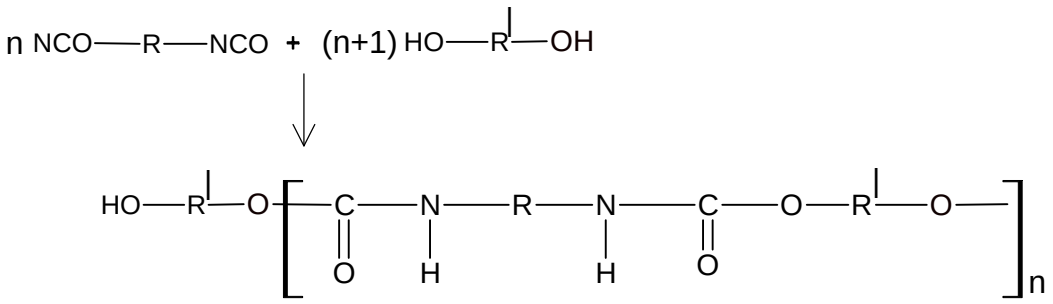
Structure : Polyurethanes are polymers containing urethane likage in the repeating units. It has the following structure.



The Urethane linkage is – NHCOO–.

Preparation :

Polyurethanes are commercially prepared by the poly addition reaction between di-isocyanate and aldol.



Properties :

1. Slightly cross - linked polyurethanes are flexible while highly cross - linked polyurethanes are rigid.
2. Their melting points are less than that of the corresponding polyamides.
3. They are reactive.
4. They react with compounds containing active H_2.

Uses :

1.They are used for the manufacture of foams, adhesives and elastomers.

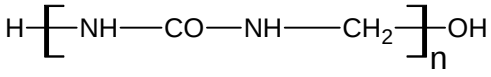
2. Rigid polyurethane foams are used for making artificial limbs.

3. Semirigid polyurethanes forams are used and for packaging.

3. Flexible polyurethane foams are used in cushions and car crash pads.

2.5.8 Urea formaldehyde Resins (Synthetic Glass) : (UF resins)

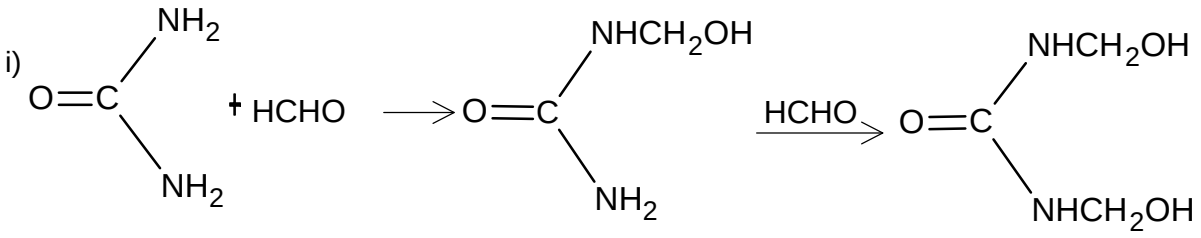
Resins formed by the condensaction of formaldehyde are called urea- formaldehyde resins. It has the following structure.



Preparation :

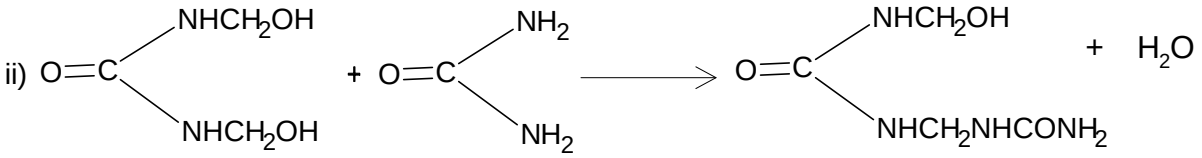
Sodium hydroxide is added to formalin to make its PH 8. To this urea is added and refluxed for 15 minutes. It is acidified with formic acid and boiled for 20 minutes. The product is neutralised with NaOH and evaporated under pressure to get solid resin.

i)



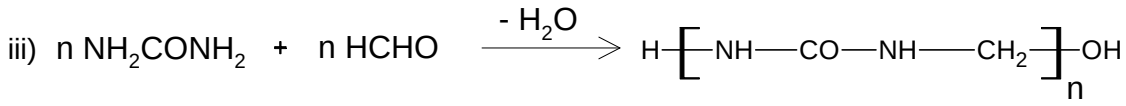
dimethylol urea

ii)



and soon

iii)



Properties :

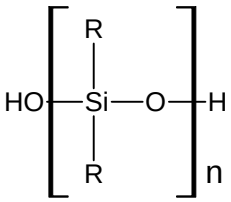
1. These are colourless and glass like known as synthetic glass.
2. These are linear polymers.
3. They have greater tensile strength and hardness.
4. They have haeat resistance and moisture resistance.

Uses :

1. These are used for domestic electrical fittings.
2. These are used as wood adhesives.
3. These are useful as surface coatings and textile finishing.

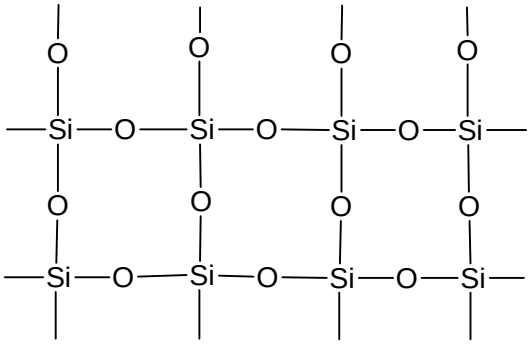
2.5.9 Siliconeresins :

Silicone resins are polymers containing silicone linkage (– Si –O-Si–) in the repeating units. It has the following structure.



Preparation :

Silicone resins are obtained by the hydrolysis of trichloro silanes.



Preparation :

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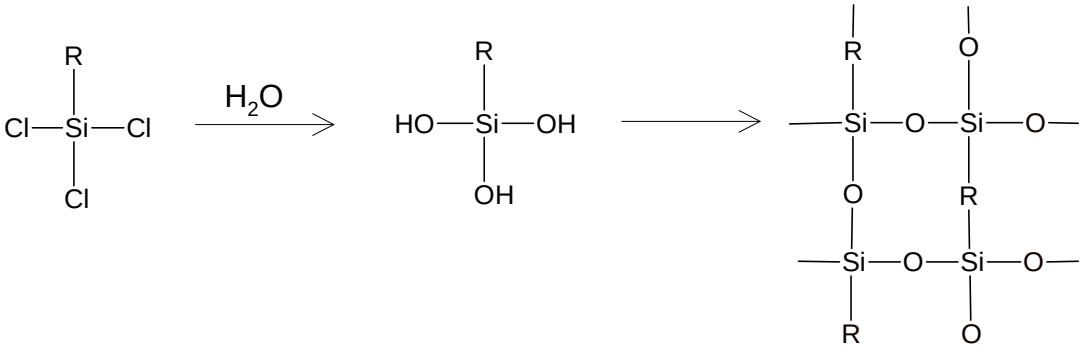


Properties :

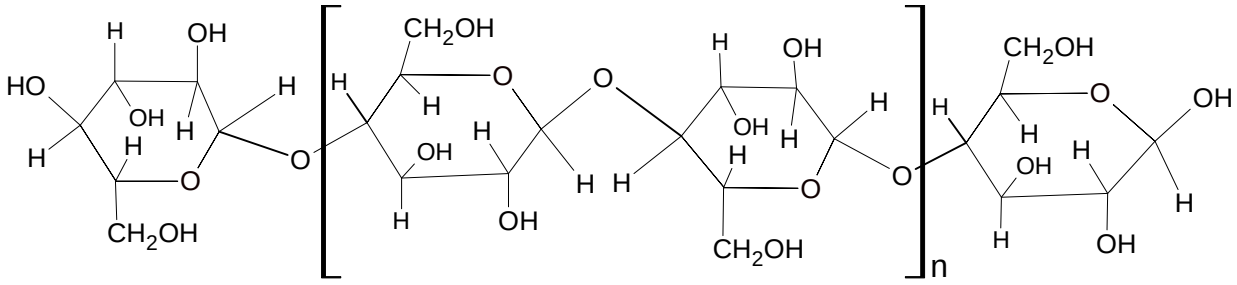
1. They are available in liquid, waxy and rubbery forms.
2. They are water repellant.
3. They are chemically inert.
4. These are thermally very stable.

Uses :

1. Foams made of silicone resins are used in aeroplanes and missiles.
2. These are used for the manufacture of industrial paints.
3. Silicone resins are used for making non - stick frying pans.

2.5.10 Cellulose and It's Derivatives :

Cellulose is a naturally occuring linear, stereo - regular polysaccharide. It is made up of β D(+) glucose residues. It has the following structure.



Cellulose is plenty in nature in the form of cotton, hemp, jute etc. Wood contains a good percentage of cellulose.

Properties :

1. It has high crystallinity.
2. Highly stereo - regular.
3. It is insoluble in many solvents.
4. It has high metting point.

Cotton Fabrics :

Cotton fabrics contain high percentage of cellulose.

Uses :

1. The strength of cotton fibre is 25% higher in wet condition than in dry condition. So, Cotton fabries launder well.
2. Cotton fabrics can be folded and unfolded several times without loss of strength.
3. In comparison to silk or wool, cotton is a better conductor of heat and has excellent moisture absorption capability so, cotton fabrics are ideal to wear in humid summer weather.

Rayon and Cellophane :

Rayon or Cellophane is regenerated cellulose.

a) Preparation of Viscose Solution :

The cellulose obtained from wood pulp is treated with strong alkali at low temperature to produce alkali celloulose. It is treated with carbondisulphide to produce cellulose Xanthate. The cellulose Xanthate is dissolved in NaOH solution. It is industrially known as Viscose solution.

$$\text{Cell} - \text{OH} + \text{NaOH} \rightarrow \text{Cell} - \text{ONa} + H_2O$$

Celllose alkali cellulose

$$\text{Cell} - \text{ONa} + CS_2 \rightarrow \text{Cell} - \text{O} - \text{C}(=\text{S})(-\text{SNa})$$

Cellulose Xanthate

b) Rayon :

Viscose solution is injected into a bath containing sulphuric acid,sodium sulphate and ammonium sulphate as fine jets. Cellulose is regenerated in the form of glossy filments known as Rayon.

$$\text{Cell} - \text{O} - \text{C}(=\text{S})(-\text{SNa}) + H_2O \rightarrow \text{Cell} - \text{OH} + \text{NaOH} + CS_2$$

Uses :

1. It is used for the manufacture of fibres.

Cellophane :

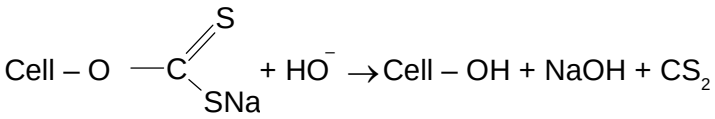
Preparation :

a) Preparation of Viscose solution :

The cellulose obtained from wood pulp is treated with strong alkali at low temperature to produce alkali celloulose. It is treated with carbondisulphide to produce cellulose Xanthate. The cellulose Xanthate is dissolved in NaOH solution. It is industrially known as Viscose solution.

b) Cellophane :

Viscose solution is made into a thinfilm and pass through a trough containing sulphuric acid, sodium sulphate and ammonium sulphate. Cellulose is regenerated.



It is then passed through another trough containing glycerol. On drying this, a thin film of cellophane is produced.

Uses :

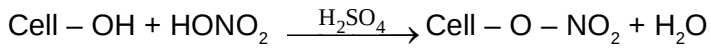
1. Cellophane is a trasperant film used in day to day life.
2. It finds extensive use in the package and wrapping industries.

Cellulose Nitrate :

It is an important cellulose polymer also known as nitrocellulose (NC).

Preparation :

It is produced by the action of nitric acid, sulphuric acid and small quantity of water on cellulose at 20°c. The product is seperated by centrifuge, purified by washing, stabilised with dilute alkali and bleached.



Uses :

1. NC with 10.5 - 11% Nitrogen is used as celluloid plastic.
2. NC with 12 - 12.3% Nitrogen is used as Photographic film.
3. Nitro cellulose containing more than 12.3% Nitrogen is used as explosive.

Disadvantage :

It is highly inflamable. So, present day photographic films are made of cellulose acetate instead of cellulose nitrate.

Cellulose acetate :

It is an important cellulose plastic.

Preparation :

It is produced by the action of acetic anhydride on cellulose. The catalyst used is sulphuric acid or perchloric acid.

$$\text{Cell} - \text{OH} + (CH_3CO)_2O \xrightarrow{H_2SO_4} \text{Cell} - O - COCH_3 + CH_3COOH$$

Uses :

1. The primary cellulose acetate (cellulose triacetate) is used for the manufacture of fibres.
2. Secondary cellulose acetate obtained by the partial saponification of primary cellulose acetate is used for the manufacture of non - flamable cinematographic films.

2.5.11 Model Questions :

1. Write preparation, properties and uses of polyethylene.
2. How polypropylene is prepared ? What are its properties and uses ?
3. Give preparation, properties and uses of polystyrene.
4. Write the structure, preparation, properties and uses of polyurethanes.
5. What are polyvinyl chlorides ? Give their preparation, properties and uses.
6. Explain Urea formal dehyderesins.
7. What are silicones. Give preparation and uses.
8. Give the source, properties and uses of cellulose.
9. Write about the derivatives of cellulose.
10. Write about polyisoprenes.

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Lesson – 6

POLYMER PROCESSING TECHNIQUES

2.6.1. Polymer processing techniques - Diecasting, Calendaring, Rotational casting, Reinforcing, Fibrespinning and Foaming.

2.6.2 In Polymer processing techniques. The polymeric materials are converted into finished products. They are -

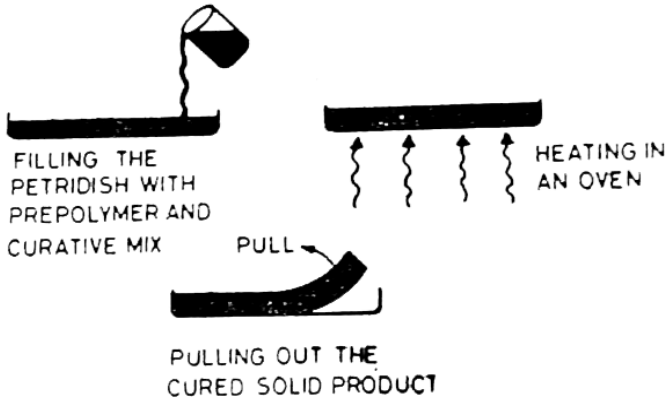
1. Die - casting
2. Calendering
3. Rotational casting
4. Reinforcing
5. Fibre spinning
6. Foaming.

2.6.3 Die - casting :

1. In Die casting liquid polymer can be converted into a solid object with the desired shape. Die casting is relatively a low cost process.
2. In Die- casting sheets, tubes and rods of limited lengths are made.

Ex : Acrylics, epoxides, polyesters, phenolics and Urethanes are suitable for die casting.

The apparatus used for this process is shown below.



Simple illustration demonstrating the casting process

The prepolymer compounded with a curative mix and other ingradients is poured into a petridish known as die. The dies are made of plaster of paris or lead or glass. The die is kept in an oven at elevated temperature for few hours. On cooling to room temperature, the solid product thus cast will have shape identical to the interior surface of the petridish. Instead of petridish if a cylindrical glass tube is used, we get the product as a cylindrical rod.

2.6.4 Calendering :

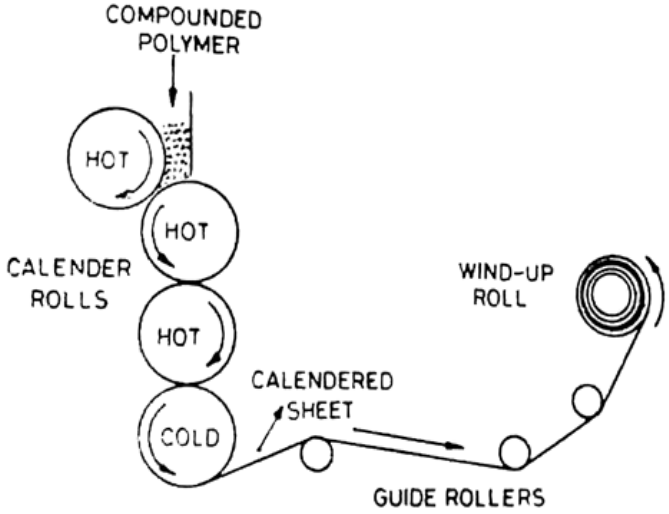
In calendering continuous films, sheets of suitable designs can be produced.

Ex : 1. Polyvinyl Chloride

2. Polyethylene, Acrylonitrile, Butadiene

3. Rubbers.

The machine used for Calendering is shown below.



Schematic diagram of a calendering machine

The main part of Calendering machine is a set of highly polished metal rollers rotating in opposite directions. It has provision for precise adjustment of gap between the rollers which determine the thickness of the sheet.

The compounded polymeric material is fed between the rollers which are at elevated temperature. The sheet emerging from the hot rollers is cooled by passing through the cold rollers. The sheets are finally wind up in rolls.

Advantage :

Special decorative effects like marbleisation can be achieved by feeding the calender with polymeric materials of different colours.

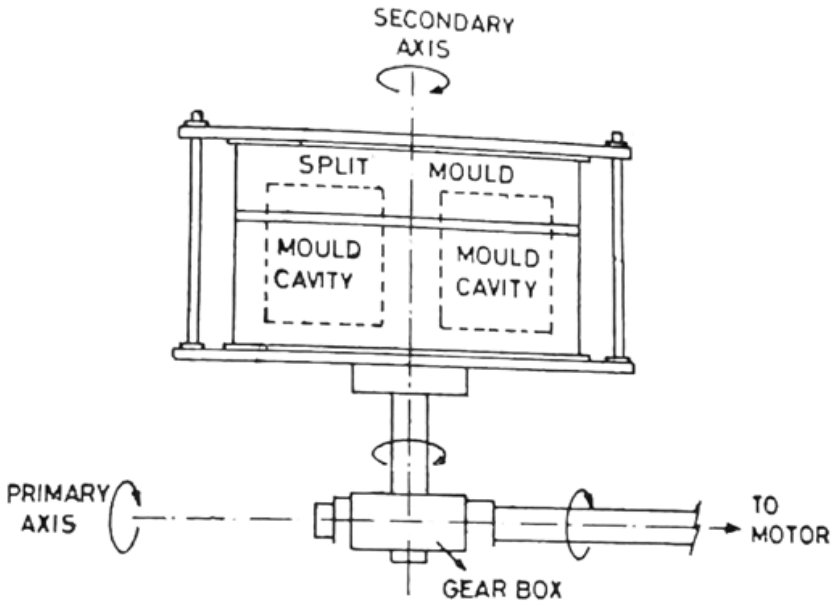
Ex : Floor tiles made of PVC.

2.6.5 Rotational Casting :

In rotational casting hollow articles can be produced.

Ex : Thermoplastic and Thermosetting materials.

The apparatus used for this process is shown below.



Hollow moulds filled with the polymeric material being rotated simultaneously along the primary as well as the secondary axis during rotational moulding

The compounded polymeric material in the form of a fine powder is taken in a hollow mould. The mould is closed, heated and rotated. It has provision for rotating the mould simultaneously along the primary and the secondary axes. This distributes the molten plastic uniformly along the inside surface of the mould. The mould still under rotation is chilled with cold water. Now the uniformly distributed molten plastic is solidified. The product thus cast will have the shape of interior surface of the mould. Then the mould is opend and the product removed.

Rotational casting using a liquid material is called " Slush moulding ".

Advantage :

PVC articles such as rainboots, hollow balls and doll heads are made.

2.6.6 Reinforcing :

In this process fibre reinforced plastics (FRP) are produced. These have out standing properties such as

1. high strength - to - weight ratio.

2. excellent corrosion resistance

3. easy to fabricate.

Because of high strength - to - weight ratio these are used in satellites. Due to excellent corrosion resistance these are used in boat hulls and also as storage tanks for strong acids.

Ex : The common resin matrix used in FRP'S are Polyesters, epoxy, phenolic, Silicones, malamine, Vinyl derivatives and Polyimides. Natural fibres such as Sisal, Asbestos are also used for reinforcement.

Silicone reinforced plastics have excellent electrical and thermal properties.

There are several methods available for the production of reinforced plastics.

The most commonly used Techniques are :

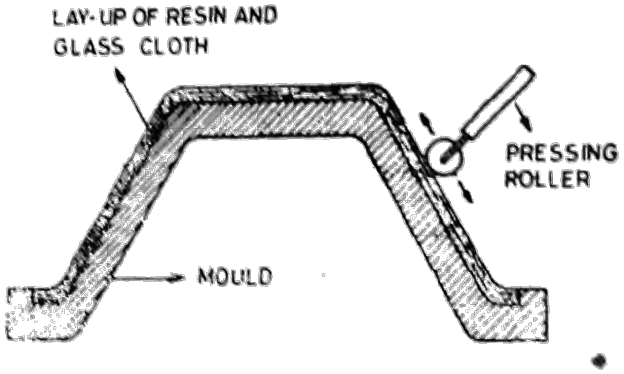
a) The Hand Lay - Up Technique

b) Filament winding Technique.

c) Spray - Up Technique.

a) The Hand Lay -Up Technique :

This is the simplest method. The quality of product depends on the skill of the operator. The hand lay - up technique it is shown by the following diagram.



Schematic diagram showing hand lay-up technique

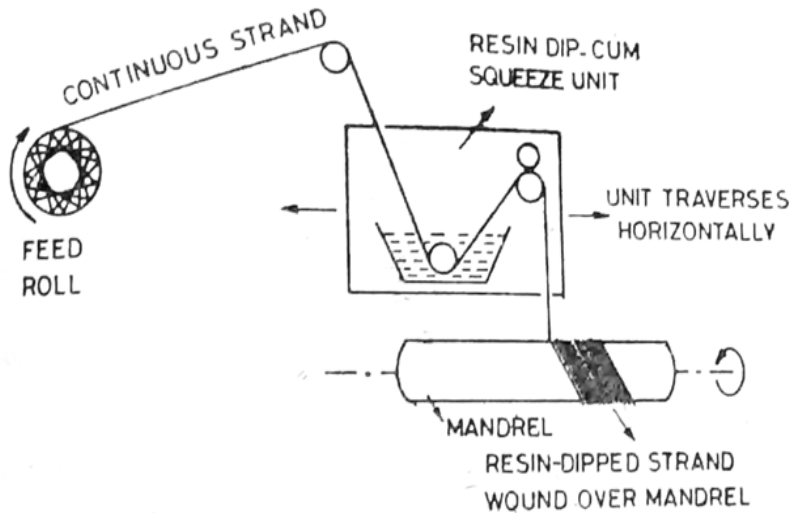
The mould is coated with a releasing agent such as polyvinyl alcohol, silicone oil or wax. This is done to prevent sticking of the fine fabricated article to the mould. Then the mould is coated with a resin matrix. A precut glass cloth is laid over the resin layer. The glass cloth on the resin layer is pressed uniformly by using roller to remove the trapped air bubbles. Now, another layer of

resin is laid over the glass cloth. Thus alternate layers of resin and glass cloth are laid. Once the required thickness is built up, it is cured at elevated temperature. After curing is completed, the reinforced material is removed from the mould. It is subjected to trimming and finishing.

Uses : Automobile body parts, Boats hulls, and Building components are made.

b) Filament - Winding Technique :

This is a very widely used method for producing reinforced plastic articles such as high pressure cylinders, storage tanks and rocket motor bodies. It can be shown by the following schematic diagram.

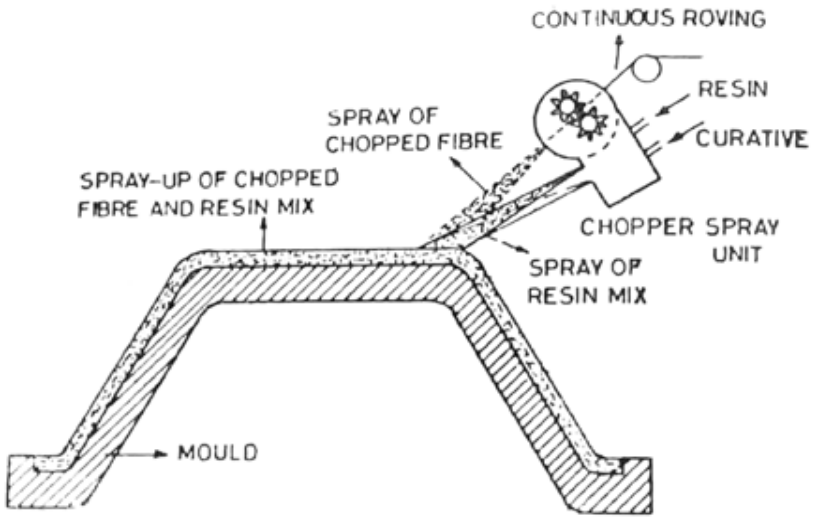


Schematic diagram of a Filament - winding machine

In this process a continuous length of strand is passed through a bath of resin and curative. As the strand comes out of the bath, the excess resin is squeezed out. The resin dipped strand is then wound over a mandrel of the required shape. It is cured under the influence of heat. The tension of the fibre and pattern of winding are very important because they influence the tensile property of the finished product.

c) Spray - Up Technique :

It is the quick method to cover large surface area of the mould. It can be shown by the following diagram.



Schematic diagram showing spray - up technique

In this technique a multiple headed spray gun is used. Form the gun, a spray of resin, curative and chopped fibre are discharged simultaneously on the surface of the mould. Once the required thickness is built up, it is cured at elevated temperature.

Uses :

Plastic articles such as truck bodies, lorry cabs, boat hulls, and storage vessels are produced by this technique.

2.6.7 Fibre Spinning :

The process of producing Fibres from polymers is called ' Spinnning'. So, in fibre spinning fibres can be produced. There are three principal spinning methods.

a) Melt Spinning

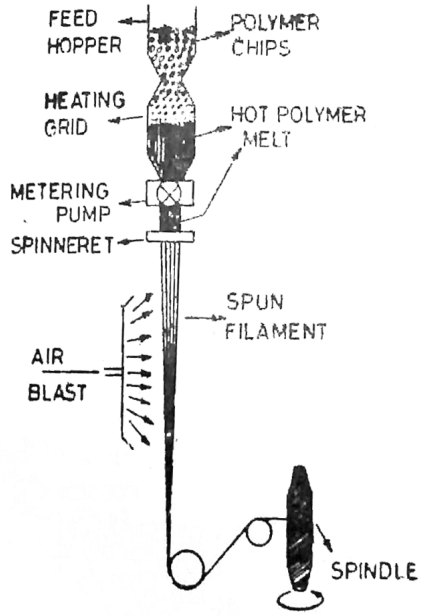
b) Dry Spinning

c) Wet Spinning

Ex : Nylon, Terylene, Poly propylene are fibre forming materials. cotton, wool and silk are natural fibre forming materials.

a) Melt Spinning :

In melt spinning the polymer chips are electrically heated. This converts the solid polymer into viscous mobile liquid. The lumps formed due to thermal degradation are removed by using a filter pack. An inert environment is created around the molten polymer to avoid oxidative degradation. The molten polymer enters into the metering pump and passes through the fine holes of the spinneret at a specified rate.



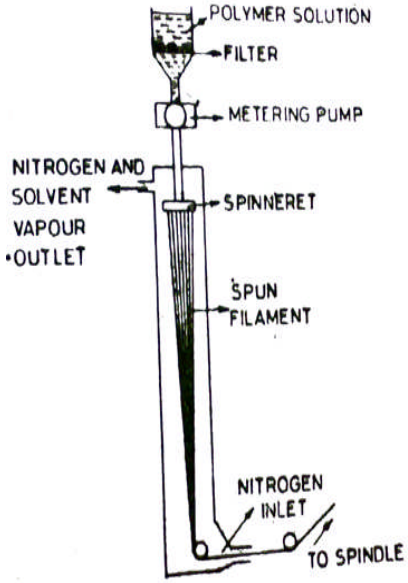
Melt - spinning

From the spinnneret continuous and fine filments emerge. These emerging filments are solidified as they come in contact with cold air. Finally they wind up on spindles.

Uses :

1. Comfort fibres are used for making shirtings, Suitings, and Undergarments etc.
2. Safety fibres are used for making carpets, curtains, seat covers etc
3. Industrial fibres are used for making tubes, pipes, tyres etc.

b) Dry Spinning : This process is shown by the following diagram.



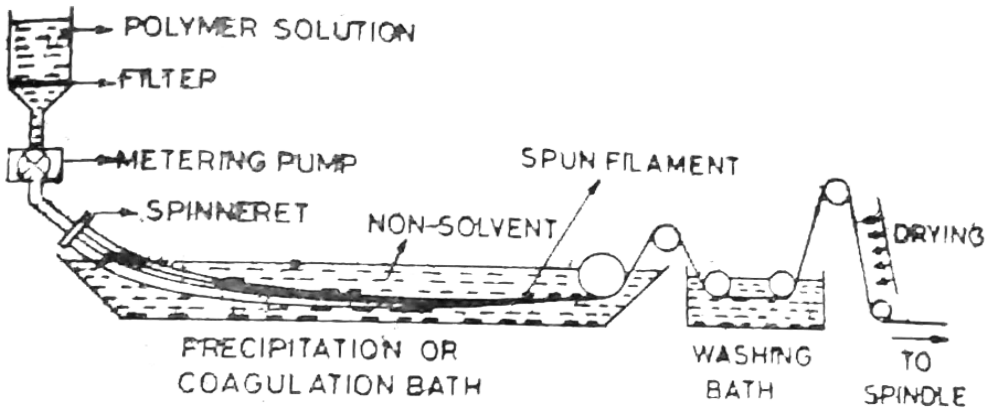
Dry spinning

In dry spinning the polymer is dissolved in a suitable solvent and pumped through the spinneret. Continuous jets of the solution emerge. These jets form fine filments by evaporation. Solvent evaporation is enhanced by passing dry nitrogen in a counter current manner. The filments formed ultimately wound up on spindles. By this process mainly cellulose acetate fibres are manufactured.

Use : Cellulose acetate, polyacrylo nitrile, PVC are converted into fibres on large scale.

c) Wet Spinning :

The process can be shown by the following diagram.



Wet spinning process

In wet spinning the polymer is dissolved in a suitable solvent and pumped through the spinneret . Continuons jets of the solution emerge. These jets are led into a coagulation bath containing large volume of the non - solvent. The jets are precipitated as fine filments.

The filments are Washed, dried and finally wind up on spindles.

Use : By this cellulose fibres, viscose rayons are manufactured.

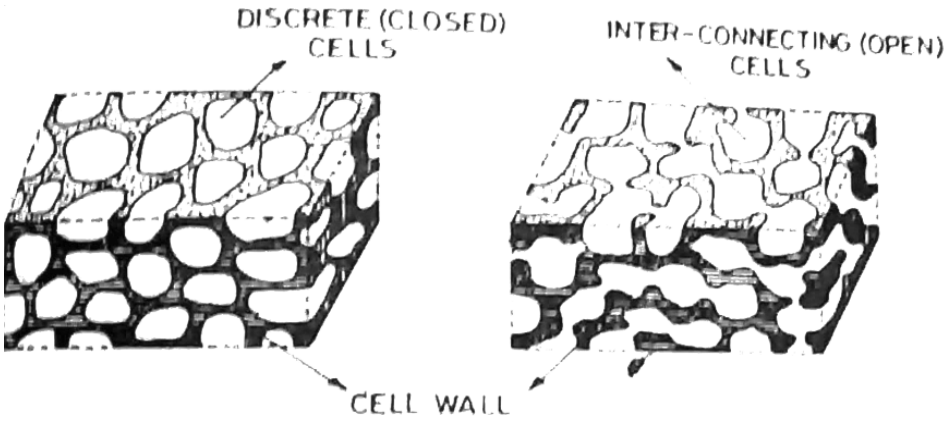
2.6.8 Foaming :

In this process expanded or spongy materials can be produced. The special properties of these materials are cushioning ability, light weight and low thermal conductivity.

Ex : Polyurethanes, Polystyrene, PVC, Polyethylene, Polypropylene, Silicones are foamable materials.

Structure :

The structure of foam material consists of either discrete unit cells or inter connecting cells. Discrete unit cells are closed cells while inter connecting cells are open cells.



Schematic representation of open type and closed type cell structures formed during foaming process.

Production :

The compounded polymeric material is melted and air or nitrogen is blown such that the whole matrix foams up. Addition of surface active agents help the foaming up process. When the required degree of foaming is achieved, the matrix is cooled and allowed to solidify in the foamed up condition.

Carbon dioxide produced by the reaction between isocyanate and water can also be used for foaming.

$$RNCO + HOH \rightarrow RNHCOOH \rightarrow RNH_2 + CO_2\uparrow$$

Ex : Foaming of polyurethane.

Stabilisation of the foam :

In the case of Thermo plastic materials the polymer mix in the foamed up condition is cooled below the softening temperature. In the case of thermosetting materials it is made to undergo crosslinking. Then the whole matrix in foaming condition attains structural rigidity. It is called stabilisation of the foam. Other wise the foam may collapse.

Uses :

1. These find prominent place in furniture and Automobile industries.
2. urethane foams are used for matresses.
3. Poly urethane rigid foams are used for making artificial limbs.
4. Polystyrene rigid foams are widely used for thermal insulation of buildings.

2.6.9 Model Questions :

1. Explain the following polymer processing techniques.
   a) Die-casting
   b) calendaring
   c) Rotational casting
2. What is Reinforcing ? How reinforced plastics are produced ?
3. What is foaming ? How is it stabilized ? What are its uses.
4. What is fibre spinning ? Discuss different spinning methods.

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Lesson – 7

INORGANIC POLYMERS

2.7.1 General properties, Glass transition temperature. Phosphorous based polymers- phosphorous based chain polymers, maddrell's salt, Kuroll's salt. Phosphorous based network polymers.

Sulphur based polymers, Boron based polymers, Silicon based polymers, properties of Silicones.

2.7.2 General Properties :

Inorganic polymers are polymers having elements other than carbon. They donot have carbon in their backbone.

Ex: Silicates, Silicones, phosphates. Inorganic polymers have the following general properties.

1. The atoms are linked together by covalent bonds.
2. They fail to burn except sulphur polymers.
3. They are hard and stiff.
4. They dissolve only in polar solvents.
5. They are less ductile.
6. They are more brittle than organic polymers.

2.7.3. Glass Transition Temperature (Tg) :

The temperature below which a polymer is hard and above which it is soft is called Glass transition temperature. It is represented by Tg.

Ex : Ordinary rubber becomes hard and brittle when cooled to -70 ^{0}c.

Explantion :

There is a temperature boundry for almost all polymers. Above this temperature the substance remains soft, flexible and rubbery. Below this temperature the substance becomes hard, brittle and glassy. This temperature is called glass transition temperature. The hard brittle state is known as glassy state.

Melting Temperature (Tm) :

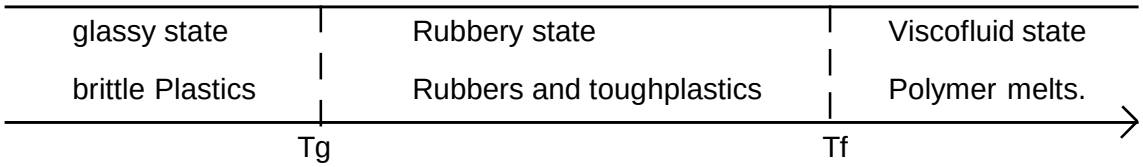
The temperature at which the polymer changes from solid to liquid is called melting temperature. It is represented by Tm.

Flow Temperature (Tf) :

The temperature at which the polymer changes from rubbery state to viscofluid state is called Flow temperature. It is represented by Tf.

Explantion :

The soft flexible state is known as rubbery state. On further heating the polymer becomes viscous liquid and starts flowing. This state is termed as viscofluid state. This temperature is called flow temperature (Tf).



Change of state with temperature in polymers.

2.7.3 Phosphorous based polymers :

These are condensed phosphates formed by the condensation process involving corner oxygen atom between PO_4 groups to give P - O bonds.

They are 3 types -

i) Metaphosphates (ring polymers)

ii) Polyphosphates (Chain Polymers)

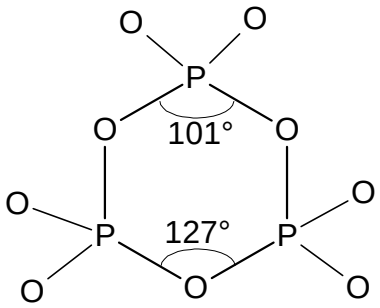
iii) Higher Polyphosphates

i) Metaphosphates :

These include mono-, di-, tri-, tetra- meta phosphates and higher meta phosphates.

In metaphosphates each PO4 group shares three oxygen atoms to form rings of $(PO_3)_n$.

Ex : Trimeta Phosphate $Na_3P_3O_9$.



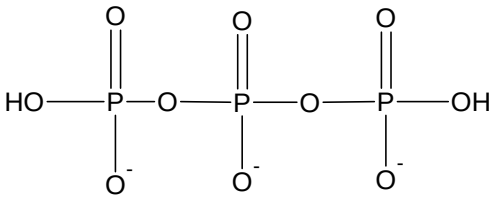
mono - PO_3
di - $(PO_3)_2$
Tri - $(PO_3)_3$
Tetra - $(PO_3)_4$
higher - $(PO_3)_n$

ii) PolyPhosphates :

These include di, tri- tetra- and long chain polyphosphates.

These are straight chain polymers having general formula $(PO_3)n\ PO_4$.

In polyphoshates PO_4 groups are linked by sharing oxygen atoms.



iii) Higher Poly Phosphates :

These are polyphosphates with an average chain of length 5 phosphorous atoms.

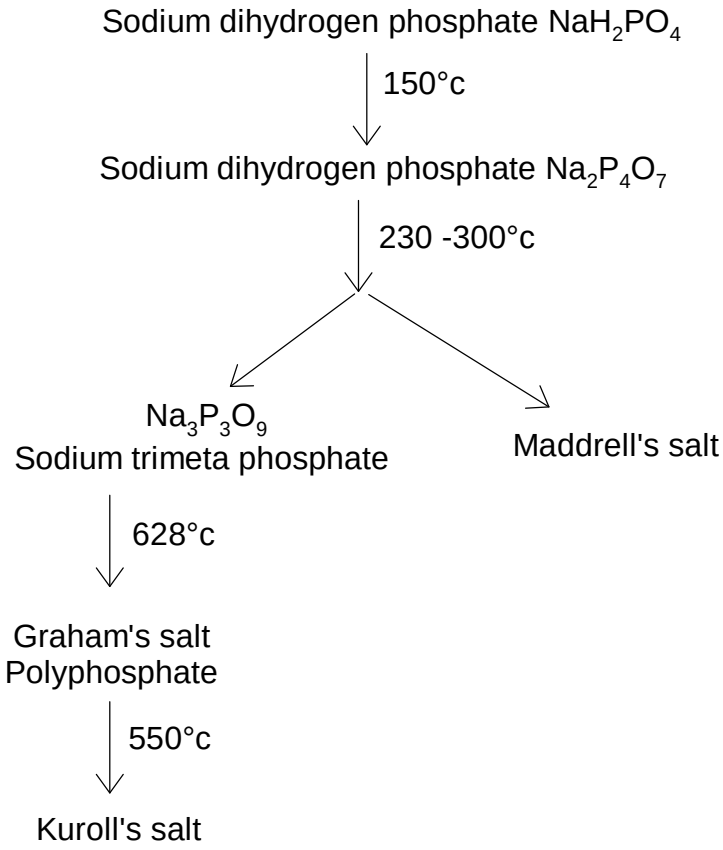
The important sodium salts are

a) Graham's salt.

b) Maddrell's salt.

c) Kuroll's salt.

Preparation :



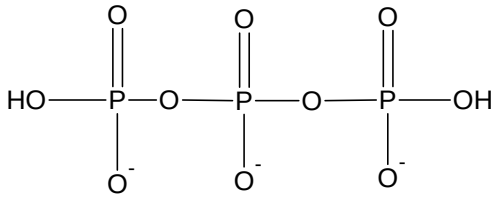
Applications :

1. The long chain sodium phosphate polymers are used in food processing industry.
2. The short chain phosphate polymers are used for deflocculation of proteins.
3. Potassium Kuroll's salt is used in the manufacture of sausages to prevent water loss.
4. Sodium Maddrell's salt is used as polishing agent in dental surgery.
5. The Borophosphate glasses are used in the manufacture of optical lenses.

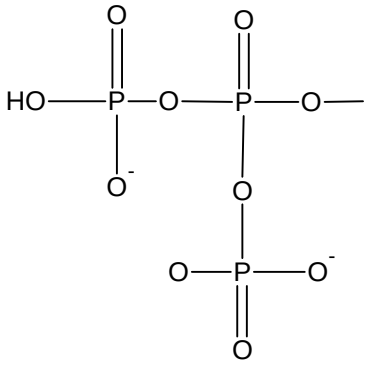
2.7.5 Phosphorous based chain polymer (Polyphosphates) :

Polyphosphates are straight chain compounds having general formula (PO_3)nPO_4.

In unbrached chains phosphate tetrahedrons are linked by oxygen atoms.



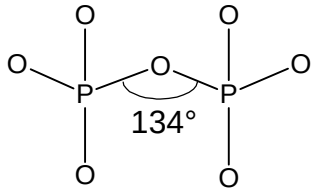
In cross linked chains phosphate groups share three oxygen atoms.



Dipolyphosphates :

It is also known as pyrophosphate.

Ex : Sodium pyrophosphate $Na_4P_2O_7$.



Preparation :

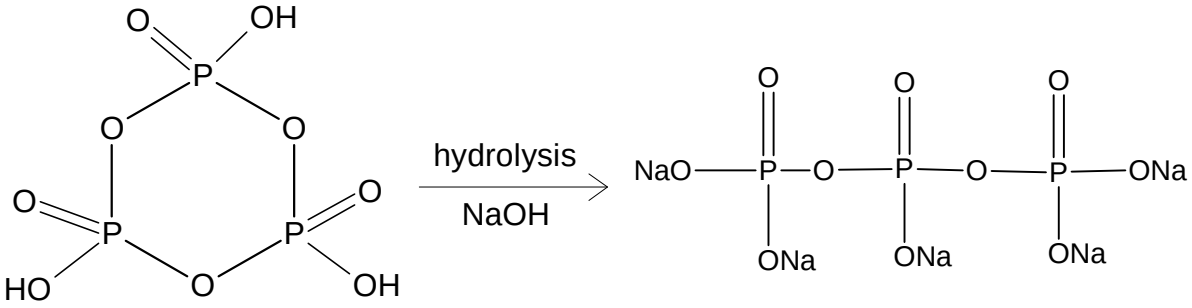
It is prepared by heating NaH_2PO_4 to 170°c

TriPolyphosphates :

It exists in two anhydrous forms as a hexahydrate $Na_2H_3P_3O_{10}$ and $Na_3H_2P_3O_{10}$

Preparation :

It is prepared by the hydrolysis of trimetaphosphate in the presence of NaOH.



Tetra Polyphosphates :

It is available as sodium hexa phosphate $Na_6P_4O_{13}$.

Preparation :

It is obtained by the hydrolysis of cyclometaphosphate and salts of large ions such as Pb^{+2}, Ba^{+2}.

Characters :

1. These are formed at elevated temperatures
2. These are soluble in water and undergo hydrolytic cleavage of P – O – P bonds.
3. The terminal 'P' are carrying one weak and one strong acid groups.
4. The body of chain carries only one acidic group.

2.7.6 Maddrell's salt :

Sodium polymeta phosphate NaPO3 - II and NaPO3 - III are known as Maddrell's salts.

It exists in two forms.

1. Maddrell's salt at high temperature

2. Maddrell's salt at low temperature

Preparation :

Sodium dihydrogen phosphate NaH_2PO_4

↓ 150°c

Sodium Pyrophosphate $Na_2P_4O_7$

↓ 230 -300°c

Madrell salt at high temperature

+

Madrell salt at low temperature

Properties :

1. These are sparingly soluble in water

2. These are readily soluble in solutions containing ammonium ions.

Structure :

X- ray studies reveal that the polymer consists of P – O – P chains made up of interconnected PO_4 groups. The pattern repeats itself after every three units and the chains donot spiral.

2.7.7. Kuroll's salt :

The polymetaphosphate $NaPO_3$ - IV, KPO_3 - IV are known as Kuroll's salts.

It exists in two forms.

1. Kuroll's salt platy.

2. Kuroll's salt fibrous.

These differ in density.

Preparation :

Sodium dihydrogen phosphate $NaH_2P_4O_7$

↓ 150°c

Sodium Pyrophosphate $Na_2P_4O_7$

↓ 230 -300°c

$Na_3P_3O_9$
Sodium trimeta phosphate

↓ 628°c

Graham's salt

↓ 550°c

Kuroll's salt platy

+

Kuroll's salt fibrous

Properties :

1. These salts are soluble in water forming viscous solution.
2. Kuroll salt platy on annealing at 400°c gives high temperature Madrell salt.

$$\text{Kuroll salt platy} \xrightarrow{400°c} \text{Madrell salt high T.}$$

3. Kuroll salt fibrous on annealing at 600°c gives trimetaphosphate.

$$\text{Kuroll salt fibrous} \xrightarrow{600°c} \text{Trimeta phosphate}$$

Structure :

X- ray studies reveal that Kuroll's salt contain P – O – P chais consisting of inter connected PO4 groups.

Each unit cell contains two different chains which spiral in opposite directions around the screw axis of the crystal.

2.7.8 Phosphorous based network polymers :

The important network polymers of phosphorous are

i) Polymeric phosphourous pentoxide

ii) Polyortho Phosphate of Boron

iii) Polymeric Aluminium orthophosphate

iv) Polymeric Ferrous phosphate

v) Ultraphosphate glass

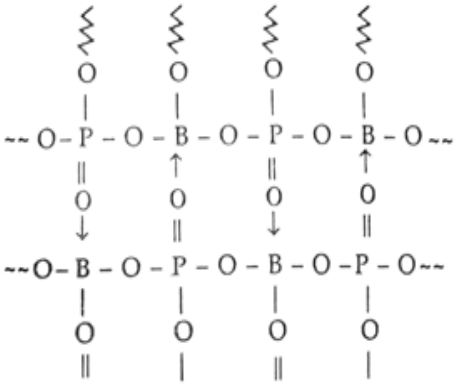
vi) Borophosphate glass.

i) Polymeric phosphate pentoxide :

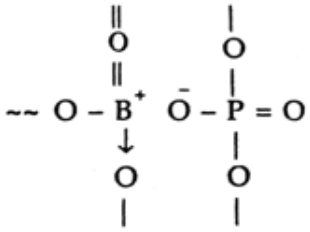
It exists in three crystalline forms. Two are sheet polymers and the third one is a glassy network structure. The glassy material has three dimensional network structure containing P– O–P bonds.

ii) Polyortho Phosphate of Boron :

The Structure of polyorthophosphate boron is similar to that of SiO_2. The P – O and B –O bonds are shorter than the corresponding single bonds. Actually it is a resonance hybrid of covalent structure I and ionic structure II.



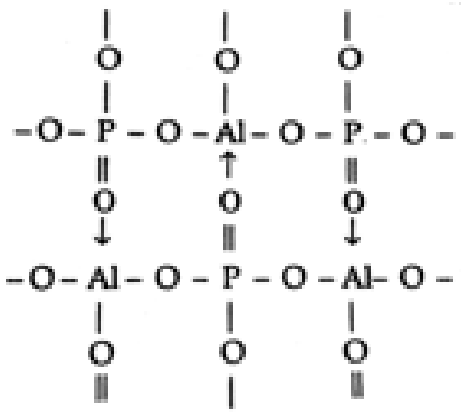
Covalent Structure I



Ionic structure II

iii) Polymeric Aluminium orthophosphate :

The structure of polymeric Aluminium orthophosphate is similar to that of Boron polyorthophosphate.

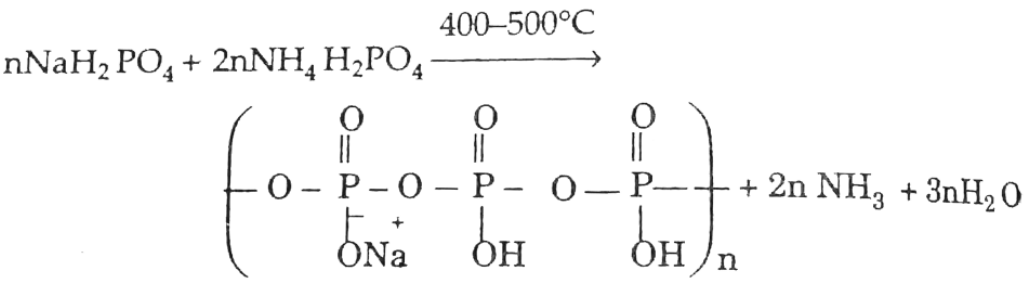


iv) Polymeric Ferrous phosphate :

In this polymer P atoms are tetrahedrally surrounded by O atoms. Fe atoms are octahedrally surrounded by O atoms, PO_4 units and H_2O molecules. There are interconnected P tetrahedra and Fe octahedra by hydrogen bonding.

v) Ultraphosphate glass :

Sodium ultraphosphate glass is obtained by heating a mixture of NaH_2PO_4 and $NH_4H_2PO_4$ It is linear polyphosphate. On heating linear polyphosphate cross linked sodium ultraphosphate is formed with the removal of H_2O molecules.



Importance : when cold glass is brought into warm humid atmosphere the water vapour form a uniform thin layer instead of discrete droplets. So there is no change in vision through ultra phosphate glass.

vi) Borophosphate glass :

Borophosphate glass is obtained by fusing a mixture of H_3PO_4, Boric oxide and calculated quantity of metal carbonate or oxide at 700°c.

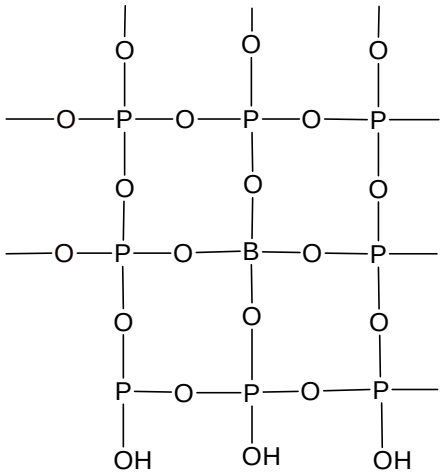
Types of Borophosphate glass : There are three types -

a) In this type of Borophosphate glass alkalimetal content is more than phosphoric acid. Almost all the Boron atoms are intrigonal BO_3 groups. The fraction of four cornered boron atoms is less than 0.1.

b) In another type of Borophosphate glass phosphoric acid content is more than alkali. All the Boron atoms are four coordinated when boron oxide is less than 10 mole percent.

c) In the third type of Borophosphate glass boric oxide and phosphoric acid are in equal proportions. As Boronoxide increases the fraction of four coordinated Boron atoms decrease steadily.

Borophosphate glass with three coordinated Boron atoms.



Borophosphate glass with four coordinated Boron atoms.

2.7.9. Sulphur based Polymers :

i) Polymeric Sulphur :

Preparation :

The long chain polymeric sulphur is prepared by heating rhombic sulphur (S_8) to 165 - 180°c and then cooling the melt in ice bath.

$$S_8 \rightleftharpoons S - S_6 - S \xrightarrow{S_8} S - S_{14} - S \xrightarrow{S_8} S - S_{22} - S \rightarrow S - S - S - S \sim\sim\sim S - S - S - S$$

Properties :

1. Pure polymeric S has Tg of 75°c.
2. Above 75°c dissociation of S – S bonds take place.

i) Polymeric Thiazyls :

a) Tetra thiazl (S_4N_4) (Tetra Sulphur Tetra Nitride)

Preparation :

It is prepared by the ammonolysis of sulphur monochloride.

$$6S_2Cl_2 + 16NH_3 \xrightarrow{CCl_4} S_4N_4 + S_8 + 12\ NH_4Cl$$

Properties :

1. It is a bright orange solid.
2. It is soluble in water and in organic solvents.
3. It reacts with Ag F_2 forming Tetrathiazyltetra fluoride.

$$S_4N_4 + 4\ AgF_2 \rightarrow S_4N_4F_4 + 4\ AgF$$

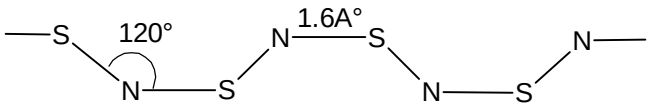
4. On reduction with $SnCl_2$/ C_2H_5OH it gives tetra sulphurtetraimide.

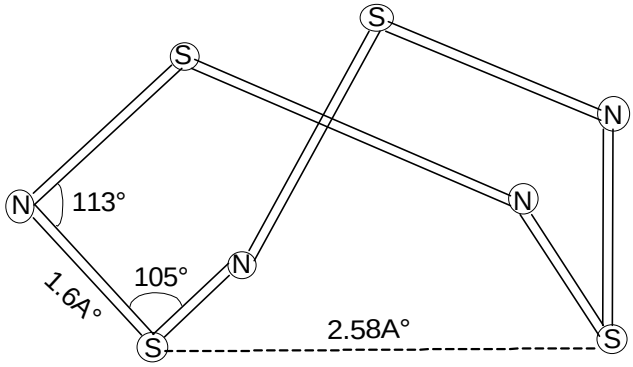
$$S_4N_4 + 4\ H \xrightarrow[C_2H_5OH]{SnCl_2} S(NH)_4$$

5. It reacts with chlorine forming trithiazyltri chloride.

$$3S_4N_4 + 6Cl_2 \rightarrow 4\ S_3N_3Cl_3$$

Structures :





S_4N_4

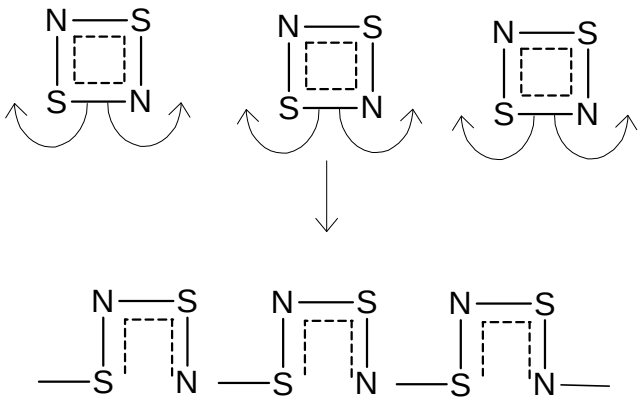
b) PolyThiazyl $(SN)_n$ (Polymeric Sulphur Nitride)

Preparation :

It is prepared by passing S_4N_4 in vacuum over Ag at 200°c. First S_2N_2 is formed which polymerises to $(SN)_n$.

$$S_4N_4 \rightarrow 2\ S_2N_2$$

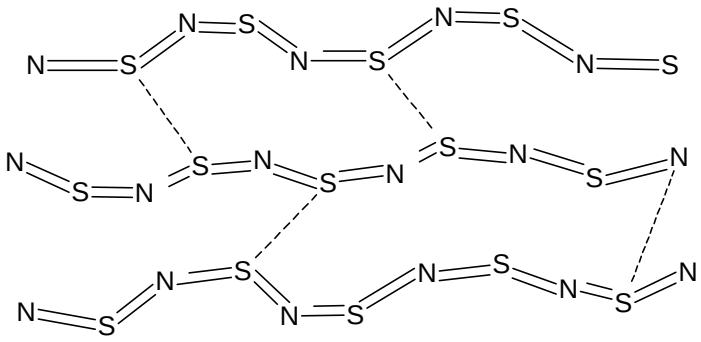
Polmerisation of S_2N_2 to form $(SN)_n$



Properties :

1. It shows property of a metal.
2. At room temperature it acts as conductor but at low temperature it becomes super conductor.
3. It is soft and malleable.
4. At 140°c it decomposes to S and N.

Structures :



c) Cross linked polymer of sulphur (Chalcogenide glass) :

The amorphous cross linked polymers formed from the compounds of chalcogens (Sulphur, Se, Te) with one or more polyvalent elements such as As, Sb, Sn are called Chalcogenide glasses.

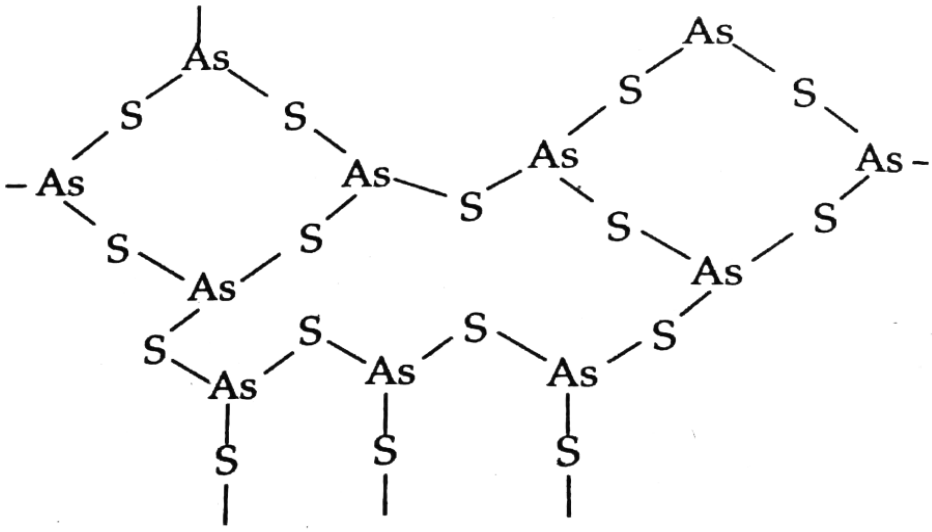
Ex : $(As_2 S_3)_n$. The naturally occuring chalcogenide glass is $(As_2 Pb_3 S_8)_n$.

Preparation :

Chalcogenide glasses are prepared by the fusion of elements under selected conditions which minimises oxidation and loss of volatalisation of the components.

Structure :

The parent network of chalocgenide glasses is a triple connected assembly of polyvalent elements through chalcogen atoms.



Properties :

1. These glasses are deeply coloured.
2. They possess lower softening point and high refractive index.
3. They have lower tensile strength.
4. The Tg of As Chalcogenide glass increases linearly.
5. Switching Phenomena : Conversion of chalcogenide glass from low conductivity to high conductivity under applied voltage is called switching.

   It can occur in two ways.

   i) Threshold switching

   ii) Memory Switching

   Swithching is due to breaking of bonds by current of high voltage in chalcogenide glass.

Uses :

1. These are used for infrared windows for civil and military optical devices.
2. These are used in ultrasonic delay lines.
3. These are used in high energy particle detector multipliers.
4. These are used for electroluminescent displays.
5. These are used in memory devices for computers.

2.7.10. Boron Based Polymers :

a) Polycarboranes :

Carboranes are the mixed hydrides of carbon and Boron. They are two types

a) Nido carboranes general formula C_2 Bn -2Hn

b) Closo Carboranes.

Preparation :

Acetylene reacts with decaborane forming ortho dicarborane.

$$B_{10}H_{10} + C_2H_2 \rightarrow C_2B_{10}H_{12}$$

Orthodicarborane

Orthodicarborane

↓ 470°c rearrangement

metadicarborane

↓ 630°c

Paradicarborane

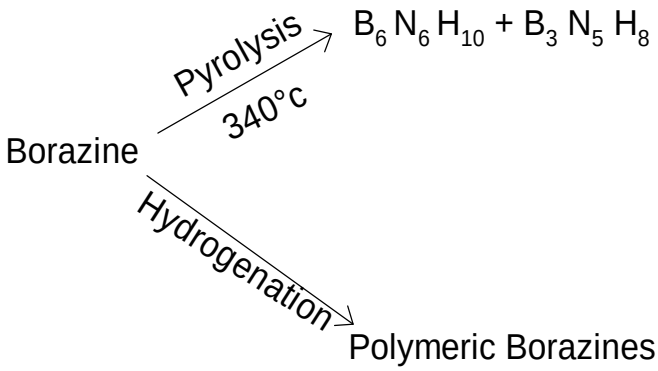
b) Polymeric Borazines :

Borazine is isoelectronic with benzene. Formula is $B_3N_3H_6$. hydrogenation of Borazine gives polymerised compounds.

Preparation :

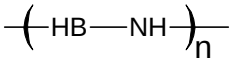
Borazine is prepared by the action of ammonia with diborane at 200°c.

$$2B_2H_6 + 6NH_3 \xrightarrow{200°c} 2B_3N_3H_6 + 12H_2$$



Structure :

It has long chains containing – BH – and – NH – groups alternatively.



c) Polymeric Borates :

Preparation :

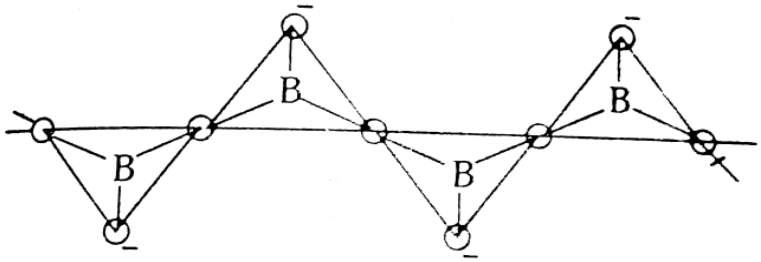
Metaborate is obtained by the action of ^{-}OH with boric acid

$$^{-}OH + H_3\ BO_3 \rightarrow BO_2^{-} + 2H_2O$$

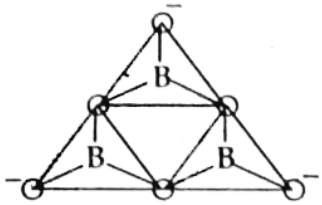
The crystals of Lithium Borate contain polymetaborate anions of endless flat Zig - Zag chains. Sodium meta borate contains cyclic trimeta borate anions.

Structure :

The Zig - Zag chains contains triangular BO_3 structural units which corresponds to Sp^2 hybridisation of the Boron atom.



$(BO_2)_n^{-n}$ anion in LiBO2



Cyclic trimeta borate anion

d) Boron Nitride :

It is also called white graphite. It exists as polymer with the formula $(BN)_n$.

Preparation :

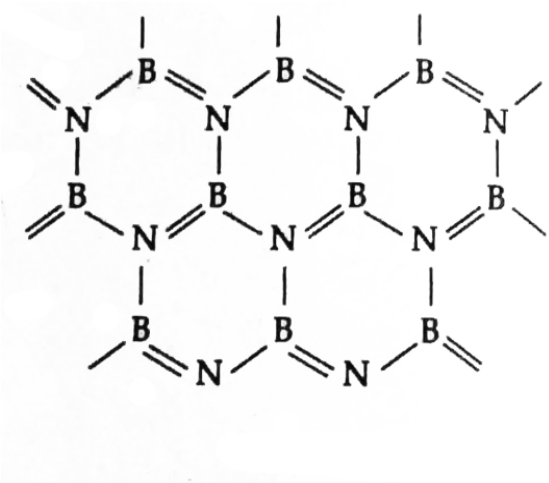
It is prepared by heating a mixture of dry ammonium chloride and borax to red hot in a platinum crucible.

$$2\ NH_4Cl + Na_2\ B_4\ O_7 \rightarrow 2BN + 2\ NaCl + B_2O_3 + 4\ H_2O$$

It is a white powder with m. p. 3275K.

Structure :

The structure of Boron Nitride resembles with that of graphite.



2.7.11. Silicon based Polymers :

These are the polymers containing silicon Si – O – Si bond.

They are mainly two types -

1) Silicates

2) Silicones

1. Silicates :

The polymers obtained by the reaction of silica (SiO_2) with alkalies are known as Silicates.

Preparation :

They are prepared by heating silica with metal carbonates or metal oxides at 1770K.

$$Si\ O_2 + Na_2CO_3 \xrightarrow{1770\ k} Na_2Si\ O_3 + CO_2$$

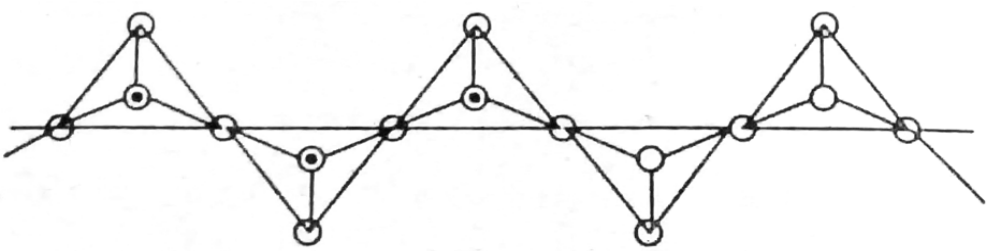
$$Si\ O_2 + Na_2O \rightarrow Na_2Si\ O_3$$

$$n\ Na_2Si\ O_3 \rightarrow (\ Na_2Si\ O_3\ )_n$$

a) Chain Silicates :

In Chain silicates two oxygen atoms per Si O_4^{-4} tetrahedron are shared forming chains.

Ex : Diapside Ca Mg ($Si O_3)_2$

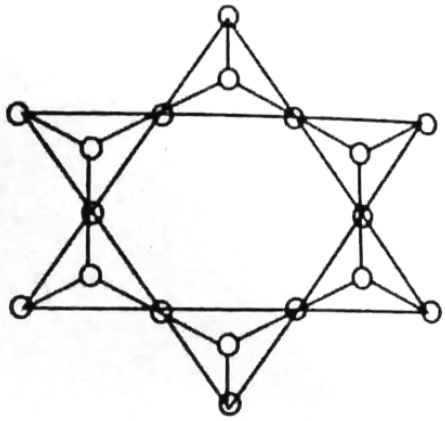


$(SiO_3)_m^{-2n}$ Chain

b) Cyclic Silicates :

In Cyclic silicates two oxygen atoms per Si O_4^{-4} tetrahedron are shared forming rings.

Ex : Beryl $Be_3 Al_2 Si_6 O_{18}$

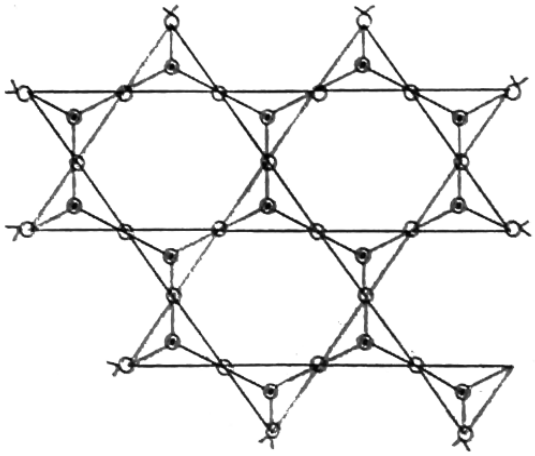


$(Si_6 O_{18})^{-12}$ion

c) Sheet Silicates :

In Sheet silicates three oxygen atoms per Si O_4^{-4} tetrahedron are shared forming two dimensional sheets. The sheets are held together by electrostatic forces of attraction.

Ex : Keolenite [Al_2 (OH) Si_2O_5]

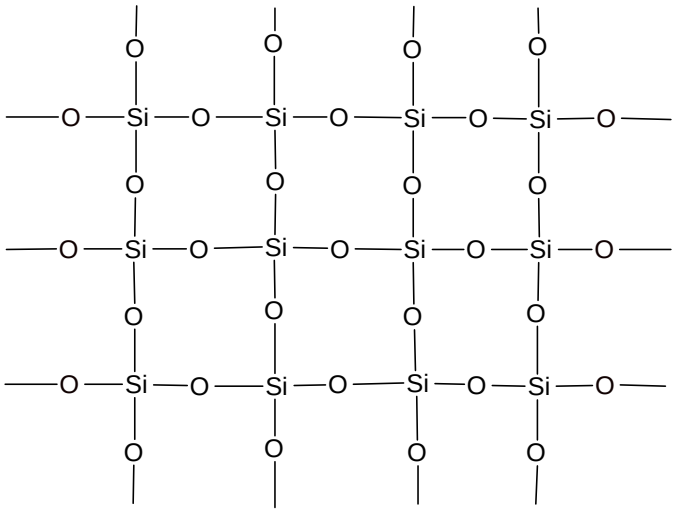


Sheet Silicate

d) Three dimensional silicates :

In Three dimensional silicates four oxygen atoms per Si O_4^{-4} tetrahedron are shared forming three dimensional latttice . They contain ($SiO_2)_n$.

Ex : Felspar, Zeolile, Quartz.



2. Silicones :

The polymers formed by the condensation of alkane silanols are known as silicones.

Preparation :

It consists of 3 steps.

i) Formation of intermediates.

ii) Hydrolysis of intermediates

iii) Chain, branching, cyclic networks.

i) Formation of intermediates :

a) Methyl chloride on heating with silicon at 300°c in the presence of copper catalyst forms dimethyl dichloro silane.

$$2\ CH_3Cl + Si \xrightarrow{Cu} (CH_3)_2 Si\ Cl_2$$

b) Methyl chloride reacts with Si and HCl forming trihalides.

$$CH_3Cl + 2HCl + Si \xrightarrow[300°c]{Cu} CH_3 Si\ Cl_3 + H_2$$

ii) Hydrolysis of Intermediates :

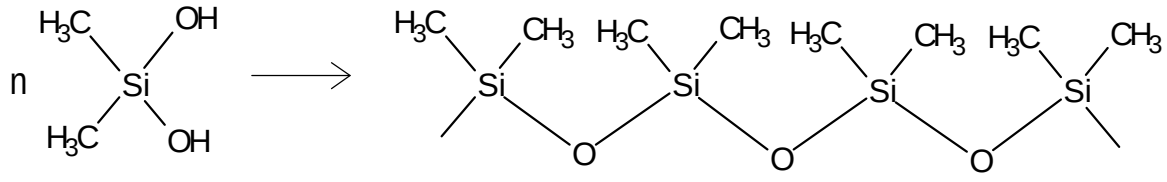
Alkyl chloro silanes on hydrolysis form alkyl silanols.

$$(CH_3)_2 Si\ Cl_2 + 2H_2O \rightarrow (CH_3)_2 Si\ (OH)_2 + 2HCl$$

$$CH_3\ Si\ Cl_3 + 3H_2O \rightarrow CH_3 Si\ (OH)_3 + 3HCl$$

ii) a) Linear Silicones :

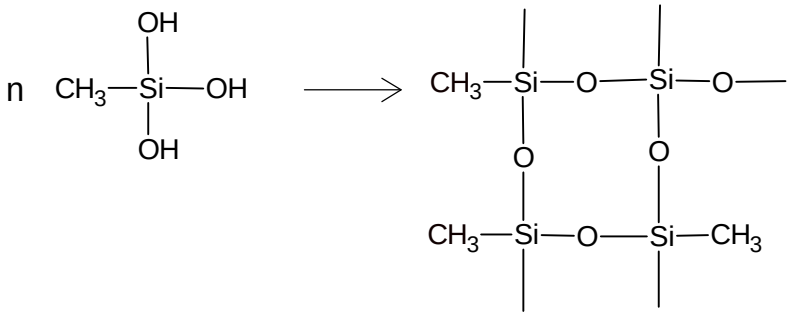
Alkyl silane diols on condensation form linear silicones.



Linear Silicone

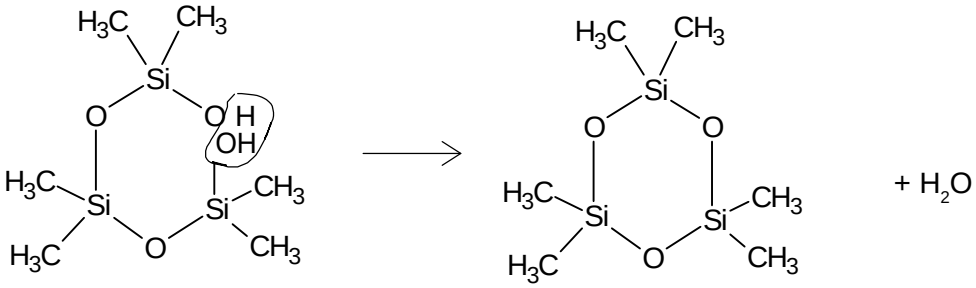
b) Cross linked Silicones :

Alkyl silane triols on polymerisation form cross linked Silicones.



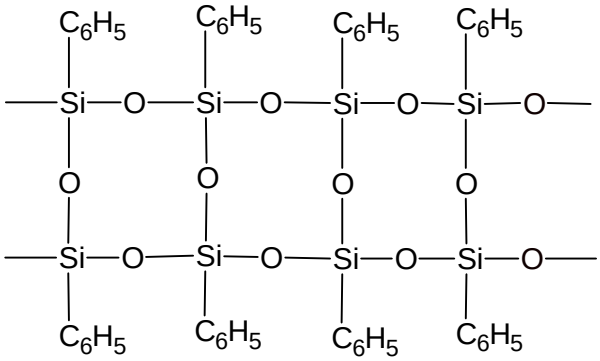
c) Cyclic Silicones :

Linear silicones on dehydration form cyclic silicones.



d) Ladder like Silicones :

Phenyl silanetriols on carefully heating form ladder like silicones.



2.7.12. Properties of Silicones:

i) Thermal Stability :

Silicon polymers can with stand upto 300 - 400°c because of Si – O – Si linkage.

The experimental values of Si – O – Si linkage are less than ionic character that means Si – O – Si linkage has ionic and also partial double bond character. So, Silicon polymers are quite stable.

ii) Viscosity :

Viscosity changes slightly with temperature of the silicone fluids.

iii) Chemical Stability :

These are chemically stable. They have no action with dil acids, bases, water and metal salts.

iv) Toxicity :

These are non - toxic.

v) Properties due to chemical structure :

a) Physical properties of polysiloxane such as compressibility, viscosity coefficient and surface properties depends on the helical structure of polysiloxane.

b) As Lubricant : At low temperature polysiloxane has linked and coiled structures. As temperature increases the linked structure opens up and increases viscosity due to thermal movement of molecules. So, It is used as lubricant both at high and low temperatures.

c) As water repellant : These are water repellent due to the presence of organic (alkyl) side groups. Materials such as paper, wool, textiles, wood, porcelain can be made water proof with a thinfilm of silicone.

d) As fabricant : Silicone rubbers retain their elasticity upto 250°c. So, artificial heart valves and heart bipass pumps are fabricated with silicone rubber.

2.7.13 Model Questions :

1. Explain

   a) Glass transition temperature

   b) Melting temperature

   c)Flow temperature.

2. Write about phosphorous based chain polymers.

3. Write notes on

   a) Maddrell's salt

   b) Kuroll's salt

4. Explain phosphorous based network polymers.
5. Write about Boron based polymers.
6. What are Silicones? Give their preparation and properties.
7. Write about Sulphur based polymers.
8. What are chalcogenised glasses. Explain

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Lesson – 8

COORDINATION POLYMERS

2.8.1 Coordination polymers, natural coordination polymers, chain coordination polymers. Two dimensional coordination polymers and with three dimensional network. Synthetic coordination polymers. Volan and quillon polymers. Polymers with cyclopentadienyl rings polymers with chelating agents, polymers with polymeric ligands, miscellaneous polymers.

2.8.2 Definition and classification of Coordination polymers :

Any micro molecule which contains coordinate covalent bond between metal and ligand is known as coordination polymer.

Ex : Polymeric cupric halides, polymeric silver sulphocyanides.

Coordination polymers are mainly two types.

a) Natural coordination polymers.

b) Synthetic coordination polymers.

2.8.3 Natural Coordination Polymers :

Natural Coordination polymers are subdivided into three types.

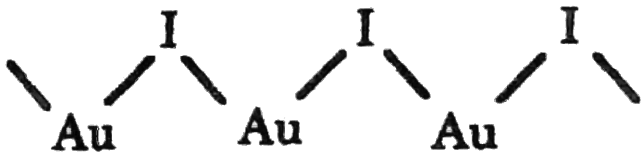
i) Chain polymers

ii) Two dimensional polymers

iii) Three dimensional network polymers.

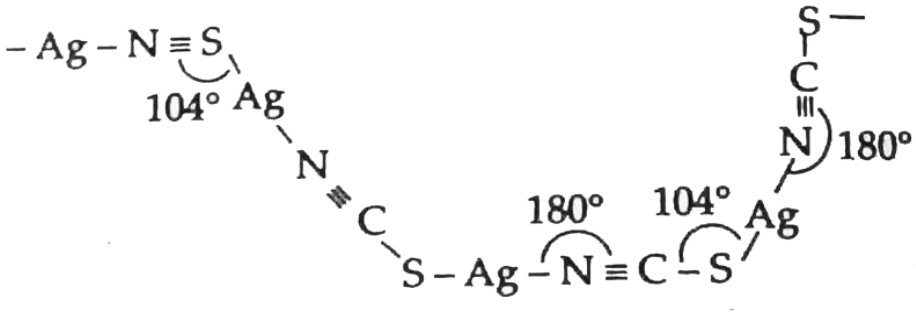
i) Chain Polymers : These are natural coordination polymers which were not synthesised as polymers but found to be polymeric in nature.

a) Polymeric gold Iodide : In AuI the bond is ionic and also fairly covalent. It exists as (AuI)n. It is a coordination polymer with coordination number 2 for Au. It has Zig-Zag chain structure.

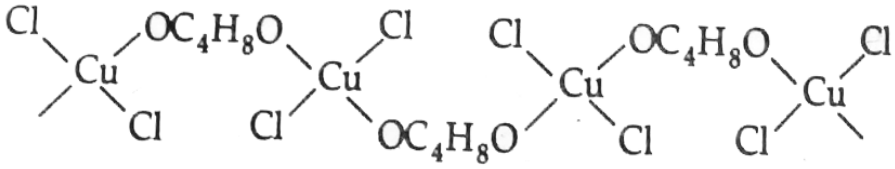


b) Polymeric gold and Silver Sulphocyanides : The polymers of gold and silver with SCN ligand are coordination polymers with Zig - Zag chain structure.

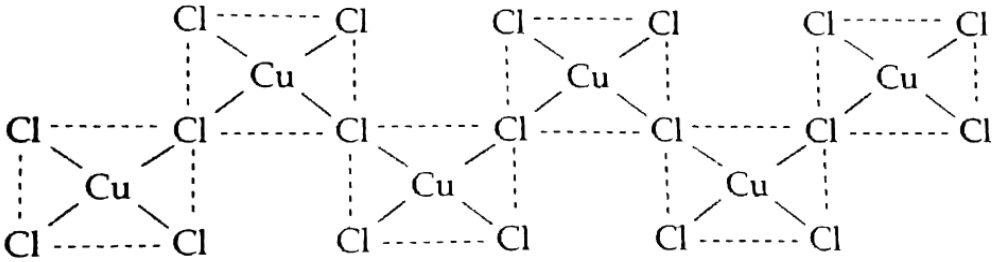
The coordination bonds of S and N are formed by the lone pairs. In these polymers coordination number is 2 for Ag or Au.



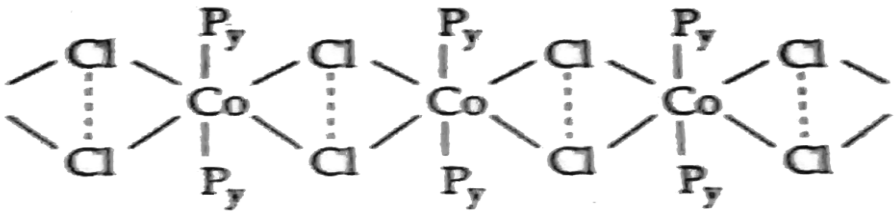
c) Polymeric $CuCl_2$ dioxane : In this polymer dioxane acts as bridging ligand. The coordination number is 4 for Cu.



d) Polymeric $(CuCl_3)_n^{n-}$: In this polymer two adjacent Cl^- ions of square planar $CuCl_4$ units are shared. The chain is arranged as spiral in the crystal lattice.

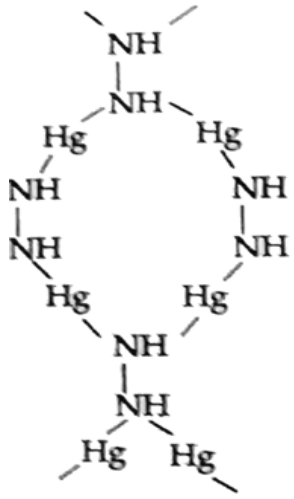


e) Polymeric [Cd (NH_3)$_2$ Cl_2]$_n$ and [Co (Py)$_2$ Cl_2]n : In these polymers the four chlorine atoms around each metal atom act as bridging ligands.



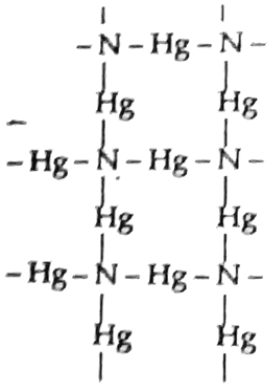
ii) Two dimensional polymers : These polymers contain metal ions with coordination number 2 having planar network structure.

Ex : $[Hg_2(N_2H_2)Br_2]_n$



In polymeric $[Ni(NH_3)_2(CN)_2]_n$ the square planar and oetahedral Ni(II) ions are present alternatively bridged by CN.

iii) Three dimensional network polymers : Compounds containing $(Hg_2N)_n^{+n}$ has three dimensional network structure. In this polymer N is Sp^3 hybridised and Hg is Sp hybridised. Tetrahedral N in $(Hg_2N)_n^{+n}$ is responsible for three dimensional network structure. The Coordination number is 2 for Hg.



In polymeric $Zn(CN)_2$, Zn in Sp^3 hybridised. It is responsible for three dimensional network structure. Tetrahedral Zn atoms are connected through linear – C N groups.

2.8.4 Synthetic Coordination Polymers :

Synthetic coordination polymers are more stable polymers synthesised. These are stable because the polymers contain bonds involving carbon atoms.

Ex : i) Volan

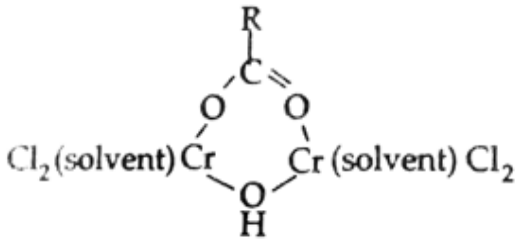
ii) Quillon

These are coordination polymers of Chromium with three dimensional network.

In volan the organic group present is methacrylate groups where as in quillon the organic group present is stearate and myristate groups.

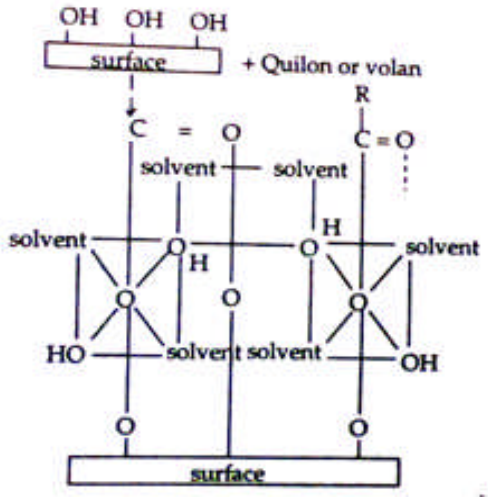
Synthesis :

A typical process for sythesis of these polymers involves the reduction of CrO_2 Cl_2 by methanol or ethanol in the presence of Carboxylic acid. This gives a solution of the following structure.



The dilution of this solution in the presence of a base leads to ionisation of chlorine and further bridging of Cr atoms by ' OH' groups.

A glass surface containing - OH, - NH_2, - COOH, - O, - $CONH_2$ etc functional groups is treated with the above solution and heated. Further polymerisation takes place yielding an insoluble coating. It is attached firmly to the surface by bridging carboxylate groups which are oriented away from the surface as shown in the following structure.

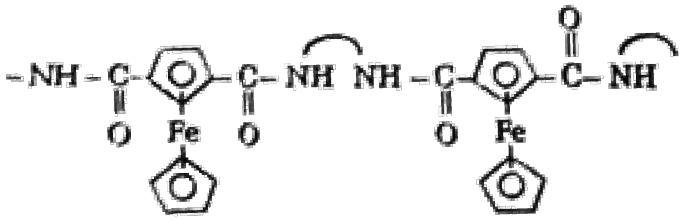


Importance :

1. Carboxylate of Quillon impart water repellance and non- adhesiveness to the treated surface.
2. Carboxylate groups having fluoro carbons impart water and oil repellent nature to the treated surface.

2.8.5. Polymers with Cyclopentadienyl rings :

a) CoCl derivative of Ferrocene reacts with diamines or dihydroxy compounds forming polymers with cyclopentadienyl rings.



b) Ferrocene undergo polymerisation in the presence of free radicals forming the polymer $(C_5H_4\ Fe\ C_5H_4)_n$.

c) Dichloro dicyclopentadienyl titanium reacts with TiCl4 followed by hydrolysis gives the polymer $[Ti (C_5H_5) ClO]_n$.

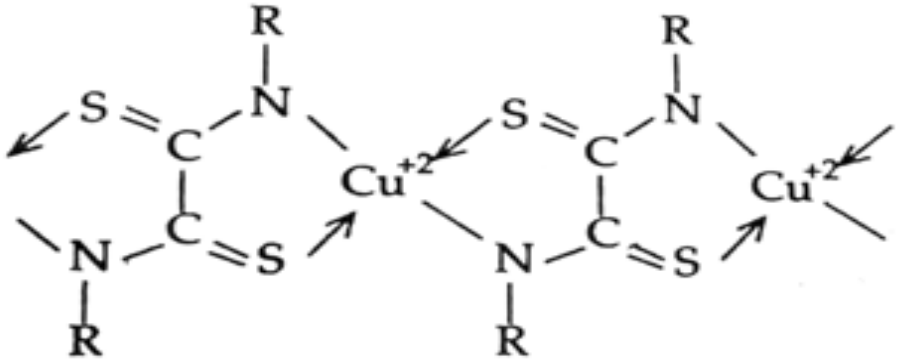
$$[Ti (C_5H_5) Cl_2] + TiCl_4 \rightarrow 2Ti (C_5H_5) Cl_3 \xrightarrow{\text{Hydrolysis}} [Ti (C_5H_5) ClO]_n$$

2.8.6 Polymers with Chelating agents :

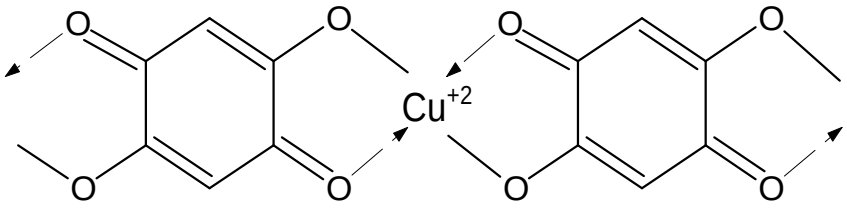
Several organic compounds act as chelating agents. One part of such ligand coordinates to one metal ion while the other part to another metal ion forming chains of ligands and metal ions.

Ex :

a) Cu^{+2} and Ni^{+2} form polymer with dithioxamide Here dithioxamide acts as bischelating agent and also known as Rubeanic acid.



b) Cu^{+2} and Ni^{+2} form polymer with dihydroxy quinones. For example 2,5 - dihydroxy - P-benzoquinone forms polymers with Cu^{+2} and Ni^{+2} .



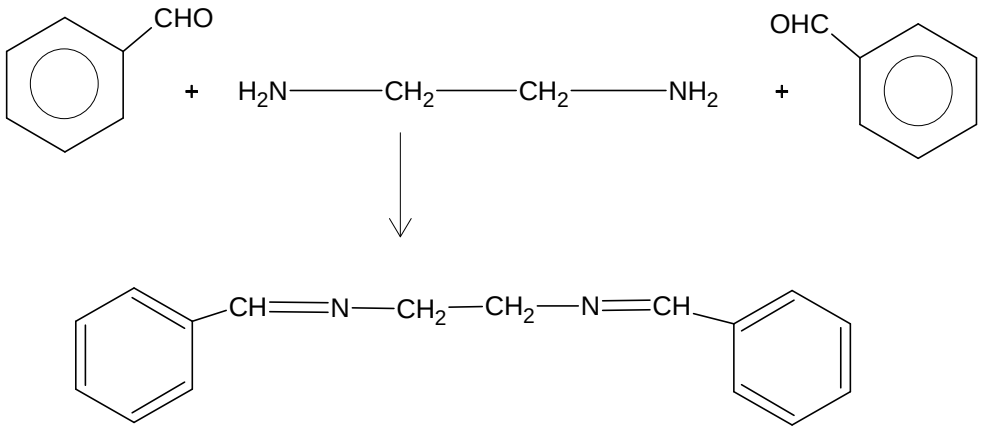
c) Be^{+2} , Co^{+2} , Ni^{+2} ,Cu^{+2} and Zn^{+2} form polymers with P- diketones such as $C_6H_5Co(CH_2)_8$ $COCH_2$ COC_6H_5

These polymers are low melting and have fibre forming nature.

2.8.7 Polymers with polymeric ligands :

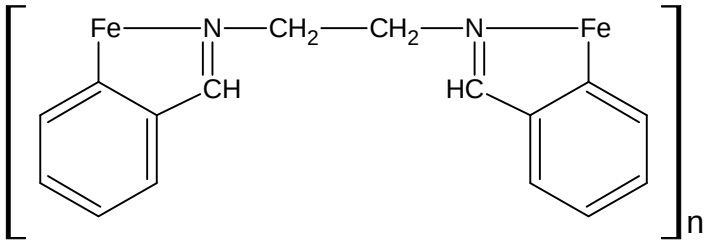
a) Polymeric shiff's base forms an important class of polymeric ligands.

Aromatic aldehydes react with diamines forming polymeric ligand. This polymeric ligand reacts with $FeSO_4$ Yielding Fe(II) polymer.

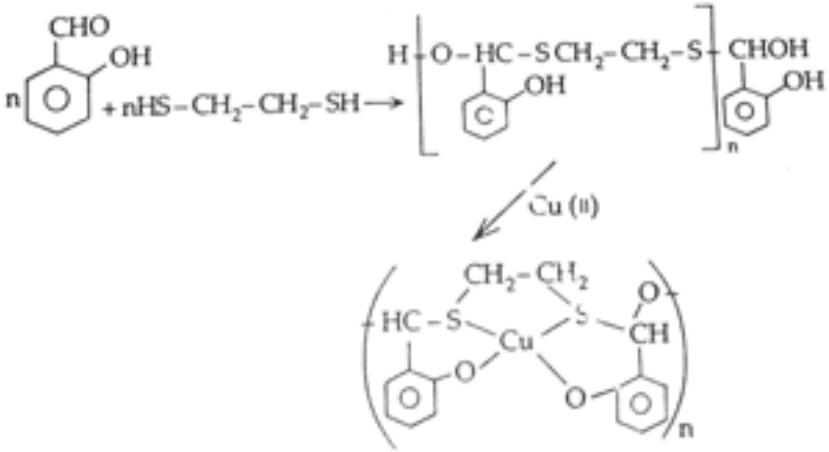


Polymeric ligand

$FeSO_4$

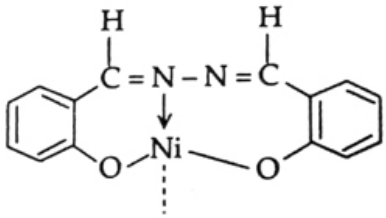


b) Salicyl aldehyde reacts with thiols forming a polymeric ligand. This polymeric ligand forms coordination polymers with salts of metals such as Cu, Co, Ni.



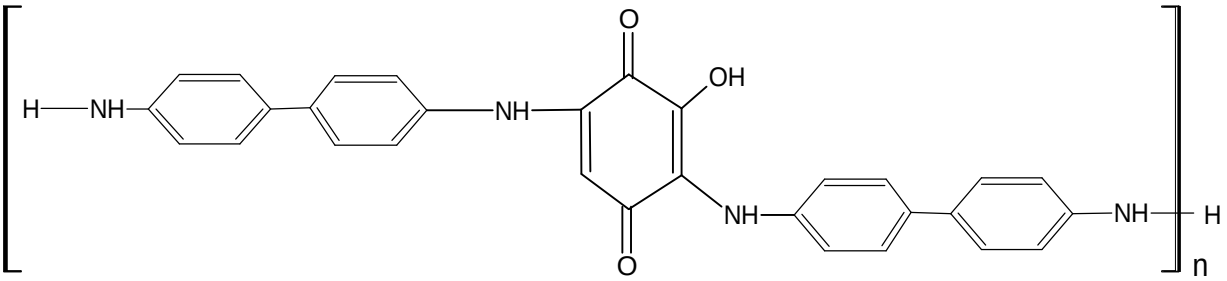
2.8.8. Miscellaneous Polymers. :

a) Co(II), Cu(II), Ni(II), Cd(II), Zn(II) etc react with Bismethyl Salicylate forming polymers with intermolecular coordination.



b) Vinyl Ferrocene undergoes polymerisation in the presence of acid catalyst forming polymeric oils.

c) Polyamino phenone is another miscellaneous polymer formed.



2.8.9 Model Questions :

1. Define and classify coordination polymers.
2. Write about chain coordination polymers.
3. Discuss two dimensional polymers.
4. Write about three dimensional network polymers.
5. Write notes on a) Volan polymer b) Quillon polymer
6. Explain a) Polymers with chelating agents b) Polymers with polymeric ligands.

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Lesson – 9

POLYMER DEGRADATION

2.9.1 Polymerdegradation, types of polymerdegradation- Thermal degradation, Mechanical degradation. Degradation by ultrasonic waves, Photodegradation, polymer degradation by high energy radiation, oxidative degradation, Hydrolytic degradation.

2.9.2 Polymer degradatioin :

Polymer degradation is defined as an uncontrolled change in molecular weight or constitution of the polymer.

Ex : Polyethylene, Polypropylene, Polymethylmetharylate etc.

Explanation :

A Plastic bucket left for long time in the sun and rain loses its lustre and strength. This detereoration in properties is due to a phenomenon called polymer degradation. The term degradation is taken to mean reduction in the molecular weight of the polymer.

A polymer suffer degradation at two stages. First, during the fabrication process and secondly during its daily usage.

Advantage :

Polymer degradation is generally undesirable. But some times it is advantage also. For example, the space craft is covered by a ' heat shield ' which is a polymer based material. When the space craft re- enters the earth's atmosphere, intense heat is generated. The heat shield encounters the intense heat generated. The polymer - based material chars, degrades and protects the space craft.

2.9.3 Types of Polymer degradation :

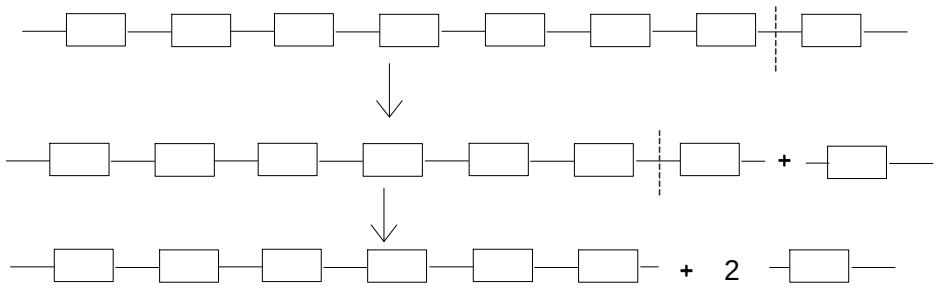
Polymer degradation is broadly two types -

1) chain - end degradation .

2) Random degradation.

1) Chain - end degradation :

Chain - end degradation starts from chain end, resulting in the successive release of the monomeric units.



Each block in the diagram represents one monomeric unit.

Ex : A good example of chain - end degradation is thermal depolymerisation of poly α - methyl styrene.

This phenomenon is actulally the reverse of propagation in chain polymerisation. It is also called depolymerisation or unzipping. In chain - end degradation mol. wt. of the polymer decreases slowly liberating the monomer simultaneously. Polymers formed by chain polymerisation undergo chain - end degradation.

Advantage :

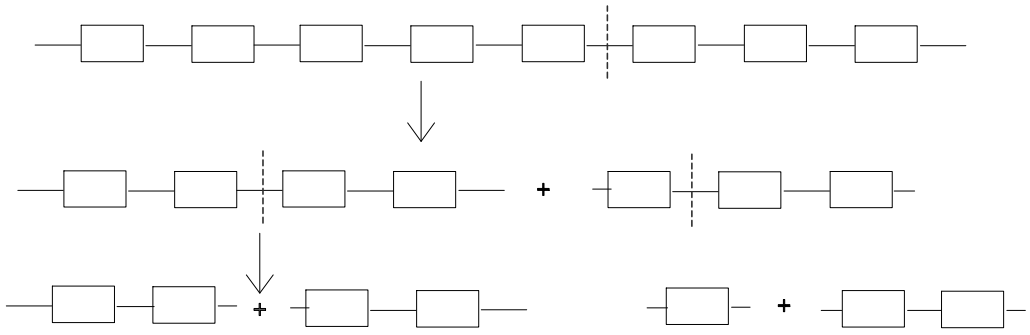
It is useful for recovering monomer from waste polymer.

Ex : From the waste polymethylmethacrylate recovery of monomer is almost 100%.

Polystyrene, Polybutadiene and Polyisoprene also undergo depolymerisation.

2. Random degradation :

Random degradation occurs at any random point along the polymer chain.



This is the reverse of polycondensation process.

$$Mn \rightarrow Mz + My$$

Ex : Polyesters, Polyethylene.

Almost all polymers undergo random degradation.

In chain - end degradation the molecular weight drops slowly and large quantity of monomer is released. In random degradation molecular weight drops suddenly and a little or no monomer is released.

2.9.4 Thermal degradation :

Def : A polymer when subjected to heat undergoes degradation called Thermal degradation.

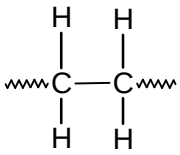
Thermal degradation of a polymer may follow either ' unzipping ' or ' random ' route. The unzipping route gives pure monomer while random degradation gives products depending on the structure of the polymer.

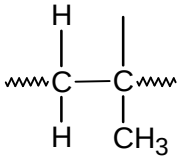
Factors effecting C – C bond or thermal stability :

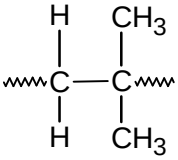
Since many polymers have a C – C chain as the back bone, their thermal stability depends on the stability of the C – C bond.

1. As no. of substituents increases thermal stability of the polymer decreases.

Ex :







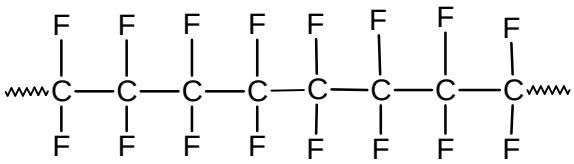
Polyethylene Polypropylene Poly iso butylene

Here polyethylene is thermally stable. The order of stability is

Polyethylene > Poly Propylene> Polyiso Propylene.

2. All Substituents do not decrease thermal stabliity. Highly electro negative substituents like fluorine protects C – C bond and increases thermal stability.

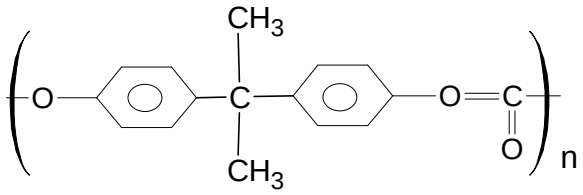
Ex : Teflon in which all hydrogen atoms of ethylene are substituted by fluorine, is the most stable polymer.



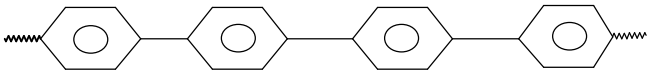
Teflon
most stable

3. Generally aromatic nucleus in a polymer chain increases Thermal stability.

Ex : Poly Phenylene is more stable than polycarbonate.



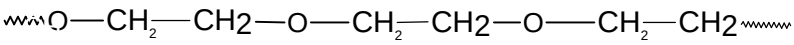
less stable



more stable

4. The branching and the presence of oxygen atom in the polymer chain decreases thermal stability

Ex : Polyethylene oxide is easily degradable.



Polyethylene oxide

less stable

5. In some reactions polymer degradation is by breaking the substituents but not the main chain.

Ex : PVC degrades at 200°c giving HCl.

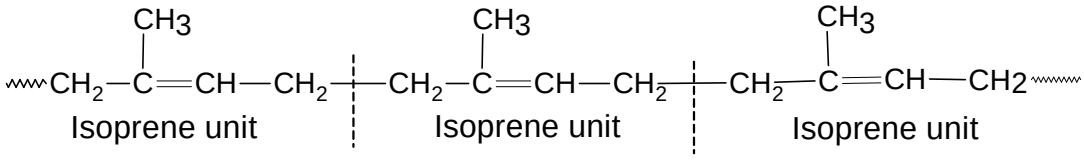
2.9.5 Mechanical Degradation :

Def : A Polymer dissolved in a solvent when subjected to vigorous stirring undergoes degradation called Mechanical Degradation.

Ex : Polystyrene, Rubber.

In rubber industry, rubber is masticated by passing it through two rotating rollers to reduce its molecular weight and make it more processable. This mastication converts hard and tough rubber into soft and semisolid mass.

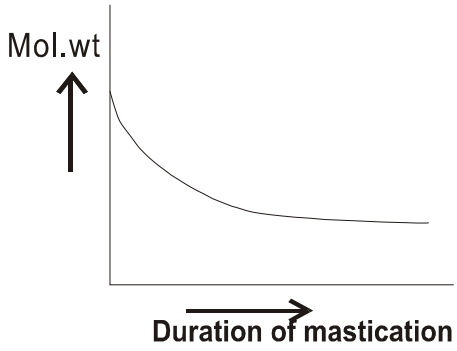
Explanation : Rubber is polyisoprene.



Poly isoprene

In Polyisoprene the bonds linking isoprene units are more Vulnerable and cleave when the polymer is subjected to stress in the form of milling or mastication.

Agitation, Grinding or Extrusion are other well known methods for effecting the mechanical degradation of the polymer. Bigger molecules are effected much more than the smaller ones during mechanical degradation.



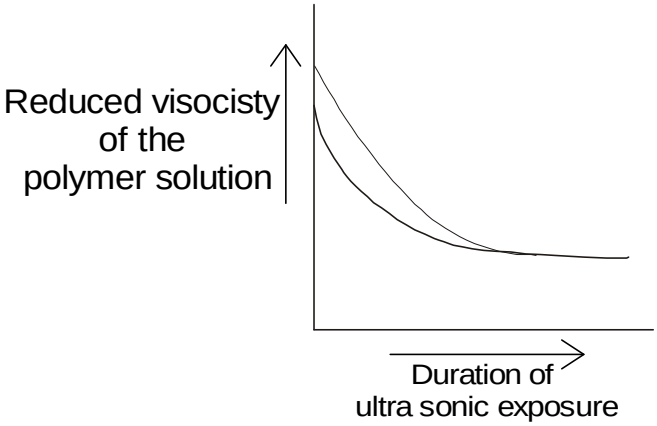
The larger the initial mol. wt. the greater the mol. wt. drop due to mechanical degradation.

Degradation is almost absent when rubber is masticated in Nitrogen atmosphere but degradation is very quick in the presence of small quantity of oxygen or air.

2.9.6. Degradation by ultrasonic waves :

Ultrasonic sound waves are sound waves of very high frequency (above 20,000 Hertz) which is beyond the audible range of the human ear.

Def : A dilute solution of high molecular weight polymer when subjected to ultrasonic waves under goes degradation. It is called degradation by ultrasonic waves. It is a special type of mechanical degradation.



1. Both in mechanical and ultrasonic degradations the decrease in molecular weight of the polymer does not go below a certain value.

2. In both the degradations bigger molecules are effected more than the smaller ones.

The above diagram shows the pattern of ultrasonic degradation with time in the case of two polymers with different initial molecular weights.

2.9.7 Photo degradation :

Def : Photo degradation is a molecular degradation brought about by ultraviolet light.

Ex : Polymethylmethacrylate, Poly α - methyl styrene. Yellowing of white synthetic garments after long use.

It was believed that free radicals are initially formed during photo degradation.

Polyethlene molecule due to structural defects or impurities contain C = C or C=O linkage and undergo photo degradation.

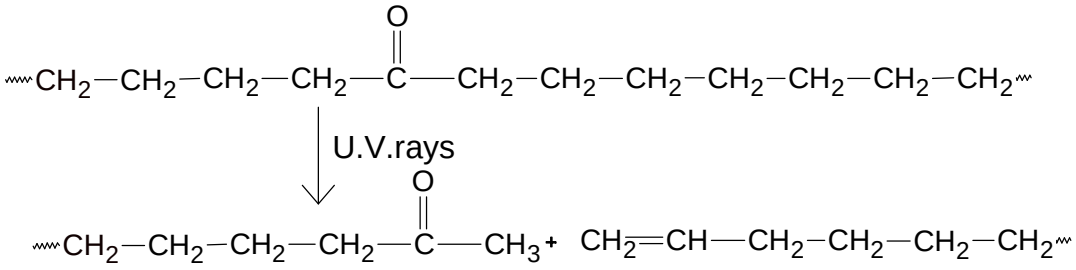


Photo Stabilisers :

Photo stabilisers are compounds which protect polymers from photo degradation to a considerable extent.

Ex : Phenyl salicylate known as salol.

2,4 - dihydroxy benzophenone known as Virnul 400.

2- hydroxy - 4- methoxy benzophenone known as Virnul M40.

The function of a photo stabiliser is to absorb U.V. radiation and dissipate the energy. Thus absorbed to the environment in harmless form.

If we represent the stabiliser by A and the hydrogen bonded structure by B, the over all reaction may be represented as

$$A \xrightarrow{h\nu} B$$

$$B \rightarrow A + \text{heat}$$

Photo stabilisers are normally used to protect polymers of bright colours. They should be of ' non - staining ' , they do not introduce any unwanted colour or discolouration of the polymer.

2.9.8 Degradation by high energy radiation :

Def : Polymers when subjected to high energy radiation undergoes degradation. It is called degradation by high energy radiation.

X - rays, gamma rays, alpha rays and beta rays are well known high energy radiations. Their energy level is much higher than that of UV rays.

Degradation by high energy radiation is more massive than that of U.V. radiations. The high energy radiations smash a polymer like a fast moving cricket ball can do to a sheet of glass. All sorts of things to happen like breaking of bonds leading to scission of its chain or cross - linking.

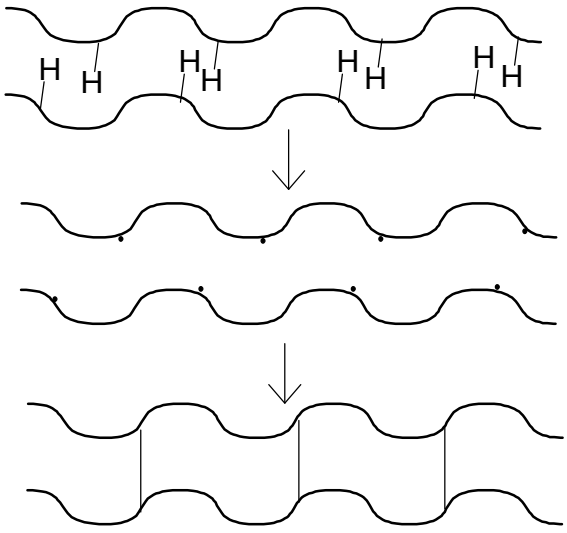
If the polymer is scissioned, there is reduction in molecular weight of the polymer. If cross-linking takes place between polymer molecules, there is increase in molecular weight.

Ex :

1) Polymers that degrade are polyisobutylene, cellulose, polymethacrylate,Poly α - methyl styrene.

2. Polymers get cross - linked are polyethylene, polypropylene, polyamides, polyisoprene, polybutadiene.

Poly ethylene and polystyrene give out hydrogen when subjected to high energy radiation. Removal of hydrogen leads to cross - linking of the polymer chain.



$+ 3H_2$

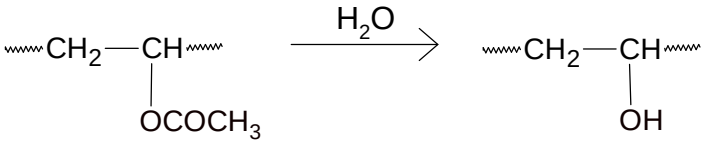
Poly isobutylene gives out methane and hydrogen when subjected to high energy radiation.

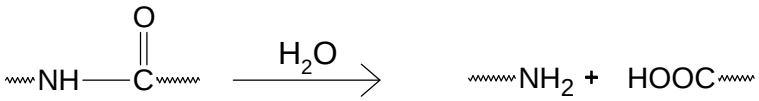
2.9.9 Hydrolytic degradation :

Def : Polymers containing ester groups in their back bone chain undergo degradation by hydrolysis. It is called hydrolytic degradation. Polymer chains containing amide and acetate groups also undergo hydrolytic degradation.

Ex :

1. Polyvinyl acetate undergo hydrolytic degradation with an alkali.



2. 

Polyanide

2.9.10 Oxidative degradation :

Def : Oxidative degradation is a molecualar degradation brough about by oxygen. Oxidative degradation usually leads to hardening, decolourisation as well as surface changes. Oxidative degradation of a polymer mainly depends on its structure.

1. Oxidative degradation of unsaturated polymers : Polyisoprene or polybutadiene containing double bonds are easily attacked by oxygen.

   i) In the first stage of oxidative degradation free radical site is formed on the back bone of the polymer chain by the attack of molecular oxygen.

   $$P \rightarrow P^{\circ}$$ where P is Polymerchain

   ii) Because oxygen has biradical nature peroxide radical is formed.

   $$P^{\circ} + O_2 \rightarrow POO^{\circ}$$

   iii) The peroxy radical now attacks the neighbouring segment.

   $$POO^{\circ} + P \rightarrow POOH + P^{\circ}$$

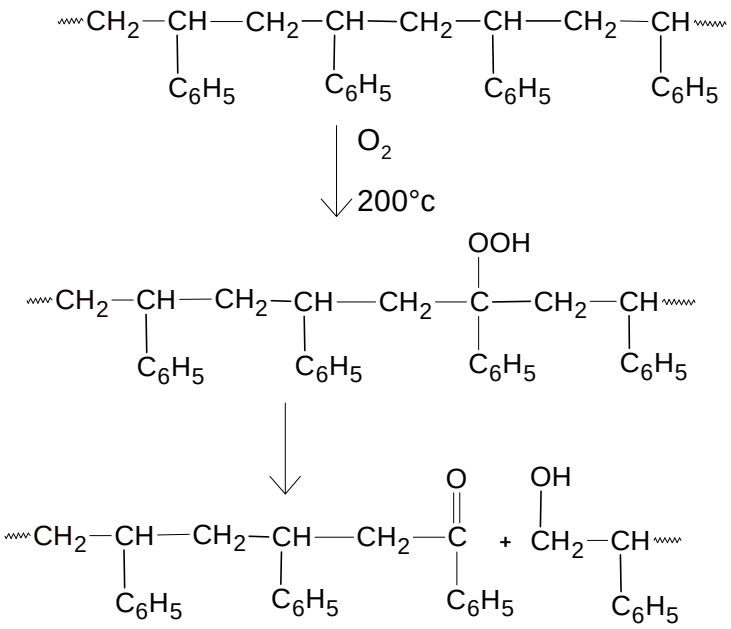
   iv) It also attacks the neighbouring double bond.

v) Termination occurs due to recombination.

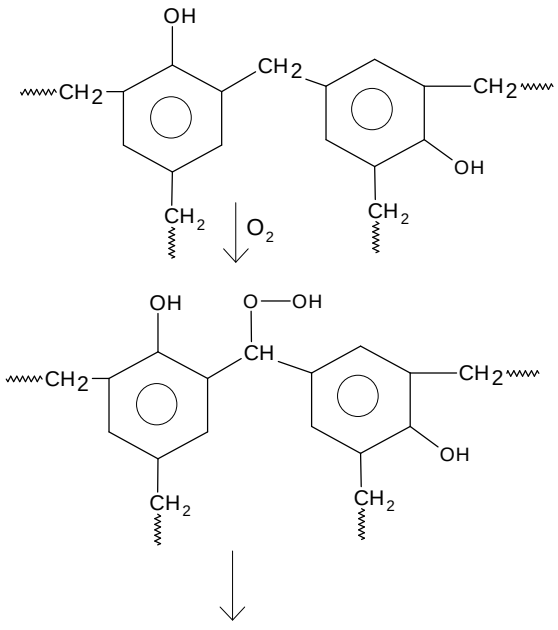
$$2\ POO^{\circ} \rightarrow POOP + O_2$$

$$2\ P^{\circ} \rightarrow P - P$$

2. Oxidative degradation of saturated molecules : Saturated molecules such as polystyrene normally resist oxidation but oxidises in the presence of sunlight or at elevated temperature of 200°c.

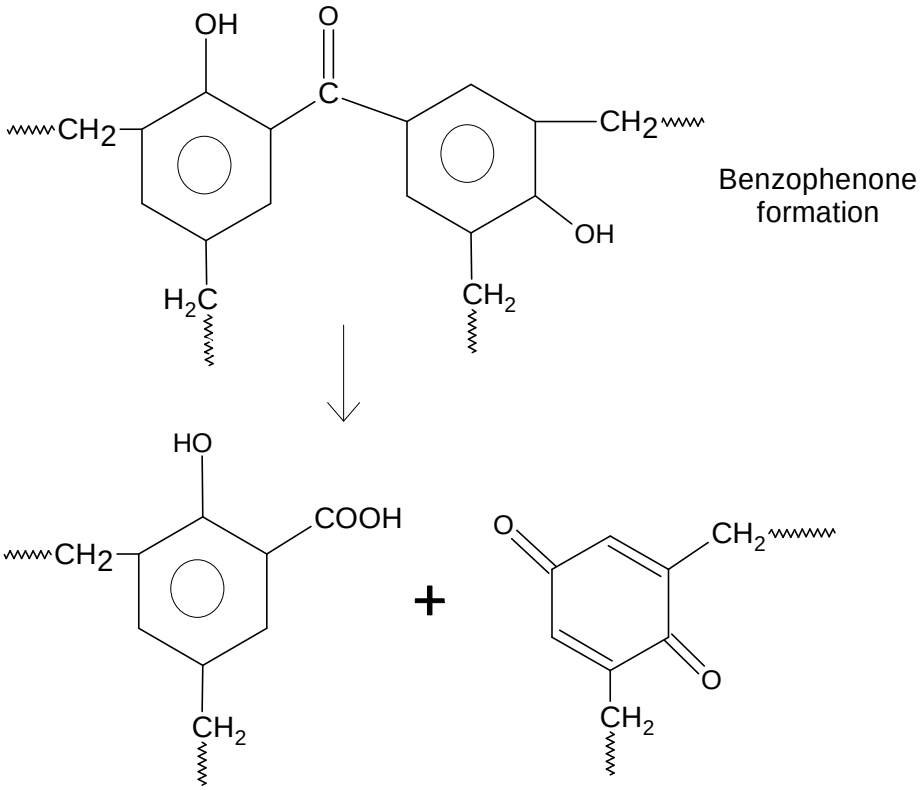


3. Oxidative degradation of resins : In the oxidative degradation of common resin phenol formaldehyde attack by oxygen commences at 200°c. Methylenic linkage are susceptible to oxidation.



Resin structure

Hydroperoxide formation



Benzophenone formation

4. Anti oxidants : Antioxidants are compounds which protect polymers from oxidative degradation. Even in small amounts antioxidants are significantly effective.

Ex : di - t- butyl P - cresol (TBC).

Phenyl β - napthylamine (PBNA)

Various reactions by which antioxidants arrest a reactive polymer are as follows -

$P^\circ + XH \rightarrow PH + X^\circ$

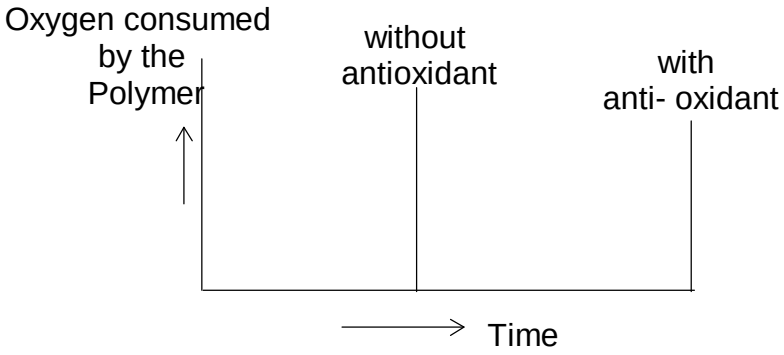
$PO^\circ + XH \rightarrow POH + X^\circ$

$POO^\circ + XH \rightarrow POOH + X^\circ$

$HO^\circ + XH \rightarrow HOH + P^\circ$

$X^\circ + X^\circ \rightarrow X_2$

PBNA is a staining antioxidant. TBC is a non - staining antioxidant.



Effect of antioxidant on oxidative degradation of a polymer.

2.9.11 Model Questions :

1. Define polymer degradation ? Give different types of polymer degradations.
2. Explain a) chain end degradation b) Random degradation.
3. Explain oxidative degradation with example
4. Write about photo degradation.
5. What are antioxidants ? How they protect polymers from degradation.
6. Write about degradation by ultrasonic waves.
7. Explain Mechanical and thermal degradations.
8. Explain degradation by high energy radiation

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Lesson – 10

PLASTICS, ELASTOMERS AND FIBERS

2.10.1: Electromeric, fibreforming and plastic materials - Introduction, Nylon - 66, Vulcanisation, Teflon, Bakelite.

2.10.2 Plastics, Elastomers and Fibres :

Depending on the ultimate form and use polymers are classified as a) plastics b) elastomers and c) fibres.

a) Plastics :

Polymers which can be shaped into hard and tough utility articles by heat and pressure are called plastics.

Ex : Polystyrene, Poly ethylene and PVC .

The word ' Plastic ' is originated from Greek. Plastic means a material which can be moulded into any shape of one's choice.

The American society of testing and materials (ASTM) defined plastic as any one of the large and varied group of materials wholly or primarly organic in composition, which may be formed into useful shapes by the application, singly or together, of heat and pressure.

Plastic Materials :

The properties of plastic materials are in between those of elastomeric and fibre forming materials. They are two types.

1. fully amorphous.

2. Partially crystalline.

Fully amorphous plastic materials :

For Fully amorphous plastic materials -

1. The glass transition temperature Tg is above the use temperature.

2. The melting temperature Tm is above use temperature.

Ex : Polystyrene with a Tg of 100°c is a good amorphous plastic.

Characters :

1. They are brittle.

2. They are in the glassy state at the ' use ' temperature.

The brittleness of a fully amorphous polymer can be improved by physically blending some elastomeric material with it.

Ex : Styrene monomer containing certain percentage of butadiene rubber on polymerisation gives high impact polystyrene.

Partially crystalline plastic materials :

For partially crystalline plastic materials -

The glass transition temperature (Tg) is below the use temperature and melting temperature (Tm) is above the ' use ' temperature.

Ex : Polyethylene with a Tg of - 125°c and a Tm of 146°c is a good partically crystalline plastic.

Characters :

1. They are tough plastics.
2. The crystalline component gives rigidity while the amorphous component gives resilience.

Plasticisation :

Plasticisation is a plastic technology used to improve softness and flexibility. The Tg of a polymer can be lowered by plasticisation.

Cross - Linking :

Cross - linking increases the upper range of the ' use ' temperature.

Ex : Phenol formaldehyde, Urea - formaldehyde and epoxy systems involve cross linking.

b) Elastomers : (Rubbers)

Polymers which have elastic properties are called elastomers. They are popularly known as rubbers.

Ex : Rubber bands, Balloons, Shoe soles, Tyres, Tubes, Gloves.

Elastomeric Materials :

Rubber band is a typical elastomeric material. When pulled it elongates many times to its length. When released, it snaps back to its original length. This is the characteristic behaviour of an elastomer.

Characters :

1. The rubbery state represent a combination of softness, strechability, resilience and toughness.
2. These materials exhibit local mobility and overall rigidity. They are amorphous in nature and exist in rubbery state.

Rubber state :

For a material to be in rubbery state

1. Glass transition temperature (Tg) should be below the ' use ' temperature.
2. The flow temperature (Tf) should be above the ' use ' temperature.

Plasticisation :

The Tg of a polymer can be lowered by internal or external plasticisation.

a) Internal plasticisation :

Copolymerisation of a polymer with small quantity of a suitable monomer is called internal plasticisation.

b) External plasticisation :

In external plasticisation. The polymer is compounded with a mutually compatible high boiling liquid known as plasticiser.

Cross - Linking :

Cross - linking is used to increase flow temperature Tf of a polymer.

Ex : All rubber technology is essentially a combination of plasticisation and cross - linking.

c) Fibers :

Polymers drawn into filments whose length is at least 100 times its diameter are called Fibres.

They are two types -

1. Natural fibres.
2. Synthetic fibres.

Ex : 1. Cotton and wool are natural fibres.

2. Nylon and terylene are synthetic fibres.

Classification of fibres :

Fibres are classified into three types -

1. Comfort fibres.
2. Safety fibres.
3. Industrial fibres.

1. Comfort fibres :

Comfort fibres are those used for making garments and undergarments.

Ex : Cotton, wool, silk , nylon.

2. Safety fibres :

Safety fibres are those used for making carpets, curtains and seat covers.

Ex : Aromatic polyamides, Polyimides, Polybenzimidazoles, Polyoxydiazoles.

3. Industrial fibres :

Industrial fibres are those used as reinforcing materials in composite structures

Ex : Aromatic polyamides, Polyesters, carbon fibres, silica fibres.

Fibre forming materials :

Nylon - 66 is a typical fibre forming material. Unlike rubber band, nylon filment does not stretch and does not snapback.

For fibre forming materials -

1. Glass tansition temperature (Tg) is above the ' use ' temperature.

2. The melting temperature (Tm) is also above the 'use' temperature.

Characters :

1. They have high rigidity or stiffness.

2. They have high tensile strength.

3. They have high degree of polymerisation.

In other words, the material should have very high crystallinity. 100% crystallinity is desirable but it is diffcult to achieve.

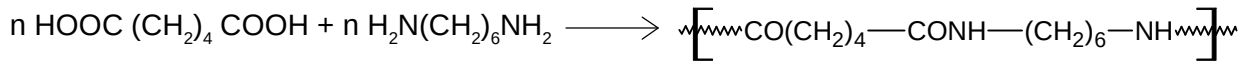
Plasticisation or Cross - linking can not be applied because they reduce crystallinity.

2.10.3 Nylon 66 :

Nylon 66 is a polyamide. It is a typical fibre forming material.

Preparation :

It is formed by the poly condensation of adipic acid and hexamethylene diamine.



adipicacid Nylon - 66

Characters :

1. Unlike rubber band Nylon filment does not stretch and does not snapback.
2. It offers considerable resistance before it can be deformed.
3. It is almost impossible to break it just by pulling.

2.10.4 Vulcanisation :

Vulcanisation is widely used in rubber technology to effect cross - linking. It was discovered by Goodyear in 1839.

Definition :

Vulcanisation is defined as any treatment of rubber that decreases its flow, increases tensile strength with out changing its extensibility.

Vulcanisation of rubber :

Crude rubber is heated with sulphur and white lead at 110 - 140°c temperature. Sulphur is attached chemically at the double bonds in rubber molecules. This causes profound change in the properties of rubber. it is called Vulcunisation or rubber.

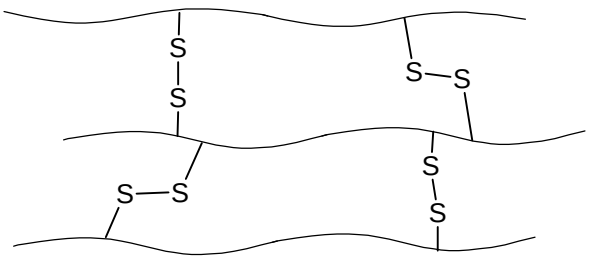
Effects of Vulcanisation :

The amount of sulphur varies from 1 to 5 parts per 100 parts of soft rubber and 40 - 45 parts per 100 parts of hard rubber.

1. Vulcanisation increases cross - linkage and decreases unsaturation.
2. The rubber becomes sensitive to heat and swells.
3. It becomes insoluble in benzene and other solvents.
4. It gets good abrasion, wear and tear resistance.
5. It becomes more elastic and less plastic.
6. It is more durable when exposed to weather.

Mechanism :

Vulcanisation convents a thermoplastic polymer into a three dimensional network resembling thermosetting polymer. The mechanism of vulcanisation is difficult to visualise. The tentative structure is shown below.



2.10.5 Teflon :

Polytetra fluoro ethylene is commercially known as Teflon.

It has the following structure

$$(- CF_2 - CF_2 -)_n$$

The monomer is tetrafluoro ethylene ($CF_2 = CF_2$).

Preparation :

It is prepared by the polymerisation of tetrafluoro ethylene. The polymerisation is carried out by emulsion method using peroxide as initiator. Redox initiators such as hydrogen peroxide and $FeSO_4$ can also be used.

$$n\ CF2 = CF2 \rightarrow (- CF_2 - CF_2 -)_n$$

Properties :

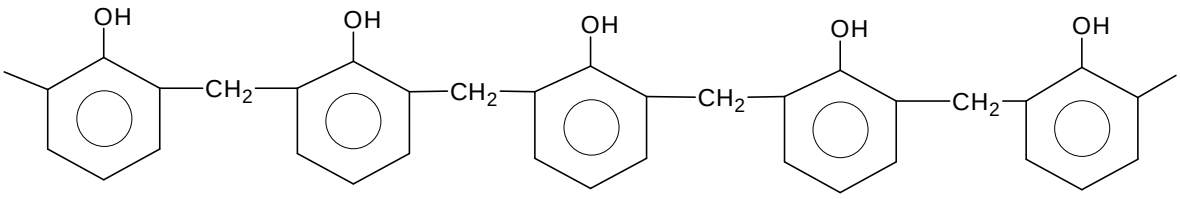
1. It is a linear polymer.
2. It has high crystallinity.
3. It is not effected by acids, alkalies and organic solvents.

Uses :

1. It is used in non - lubricated bearings.
2. It's fibre is used in belts.
3. It is used for the manufacture of pipes and pump valves.

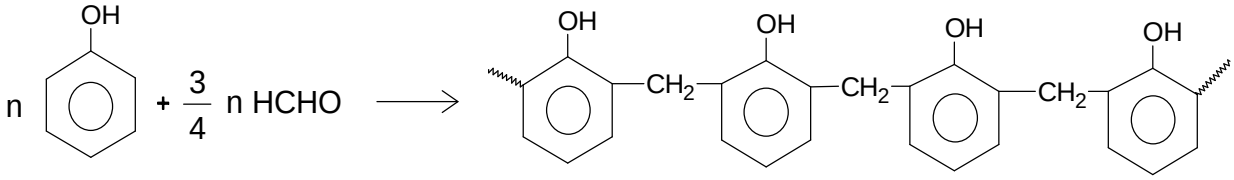
2.10.6 Phenol - formaldehyde resins (Bakelite) :

Resins formed by the polycondensation of phenol and formaldehyde are called Phenol - formaldehyde resins. The linear molecule formed is known as bakelite. It has the following structure.



Preparation of Bakelite :

It is prepared by the action of pheno with 75% of stoichiometric quantity of formaldehyde in the presence of an acid catalyst. Due to insufficient quantity of formaldehyde, only linear molecules are formed known as Bakelite.



Bakelite

Properties :

1. It can be stored for any length of time without hardening and further cross- linking.
2. It can be effected by heating with excess of formaldehyde when ever necessary.

Uses :

1. Compounded with asbestoes Bakelite resins are used for moulding telephone and electrical instruments.
2. Mixed with sand, they are used as core binders in foundries.

2.10.7 Model Questions :

1. Write notes on a) Elastomers b) Fibres c) plastics.
2. What is plasticization ? What is its utility ?
3. Write about volcunisation of rubber.
4. Write notes on nylon – 66.
5. What is Bakelite ? How is it prepared?

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B.Sc. CHEMISTRY
PAPER - IV PHYSICAL CHEMISTRY

SYLLABUS

1. Determine the specific rate constant of Acid hydrolysis of Methyl Ethyl Acetate.

2. Determine the specific rate constant of catalytic decomposition of Hydrogen peroxide.

3. Determine partition coefficient of Iodine between water and carbon tetrachloride.

4. Determine partition coefficient of Benzoic acid between Benzene and water.

5. Determine the strength of HCl conductometrically using standard sodium hydroxide.

6. Determine the strength of Fe+2 in Mohr's salt by potentiometric titration using potassium dichromate solution

7. Determine the concentration of the given $KMnO_4$ solution and verification of the BEER's Law.

8. Determine the concentration of the given $K_2Cr_2O_7$ solution and verification of the BEER's Law.

ACID HYDROLYSIS OF METHYLACETATE

Expt - 1

Aim :

To determine the rate constant of the esterhydrolysis catalysed by an acid.

Apparatus :

Reagent bottle, water trough, Burette, Graduated Pipette, Conical flask, stop watch, Measuring jar.

Principle:

The hydrolysis of methyl acetate is given by the equation.

$$CH_3COOCH_3 + H_2O \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOH + CH_3OH$$

It is a first order reaction as the change in concentration of water during reaction is neglisible.

Thus the rate constant equation for the reaction is

$$K = \frac{2.303}{t}.\log\frac{a}{(a-x)}$$

Where a and (a-x) are the intial and final concentration of the ester respectively. The course of the reaction is followed by estimating the acetic acid formed at different intervals of time upto the time of completion of reaction volumetrically with 0.1M sodium hydroxide solution. The reaction takes place in acidmedium. At zerotime, the titre value (Vo) indicates the mineral acid. At any time "t", the titre value (Vt) incidates the mineral acid + acetic acid produced. At the completion of reaction, the titre value (V_∞) indicates the mineral acid + acetic acid equivalent to ester taken initially.

Therfore,

$$a \alpha V_\infty - V_0,\ x \alpha V_t - V_0 \ \&\ (a-x)\alpha\ V_\infty - V_t$$

The rate constant becomes

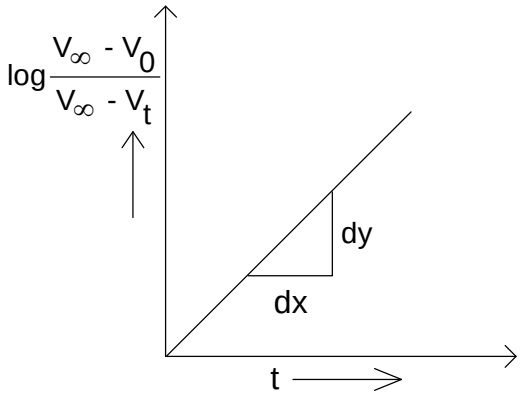
$$K = \frac{2.303}{t}.\log\frac{V_\infty - V_0}{V_\infty - V_t}$$

Procedure :

100ml of 0.5 ml HCl is transferred into the bottle with the help of a measuring jar. 5 ml of methyl acetate is added to the bottle with 5ml pipette and a stopwatch is started when the pipette is half emptied. The contents are shaken and kept in the water trough. At the interval of 10 mts, 5ml of reaction mixture is transferred into a conical flask in which some icepieces and water are already present. The reaction then ceases. The mixture is titrated with 0.1M NaOH solution using phenolpthalein indicator. The titre value V_t is noted. Similarly at the intervals of 20,30,40 and 50 minutes, the titre values are determined. Finally the reaction mixture is placed in boiling water for about 30 mts, cooled and 5ml of the reaction mixture is titrated directly (without ice) using indicator with the same 0.1 M NaOH solution. The titre value V_∞ is noted.

5 ml of 0.5 M HCl is titrated with the same 0.1 M NaOH solution and the titre value 'V' is noted. The titre value at zerotime V_0 is calculated from V. Rate constant values are calculated.

A graph is drawn between t and $\log \frac{V_\infty - V_0}{V_\infty - V_t}$ and from the slope the rate constant is determined.



Result :

Rate constant of ester hydrolysis_____

Calculations :

Volume of NaOH at zero time $V_0 = \frac{V \times 100}{105}$

S.No.	Time in minutes t	Volume of NaOH Vt	$K = \frac{2.303}{t} . \log \frac{V_\infty - V_0}{V_\infty - V_t}$
1.	10		
2.	20		
3.	30		
4.	40		
5.	50		
6	∞	V_∞ =	

If the value of k thus calculated is constant (or) nearly constant. It indicates that the reaction is of the first order.

CATALYTIC DECOMPOSTION OF HYDROGEN PEROXIDE

Expt - 2

Aim :

To study the kinetics of decomposition of H_2O_2 by using catalyst (MnO_2 powder)

Theory :

Experiment shows that this is a unimolecular reaction. The total reaction is taking place in two steps.

$$H_2O_2 \xrightarrow{\text{Slow}} H_2O + (O)$$

$$(O + O) \rightarrow O_2\uparrow$$

The overall reaction is

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Apparatus :

500ml stoppered bottle, water bath, measuring jar, 5ml pipette, stopwatch, ice, thermostat.

Chemicals :

3% H_2O_2, 0.44 N $KMnO_4$ (14gms in 1lit of H_2O), dil H_2SO_4 4N.

Catalyst for the reaction :

Fe Oxide, MnO_2, Mg (or) carbon, finely divided metals such as pt, Au, Ag (or) enzyme blood catalase (or) iodide ion.

Procedure :

10ml of 30% H_2O_2 is dissolved in 90ml of water to get 3% solution of H_2O_2.

It is taken in a 500ml stoppered bottle and placed in a thermostat (or water bath)

Into a conical flask (A) about 20ml of ice water (or) small pieces of ice 20 gms approximately is taken. To this ice water, 20 ml of dil. H_2SO_4 is added and kept ready for the transfer of 3% H_2O_2 solution.

Now about 2gms of Manganese dioxide powder is transferred into above 500ml stoppered bottle and stopwatch is started immediately. This reaction mixture is given to swirling motion from time to time . 5 ml of this reaction mixture is transferred into conical flask (A). It is titrated against $KMnO_4$ (0.44N) until permanent pale pink colur is obtained. This volume of $KMnO_4$ is noted (V_0).

5 ml of reaction mixture is transferred into the conical flask containing 20ml of icewater and 20ml of dil. H_2SO_4 in the 15th, 30th, 45th, 60th, 75th, 90th minute and titrated against $KMnO_4$ as above. The volumes of $KMNO_4$, are recorded (Vt) at the intervals of time t.

Time (mts)	**0**	**15**	**30**	**45**	**60**	**75**	**90**
Vol. of $KMnO_4$ (ml)							

S.No.	**Time in minutes**	Volume of $KMnO_4$ **(ml)**	**K =** $\frac{2.303}{t} . \log \frac{V_0}{V_t}$

A constant (or) nearly constant values of K shows that the decomposition of H_2O_2 catalysed by MnO_2 is only first order reaction.

PARTITION COEFFICIENT OF IODINE

Expt - 3

Aim :

To determine the partition coefficient of Iodine between carbontetrachloride and water.

Apparatus :

Two 500 ml glass stoppered bottles, 5 ml and 10ml pipettes, burette, conical flask, separating funnel.

Chemicals :

I_2 , KI, CCl_4, $Na_2S_2O_3$ and distilled water.

Theory :

The distribution of a solute between two immiscible solvents is called as partition (or) distribution. The ratio of the concentration of solute in the organic phase and aqueous phase is a constant known as partition coefficient.

$$K = \frac{C_{organic}}{C_{aqueous}}$$

Where K is constant

$C_{organic}$ is concentration of solute in organic layer

$C_{aqueous}$ is concentration of solute in aqueous layer

Procedure :

25ml of CCl_4 and 75ml of water are taken in two 500ml glass stoppered bottles

In the first bottle 0.5 gm of Iodine and in the second bottle 1 gm of Iodine is added. The bottles are stoppered tightly and shaken well for about an hour. On standing the contents of the bottles are separated into two layers (lower CCl_4, upper water). The two layers are separated by separating funnel into two beakers.

5 ml of organic layer of first bottle is transferred into conical flask with the help of the pipette. To this 10 ml of 10% KI solution and 100ml of distilled water are added and shaken well. The solution is titrated against 0.1M hypo until it turns to pale yellow. Then 5 ml of starch is added where the solution turns to deep blue. Addition of hypo is continued until the solution turns colourless. The titration is repeated and the values are tabulated. Similarly titrations are conducted with the organic layer in the second bottle.

10 ml of aqueous layer of the first bottle is transferred into the conical flask. With the help of the pipette. To this 10 ml of 10% KI solution and 100ml of distilled water are added and shaken well. The solution is titrated against 0.01 M hypo until it turns to pale yellow. Then 5ml of starch is added. The formed blue coloured solution is titrated against hypo until it turns colourless. The titration is repeated and the values are tabulated. Similarly two titrations are conducted with the second bottle aqueous layer.

Result :

The partition coefficient of iodine between CCl_4 and water is _____.

Calculations :

Bottle - I

S.No.	Volume of organic layer (ml)	Burrette readings		Volume of 0.1M hypo rundown (ml) V_1
		Initial	final	
1.	5.0			
2.	5.0			

S.No.	Volume of aqueous layer (ml)	Burrette readings		Volume of 0.01M hypo rundown (ml) V_2
		Initial	final	
1.	10.0			
2.	10.0			

Partition Coefficient $K_1 = \frac{V_1}{V_2} \times 20$

= _____

Bottle - I

S.No.	Volume of organic layer (ml)	Burrette readings		Volume of 0.1M hypo rundown V_1 (ml)
		Initial	final	
1.	5.0			
2.	5.0			

S.No.	Volume of aqueous layer (ml)	Burrette readings		Volume of 0.01M hypo rundown V_2 (ml)
		Initial	final	
1.	10.0			
2.	10.0			

Partition Coefficient $K_2 = \frac{V_1}{V_2} \times 20$

= _____

$\therefore$ Partition Coefficient (K) of $I_2 = \frac{K_1 + K_2}{2}$

= _____

PARTITION COEFFICIENT OF BENZOIC ACID

Expt - 4

Aim :

To determine the distribution (or) partition coefficient of Benzoic acid in between benzene and water at room temperature and to prove the benzoic acid exists as dimer in benzene.

Apparatus :

Two 500 ml glass stoppered bottles, 5 ml and 10ml pipettes, 50 ml burette, conical flask, separating funnel etc.,.

Chemicals :

Benzoic acid, Benzene, NaOH, Hypo, Phenolphthalein.

Theory :

According to nernst Distribution law " When two immiscible liquid solvents are in contact with each other and a substance soluble in both the liquids is mixed, then the substance distributes itself between the two layers so that its concentrations in the two layers bear a constant ratio at constant temperature ". This is independent of the actual quantities of the liquids and substance. But this law is applicable when the substance is present in the same molecular form in both the liquids. Benzoic acid distributes in between water and Benzene. But it is present as dimer in benzene. Instead of concentration ratio, the value $C_{aqueous} / \sqrt[n]{C_{organic}}$ remains constant as partition coefficient. Here n=2. Hence, $C_{aq} / \sqrt{C_{org}}$ is shown as constant, then the dimer state of benzoic acid is proved.

Partition coefficient $K = \frac{C_{aqueous}}{\sqrt{C_{organic}}}$

Procedure :

15ml Benzene, 75 ml water and 10 ml benzoic acid solutions are taken in 1st 500ml glass bottle. 10ml benzene, 75ml water and 15 ml benzoic acid solutions are taken in 2nd 50 ml glass bottle. The bottles are stoppered tightly and shaken well for about 40 minutes. On standing the contents of the bottles are separated into two layers. (Lower aqueous layer and upper benzene layer). The two layers are separated by using separating funnel into beakers.

5 ml of organic layer of 1st bottle is transferred into conical flask with the help of pipette. Nearly 20 ml of distilled water and 1 drop of phenolphthalein are added. The solution is titrated against 0.1 M sodium hydroxide solution to the end point where the solution changes from colourless to pink. Titration is repeated and the values are tabulated. Similarly titrations are conducted with the organic layer in the 2nd bottle.

10ml of the aqueous layer of the 1st bottle is transferred into the conical flask with the help of the pipette. Nearly 20 ml of distilled water and 1 drop of phenolphthalein are added. The solution is titrated against 0.01 M sodium hydroxide solution to the end point where the solution changes from colourless to pink. Titration is repeated and the values are tabulated. Similarly titrations are conducted with the aqueous layer of the 2nd bottle.

Result :

Partition coefficient of benzoic acid between water and benzene = _____.

As $\frac{Caq}{\sqrt{Corg}}$ is found constant, the dimer state of benzoic acid in benzene liquid is confirmed.

Calculations :

Bottle. No.	**Volume of organic layer (ml)**	**Burrette readings**		**Volume of 0.1M NaOH V_1 (ml)**	**Corg = $\frac{V_1 \times 0.1}{5}$**
		Initial	**final**		
1.	5.0				
	5.0				
2.	5.0				
	5.0				

Partition coefficient $K_1 = \frac{Caqueous}{\sqrt{Corganic}}$

= _____

Bottle. No.	Volume of aqueous layer (ml)	Burrette readings		Volume of 0.1M NaOH V_2 (ml)	Caqueous = $\frac{V_2 \times 0.1}{10}$
		Initial	final		
1.	10.0 ml				
	10.0 ml				
2.	10.0 ml				
	10.0 ml				

Partition coefficient $K_2 = \frac{\text{Caqueous}}{\sqrt{\text{Corganic}}}$

= _____

$\therefore$ Partition Coefficient K = $\frac{K_1 + K_2}{2}$

= _____

The partition coefficient of benzoic acid between water and benzene is _____

CONDUCTOMETRY

Expt - 5

Aim :

To estimate the amount of HCl by titrating it conductometrically with standard NaOH solution.

Apparatus :

Burette, Pipette, Conductometer, double distilled water, 100 ml beaker, glass rod, conductivity cell etc.,.

Principle :

The concentrations of the electrolyte solutions can be determined by measuring their specific conductivities. The conducatnce of 1cc electrolyte solution is its specific conductance.

The endpoint in an acid (HCl), base (NaOH) titration can be determined by measuring the conductivities at the successive additions of titrant to the titrate and plotting a graph. The HCl solution exhibits fairly large conductivity due to the high mobility of H^+ions. In the course of titration with NaOH resulting a decrease in the conductivity of the solution. This reaches minium at the end point. After the endpoint further addition of excess NaOH solution, causes an increase of conductivity due to high mobility of unreacted OH^- ions. A graph is plotted for conductance values against volume of NaOH added. The faraway points on either side of the endpoint form straight lines to intersect showing the minimum conductivity. The volume of NaOH solution corresponding to the minimum of graph is titre value, from which the acid is estimated.

Procedue :

a) Preparation of standard oxalic acid (0.05M) :

About 1.5 gms of oxalic acid is taken in a weighing bottle and its exact weight (W1) is determined. The substance is transferred into 250ml volumetric flask with the help of a funnel. The substance is dissolved in distilled water made up to the mark and shaken well. The weight of empty weighing bottle (W_2) is determined. Molarity is calculated.

$$\text{Molarity of solution} = \frac{W_1 - W_2}{126} \times \frac{1000}{250}$$

$$= \_\_\_\_\_ \text{ M}$$

b) Standardisation of NaOH solution :

Burette is filled with NaOH solution. 20.0 ml of oxalic acid solution is pipetted out into a conical flask. 1 (or) 2 drops of phenolphthalein indicator is added. The solution is titrated with NaOH solution from burette to the end point. At the endpoint the colourless solution gets sharp pale pink. Titre value is noted. The titrations are repeated to get two equal successive titre values. Molarity of NaOH is calculated.

c) Conductometric Titration :

The given HCl solution in 100ml volumetric flask is made up to the mark with distilled water and shaken well. 20.0ml of this solution is pipetted out into 100ml beaker and 30ml distilled water is added. The solution is stirred with glass rod and conductivity cell is placed in it without taking out glass rod. Initial reading of the conductivity is noted. Burette is filled with NaOH solution. NaOH solution is added to the beaker in 2ml portions with constant stirring upto 30ml. At each addition the resultant conductivity is noted in a table and volume corrections are made to it due to dilution.

A graph is plotted by taking conductance on y- axis and volume of NaOH on x -axis. The straight lines are drawn and from the intersection point, the titre volume is noted. Calculations are made.

Result :

Amount of HCl present in 1 litre of solution = _____.

Procedue :

a) Preparation of standard oxalic acid solution :

Weight of weighing bottle + oxalic acid (W_1) = _____ gms.

Weight of empty weighing bottle (W_2) = _____ gms.

Weight of oxalic acid taken = $W_1 - W_2$ = _____ gms.

Molarity of oxalic acid = $\frac{W_1 - W_2}{126} \times \frac{1000}{250}$ = _____ M_1

b) Standardisation of NaOH solution :

S.No.	Volume of Oxalic acid V_1 (ml)	Burrette readings		Volume of NaOH rundown (ml) V_2
		Initial (ml)	final (ml)	
1.	20.0 ml			
2.	20.0 ml			
3.	20.0 ml			
4.	20.0 ml			

$$H_2C_2O_4 + 2NaOH \rightarrow Na_2C_2O_4 + 2H_2O$$

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

Where M_1 = Molarity of oxalic acid =

V_1 = volume of oxalic acid = 20.0ml

n_1 = no.of moles of oxalic acid = 1

M_2 = Molarity of NaOH = ?

V_2 = Volume of NaOH = _____ ml

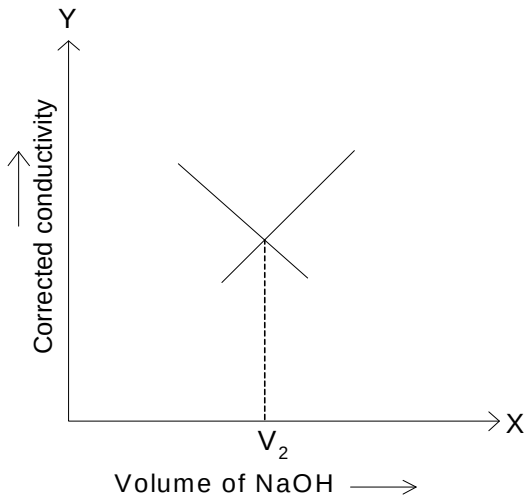
n_2 = no. of moles of NaOH = 2

$$\therefore M_2 = \frac{M_1V_1}{n_1} \times \frac{n_2}{v_2}$$

= _____M.

S.No.	Volume of HCl (V)	Volume of NaOH (V^1)	Conductivity (C)	Corrected conductivity $= C\left(\frac{V+30+V^I}{V}\right)$

Graph :



$$NaOH + HCl \rightarrow NaCl + H_2O$$

Volume of acid taken = V_1 = V = 20.0ml

Molarity of acid = M1 = ?

Moles of acid = n_1 = 1

Volume of NaOH required = V_2 =

Molarity of NaOH = M_2 = _____

Moles of NaOH = n_2 =1

$$\therefore M_1 = \frac{M_2 V_2}{n_2} \times \frac{n_1}{v_1}$$

= _____M.

Amount of HCl present in 1 litre = M1 x 36.5

= _____gms.

POTENTIOMETRY

Expt - 6

Aim :

To estimate the amount of Fe++ present in the given Mohr's salt using standard dichromate solution potentiometrically.

Apparatus :

Potentiometer, Electrodes, Volumetric flask, Burette, Pipette, Magnetic paddle etc.,.

Principle :

The reaction between Fe++ and dichromate is a redox reation.

$$Cr_2O_7^{-2} + 6\ Fe^{+2} + 14H^+ \rightarrow 2Cr^{+3} + 6\ Fe^{+3} + 7H_2O$$

The standard potential of Fe^{+2} / Fe^{+3} is 0.77 at 25°c and that of Cr^{+3} / Cr^{+6} is 1.33. When an indicator electrode is placed in Fe^{+2} solution where the reaction is $Fe^{+2} - e^- \rightarrow Fe^{+3}$, the electrode acquires a potential E as given below.

$$E = E° + \frac{0.0591}{1} \log \frac{\left[Fe^{+3}\right]}{\left[Fe^{+2}\right]}$$

The potential is thus controlled by the concentration ratio. During the titration with dichromate solution the ratio changes and so the potential changes. The potential changes more rapidly in the vicinity of the end point and after wards reaches the potential of Cr^{+3} / Cr^{+6} system. Due to this large gap in the potentials, when a graph is drawn taking potenitals versus volumes of titrant a sudden jump is obtained at the end point from which titre value is noted. The addition of phosphoric acid increases the range of sudden jump by reducing the Fe^{+2} / Fe^{+3} potential

Procedure :

1) Preparation of standard dichromate solution :

About 1.5 gms of dichromate is weighed correctly in a weighing bottle (W_1). The substance is transferred into a 250ml volumetric flask with the help of funnel. The weight of empty weighing bottle (W_2) is determined. The substance in the flask is dissolved by adding distilled water and made upto the mark with distilled water. It is stirred well and calculated the concentration.

$$\text{Concentration of } Cr_2O_7^{-2} = \frac{(W_1 - W_2)}{294.1} \times \frac{1000}{250}$$

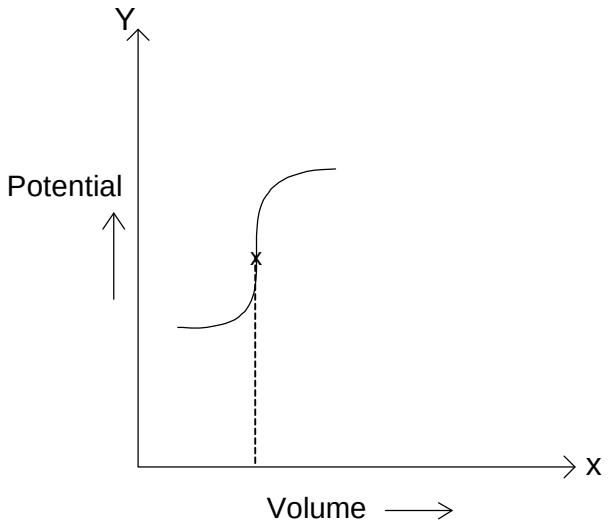
2) Potentiometric titration :

a) Pilot titration : 20.0 ml of Mohr's salt solution is taken into a beaker with a pipette. 6ml of 1:1 sulphuric acid and 5 ml of phosphoric acid are added. About 20ml of distilled water is added. Magnetic paddle, standard electrode and indicator electrodes are placed in the beaker. Operating the magnetic paddle, the intial potential reading is noted. Dichromate solution is filled in the burette and 1 ml increments of dichromate solution are added to the beaker. Every time the stable potential is noted. The range of large potential change is noted.

b) Regular titration : 20.0 ml of Mohr's slat solution is taken into a beaker with a pipette. 6ml of 1:1 sulphuric acid, 5 ml of phosphoric acid and 20ml of distilled water are added. Magnetic paddle, standard electrode and indicator electrodes are placed in the beaker and started stirring the magnetic paddle. 1 ml increments of dichromate solution from burette are added to the solution upto the begining of wide potential change. Then 0.1 ml increments of dichromate are added until the change of potential ceases. Every time potential is noted. Afterwards the titration is continued by adding 1 ml increments of 10ml dichromate solution. The potentials are noted

A graph is plotted by taking volumes of dichromate on x - axis and potential values on the y - axis. A graph shown in fig. is obtained. The volume of dichromate solution corresponding to the mid point of inflexion of the curve is the titre volume. The Fe^{+2} is estimated from the titre volume.

Graph :



Calculations :

Weight of weighing bottle + $K_2Cr_2O_7$ (W_1) = _____ gms.

Weight of empty weighing bottle (W_2) = _____ gms.

Weight of $K_2Cr_2O_7$ taken = $W_1 - W_2 = W$ = _____ gms.

Concentration of dichromate solution = $\frac{W \times 4}{294.1}$ = _____ M

S.No.	Volume of dichromate solution (ml) V_I	Potential value mv	S.No.	Volume of dichromate solution (ml) V_I	Potential value mv

6 moles of Mohr's salt = 1 mole of dichromate.

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

Where M_1 = Molarity of dichromate solution = _____M

V_1 = Volume of dichromate = _____ml
(from graph)

n_1 = no.of moles of dichromate = 1

M_2 = Molarity of Mohr's salt solution = ?

V_2 = Volume of Mohr's salt solution = 20.0 ml

n_2 = no. of moles of Mohr's salt = 6

$\therefore M_2 = \frac{M_1V_1}{n_1} \times \frac{n_2}{v_2}$ = _____M.

Weight of Fe^{+2} present in the given 100ml solution = $\frac{M_2 \times 56}{10}$ = _____gms.

BEER'S LAW

Expt - 7

Aim :

To verify Beer's law and to determine the concentration of $KMnO_4$ in the given 100ml solution.

Apparatus :

250 ml standard volumetric flask, 100ml volumetric flasks - 8, Burette, pipette, conical flask, colorimeter, Cuvets etc.,.

Principle :

Beer's law can be stated mathematically as,

Absorbance (or) optical density (o.d) = $\in$ ct

Where $\in$ = molar extinction coefficient

c = concentration of solution

t = width of the solution.

As $\in$ and t are constants for a given solution and colurimeter.

Absorbance α C

Manganese (VII) i.e, $KMnO_4$ is not a primary standard. Hence, it is standardised by preparing 0.05 M standard oxalic acid solution by volumetric procedure.

Procedue :

1) Preparation 0.01 M $KMnO_4$ solution :

3.50 gms of $KMnO_4$ is weighed and dissolved in 200 ml distilled water, boiled, allowed to cool, filtered using glass wool (or) sintered funnel and diluted to 2 litres.

2) Preparation of standard oxalic acid solution (0.05M) :

About 1.5 gms of oxalic acid is taken in a weighing bottle and its exact weight (W_1) is noted. The substance is transferred into a clean 250 ml volumetric flask with the help of a clean funnel. The weight of empty weighing bottle is determined (W_2). The substance in the funnel is washed into the flask with distilled water. The substance is dissolved and the solution is made upto the mark and homogenised. The concentration of the solution is calculated.

$$\text{Molarity of oxalic acid} = \frac{(W_1 - W_2)}{126} \times \frac{1000}{250}$$

= _____ M

Standardisation of $KMnO_4$ solution :

10.0ml of standard oxalic acid is transferred into a conical flask. To it 20 ml of dil. sulphuric acid is added and the solution is heated to near boiling point. The burette is filled with $KMnO_4$ solution in the burette to a permanent pale pink end point. The readings are tabulated and the concentration of $KMnO_4$ solution is calculated.

S.No.	Volume of Oxalic acid taken (ml)	Burrette readings		Volume of $KMnO_4$ taken (ml)
		Initial (ml)	final (ml)	

$$\frac{V_1M_1}{n_1} = \frac{V_2M_2}{n_2}$$

Where V_1 = Volume of oxalic acid

M_1 = Molarity of oxalic acid

n_1 = no.of moles of oxalic acid = 5

V_2 = Volume of $KMnO_4$ =

M_2 = Molarity of $KMnO_4$

n_2 = no. of moles of $KMnO_4$ = 2

Preparation of solutions for the construction of Beer's law graph :

7 to 8 clean 100ml volumetric flasks are taken and labelled as A,B,C ..... The standardised $KMnO_4$ solution is transferred into them using burette as indicated in the Table - III The solutions are diluted and made upto the mark with distilled water. They are shaken well to homogenise the solutions.

S.No.	Lable	Vol. of $KMnO_4$
1	A	1.0ml
2.	B	2.0ml
3.	C	3.0ml
4.	D	4.0ml
5.	E	5.0ml
6.	F	6.0ml
7.	G	7.0ml

Preparation of unkown for measurement of absorbance :

The unknown volumes of $KMnO_4$ given in the 100ml volumetric flasks are diluted and made upto the mark with distilled water. The solutions are shaken well.

Measurement of absorbance :

The measurement of absorbance with colorimeter consists of two parts (i) selection of wave length (or) fitter of maximum absorbance value (λ max) (ii) Measurment of absorbance values.

The measurement of absorbance involve two steps.

i. The adjustment of absorbance value to zero when the reagent blank is in the light path.

ii. Measurment of absorbance of the sample when it is in the path. For selecting the wavelength (or) filter and adjusting the absorbance to zero with blank provisions are available in the colourimeter.

The cells (or) cuvets are taken. One cuvet is for reagent blank (here distilled water) and the other for sample. The blank and sample are taken in the cell (or) cuvet. using the provision to select the filter / wave length one filter is selected. The cell with blank was introduced into the colorimeter. The absorbance is adjusted to zero. The blank is replaced with the sample. The absorbance value is noted. In the same way the absorbance of sample with all the filters are measured. The results are tabulated.

S.No.	Filter no.	Absorbance
1.	45	
2.	47	
3.	51	
4.	52	
5.	54	
6.	57	
7.	60	
8.	67	

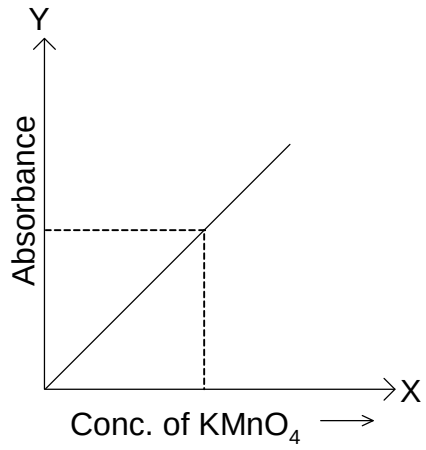
From the table the filter/ wavelength of maximum absorbance was identified.

Using the filter / wave length of maximum absorbance the absorbance values of the solutions prepared for the verification of Beer's law and the unknown are measured and noted down (Table-III). In measuring the absorbance values the procedure described above i.e. adjustment of zero absorbance with the blank and measurement of absorbance of the sample was followed.

Table - III

Sample	Vol. of $KMnO_4$ (ml)	Concentration of $KMnO_4$	Absorbance
A	1.0ml		
B	2.0ml		
C	3.0ml		
D	4.0ml		
E	5.0ml		
F	6.0ml		
Unknown	-		

A graph is plotted by taking the concentration of $KMnO_4$ on the x - axis and the absorbance values on the y - axis the graph is a straight line. Using the absorbance values of the unknown, the concentration of $KMnO_4$ is determined from the graph.



Note :

1) Whenever the solution in the cuvet (or) cell is changed the cuvet is rinsed twice with the solution which is to be taken into it

2) The solution on the outside walls of the cuvet is removed with a soft filter paper (or) tissue paper by gentle pressing.

BEER'S LAW

Expt - 8

Aim :

To verify Beer's law and to determin the concentration of dichromate $K_2Cr_2O_7$ in the given 100ml solution.

Apparatus :

100ml volumetric flasks - 8, Burette, pipette, conical flask, colorimeter, Cuvets etc.,.

Principle :

Beer's law can be stated as,

Absorbance $= \in ct$

Where $\in$ = molar extinction coefficient

c = concentration of solution

t = width of the solution.

As $\in$ and t are constants for a given solution and colorimeter.

Absorbance α C

Procedure :

Step - 1 : Preparation of dichromate solution :

About 1.5 gms of potassium dichromate is taken in a weighing bottle and its exact weight (W_1) is determined. The substance is transferred into 100 ml volumetric flask with the help of a funnel. The substance is dissolved in distilled water and made up to the mark. The weight of empty weighing bottle (W_2) is determined. Form the weights molarity of solution is calculated (stock solution).

The stock solution is taken in six 100ml volumetric flasks labelled A,B,C,D,E and F with the help of burette as shown below.

Flask	A	B	C	D	E	F
Volume of Dichromate	1.0ml	2.0ml	3.0ml	4.0ml	5.0ml	6.0 ml

The solutions are made up to the mark with distilled water and shaken well.

Step - 2 : Selection of filter :

In cleaned cuvet distilled water is taken (Reagent blank) and placed in the colourimeter. A filter is placed and absorbance is adjusted to Zero. Into another cuvet sample solution is taken and the reagent blank is replaced with the cuvet. The absorbance is noted. By changing the filters and following the same procedure, the absorbance values are measured. The filter which gives maximum absorbance is noted and selected for the experiment.

Step - 3: Measurement of absorbance of solutions :

The selected filter is fixed in position and the absorbance values of all solutions are measured and tabulated. A graph is plotted by taking absorbance values of y - axis and concentration of solutions on x - axis. A straight line is obtained.

The unknown solution in 100 ml volumetric flask is diluted up to the mark and shaken well.

The absorbance of this solution is measured using the same filter. Form the absorbance value, the concentration of given dichromate solution is determined from the graph.

Result :

Concentration of given dichromate solution = _____.

Precautions :

1. Whenever the solution in a cuvet is changed, the cuvet must be rinsed with the solution to be taken in it.
2. The soution, if any on the outside walls of the cuvet is to be wiped out gently with a soft filter paper.

Calculations :

Weight of weighing bottle + $K_2Cr_2O_7$ (W_1) = _____ gms.

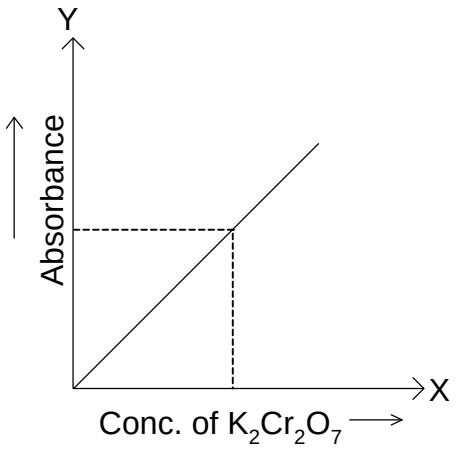
Weight of empty weighing bottle (W_2) = _____ gms.

Weight of $K_2Cr_2O_7$ taken = $W_1 - W_2 = W$ = _____ gms.

$$\text{Concentration of dichromate solution} = \frac{W \times 10}{294.1}$$

= _____ M

Graph :



S.No.	Filter no.	Absorbance
1.	45	
2.	47	
3.	51	
4.	52	
5.	54	
6.	57	
7.	60	
8.	67	

Filter number selected =

S.No.	Sample	Vol. of $K_2Cr_2O_7$ taken	Concentration of $K_2Cr_2O_7$	Absorbance
1	A	1.0ml		
2.	B	2.0ml		
3.	C	3.0ml		
4.	D	4.0ml		
5.	E	5.0ml		
6.	F	6.0ml		
7.	Unkown	–		

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