Swetha N

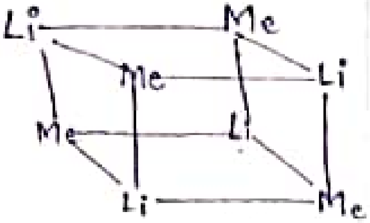
Structure of Methyl lithium:-

→ Simple monomeric formula is CH_3-Li.

→ The Raman bands (in diethyl ether solution) of CH_3Li at 486, 277, 209 and 171 cm^{-1} are characteristic of cluster modes of tetrameric units.

→ Low C-H stretch in IR frequencies at 2840 cm^{-1} represents ~~uni~~ tetrameric units. Hence CH_2-Li is said to exist in tetrameric unit $(CH_3-Li)_4$.

→ This comprise of four lithium atoms at the corners of a tetrahedron and alkyl group (methyl = Me) are located at other four corners of a tetrahedron.



→ Each C atom is associated through three equidistant lithium atoms, thus acting as triply bridging hydro-carbyl groups using four centre Li_3C Bond.

→ Each C atom utilises one sp^3 hybrid orbital to overlap with the three sp^3 hybrid atomic orbital provided by the three lithium atoms. All the four hybrid orbital are directed towards the centre of Li_3C in trigonal pyramid geometry.

→ The bonding in CH_3-Li consists of a set of localised molecular orbitals. The symmetric combination of three Li (sp^3 orbital) on each face of the Li_4 tetrahedron and one sp^3 orbitals from CH_3 gives an orbital that can accomodate a pair of electron to form a 4c-2e bond.

Structure of Zeise's Salt:

→ It is Potassiumtrichloro(η^2-ethene)platinate(II) = $K[PtCl_3(\eta^2-C_2H_4)]$

→ It was the first organometallic compound to be isolated in pure form. It is a square planar complex.

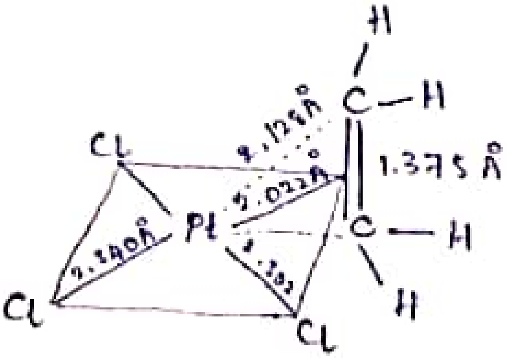
→ The Dewar-Chatt-Duncanson model explains the type of chemical bonding between an metal Pt and ligand

→ The π-acid ligand donates electron density in to metal d orbital. The metal donates electrons back from a filled d-orbital into the the empty π^* ($2p_z$) antibonding orbital of the ligand. (hence the description π-acid ligand). Both these effects tends to reduce the C-C bond order in ethene, leading to an elongation.

→ The complexation (interaction) can cause C-atoms to rehybridise from sp^2 towards sp^3, which is indicated by the bending of the H-atoms on the ethene back (away) from the metal.

→ The trans-Pt-Cl bond is 2.340 Å is significantly longer than the cis Pt-Cl bond (2.302 Å).

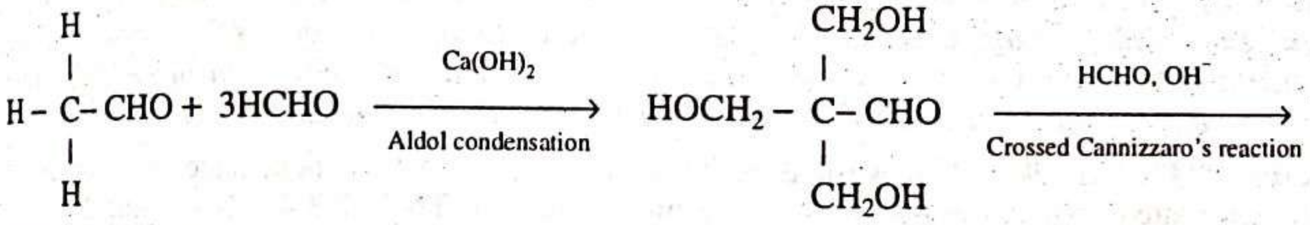
→ The C-C distance is 1.375 Å which is slightly longer than the value found in the free ethene (1.33 Å) indicating some $d\pi$-$p\pi^*$ back bonding from Pt to C_2H_4.



(8) *The [illegible] water, washed by boiling and again washed in a beater.*

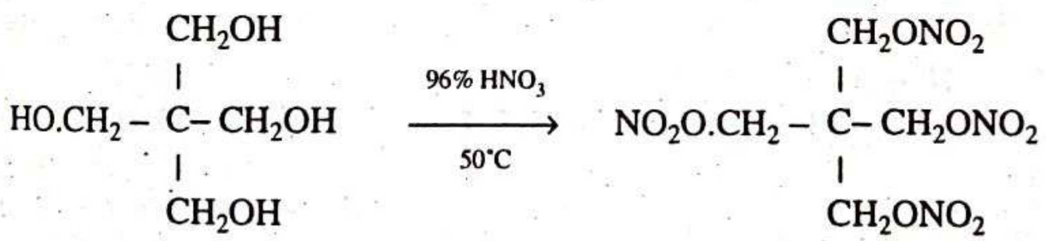
PETN OR PENTHRIT

Pentaerythritol tetra nitrate [$C(CH_2ONO_2)_4$] is one of the most brisant and sensitive military high explosive. For use as a **booster explosive**, a bursting charge or a plastic demolition explosive, it is desensitized by admixture with TNT (the mixture is called **pentrolite**) or by the addition of wax. PETN is prepared by the nitration of pentaerythritol with strong 96% HNO_3 at about 50°C.



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-CHO + 3HCHO \xrightarrow[\text{Aldol condensation}]{Ca(OH)_2} HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CHO \xrightarrow[\text{Crossed Cannizzaro's reaction}]{HCHO,\ OH^-}$$

Acetaldehyde



$$HO.CH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH \xrightarrow[50^\circ C]{96\%\ HNO_3} NO_2O.CH_2-\overset{\displaystyle CH_2ONO_2}{\underset{\displaystyle CH_2ONO_2}{C}}-CH_2ONO_2$$

Pentaerythritol PETN

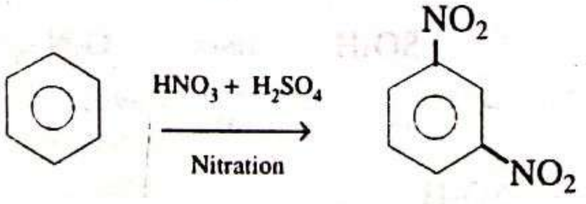
The decomposition of PETN probably takes place in the following manner.

$$C(CH_2ONO_2)_4 \rightarrow 4H_2O + 3CO_2 + 2CO + 2N_2$$

The high sensitivity of PETN allows it to be detonated by the impact of a rifle bullet.

DINITRO BENZENE (DNB)

Dinitro benzene is prepared by the nitration of benzene with the nitrating mixture consisting of 40 parts HNO_3 and 60 parts of H_2SO_4 at about 100°C. A mixture of all the three isomeric dinitrobenzene is thus obtained, but the m-dinitrobenzene predominates in the mixture.



DNB

also added. The gun powder or black powder thus obtained in finally dried at about 40°C.

RDX OR CYCLONITE

RDX or cyclonite is sym-trimethylene trinitramine $[(CH_2)_3N_3(NO_2)_3]$. It is one of the most powerful explosives known at present time. It can be prepared by the following methods.

(a) Hale method- A British chemist **G.C.Hale (1925)** prepared RDX by destructive nitration of hexamethylene tetramine with conc. HNO_3.

$$\underset{\text{Hexamethylene tetramine}}{(CH_2)_6N_4 \text{ or } C_6H_{12}N_4} + 3HNO_3 \rightarrow \underset{\text{RDX or Cyclonite}}{C_3H_6O_6N_6} + 3HCHO + NH_3$$

(b) Ebele-Schlessler-Ross method- This method consists in addition of paraformaldehyde and ammonium nitrate to acetic anhydride at 70°C.

$$3HCHO + 3NH_4NO_3 + 6(CH_3CO)_2O \rightarrow \underset{\text{RDX or cyclonite (60\% yield)}}{[(CH_2)_3N_3(NO_2)_3] \text{ or } C_3H_6O_6N_6} + 12CH_3COOH$$

The process takes place in two stages.

(a) $6HCHO + 4NH_4NO_3 + 3(CH_3CO)_2O \rightarrow (CH_2)_6N_4 + 4HNO_3 + 6CH_3COOH + 3H_2O$

(b) $\underset{\text{Hexamethylene tetramine}}{(CH_2)_6N_4} + 4HNO_3 \rightarrow \underset{\text{RDX}}{(CH_2N.NO_3)_3 \text{ or } C_3H_6O_6N_6} + NH_4NO_3 + 3HCHO$

The formaldehyde and ammonium nitrate from the step (b) are further utilized alongwith more ammonium nitrate and acetic anhydride and the process is thus repeated. But the yield of cyclonite is about

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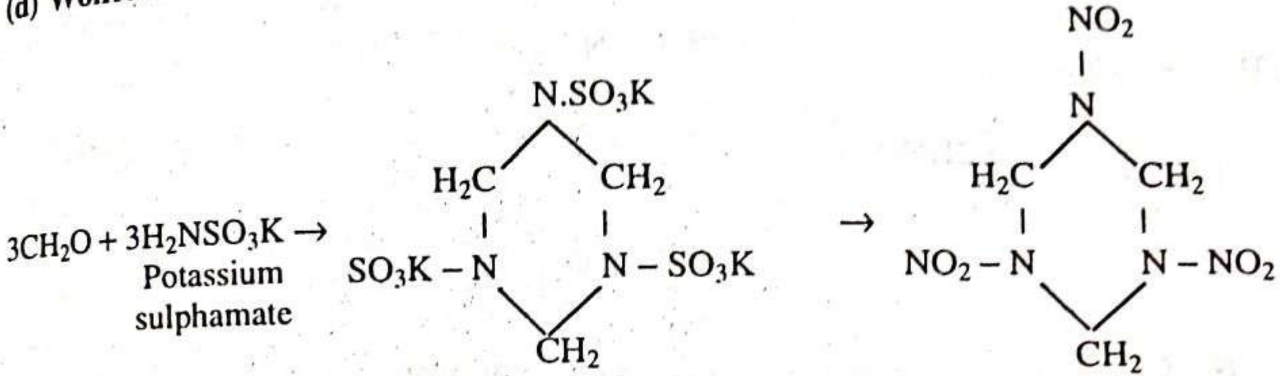
60%, because some HCHO gets converted into unreactive methylene and polymethylene diacetates.

(c) Bachmann method: A combination process was developed by **Bachmann (1949),** who utilized the by product to get a second mole of RDX. This is the combination of above two methods.

$$(CH_2)_6N_4 + 2NH_4NO_3 + 4HNO_3 + 6(CH_3CO)_2O \rightarrow \underset{\text{Cyclonite (80\% yield)}}{2C_3H_6O_6N_6 \text{ or } 2(CH_2N.NO_2)_3} + 12CH_3COOH$$

(d) Wolfram method: This method was developed in Germany and involves the following steps :



Isomer of potassium methylene sulphamate

RDX

RDX is used in a mixture with TNT and aluminium, known as **Torpex**, for mines, depth charges and torpedo warheads. It is also used as an ingredient for explosive for shells and bombs and it is desensitized by wax or oily material.

EDNA

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Hexyl

Hexyl is generally used with other explosives as a filler for bombs, mines and warheads for torpedoes.

LEAD AZIDE

Lead azide can be prepared by treating sodium azide (prepared from sodium amide and nitrous oxide) with lead acetate or lead nitrate.

$$NaNH_2 + N_2O \rightarrow \underset{\text{Sodium azide}}{NaN_3} + H_2O \ ; \ NaNH_2 + H_2O \rightarrow NaOH + NH_3$$

$$2NaN_3 + Pb(CH_3COO)_2 \rightarrow \underset{\text{Lead azide}}{Pb(N_3)_2} + 2CH_3COONa$$

Lead azide has partially replaced mercury fulminate as an initiating or primary explosive for blasting caps. Mercury fulminate is somewhat less stable than desired and needs costly raw material Hg. Lead azide and mercury fulminate decompose exothermically on being struck in the following manner.

$$Pb(N_3)_2 \rightarrow Pb + 3N_2 + 0.6 \text{ k. cals.}$$

$$Hg(ONC)_2 \rightarrow Hg + N_2 + 2CO + 117 \text{ k. cals.}$$

DINOL

Dinol is diazodinitrophenol or 4,6-dinitrobenzene 1,2 diazoxide. It was first diazo compound ever discovered by **Griess (1858)**. It is generally used as a primary explosive and prepared by diazotizing picramic acid.

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iron can not be for changing its physical properties. It is a highly refined metallic iron, containing a little slag, which is distributed throughout the iron in fine fibrous and film forms. Due to the presence of slag in wrought iron, it resists corrosion.

STEEL

Steel is an **alloy** of carbon and iron and has less carbon than what is present in cast iron. Normally steel contains 0.25-2.5% of carbon as cementite (Fe_3C) and traces of S,P, Mn and Si as impurities. We therefore see that percentage of carbon in steel is intermediate between that in wrought iron and in cast iron. Sulphur and phosphorus are the objectionable impurities, which are present usually below 0.05% depending on the method used for the manufacture of steel. Silicon usually lies between 0.15-0.35% and is present as iron silicide (FeSi) which is soluble in ferrite. Mn is added to steel during its manufacture and it acts as a **deoxidiser** to reduce any FeO to MnS which is inert, while FeS makes steel brittle in hot working. Generally the properties of steel are governed by the amount of carbon it contains and on the state (i.e., free or combined) in which it is present in the steel. Some other elements such as Mn (**in killed steel**), S (**in rimmed steel**) have modified the strength and machinability of steel. Usually carbon contents vary from 0.2-1% in most steels, but there are steels containing carbon from 0.08-below 2% and others containing carbon from 1–1.5%. For example, **tool steel** contains 0.9-1.5% carbon, **structural steel** contains 0.2-0.6% carbon, and **mild steel** contains 0.2% or less carbon. Properties of **alloy steel** are greatly changed by the presence of other metals, such as Mn, Ni, Cr, Mo, V etc. These alloys in addition to carbon, contain one or more of these metals. The process of **tempering** also changes the physical properties of steel, because **tempering** also changes the physical properties of steel, as tempering adjusts the deposition of carbon in steel.

MANUFACTURE

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With the development of various new processes, such as **Bessemer process, open hearth process, electric furnace process, L.D. process etc,** the cementation and crucible processes are now not much in use.

(3) BESSEMER PROCESS

This process was discovered by Henry Bessemer in England (1856). In this process low phosphorus pig iron (below 0.09%) is treated by acid Bessemer process and high phosphorus pig iron (more than 1.5%) is treated in basic Bessemer process. In both the processes steel is made by first blowing cold air through molten pig iron at about 2 atmospheric pressure, oxidising the impurities and simultaneously converting pig iron to steel. The process mainly differs in the use of acid and basic refractory linings of the converters.

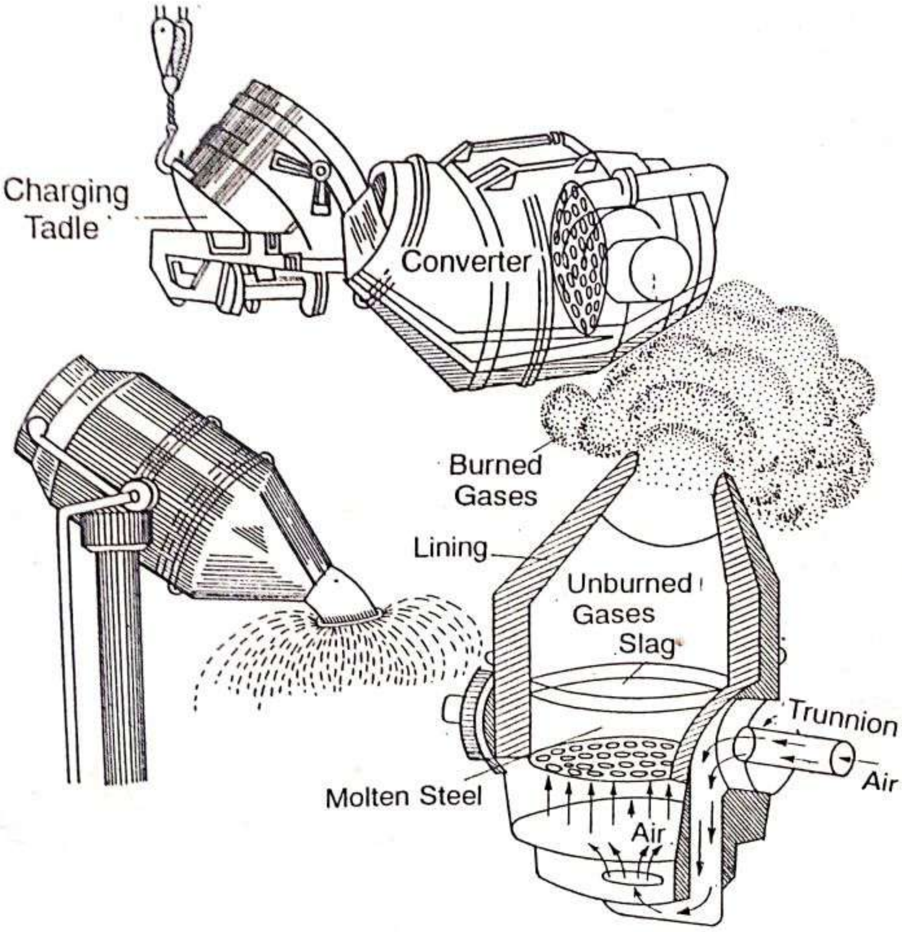

Fig. 5. Bessemer converters.

The converter is a pear shaped furnace about 6 m high and 3 m in diameter. It is made of steel plates and is lined inside with silica or magnesia (MgO), depending upon the nature of impurities present in the pig iron. If the impurities present in the pig iron are basic, e.g., manganese, a lining of silica brick is used and the process is known as **acid Bessemer process.** If impurities are acidic, e.g., sulphur, phosphorus etc., a basic lining of lime (CaO) or magnesia (MgO) is used in the converter and process is then known as **basic Bessemer process.** The capacity of the converter is from 10-25 tonnes of charge at a time. The converter is mounted on shafts or trunnions, one of which is hollow and serves as a wind pipe and upon which the converter can rotate in any position. The converter is also provided with a number of holes at the bottom through which a hot blast of air can be introduced.

The molten pig iron is mixed in mixers and then charged into converter. About 15-16 tonnes of iron can be charged at a time. The converter is first set in the horizontal position and after charging the converter is adjusted in vertical position. After charging a blast of cold air is admitted through the holes provided at the bottom at a pressure of about 2-3 kg/cm^3. The blast is continued for about 15 minutes during which the impurities are oxidised. Mn is oxidised to MnO and Si is oxidised to SiO_2. Carbon is also oxidised to CO. The resulting oxides of Mn and Si (MnO and SiO_2) combine together to form slag of manganese silicate.

$$2Mn + O_2 \rightarrow 2MnO$$

$$Si + O_2 \rightarrow SiO_2$$

$$2C + O_2 \rightarrow 2CO$$

$$MnO + SiO_2 \rightarrow \underset{\text{Slag}}{MnSiO_3}$$

Carbon is oxidised to CO which burns with a blue flame at the mouth of the converter. When the flame dies out, it indicates the complete oxidation of impurities.

Similarly, **in basic Bessemer process,** phosphorus is slagged off as calcium phosphate and is known as **Thomas slag.** This slag is used as a fertilizer.

$$4P + 5O_2 \rightarrow 2P_2O_5 \text{ or } P_4O_{10}$$

$$6CaO + P_4O_{10} \rightarrow \underset{\text{Thomas slag}}{2Ca_3(PO_4)_2}$$

After complete oxidation of impurities, **spiegeleisen** (an alloy of iron, manganese and carbon) is added and the blast of air continued for a short period to effect thorough mixing. Mn and carbon act as **deoxidisers** in the first instance and reduce any FeO which may be present. The excess of manganese and carbon dissolve in the molten metal, the carbon being the necessary constituent of steel and manganese makes it harder and also increases the tensile strength. Sometimes, a small and calculated amount of ferro-silicon or aluminium is added to the finished product. It serves as **scavenger** and reduces any CO dissolved in the metal to carbon, thereby producing steel which is free from enclosed bubbles of the gas called, **blow holes.** Aluminium also removes nitrogen forming aluminium nitride. The scavenger elements get oxidised and separate as slag.

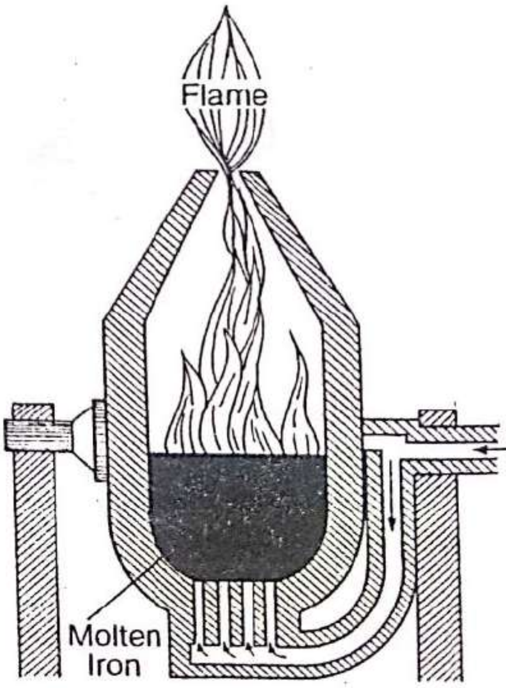

Fig. 6. Bessemer converter adjusted in the horizontal position.

The slag is held back by a skimmer and the **finished steel** is then transferred to a bucket shaped refractory lined steel shell with a hole at the bottom through which molten metal is allowed to flow into moulds. When the ingots have cooled sufficiently, these are reheated and rolled to various shapes and sizes. After the removal of the steel, the converter is turned bottom up so that the slag drops into buggies and is removed for disposal.

(4) LINZ DONAWITZ OR LD PROCESS

This process was developed in Australia in 1951 and is in use at many places throughout Asia, Europe and other places. In India, Hindustan Steel Ltd. at Rourkela uses this process. This is a modification of basic Bessemer process. The converter has a solid bottom and is lined inside with a basic lining of tarred

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energy. (5) Continuous flow of ingots to the rolling mills. (6) As the ore itself acts as the oxidising agent, greater amount of output is obtained with the same amount of pig iron. (7) Greater variety of products can be manufactured.

(5) OPEN HEARTH PROCESS

The open hearth process is based on the regenerative principle of heat economy proposed by William Siemens (1857). In this method the waste heat of the products of combustion of a gaseous fuel is utilized. This process is also of two types, the acid hearth process and basic hearth process similar to Bessemer process. In fact, both acid and basic open-hearth processes are essentially same processes, the difference being only that of lining in the furnace. The hearth is lined inside with either silica or calcined dolomite ($CaO.MgO$). The choice of lining material depends upon the nature of the impurities present in pig iron as in case of Bessemer process.

The open hearth process consists in heating pig iron or cast iron, steel scrap and iron ore (haematite) on the hearth of furnace by the heat produced by burning fuel in air (both preheated) or by producer gas. The gaseous fuels are burned with controlled amount of oxygen to produce high temperature required for steel making. The furnace is regenerative type with brick checker work to utilize heat of the outgoing gases by heating the incoming air by contact with checker work previously heated by the flue gases.

Iron is placed in the hearth H and producer gas is passed through generator G_1 which is previously heated and air is passed through the generator G_2 which is also heated. Thus during the first phase of the cycle, producer gas and air are separately passed through previously heated generators or chambers G_1 and G_2, while the products of combustion flow through the checker work in G_3 and G_4. The combustion takes place rapidly because the gases have been preheated to high temperature. Subsequently the cycle is reversed, so that flue gases are passed through G_1 and G_2 and air and producer gas are being preheated in G_3 and G_4 respectively. In this way cycle is repeated in an alternative manner. Every few minutes the direction of gases is reversed so that incoming gases are always preheated.

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Due to the burning of the producer gas, the charge melts and the impurities of S, P, Si and C are oxidised by haematite.

$2Fe_2O_3 + 3S \rightarrow 4Fe + 3SO_2$ (Sulphur removed)

$5Fe_2O_3 + 6P \rightarrow 10Fe + 3P_2O_5$

$2Fe_2O_3 + 3Si \rightarrow 4Fe + 3SiO_2$

$Fe_2O_3 + 3Mn \rightarrow 2Fe + 3MnO$

$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$ (Carbon removed)

$P_2O_5 + 3CaO \rightarrow \underset{\text{Slag}}{Ca_3(PO_4)_2}$ (Phosphorus removed)

$SiO_2 + CaO \rightarrow \underset{\text{Slag}}{CaSiO_3}$ (Silicon removed)

$MnO + SiO_2 \rightarrow \underset{\text{Slag}}{MnSiO_3}$ (Manganese removed)

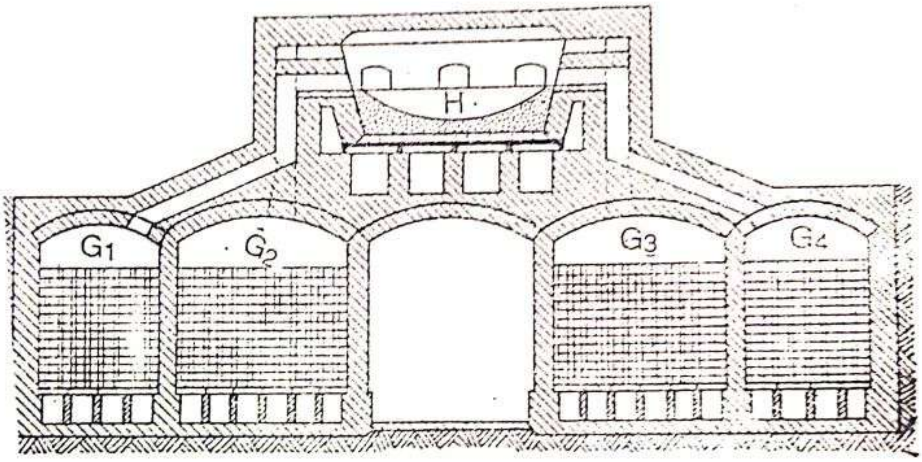

Fig. 7. Open Hearth Process,

From time to time samples are taken out from the furnace and analysed for carbon content. When the metal is found to contain desired amount of carbon, calculated amount of ferro manganese and aluminium are added as in Bessemer process. Calculated amount of other metals are added if special steels are to be prepared. The final product is removed from the furnace by tilting the hearth.

Advantages :

(1) It is better suited to all grades of pig iron containing upto 1% of phosphorus. (2) Due to the development of high temperature almost all types of scrap steel can be used. (3) Iron ore, scrap steel and pig iron are directly converted in to steel. (4) As the elimination of impurities can be controlled by analysis of the drawn samples of metal and slag, various grades of steels, according to specification can be easily produced. (5) Due to lower amount of FeO and N_2, this process is superior to Bessemer process and the steel formed by this method is also of better quality. (6) This process gives more uniform steel. (7) Cast iron from lower grade ores can be converted into steel. (8) Much fuel is saved in the process as it works on the regenerative principle of heat economy. (9) As the ore itself acts as the oxidising atgent, greater amount of steel can be produced with same amount of pig iron. (10) There is a better control of temperature and composition in the furnace.

(6) ELECTRIC FURNACE METHOD

In this process, the steel is obtained by heating the materials to very high temperature without introducing the undesirable impurities. Thus steel obtained by this method is free from S , P and gas bubbles and contains only some solid non-metallic impurities, called **sonims.** This process is thus much superior than Bessemer and open hearth processes. The heating is done in an **arc furnace** to facilitate rapid steel production. ***In fact, furnaces are of two types :***

(a) Arc furnace. (b) Induction furnace.

In the case of **arc,** the arc can be between two electrodes of carbon or between carbon and molten charge. In case of **induction,** charge is heated by induction currents.

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for making transformer cores and poles of dynamos and motors. It is also used for making automobile valves and springs.

A summary of the principal effects of the alloying elements is given in Table 2.2.

2.7 FERROALLOYS

Ferroalloys are an important group of metallic materials required for use in the steel industry. They are the major source of elements such as Si and Mn which are required for plain carbo steels and Cr, V, W, Ti and Mo which are added as alloying elements to low and high carbo steels. The major application of ferroalloys is as deoxidisers and desulphurisers in steel industry and as specified additives to impart desired properties to steel.

The characteristic feature of ferroalloys is that they are brittle and as such they ar unsuitable for engineering applications; but their addition to plain carbon steels greatly increas the service value of steels. The ferroalloys contain appreciable amounts of iron and their meltin points are lower than that of the pure metals. As a result they readily dissolve in molten steel. Th other elements in ferroalloys act as protecting devices against oxidation of the principal alloyin element. Some important ferroalloys and their composition are given in Table 2.4. In all cases th balance is Fe.

Table 2.4 Ferroalloys and their composition

	% Composition							
Ferroalloy	Mn	Si	C	Cr	Mo	Al	Ti	V
Ferromanganese								
Standard	78 - 82	1.25	0.75					
Medium carbon	80 - 85	1.25 - 2.5	1 - 3					
Low carbon	80 - 85	1.25 - 7.0	0.75					
Ferrosilicon		47 - 52	0.15					
Ferrochromium								
High carbon		1 - 2	4.5 - 6.0	67 - 70				
Low carbon		0.3 - 1.0	0.03 - 2.0	68 - 71				
Ferromolybdenum (high carbon)		1.5	2.5		55 - 70			30 - 40
Ferrovanadium (high carbon)		13.0	3.5					
Ferrotitanium (low carbon)		3 - 5	0.1				6 - 10	38 - 43

The most common method of production of ferroalloys is by heating the charge in electric arc furnace. Three important alloys which are produced in large quantities are ferrosilico ferromanganese and ferrochrome.

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Ferrosilicon

The charge consisting of a mixture of quartz (silica), coke, haematite and iron (as turnings) is melted in an electric furnace. The principal reaction is the the reduction of silica by carbon to silicon which dissolves in molten iron giving the ferroalloy.

$$SiO_2 + 2C \rightarrow Si + 2CO$$

The ferrosilicon is periodically removed from the bottom of the furnace. After solidification the alloy is crushed to specified size.

Ferrosilicon is employed on a large scale as a reducing agent in steel industry. It decreases the solubility of carbon in iron leading to its deposition as graphite. This property is used for making silicon steels which are corrosion resistant and have magnetic permeabilities.

Ferromanganese

High carbon ferromanganese is made by the reduction of pyrolusite mixed with iron oxide using anthracite in a blast furnace. Manganese with a low silicon content containing at least 40% Mn and with Mn : Fe ratio of 9: 11 are required for this purpose.

Low carbon ferromanganese is made by the silico - thermic reduction of pyrolusite mixed with iron oxide in an electric furnace. This alloy contains 69 - 71% Mn, 18 - 22% Si, 4 - 6% Fe and less than 1.0% Co.

Ferromanganese is used as a deoxidiser and desulphuriser and is added to steels to impart hardness, toughness and wear resistance.

Ferrochromium High chromium ferrochromium is obtained by the direct reduction of chromite with carbon in an electric furnace (Sec. 1.28). Low carbon ferrochromium (0.03 - 0.1%) is produced by the removal of carbon from high carbon ferrochromium by iron oxide in a vacuum furnace.

The principal application of ferrochromium is in the production of stainless steels.

2.8 HEAT TREATMENT OF STEEL

The characteristic of steel is that, depending on the composition, it possesses a wide range of properties. For example it can be soft and ductile or hard and strong. These properties can be controlled not only by changing the percentage of carbon but also by subjecting it to a process called *heat treatment*. Heat treatment brings about structural changes in steel which are attributed to the polymorphism of iron. Heat treatment is possible because of the change from a FCC structure to one which is nearly BCC that occurs when iron is cooled to 910°C. Heat treatment is defined as a *series of operations involving heating and controlled cooling which brings about a change in the properties of steel as a consequence of the changes in its structure.* In general heat treatment processes depend only on the rate of cooling and not on the rate of heating. The various heat treatment processes are described below.

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Normalising

Normalising is a relatively simple heat treatment. In this process steel is heated in a furnace to above (about 50°C) its upper critical temperature and allowed to remain at that temperature for a sufficiently long period of time so that the steel acquires uniform temperature throughout its body. It is then taken out of the furnace and allowed to cool to room temperature in still air.

The object of normalising is to obtain a structure which is uniform throughout the steel. Heating produces a uniformly fine grained austenite structure from a coarse structure. On cooling this converts to a uniformly fine grained ferrite and pearlite.

Annealing

Annealing is similar to normalising, but differs only in the method of cooling. The steel is heated to some 50°C above the upper critical temperature so that the coarse grain structure is transformed into fine grained austenite. It is held at that temperature for a sufficient time for steel to attain uniform temperature. The steel is then allowed to cool in the furnace itself to ensure the removal of all stress without causing any appreciable increase in grain size. Annealing greatly improves the toughness and ductility of steel.

Hardening

Normalising and annealing are simple methods of heat treatment in which the structure of steel remains unchanged or transforms basically into pearlite. However, the more commonly used heat treatment processes are those which involve cooling the austenite at such a rate that the pearlite formation is prevented. These processes - hardening and tempering - lead to the development of hardness and strength.

In *hardening* steel containing sufficient carbon is heated to above its upper critical temperature and then *quenched (cooled quickly)*. The quenching agents are cold water and brine or caustic soda solution for drastic quenching and oils for less drastic quenching. Quenching oils are of animal, vegetable or mineral origin. Whale oil was commonly used for this purpose. This has now been replaced by synthetic organic compounds based on polyalkane glycols in water solution. Quenched steel is extremely hard. The hardness of steel is explained as follows.

Rapid cooling of steel arrests the formation of pearlite; however the austenite phase is

Fig 2.3 TTT diagram

Tempering

The hardened steel is brittle and is commonly associated with stresses developed during quenching. These properties make steel less useful unless extreme hardness is required. In such cases the material is reheated (in the range of 200 - 700°C) in such a way that the internal stresses are removed and the steel is rendered less hard and more ductile. This process of heat treatment of hardened steel is referred to as *tempering*.

In this process the martensite structure which is supersaturated solid solution of carbon in ferrite rejects carbon which precipitates as finely divided carbide phases. The tempered steel will have a fine dispersion of carbides in a matrix of α - iron.

High carbon steels are usually tempered in the range of 200 - 300°C where hardness is the criterion. The medium carbon steels are tempered in the range of 400 - 600°C where toughness and strength are important.

Structural changes during tempering

There is no perceptible change in the structure of steel up to about 200°C. However, at this temperature, the quenching stresses are reduced slightly and the steel may become a little harder since the residual austenite will transform into martensite. At about 230°C extremely small crystals of cementite begin to separate which continues till a temperature of about 400°C is reached. The resulting structure is tougher but softer than the martensitic steel, and is referred to as *troostite*. Above 400°C the tiny particles of cementite fuse together and the formation of cementite continues. The structure is now granular and is known as *sorbite*. Sorbite is tougher and softer than troostite

A conventional method of tempering is *temper by colour*. In this method the quenched steel is first cleaned to give a bright surface. It is then heated in a furnace by circulating hot air through it until the thin oxide film formed on the surface acquires the desired colour. The method is applicable only to plain carbon steels. Some tempering colours, tempering temperature and the application of such tempered steels are summarised in the Table 2.3.

Table 2.3 Temper colours of plain carbon steels

Temperature (°C)	Colour	Typical uses
230	straw yellow	razor blades
250	light brown	penknife blades, wood working tools
270	purple	surgical tools
290	bright blue	screw drivers
300	dark blue	springs

2.9 CASE HARDENING OF STEEL; CARBURISING

Certain components of steels require a combination of toughness and ductility and at the sam time be associated with hardness and wear resistant characteristics. It is to be noted that ductil materials are usually soft whereas hard materials are brittle. A blend of such opposite set o properties can be achieved by the use of steel which has different compositions at the surface an in the interiors. One of the processes by which the composition gradient can be maintained i referred to as *case hardening* or *surface hardening*. A particular case of surface hardening i *carburising*.

Carburising is based on the fact that carbon dissolves in solid iron in its FCC lattice. I view of the small size the carbon atoms penetrate the layers between the larger atoms of iron a shown in Fig 2.4.

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The steel must be case hardened only at a temperature above the upper critical temperature because carbon will dissolve only in FCC iron.

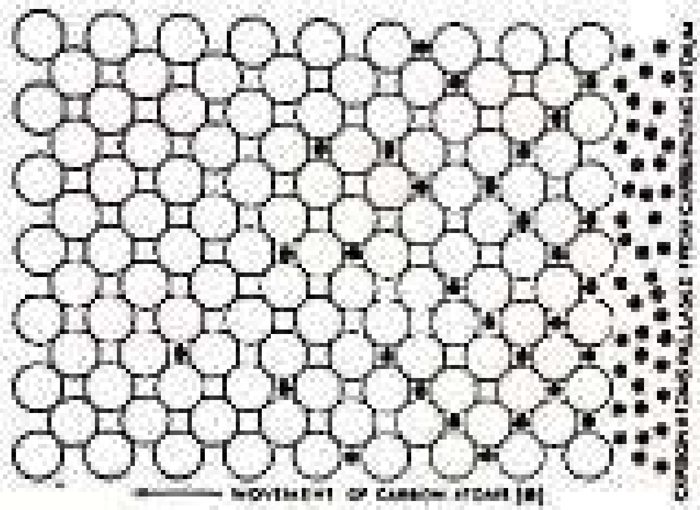

Fig 2.4. Penetration of carbon atoms into FCC lattice of iron

Carburising can be carried out in solid, liquid or gaseous media. Carburising in solid medium is called *pack carburising*. In this process, the components to be carburised are packed into steel boxes along with charcoal and an activator like barium carbonate. The sealed boxes are heated slowly to about 900 - 950°C (carburising temperature) for up to six hours depending on the case depth (thickness of carbon layer).

Liquid carburising or cyanide carburising is carried out in a bath of sodium cyanide-carbonate mixture. The cyanide bath is heated to about 870 - 950°C and the steel components placed in wire basket are immersed in molten bath for a few minutes according to the depth of the case required.

In this process carburising takes place owing to the decomposition of sodium cyanide releasing both free C and N atoms at the surface. Thus cyanide hardening involves absorption of both C and N. The advantages of cyanide carburising include the following.

(1) Temperature of liquid bath is uniform and can be controlled.

(2) Steel component can be quenched direct from the bath.

(3) Surface of the component remains clean.

The disadvantage of the process is the poisonous nature of sodium cyanide and the disposal of process waste poses environmental problems.

Gas carburising is the most efficient and the large scale industrial carburising method. The steel component is heated at about 900°C for three hours or more in an atmosphere of natural gas (methane) or propane mixed with a carrier gas (a mixture of nitrogen, hydrogen and carbon monoxide). The advantages of gas carburising include the following.

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(1) Surface of the component is clean after treatment.

(2) Gas carburising plant is compact.

(3) Carbon content at the surface can be more accurately controlled.

The carburised steel is again subjected to heat treatement, by first normalising then by heating
760°C and followed by quenching.

The relation between time of treatment and the case depth at 900°C for 0.15% steel for
liquid, and gaseous carburising is given in Fig. 2.5.

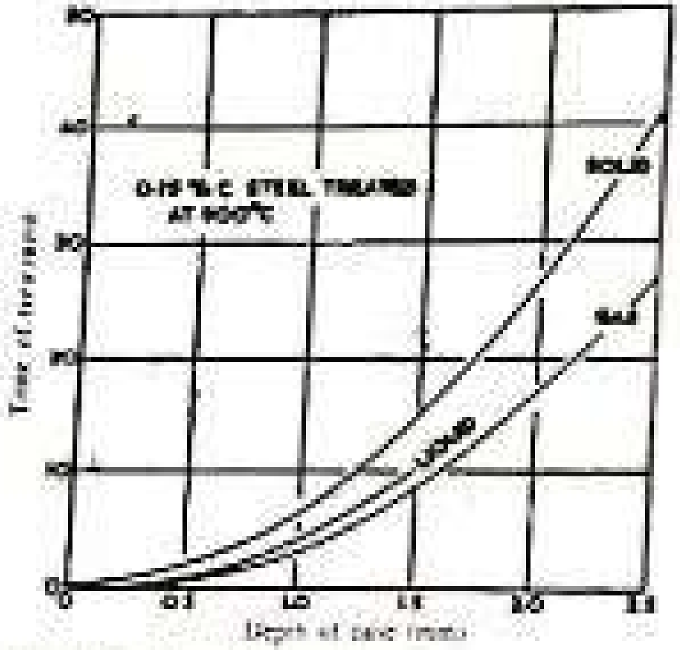

Fig 2.5 *Time case depth relationship for a typical plain carbon steel*

2.10 NITRIDING

Nitriding is another method of case hardening. The process involves the interstitial solid solution nitrogen atoms to form a very hard case on the surface of the steel. Nitriding is employed in the case of alloy steels containing about 1% or less of any one of the elements namely aluminium chromium, molybdenum or vanadium. Ordinary carbon steels cannot be nitrided since the iron nitrogen compound which is formed will diffuse into the core. However, the nitrides of aluminium vanadium, chromium and molydenum are retained near the surface of the steel providing extremely hard skin.

Nitriding is carried out at a relatively low temperature. Hence it constitutes the last operation (since all other operations are carried out at temperatures above 700°C) in the manufacture of the steel component. The steel is maintained at 500°C for 40 to 100 hours in an atmosphere of ammonia in a gas tight chamber. Ammonia dissociates releasing nitrogen atoms.

$$NH_3 \rightarrow N + 3H$$

The atomic nitrogen released is at once absorbed by and interstitially dissolves in the surface of the steel. Nitriding is not possible with atmospheric nitrogen since dinitrogen (N_2) is not absorbed by steel. The advantages of nitriding over carburising are as follows.

(1) Since no quenching is required after nitriding, cracking and distortion are unlikely.

(2) An extremely high surface hardness is attainable with some alloy steels.

(3) Corrosion and fatigue resistance are good.

(4) Hardness is retained up to 500°C whereas carburising hardened steel begins to soften around 200°C.

The major disadvantage of nitriding is that the initial outlay for nitriding plant is higher. Further if a nitrided steel is over heated, the surface hardness is lost permanently.

Sometimes steel is subjected to *carbonitriding*. Carbonitriding is a surface hardening process which makes use of a mixture of a hydrocarbon and ammonia. It is particularly limited for hardening small components whose wear - resistance is an important parameter.

2.11 STEEL INDUSTRY IN INDIA

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adherent film of oxide to steel

(5) Displacement of eutectoid point The alloying elements will cause a displacement of the eutectoid point. This occurs in such a way that the structure is completely pearlitic. The eutectoid temperature may be lowered or raised.

The influence of a few typical alloying elements are given below.

(a) Manganese Steels usually contain a small percentage of manganese remaining from the deoxidation. However, it is regarded as an alloying element only when its composition exceeds 1.0%. The structure of manganese is similar to that of austenite (FCC). Hence, when added to steel it stabilises the austenite structure even at lower temperatures. For example, when 12.0% manganese is added to a steel containing 1.0% carbon, the structure remains austenitic even after the steel has been slowly cooled to room temperature. As a result the steel will have a soft but tough austenitic core with a hard wear resistant carbide shell. Such a steel resists mechanical shock and severe abrasion. Manganese steel is used in rock crushing machinery and steel helmets.

(b) Chromium Some of the chromium dissolves in ferrite and stabilises it. However, most of the metal forms chromium carbide which is harder than iron carbide. This increases the hardness of steel. The disadvantage of chromium is that it introduces brittleness because of the course grains produced (grain growth). Chromium imparts stainless properties to steels by forming a dense adherent oxide film on steel which protects the surface from further attack. There are two types of stainless steels.

Those which contain 13% chromium and which are used to manufacture articles such as domestic kitchen - sinks, refrigerator parts and tableware.

Those which contain 18% Cr or and 8% Ni used in chemical plant where acid resisting properties (corrosion resistance) are important.

(c) Nickel Like chromium, nickel also dissolves in ferrite strengthening it. Steels containing up to 5% Ni, toughens the steel which may be attributed to the fine grains produced. The disadvantage of nickel is that it does not form the carbide and in fact destabilises cementite.

Chromium and nickel have opposite effects on the properties of steel. While chromium produces course grains, nickel promotes fine grain growth. Further chromium stabilises the carbide whereas nickel destabilises it. Addition of these two metals together have some advantages. Molybdenum added in amounts of about 0.3% further improves the properties of steel.

(d) Vanadium Vanadium has a very strong tendency to form the carbide. It also promotes the fine grain growth and induces resistance to softening at high temperatures. Steel containing 0.35% V is used for making turbine blades and discs and some gas turbine components.

(e) Tungsten Tungsten is an important alloying element of high speed steels. High speed tools are those which retain their temper even when heated to redness. Tungsten dissolves in both

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and γ-iron. It forms carbides WC and W_2C with carbon. A compound with iron Fe_2W, provides an age hardening system. It refines the grain size and produces less tendency to decarburisation during working. Tungsten renders the phase transformation sluggish and this property is used in high speed tool and die steels.

Table 2.2 Effects of alloying elements on steels

Element	Principal effect	Composition of typical alloy	Application
Manganese	forms stable carbide, stabilises austenite, hardens on abrasion	12% Mn, 1% C rest Fe	rock drills, rails, steel helmets
Chromium	forms hard carbide, increases hardness of steel, increases resistance to corrosion	13% Cr, .3% Mn, 0.3% C, rest Fe 18% Cr, 8.5% Ni, 0.3% C, rest Fe	cutlery, sharp edged tools domestic and decorative ware.
Nickel	toughens steel by refining gains, strengthens ferrite, low coefficient of thermal expansion	18% Ni, 8.5%Cr, 3% Mn, 0.2% Ti, 0.1% Al, 0.01%C, rest Fe	crockery
		36% Ni, 64% Fe (invar)	clock pendulums
		40 -50% Ni rest Fe (same coefficient as expansion of glass)	metal glass seals
		16% Ni, 12%Co, 9% Al, 5% Cu, 1% Ti, rest Fe (Alnico)	permanent magnets
Vanadium	stabilises carbide, raises softening temperature of hardened steel	0.35% V, 1.30% Mn 2.5% Ni, 12% Cr 0.7% Mn, 0.1% C, rest Fe	turbine blades
Tungsten	Forms very hard stable carbides, raises softening temperature and renders transformation very sluggish and promotes fine grains	18W, 4.25%Cr, 1.2% V, 0.75% C, rest Fe	lathe cutting tools hacksaw blades
Silicon	improves oxidation resistance at high temperature	4Si, 96Fe	electromagnets transformer
	increases magnetic permeability	0.6 Si, 28 Cr, 0.35 C	furnace parts

(f) Silicon Silicon dissolves in ferrite and stabilises it. Addition of silicon to low carbon steels improves the oxidation resistance at high temperatures. An iron - silicon alloy containing about 4% Si and practically no carbon has a high magnetic permeability and chemical resistance. It is used

Primary detonating explosives are extremely sensitive and explode by the application of heat, friction or impact for a very short period. They are used in small quantities to initiate the detonation of less sensitive secondary explosives. Some examples of this type include mercury fulminate $Hg(ONC)_2$, lead azide $Pb(N_3)_2$, lead styphanate $C_6H(NO_2)_3O_2Pb$, nitromannite $C_6H_8(ONO_2)_6$ and dinitrodiazophenol $C_6H_2N_4O_5$.

Secondary detonating explosives are insensitive to mechanical shock and fire. They explode violently only when stimulated by the shock waves caused by the detonation of primary explosives. Their burning proceed at a rate of about 6000 ms^{-1} and extremely high pressures are built up in a fraction of a second. As a result they exert a very high shattering effect. Examples of secondary explosives include trinitrotoulene (TNT), dynamite, tetryl (2, 4, 6 trinitrophyenylmethyl nitroamine) and RDX.

5.16 PROPERTIES OF EXPLOSIVES

The following properties of explosives determine their use for particular applications.

(1) Sensitivity Sensitivity to impact, is important in the case of primary detonating explosives. This is usually determined by dropping a standard weight from a height on to the explosive to be tested. The minimum height from which the fall of standard weight triggers the detonation is taken as a measure of sensitivity.

(2) Brisance Brisance derived from the French word *briser* (to break) is a measure of the shattering action of explosives. It can be determined by sand bomb test or Trauzl's lead block test.

In the sand bomb test 200g of standard sand (-20 to +30 mesh) is taken in a thick-walled metal cylinder. An accurately weighed quantity (0.4g) of the explosive is introduced into the metal cap and placed into the sand. The cylinder is closed and the detonator is exploded using a suitable device. After the blast, the crushed sand is removed and allowed to pass through a +30 mesh sieve. The mass of the sand which passes through the sieve gives a measure of brisance.

In the Trauzl lead block test one gram of the explosive fitted with a suitable detonator is placed a standard lead block (20 cm in height as well as diameter with a hole of 2.5cm width). The charge is covered with sand and blasted. The net expansion (ballooning) of the cavity is a measure of brisance.

(3) Stability The temperature at which an explosive decomposes on heating is a measure of its stability. A method of assessing stability is to heat the explosive carefully to a high temperature and the oxides of nitrogen released are brought in contact with a starch iodide paper. The blue colour produced is compared with standard tints to evaluate the stability.

5.17 TRINITROTOLUENE (TNT)

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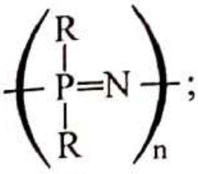
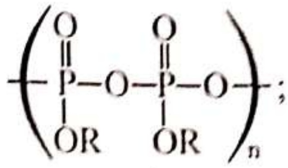
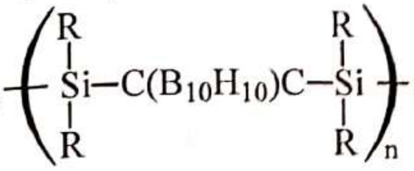
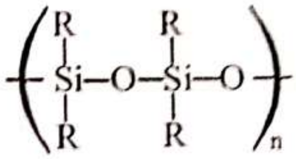
INORGANIC POLYMERS

Inorganic polymers are giant molecules composed of atoms other than carbon. These atoms are linked together mainly by covalent bonds. Some common examples of inorganic polymers are :

Polyphosphazines,  $\left(-\overset{R}{\underset{R}{P}}{=}N-\right)_n$; Polyphosphates,  $\left(-\overset{O}{\overset{\|}{\underset{OR}{P}}}-O-\overset{O}{\overset{\|}{\underset{OR}{P}}}-O-\right)_n$; Polymeric sulphur nitride, $(SN)_n$; Polycarboranes,  $\left(-\overset{R}{\underset{R}{Si}}-C(B_{10}H_{10})C-\overset{R}{\underset{R}{Si}}-\right)_n$; Silicones,  $\left(-\overset{R}{\underset{R}{Si}}-O-\overset{R}{\underset{R}{Si}}-O-\right)_n$ and a majority of silicate minerals.

General Properties of Inorganic Polymers

1. With a few exceptions (such as sulphur), inorganic polymers do not burn. They only soften or melt at high temperatures.

2. Inorganic polymers which have cross-linked structures with a high density of covalent bonds are generally stiffer and harder than the organic polymers.

3. The chain segments between cross links in polymers having cross-linked structures, are usually short and stiff. Consequently, these structures are not flexible enough to permit intercalation of solvent molecules. As a result there are very few inorganic polymers which swell reversibly imbibing solvent molecules.

4. Most of the inorganic polymers are built up of highly polar repeat units. These polymers would, therefore, dissolve only in polar solvents. Most of these polymers, however, react with the solvents. There are thus only a few inorganic polymers which actually dissolve in appropriate solvents.

5. Inorganic polymers are generally much less ductile than the organic polymers. Thus, while organic polymers such as polyethylene can extend by about 20 per cent or more before fracture, inorganic polymers break even when extended by about 10 per cent.

6. Inorganic polymers can usually be obtained in pure crystalline as well as in pure amorphous forms. Organic polymers, on the other hand, have structures which are partly crystalline and partly amorphous.

7. Inorganic polymers, in general, are stronger, harder and more brittle than the organic polymers.

Glass Transition Temperature, T_g. The glass transition temperature is defined as the temperature at which the internal energy of polymer molecules increases to such an extent that the chain segments of the polymer molecules are just ready to leave their lattice positions. At this temperature, the chain segments start moving past one another even if an infinitesimally small strain is applied to the polymer.

The glass transition temperature depends upon the chain length and the degree of cross-linking. It also depends upon the barrier restricting internal rotation round the chain links. Below the glass transition temperature, the chain segments of the polymer are 'frozen' on the lattice sites. The polymer in this condition is hard, invariably brittle and hence breakable like glass. Above the glass transition temperature,

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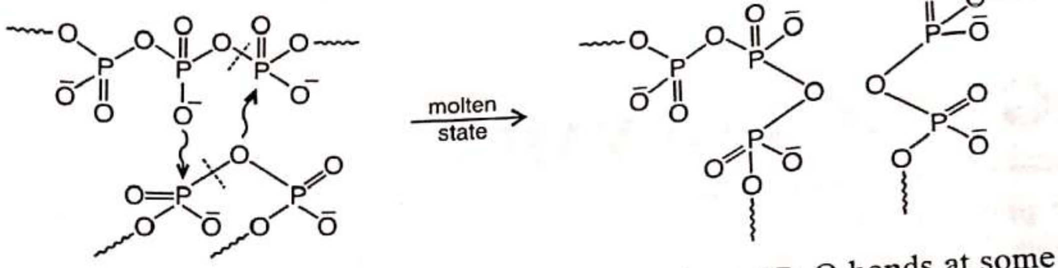
the segments of the polymer begin to exhibit diffusional motion as do the molecules of a liquid. At temperatures sufficiently higher than T_g, the polymer is present in the molten state. In this state there is exchange of bonds between the atoms, as shown below in the case of a polyphosphate.



As can be seen, the above exchange reaction involves breaking of P–O bonds at some places and the formation of new P–O bonds at other places. This gives sufficient mobility to the chain segments of the polymer in the molten state.

The cross-linked inorganic polymers show a wide range in their glass transition temperatures. In this temperature range, they change from rigid solids to leathery solids, from leathery solids to rubbery solids and finally to highly viscous liquids.

The glass transition temperature of a linear polymer is fairly sharp. This is because the movement of chain segments from one site to another does not involve the exchange of bonds as happens in the case of cross linked inorganic polymers. The chains in a linear polymer are held together by weak van der Waals forces which are overcome by the supply of even a small amount of energy. Therefore, the energy required for the movement of chains in such polymers is small. Consequently, the glass transition temperature of a linear polymer is lower than that of a cross-linked polymer in which the movement of chain segments requires the breaking of bonds.

IMPORTANT INORGANIC POLYMERS

There is a very wide variety of inorganic polymers, important amongst which are :

I. *Phosphorus-based Polymers* II. *Sulphur-based Polymers*

III. *Boron-based Polymers* IV. *Silicon-based Polymers* and

V. *Coordination Polymers*

The various types of polymers mentioned above have been described below in some details. E before this, it is important to mention that the type and the extent of association between the atoms in c polymer may be totally different from those in the other polymer. Therefore, the lines between the atoms the structures of polymers signify only the association between the atoms and not the exact bond type the bond orders.

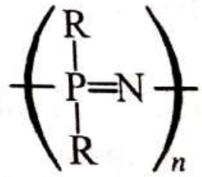
I. PHOSPHORUS-BASED POLYMERS

The phosphorus-based polymers can be divided into two categories, *viz., the chain polymers* and *network polymers,* depending upon the type of linkage involved between their atoms.

A. Phosphorus-Based Chain Polymers

These include polyphosphazines, polyphosphoryl halides, vitreous polyphosphates, crysta polymetaphosphates, plasticised and flexible polyphosphates and polyphosphoric acids.

1. Polyphosphazines. These polymers have the general structure



$$\left(\begin{array}{c} R \\ | \\ -P{=}N- \\ | \\ R \end{array}\right)_n$$

where R usually for Cl, OCH_3 and OC_2H_5. The polymers with R as Cl are known as polyphosphonitrilic chlorides an

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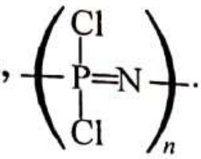
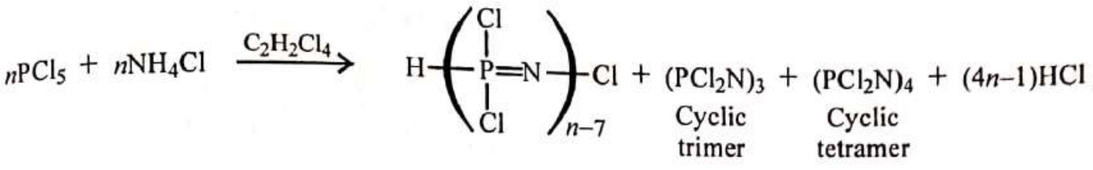
with R as OCH_3 and OC_2H_5 are, respectively, known as polydimethoxy and polydiethoxyphosphazines. These are discussed below.

Polyphosphonitrilic chlorides,  $\left(\!-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{P}}}=\mathrm{N}-\right)_n$. These polymers constitute what is known as inorganic rubber. They exhibit high elasticity and can be stretched several-fold with almost complete recovery. However, they undergo degradation under normal atmospheric conditions more rapidly than do the organic rubbers. Hence these polymers do not find much commercial use.

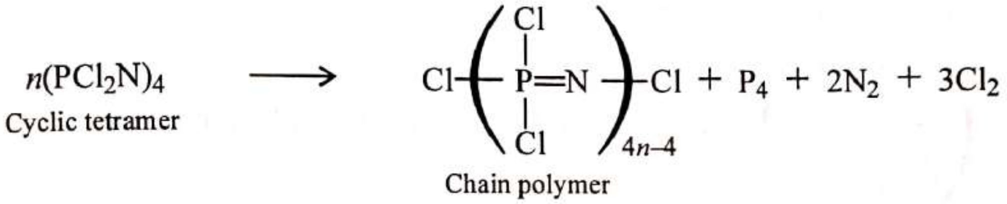
Polyphosphonitrilic chlorides can be prepared as follows :



$$n\mathrm{PCl_5} + n\mathrm{NH_4Cl} \xrightarrow{\mathrm{C_2H_2Cl_4}} \mathrm{H}\left(\!-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{P}}}=\mathrm{N}-\right)_{n-7}\mathrm{Cl} + \underset{\substack{\text{Cyclic}\\ \text{trimer}}}{(\mathrm{PCl_2N})_3} + \underset{\substack{\text{Cyclic}\\ \text{tetramer}}}{(\mathrm{PCl_2N})_4} + (4n-1)\mathrm{HCl}$$

The above reaction yields a mixture of cyclic trimers and tetramers along with a series of linear polymers. The linear polymerisation is terminated by H and Cl atoms.

The cyclic trimer or tetramer when heated in vacuum at 250° C, changes into a chain polymer :

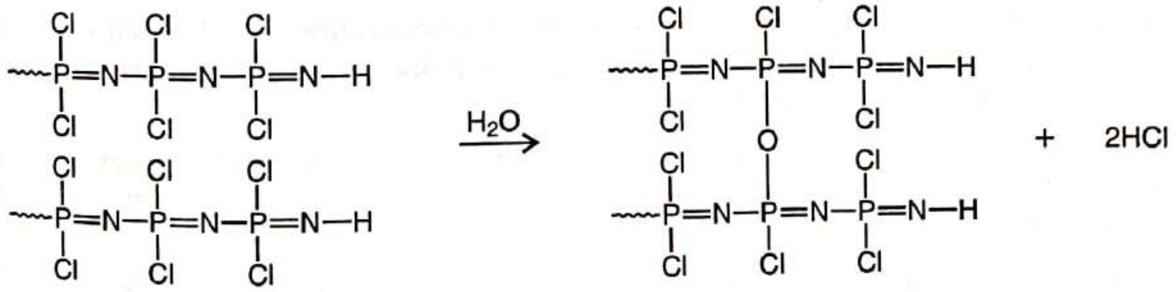


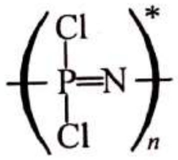
$$\underset{\text{Cyclic tetramer}}{n(\mathrm{PCl_2N})_4} \longrightarrow \underset{\text{Chain polymer}}{\mathrm{Cl}\left(\!-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{P}}}=\mathrm{N}-\right)_{4n-4}\mathrm{Cl}} + \mathrm{P_4} + 2\mathrm{N_2} + 3\mathrm{Cl_2}$$

The resulting chain polymer is somewhat cross-linked and hence has limited solubility in inorganic solvents. Polyphosphonitrilic chloride is at least as good an elastomer as vulcanised rubber.

The freshly prepared polyphosphonitrilic chlorides are soluble in chloroform but insoluble in petroleum ether. When the solutions are allowed to stand, the polymers get cross-linked and slowly gel.

When samples of highly elastic inorganic rubber are stored in absence of air, there is no change in their elastic properties. However, storage in air makes the material brittle. This is due to the action of water present in air in forming oxygen bridges between the chains so that there is reduction in average length of chain segments at lattice sites, as shown below.



The Cl atoms of the polymerising units of chain polymers  $\left(\!-\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{P}}}=\mathrm{N}-\right)_n^{*}$ can be replaced by other substituents such as OCH_3, OC_2H_5, etc. These substituted polyphosphazines are generally chain polymers. But,

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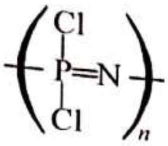
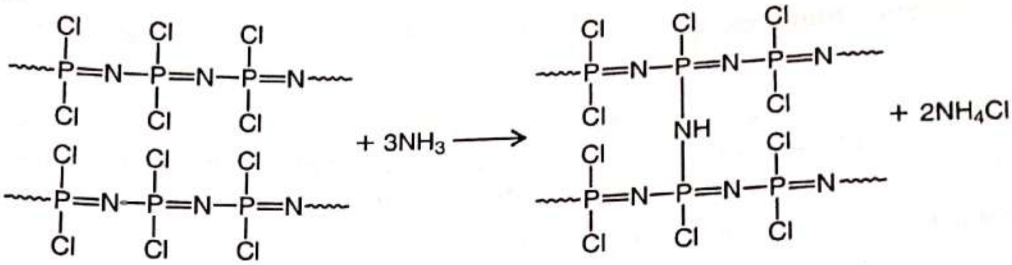
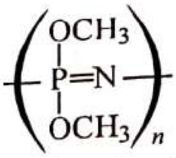
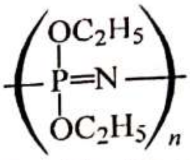
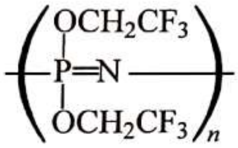
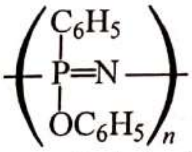
when  $\left(\begin{array}{c}\text{Cl}\\|\\-\text{P}=\text{N}-\\|\\\text{Cl}\end{array}\right)_n$ reacts with ammonia it produces cross-linked polymers, as shown below :



Polydimethoxy and polydiethoxyphosphazines,  $\left(\begin{array}{c}\text{OCH}_3\\|\\-\text{P}=\text{N}-\\|\\\text{OCH}_3\end{array}\right)_n$,  $\left(\begin{array}{c}\text{OC}_2\text{H}_5\\|\\-\text{P}=\text{N}-\\|\\\text{OC}_2\text{H}_5\end{array}\right)_n$. Polydimethoxy and polydiethoxyphosphazines can be prepared by reacting phosphonitrilic chloride with sodium methoxide and sodium ethoxide, respectively, when the chlorine atoms get replaced by the alkoxy groups.

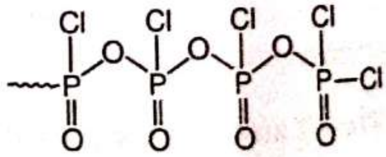
Polydimethoxy and polydiethoxyphosphazines are colourless, transparent film-forming thermoplasts. They are, however, unstable and when heated above 100°C, they slowly get converted into cyclic $[P(OR)_2N]_3$ and $[P(OR)_2N]_4$ polymers where R is CH_3 or C_2H_5.

The polymer,  $\left(\begin{array}{c}\text{OCH}_2\text{CF}_3\\|\\-\text{P}=\text{N}-\\|\\\text{OCH}_2\text{CF}_3\end{array}\right)_n$, *viz.,* polydi(trifluoroethoxy) phosphazine, can be transformed into inflexible films and can also be spun into fibres. This polymer is crystalline upto its melting point, *i.e.,* 240°C. It is soluble in acetone, tetrahydrofuran, ethyl acetate, dimethyl ether, etc. It does not burn in air but starts decomposing at 150°C.

Polydiaryloxyphosphazines are more stable than the polydialkoxy phosphazines. Thus, polyphenylphenoxyphosphazine  $\left(\begin{array}{c}\text{C}_6\text{H}_5\\|\\-\text{P}=\text{N}-\\|\\\text{OC}_6\text{H}_5\end{array}\right)_n$ can be spun into fibres from melts at 225°C. The Young's modulus of the fibre is similar in magnitude to that of nylon.

All the polyphosphazines have a much lower electrical conductivity than the analogous carbon-based unsaturated polymers suggesting that pi bonds are not as delocalised in polyphosphazines as are the double bonds in carbon-based unsaturated polymers.

X-ray analysis of polyphosphazines depicts patterns which are typical of semicrystalline polymers. The chain repeat distance in these polymers is 4·9 Å which is hardly affected by the type or the size of the substituents present on P atoms.



Polyphosphoryl Chlorides. These polymers have the general formula $P_nO_{2n-1}Cl_{n+2}$ and have the general structure as shown.

Preparation. Polyphosphoryl chlorides are prepared by reacting phosphorus oxychloride with phosphorus pentoxide.

$$(n+2)POCl_3 + (n-1)P_2O_5 \longrightarrow 3P_nO_{2n-1}Cl_{n+2}$$

The nature of the product depends upon the Cl/P ratio. The polymer obtained at Cl/P ratio of 1·1 is a clear amorphous mass exhibiting considerable elasticity. It can be flexed to a large extent without breaking.

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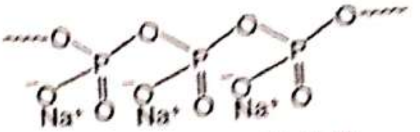
Polyphosphoryl chlorides are strongly acidic being similar in properties to acid chlorides. In air, they give fumes of HCl due to their interaction with moisture. They act as good chlorinating agents in organic reactions.



Vitreous Polyphosphates (Phosphate Glasses). In vitreous polyphosphates, the charges on polyphosphate anions are neutralised by the charges on cations like Na^+, K^+, etc., as shown.

Vitreous sodium polyphosphate can be readily obtained by heating $Na_4P_2O_7$ or Na_3PO_4 with P_2O_5.

The polyphosphate anions in these polymers have long straight chains. But, on an average, one P atom out of every thousand P atoms is a part of a branching unit thereby forming a cross link between the chains. These cross links, however, disappear within 12 hours when the polymer is dissolved in water or in a neutral aqueous salt solution.

Crystalline Polymetaphosphates. Insoluble crystalline poly-metaphosphates of alkali metals have been known for over 100 years. These have been synthesised by the selective condensation of disodium hydrogen pyrophosphate or its potassium analogue. By varying the experimental conditions of condensation, a number of polymetaphosphates, designated as Na(or K)PO_3–II, Na(or K)PO_3–III and Na(or K)PO_3–IV, having the same general formula ($NaPO_3$) but different properties, are isolated. The various metaphosphates, though conventionally written as monomers, are actually polymeric with the general formula $(NaPO_3)_n$.

Maddrell's Salts. Sodium polymetaphosphates $NaPO_3$–II and $NaPO_3$–III are known as Maddrell's salts. These salts are negligibly soluble in water and in saline solutions at room temperature. However, at elevated temperatures and in the presence of salts of alkali metal ions (other than Na^+ ions) and ammonium ions in solution, these metaphosphates dissolve at a higher rate. Also $NaPO_3$–II dissolves more readily than $NaPO_3$–III under the conditions mentioned above. The potassium Maddrells' salts KPO_3–II and KPO_3–III behave in a similar manner.

The X-ray studies on Maddrell's salt, $NaPO_3$–II, reveal that the polymer consists of long –P–O–P– chains made up of interconnected PO_4 groups. However, the pattern repeats itself after every three units and the chains do not spiral.

Kuroll's Salts. The polymetaphosphates Na(or K)PO_3–IV are known as Kuroll's salts. These are somewhat more soluble than the corresponding Maddrell's salts in pure water. If a Kuroll's salt is kept in ice-cold distilled water for a few days or in hot water for a few hours, its crystals swell and become gummy. Eventually they dissolve completely to give a highly viscous solution. The dissolution of sodium Kuroll's salt is greatly speeded up by the presence of salts having cations other than Na^+ ions. The potassium Kuroll's salt behaves in a similar manner.

Properties and Structures of Crystalline Polymetaphosphates. The process of dissolution of Kuroll's and Maddrell's salts in solutions of simple salts containing cations other than those appearing in the polymetaphosphate which is being dissolved, is an exchange process between cations of the salt and the cations of polymetaphosphates.

The dissolution of long chain polymeric metaphosphates in the presence of salts is due to the introduction of cations of different sizes of the salt in place of cations present in the crystal lattice of difficultly soluble metaphosphates so that the long chains of these polymers are now loosely held at their lattice positions and can be effectively removed from these positions in the aqueous medium. However, a salt containing the same cation as the one contained in the polymeric metaphosphate will not be able to cause such 'loosening' of long chains because the exchange of cations of the salt now occurs with the identical cations of the polymer. Therefore, in such a case, or in a case where no salt is added for dissolving the polymer, the latter is insoluble.

The chain phosphates exhibit optical bifringence and anisotropic electrical conductivity and both these properties increase with increase in the chain length of the polymers. The molar masses of chain polymers are extremely high (250000 to several million).

X-ray studies on rubidium Kuroll's salt reveal that its structure consists of –P–O–P– chains running in the direction of fibrous cleavage and consisting of interconnected PO_4 groups. Each unit cell contains

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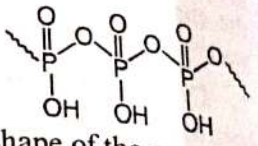
a portion of two different chains which spiral in opposite directions around the screw axis of the crystal. The pattern repeats itself after every two P atoms in the chains. Thus there are four units of $RbPO_3$ per unit cell. The P–O distances within the chains are 1·62 ± 0·03 Å and the angles O–P–O and P–O–P in the chains are 99·5° and 129°, respectively.

When potassium Kuroll's salt is dissolved in sodium chloride solution, a gummy mass is readily precipitated by the addition of alcohol to the solution. By warming the mass in alcohol-water mixture, a rubber-like solid is produced. The material bounces when dropped on a hard surface. If this material is allowed to remain in a container for some time, it flows out and adheres to the surface of the container in the form of a flexible mass called **plasticised polyphosphate**. The exposure of this mass to moist air results in the formation of powder crust due to the hydrolysis of the plasticised polyphosphate.

Polyphosphoric Acids. The polyphosphoric acids consist of long straight chains of –P–O–P– units, as shown.



The H_2O/P_2O_5 molar ratio of these amorphous solids is 1. These polyacids when put in sealed containers start flowing slowly after a few days and assume the shape of the container. The amorphous polyacids are tough and not rubber-like because of hydrogen bonding in the chains. They are highly hygroscopic and hydrolyse rapidly.

B. Phosphorus-Based Network Polymers

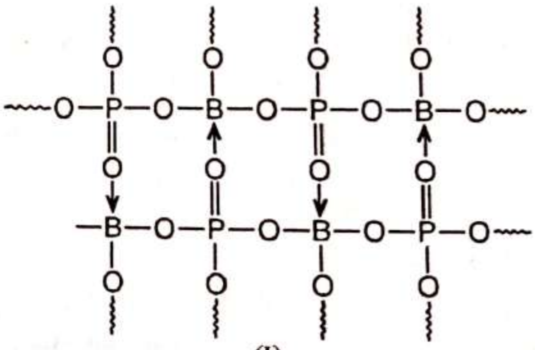
These include polymeric phosphorus pentoxide, polymeric orthophosphates of boron, aluminium and iron, sulphur-phosphorus polymers, ultraphosphate glasses, borophosphate glasses, etc.

Polymeric Phosphorus Pentoxide. Polymeric phosphorus pentoxide exists in three crystalline forms, two of which are sheet polymers and the third is a glassy material having a three-dimensional network structure. All the three forms contain P–O–P linkages. One sheet form consists of large rings containing ten P and ten O atoms each while the other sheet form consists of rings containing six P and six O atoms each.

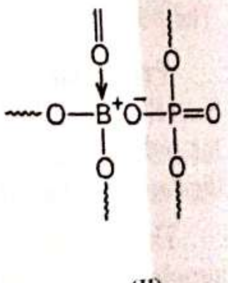
In all the three forms of polyphosphorus pentoxide, each P atom is tetrahedrally surrounded by four oxygen atoms, three oxygens being shared with adjacent PO_4 tetrahedra.

Polymeric Boron Orthophosphate, $(BPO_4)_n$. The crystal structure of boron polyphosphate is similar to that of silica. The P–O distance is 1·55 Å and B–O distance is 1·44 Å. A simplified picture of the structure (in two dimensions) is as shown.

However, the P–O and B–O distances reported above are shorter than the corresponding normal sigma bonds. Since a number of covalent structures of type I and ionic structures of type II are possible, the actual structure appears to be a resonance hybrid of the covalent structure I and the ionic structure II. Ionic structure II explains the shortening of the P–O bond due to fractional pi bond and a slight shortening of the B–O bond due to partial ionic bond.



(I)



(II)

Because of its rigid three-dimensional network structure resembling that of $(SiO_2)_x$, boron polyphosphate is unusually stable.

Polymeric aluminium orthophosphate, $(AlPO_4)_n$. Polymeric aluminium orthophosphate is similar in structure to polymeric boron orthophosphate. Like SiO_2, the polymeric aluminium phosphate also exists in several crystalline modifications.

Polymeric silver phosphate, $(Ag_3PO_4)_n$. Polymeric silver phosphate is a yellow crystalline substance in which each Ag is surrounded by four O atoms (Ag–O distance is 2·34 Å). In addition to these O atoms each Ag atom has two other Ag atoms as its neighbours (Ag–Ag distance is 3·00 Å compared to th

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distance of 2·88 Å in silver metal). As in $(BPO_4)_n$, there appears to be a fractional pi bond character in P–O bonds of PO_4 units in this case.

Polymeric ferrous phosphate, $[Fe_3(PO_4)_2.8H_2O]_n$.** In this polymer, P atoms are tetrahedrally surrounded by O atoms and Fe atoms are octahedrally surrounded by O atoms, PO_4 units and H_2O molecules. There are complex bonds of interconnected P tetrahedra and Fe octahedra extending throughout the crystal with the individual bonds apparently held together by hydrogen bonds between H_2O molecules.

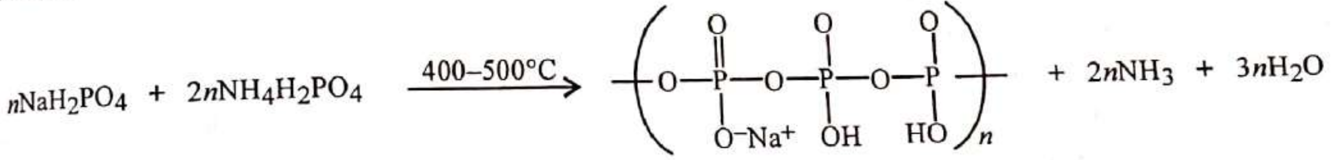
Sulphur–Phosphorus Polymers. The liquid sulphur at 160–250°C, when rapidly cooled, gets transformed into highly elastomeric form S_μ. This form contains long chains of S atoms. The S atom chains terminate into free radicals, *viz.*, $S–S_x–S$. It is known from ESR that there are, on an average, 10^5 S atoms in the chains.

The elastic properties of S_μ can be changed by the addition of a small percentage of P. The Young's modulus decreases rapidly with increasing P content. It appears that P vulcanises elastic S_μ in about the same way as S vulcanises natural rubber, *i.e.*, through cross-linking. The incorporation of ten or higher percentage of P increases the cross-linking of S_μ to such an extent that the resulting material loses elastomeric properties almost completely.

Ultraphosphate Glasses. These are amorphous polyphosphates in which the molar ratio of phosphate anion/metal cation is greater than unity. They can be considered to be derived from P_2O_5 polymer by interruption of a portion of P–O–P bonds by metal cations and hydroxy groups or from linear metaphosphates $(MPO_3)_n$ by successive substitution of pairs of M^+ ions by an oxygen cross link.

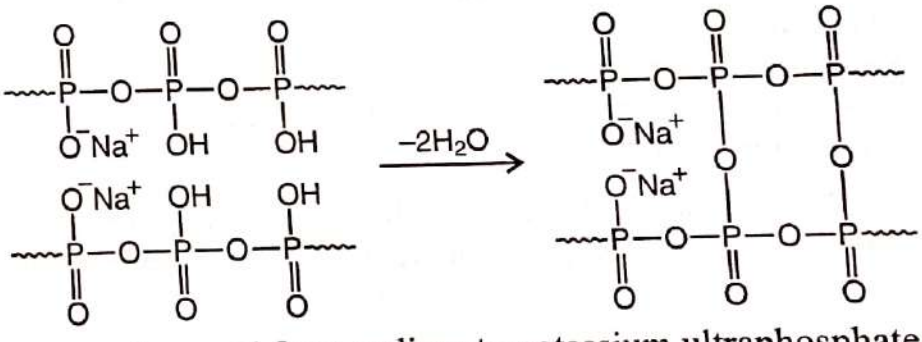
The ultraphosphate glasses resemble the glassy organic plastics in processability.

Amongst the alkali metal ultraphosphates, sodium ultraphosphate is prepared by heating a mixture of NaH_2PO_4 and H_3PO_4 or a mixture of NaH_2PO_4 and $NH_4H_2PO_4$, the molar ratio depending upon the cross link density of the polymer required. Thus, when NaH_2PO_4 and $NH_4H_2PO_4$ are heated together, polycondensation occurs to form linear polyphosphate,



$$nNaH_2PO_4 + 2nNH_4H_2PO_4 \xrightarrow{400\text{–}500°C} \left(-O-\underset{O^-Na^+}{\overset{O}{\overset{\|}{P}}}-O-\underset{OH}{\overset{O}{\overset{|}{P}}}-O-\underset{HO}{\overset{O}{\overset{|}{P}}}- \right)_n + 2nNH_3 + 3nH_2O$$

Further heating of $(NaH_2P_3O_9)_n$ formed to still higher temperatures produces cross links by removing H_2O molecules from hydroxy groups of different polyphosphate chains to yield sodium ultraphosphate, as shown.



Simple alkali metal ultraphosphates are rapidly attacked and dissolved by water. The rate of attack increases as we move from lithium to sodium and from sodium to potassium ultraphosphate. The ultraphosphate of alkaline earth metal cations are much more resistant to hydrolysis. The durability o ultraphosphates increases with cross link density. The more tightly bound the network, the more resistan is the ultraphosphate to hydrolytic attack. The durability of ultraphosphates is also strongly *p*H-dependent At lower *p*H, the rate of attack decreases as *n* increases while at higher *p*H, the reverse is true Ultraphosphates of lithium and sodium have higher Young's modulus than the ultraphosphates of bulkie cations.

The surface of an ultraphosphate glass in normal atmosphere gets covered with a very thin layer absorbed water and partially hydrolysed glass at an equilibrium concentration that depends upon th

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**Normally [illegible] used in the formulae of polymers to denote polymerising units. But, in

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humidity. This layer makes the surface non-misting, that is, when a cold glass is brought into a warmer humid atmosphere, the water vapours which condense on the glass surface form a uniform thin layer instead of discrete droplets (as happens in the case of ordinary glass) so that the vision through the ultraphosphate glass remains un-impaired.

Borophosphate Glasses. The borophosphate glasses are readily produced by melting together H_3PO_4, boric oxide and appropriate quantities of alkali metal carbonates or oxides. The optimum temperature for polycondensation is around 700°C.

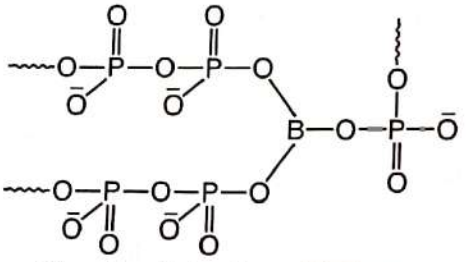
Borophosphate glasses fall in three distinct categories :

1. Those in which there is stoichiometric excess of alkali over phosphoric oxide. In this category of glasses, practically all the boron atoms are present as trigonal BO_3 groups. The fraction of four-coordinated boron atoms is less than 0·1.

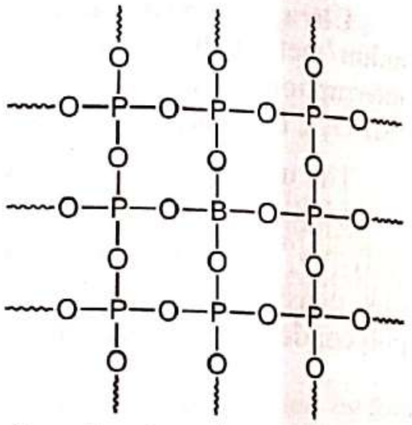
2. Those in which there is excess of phosphoric oxide over alkali. In this class, if there is less than 10 mole percentage of boric oxide, practically all the boron atoms are four-coordinated. As the proportion of boric oxide goes above 10 mole per cent, the fraction of four-coordinated boron atoms decreases rapidly and becomes one third at 33 mole per cent of B_2O_3.

3. Those in which alkali and phosphoric oxide are present in equivalent proportions (in moles). The fraction of four-coordinated boron atoms decreases steadily with increase in the content of B_2O_3, this being about one-third at low concentration of B_2O_3 and almost zero at about 47 mole per cent of B_2O_3.

The structure of borophosphate glasses with boron atoms occupying three coordination sites and four coordination sites are as shown.



Borophosphate glass with three-coordinated boron atoms.



Borophosphate glass with four-coordinated boron atoms.

For acidic borophosphate glasses, *i.e.*, when there is excess of P_2O_5 over alkali, the glass transition temperature of any chosen composition increases with continued condensation and removal of OH groups in the same way as it does with simple ultraphosphate glasses. Also there is a direct relationship between cross link density in the polymer and the glass transition temperature between 0–10 mole percentage of boric oxide.

The simple alkali borophosphates with composition around 80 mole per cent P_2O_5 and 5 mole per cent B_2O_3 dissolve fairly easily in water. The solubility, however, decreases with increase in the fraction of four-coordinated boron atoms. Borophosphate glasses containing both alkali and alkaline earth metal cations are considerably more durable than simple ultraphosphate glasses of similar compositions. The addition of 5 mole per cent B_2O_3 to an ultraphosphate polymer with composition : Li_2O 10 mole %, Na_2O 10 mole % and BaO 5 mole %, increases the durability of the resulting polymer towards running water. A number of multicomponent borophosphate glasses have been prepared which are as durable as ordinary silica glass at similar temperatures. For instance, the rate of dissolution in running water of borophosphate glass with composition : P_2O_5 55 mole %, B_2O_3 5 mole %, MgO 9 mole %, CaO 9 mole %, Li_2O 7 mole % and Na_2O 15 mole %, is as low as 5×10^{-6} mole per year at 20°C. This rate is the same as that of a reasonably durable silica glass. However, the rate of attack by water on borophosphate glasses increases with increase in temperature much more rapidly than on silica glass.

As happens in the case of ultraphosphate glasses, the water vapours on borophosphate glasses condense in the form of a thin layer and not in the form of minute water droplets. The visibility through borophosphate glasses is thus not impaired. This is the reason why these glasses are ideal for the manufacture of spectacles and other lenses.

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Applications of Phosphorus-Based Polymers. 1. The long chain vitreous sodium phosphate polymers are employed in food processing industry. Their use in this industry is based on the interaction of phosphates with proteins.

2. The short chain vitreous phosphate polymers are used for deflocculation of proteins.
3. The potassium Kuroll's salt is employed in the manufacture of sausages to prevent water loss.
4. The sodium Maddrell's salt is used as a polishing agent in dental surgery.
5. The borophosphate glasses are used for manufacturing optical lenses.

II. SULPHUR-BASED POLYMERS

A large number of sulphur-based polymers are now known. These include linear chain polymers as well as network polymers. The most important linear chain polymers are polymeric sulphur and polymeric sulphur nitride. The important network polymers comprise of chalcogenide glasses. All of these are discussed below.

Polymeric Sulphur

It is prepared by heating rhombic sulphur (S_8) to 165–180°C and then suddenly cooling the melt in ice bath. The cyclic S_8 structure of rhombic sulphur opens up to produce $\cdot S{-}(S)_6{-}S\cdot$ radical which recombines with S_8 unit to produce $\cdot S{-}(S)_{14}{-}S\cdot$ radical which further combines with S_8 unit and so on, as illustrated below :

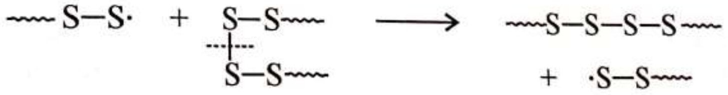
$$\cdot S{-}(S)_6{-}S\cdot \;+\; S_8 \xrightleftharpoons{165\text{–}180^\circ C} \cdot S{-}(S)_{14}{-}S\cdot$$

$$\cdot S{-}(S)_{14}{-}S\cdot \;+\; S_8 \rightleftharpoons \cdot S{-}(S)_{22}{-}S\cdot \text{ and so on}$$

{$(S)_6$, $(S)_{14}$, $(S)_{22}$, etc., are actually zigzag chains of 6, 14, 22, etc., of sulphur atoms, respectively.}

The final product is washed with carbon disulphide to remove the traces of S_8 rhombic sulphur.

The pure polymeric sulphur has a glass transition temperature of 75°C. Above this temperature, the sulphur chains undergo dissociation and re-association, as shown below :



$$\sim\!S{-}S\cdot \;+\; \begin{array}{l} S{-}S\sim \\ \vdots \\ S{-}S\sim \end{array} \longrightarrow \begin{array}{l} \sim S{-}S{-}S{-}S\sim \\ +\;\cdot S{-}S\sim \end{array}$$

At temperatures below the melting point of sulphur, *viz*., 114°C, the polymeric sulphur is unstable and reverts back to rhombic sulphur, S_8. The transition from polymeric sulphur to rhombic sulphur is facilitated by the presence of S_8 in the polymer. The removal of S_8 by washing the polymer with carbon disulphide slows down the transition.

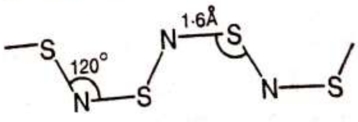
Polymeric Sulphur Nitride, $(SN)_n$

Polymeric sulphur nitride was first prepared in 1910 by Burt by passing vapours of S_4N_4 over silver gauze or silica wool at 100–300° C. In 1973, Labes and coworkers synthesised crystalline polymeric sulphur nitride in the form of bundles of fibres and found that the material possesses metallic conductivity in a direction parallel to the length of the fibre.

Pure $(SN)_n$ can be prepared by passing S_4N_4 vapour over silver wool at 220° C. The gaseous S_2N_2 formed is condensed to solid state by passing through a liquid nitrogen-cooled trap. It is then sublimed into an ice-cooled trap from which it is slowly allowed to warm upto the room temperature. The S_2N_2 during this process of slow warming, gets polymerised to $(SN)_n$.

Polymeric sulphur nitride consists of layers of fibres stacked parallel to one another. The polymer shows metallic conductivity and metallic ductility. It is soft and malleable. The polymer is slowly attacked by moisture when exposed to it for several months. It decomposes in vacuum at 140° C to give sulphur and nitrogen.

The structure of the polymer comprises of nearly planar chains of S–N bonds of approximately the same length (1·6 Å). The structure of a portion of the polymer is as shown.



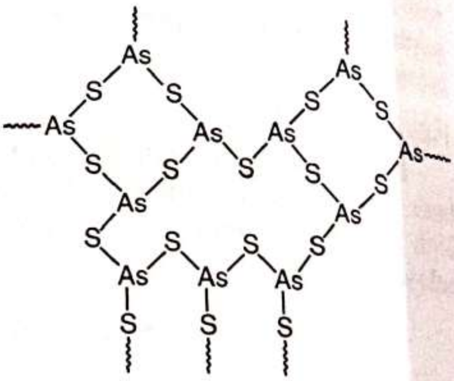
The electrical conductivity of the polymer $(SN)_n$ is in the range of 1200–3700 S cm^{-1} and increases 50–200 times when the temperature is lowered to 4·2 K. It has been found recently that the polymer becomes a superconductor at 0·26 K. The polymer is the first example of a non-metallic superconductor.

Chalcogenide Glasses

The chalcogenide glasses are a family of amorphous cross-linked polymers formed by compounds of chalcogens (S, Se, Te) with one or more of the polyvalent elements such as antimony, arsenic, bismuth, germanium, indium, phosphorus, tin and thalium. While the best known two-component chalcogenide glass is $(As_2S_3)_n$, there are many multicomponent chalcogenide systems like Si–P–Te, Si–Sb–Te, Ge–P–Se, Si–Sb–S and As–Ge–Si–Te. The chalcogenide glass $(As_2Pb_3S_8)_n$ occurs as such in nature.

Chalcogenide polymers are generally prepared by the fusion of the elements under conditions selected for minimising oxidation and loss of volatilisation of the components.

The X-ray studies reveal that chalcogenide glasses consist of short chains of chalcogen atoms linked together by polyvalent atoms which serve as branching and cross-linking sites. Thus, the parent network of As, Sb, P chalcogenides, is a triple-connected assembly of As, Sb or P atoms linked through S, Se or Te atoms. A typical As–S polymer network is as shown :



These polymers resemble organic polymers. Compared to inorganic polymers such as ultraphosphate and borophosphate glasses, these polymers have lower softening points, higher refractive indices and lower tensile strengths.

Chalcogenide glasses are fairly stable to acids but are attacked by concentrated alkalies. Most of the polymers begin to oxidise in air at about 3000° C. But some of these polymers can be distilled in vacuum without showing any sign of decomposition – a property most unlikely of polymers. This happens because of the dissociation of polymeric network into small fragments in vapour phase in vacuum which recombine spontaneously when the vapours condense. The glass transition temperatures of As and Ge chalcogenides increase linearly with As or Ge content of the glass. In the range of 5–15 mole % As and 3–8 mole % Ge, the chalcogenide glasses show distinct rubbery properties although over a small range of temperature. In this respect the chalcogenide polymers differ markedly from the oxide glasses (*e.g.,* borate, phosphate and silica glasses) which do not exhibit rubber-like properties in any temperature range.

Chalcogenide glasses are deeply coloured. However, most of them are good infrared transmitting materials and have been used for the fabrication of IR windows for army and civil optical devices.

Switching Phenomenon in Chalcogenide Glasses. The chalcogenide glasses undergo reversible change from low conductivity to high conductivity state under applied voltage. This phenomenon is known as **'switching.'** It can occur in two forms, *viz.,* threshold switching and memory switching.

In **threshold switching**, the chalcogenide glass maintains a high resistance until a certain threshold voltage gradient (*i.e.,* 10^4 volts/cm) is reached. At this voltage gradient the chalcogenide glass changes suddenly into a low resistance state which has about a thousand-fold greater conductivity than the state prior to the application of threshold voltage. The chalcogenide glass continues to remain in this high conductivity state as long as a certain minimum current (called 'holding current') is maintained. If the current falls below the holding current value, the chalcogenide glass returns to the high resistance state once again.

In the **memory switching**, the chalcogenide glass exhibits a high resistance until a threshold voltage gradient is exceeded. At this stage, the chalcogenide glass suddenly changes into a high conductivity state. The material then remains in this condition even after the current is switched off. It can, however, return to high resistance state by passing a short current pulse that exceeds the original threshold voltage gradient.

The switching phenomenon is probably due to the fact that the current of high voltage causes decomposition of bonds in the chalcogenide glass so that when the voltage gradient becomes high

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enough, a conducting path within the glass is produced. A detailed discussion of switching is, however, beyond the scope of the book.

Some of the chalcogenide glasses are used for infrared transparent windows in civil and military devices.

The chalcogenide glasses have a great potential for their use in ultrasonic delay lines, high energy particle detector multipliers, memory devices for computers, electroluminiscent displays, etc.

III. BORON-BASED POLYMERS

Boron-based polymers constitute an important class of inorganic polymers. Amongst these the most important ones are polycarboranes and polymeric boron nitride.

1. Polycarboranes

These are mainly linear polymers in which meta or para carboranes are linked through a variety of hetero atom bridges such as P–O–P.

When acetylene is added to decacarborane, $B_{10}H_{10}$, it forms a closed icosahedral molecule $C_2B_{10}H_{12}$ with a diameter of about 4·0 Å in which the two carbon atoms are adjacent to each other. This product is named ortho (or 1,2)-dicarbaclosododecacarborane.

$$\underset{\text{Decaborane}}{B_{10}H_{10}} + C_2H_2 \longrightarrow \underset{\substack{\text{Ortho dicarbocloso}\\ \text{dodecacarborane}}}{C_2B_{10}H_{12}}$$

When the ortho product is heated to 475°C, it undergoes an intramolecular rearrangement to give the isomeric meta carborane in which the two carbon atoms are separated by one boron atom. On further heating above 630° C, the material isomerises to para carborane in which the carbon atoms lie at opposite vertices of the cage. The skeletal structures of ortho, meta and para carboranes are shown in Fig 1.

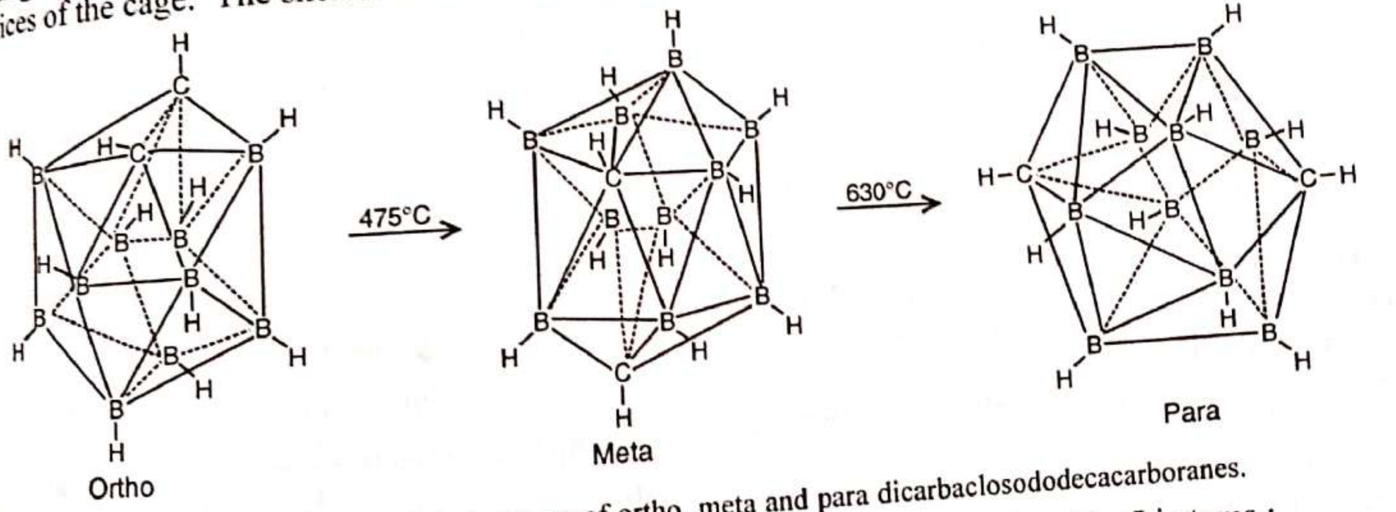
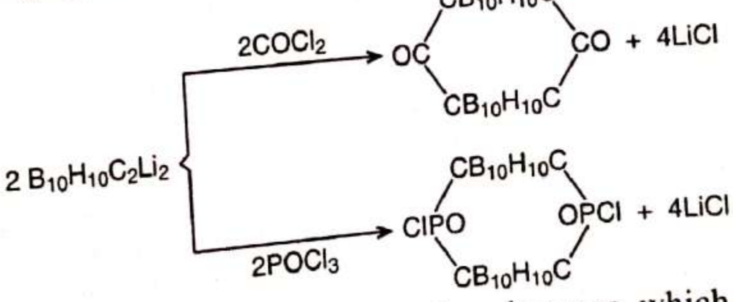


Fig. 1. The skeletal structures of ortho, meta and para dicarbaclosododecacarboranes.

In these compounds, the H atoms attached to C atoms can be easily replaced by Li atoms :

$$C_2B_{10}H_{12} + 2Li \longrightarrow C_2B_{10}H_{10}Li_2 + H_2$$

The dilithium salts of ortho, meta and para carboranes then easily react with halogen-containing compounds such as $COCl_2$, $POCl_3$, etc., to give cyclic or linear polycarboranes.



The main products in the reaction of ortho $C_2B_{10}H_{10}Li_2$ with halogen compounds are cyclic polymers, as shown.

The lithium derivatives of meta and para carboranes give rise to linear polycarboranes which, however, do not contain more than five repeat units. In other words, these polycarboranes are only low molar mass polymers.

The lithium derivatives of meta and para carboranes react with $(CH_3)_2SnCl_2$ to give crystalline polymers of reasonable chain lengths containing 20–30 repeat units.

$$nLi_2C_2B_{10}H_{10} + n(CH_3)_2SnCl_2 \longrightarrow -\!\!\left[CB_{10}H_{10}CSn(CH_3)_2\right]\!\!-_n + 2nLiCl$$

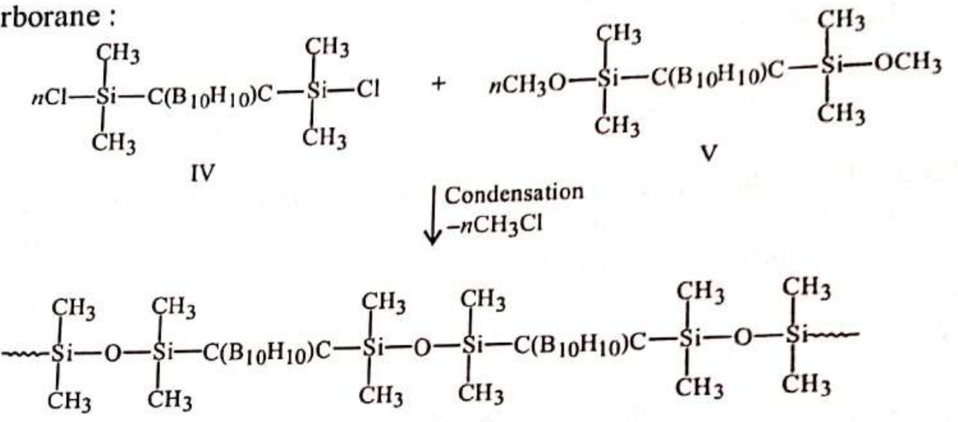
The most interesting polycarboranes are those in which the carboranes are bound by **polysiloxane bridges**. If meta $Li_2C_2B_{10}H_{10}$ is made to react with $(CH_3)_2SiCl_2$, it produces $ClSi(CH_3)_2C(B_{10}H_{10}CSi(CH_3)_2Cl$, as shown below :

$$\underset{\substack{\text{(meta)}\\ \text{III}}}{LiCB_{10}H_{10}CLi} + 2(CH_3)_2SiCl_2 \longrightarrow \underset{\substack{\text{(meta)}\\ \text{IV}}}{ClSi(CH_3)_2C(B_{10}H_{10})CSi(CH_3)_2Cl} + 2LiCl$$

The product IV is then reacted with methanol to give the methoxy derivative:

$$\text{IV (meta)} + CH_3OH \longrightarrow \underset{\text{V (meta)}}{CH_3OSi(CH_3)_2C(B_{10}H_{10})CSi(CH_3)_2OCH_3}$$

Compounds IV and V then condense at 140°C in the presence of ferric chloride (catalyst) to yield the long chain polycarborane :



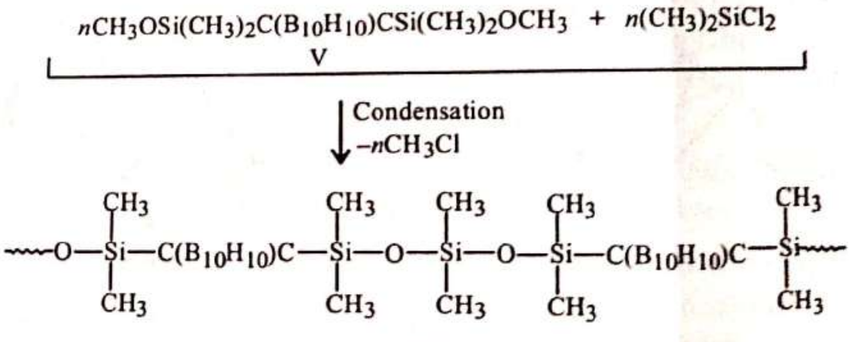
$$n\,Cl{-}Si(CH_3)_2{-}C(B_{10}H_{10})C{-}Si(CH_3)_2{-}Cl\ (\text{IV}) + n\,CH_3O{-}Si(CH_3)_2{-}C(B_{10}H_{10})C{-}Si(CH_3)_2{-}OCH_3\ (\text{V}) \xrightarrow[-nCH_3Cl]{\text{Condensation}} \sim Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}C(B_{10}H_{10})C{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}C(B_{10}H_{10})C{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2\sim$$

Long chain polymer
VI

A similar polymer is obtained if dilithium para carborane is taken in place of dilithium meta carborane.

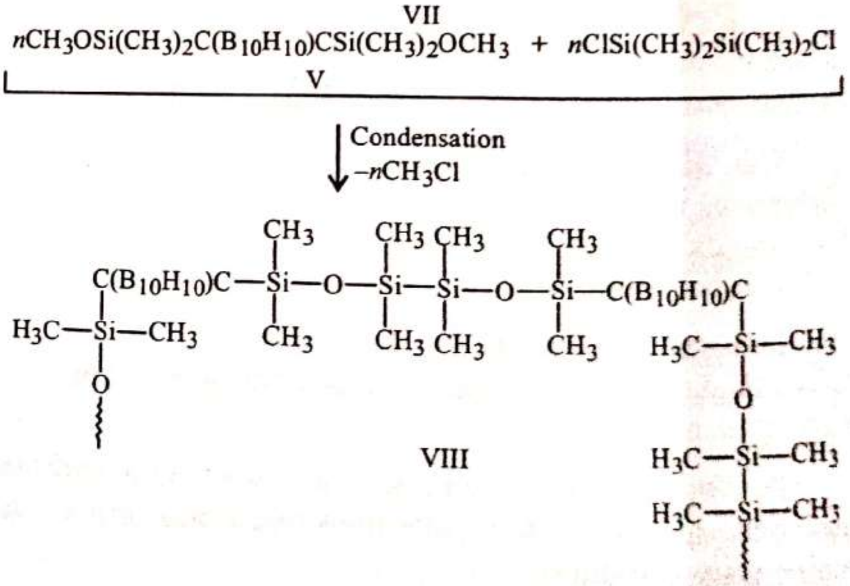
The reactions of compound V (meta or para) with $(CH_3)_2SiCl_2$ as also with $ClSi(CH_3)_2Si(CH_3)_2Cl$ produce long chain polymers VII and VIII having structures similar to that of VI, as shown.

All polycarboranes containing Si–O–Si linkages are partially crystalline elastomers whose glass transition temperatures decrease with increasing number of Si atoms in the linking groups. To make these elastomers useful as rubbers, a small quantity of 1-venyl 2-methyldichloro 1,2 dicarbaclosododecacarborane is added to the condensation reaction. The resulting elastomer is cross-linked with peroxide initiators. The properties of the cross-linked material as rubber can be further improved by compounding it with finely divided silica fillers. The final product is stable upto 260°C. However, its oxidative decomposition begins at about 300° C. This puts a limitation to their use at high temperatures.



$$\underbrace{nCH_3OSi(CH_3)_2C(B_{10}H_{10})CSi(CH_3)_2OCH_3}_{\text{V}} + n(CH_3)_2SiCl_2 \xrightarrow[-nCH_3Cl]{\text{Condensation}} \sim O{-}Si(CH_3)_2{-}C(B_{10}H_{10})C{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}C(B_{10}H_{10})C{-}Si(CH_3)_2\sim$$

VII



$$\underbrace{nCH_3OSi(CH_3)_2C(B_{10}H_{10})CSi(CH_3)_2OCH_3}_{\text{V}} + nClSi(CH_3)_2Si(CH_3)_2Cl \xrightarrow[-nCH_3Cl]{\text{Condensation}} \sim O{-}Si(CH_3)_2{-}C(B_{10}H_{10})C{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}C(B_{10}H_{10})C{-}Si(CH_3)_2{-}O{-}Si(CH_3)_2{-}Si(CH_3)_2\sim$$

VIII

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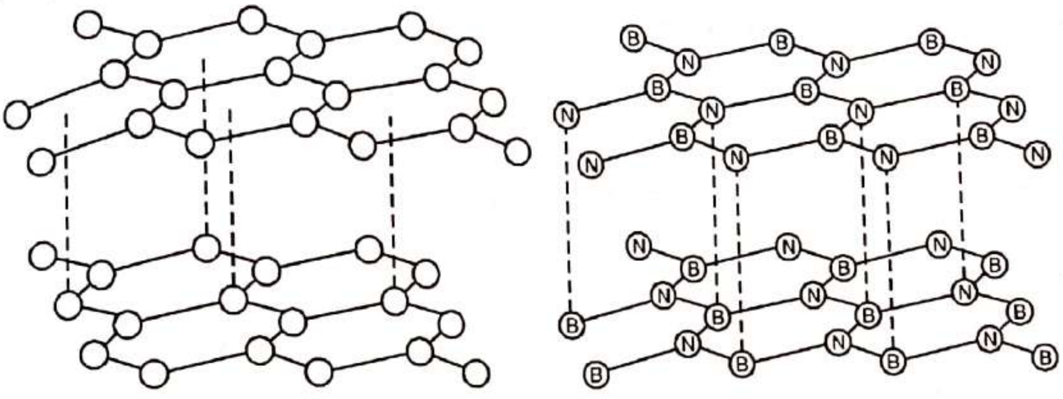
Polymeric Boron Nitride

The polymeric boron nitride, $(BN)_n$, exists in two forms, *i.e.*, as a layer polymer and as a three-dimensional network polymer.

Layer Polymer. This form resembles graphite and was first discovered by Balmain in 1842. It can be obtained by a variety of methods. A common method involves heating of boric acid with urea in an atmosphere of nitrogen at 600° C followed by the treatment of the product with ammonia at 950° C. The final product is an amorphous powder.

The structure of boron nitride resembles that of graphite. It thus consists of infinite sheets of six-membered rings of alternating boron and nitrogen atoms stacked in layers. There is, however, an important difference between the structure of polymeric boron nitride and graphite. In boron nitride, the sheets are stacked over one another in such a manner that the atoms in each successive layer are directly superimposed whereas in graphite, the atoms in one layer lie opposite to the centres of the six-membered rings in the next layer, as shown in Fig. 2.



Graphite

Boron nitride.

Fig. 2. Layer structures of graphite and boron nitride.

The crystallographic unit cell constants of boron nitride are very similar to those of graphite, the B–N distance in $(BN)_n$ being 1·45 Å compared to C–C distance of 1·42 Å in graphite. The interlayer separation in $(BN)_n$ is 3·3 Å compared to 3·5 Å in graphite.

There is, however, a distinct difference between the two polymers. Unlike graphite, the polymeric boron nitride is an electrical insulator. This is because the nitrogen atom in one layer of $(BN)_n$ is always adjacent to a boron atom so that the lone pair of electrons on each N atom in a layer is bound to the electron-deficient B atom of the adjacent layer. In other words, the electrons in boron nitride are highly localised making the polymer non-conducting.

Boron nitride is soft like graphite and can be easily machined. The articles fabricated from this polymer, either by sintering or by machining, can be safely exposed to atmosphere upto a temperature of about 800°C. The melting point of polymeric boron nitride (under an atmosphere of nitrogen) is about 3000° C.

Three-Dimensional Network Polymer. If the layer form of polymeric $(BN)_n$ is heated at 1500–2000°C under extremely high pressure in the presence of a catalyst, it gets converted into a three-dimensional network polymeric form. This form is isomorphic with diamond and is comparable with the latter in hardness. It is, therefore, used as a substitute for diamond in jewellery as also for the fabrication of cutting tools. It shows signs of surface oxidation in air around 200°C.

IV. SILICON-BASED POLYMERS

Silicon-based polymers constitute the most important class of inorganic polymers. These include organopolysiloxanes, commonly known as **silicones.**

Organosilicones or Organopolysiloxanes

Organosilicon polymers have been described briefly in Chapter 16. However, since these polymers constitute an important class of inorganic polymers, it would be pertinent to describe them in some more details alongwith other inorganic polymers.

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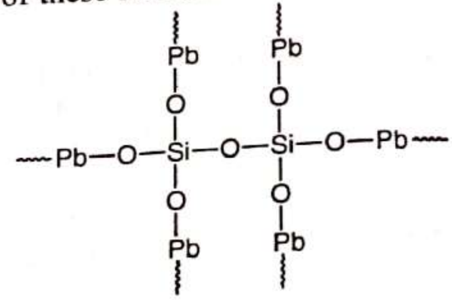
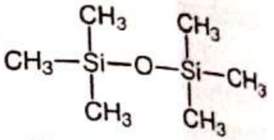
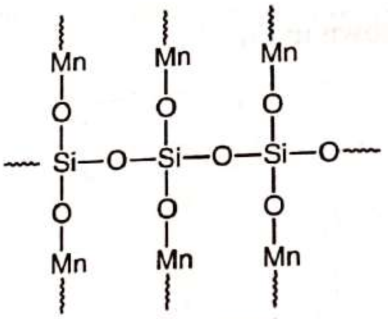
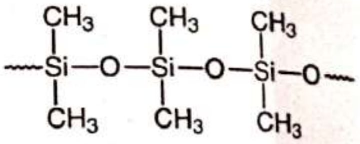
The chemical constitution of organosilicones can be represented as $(R_xSiO_{2-x/2})_n$ where n is very large while x varies from 0 to 4. On one extreme of these silicones is silica (x=0) which is an inorganic polymer and on the other extreme is tetraorganosilane (x=4) which is an organometallic compound and is monomeric, *e.g.*, $(CH_3)_4Si$. In between x=0 and x=4 are the polymeric silicones which can be categorised both as organic as well as inorganic polymers. These polymers resemble inorganic polymers in having a high percentage of ionic character of Si–O bonds and they resemble organic polymers in having organic groups on silicon atoms.


Barysilite mineral

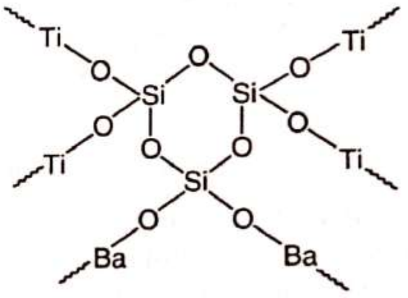

Hexamethyl disiloxane

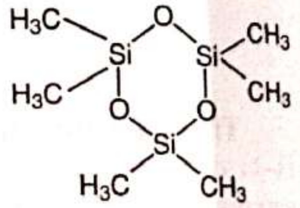
Organosilicon polymers contain chains or network of alternating silicon and oxygen atoms in their structures, that is, they have polysiloxane structure exhibited by some natural silicon minerals such as barysilite, rhodonite, benitoite, as shown.


Rhodonite mineral


Polydimethyl siloxane

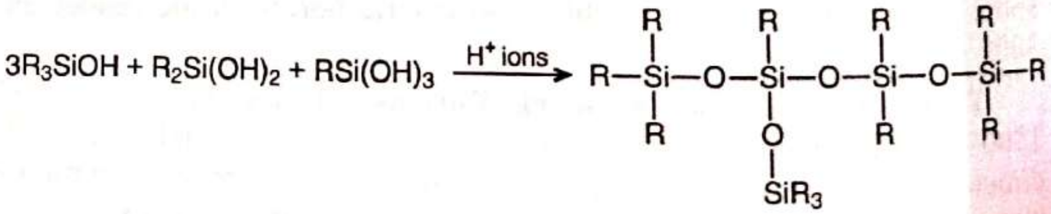
But, whereas the polysiloxane structures in natural silicon minerals are cross-linked through metaloxy groups, the polysiloxane structures of the corresponding siloxanes contain non-bridging alkyl (*e.g.*, CH_3) groups on silicon atoms. There is thus no cross linking. The polymeric molecules in silicones are held together by weak van der Waals forces with the result that the silicones are either liquids of varying viscosity or gums or solids containing polymeric molecules which are generally soluble in organic media.

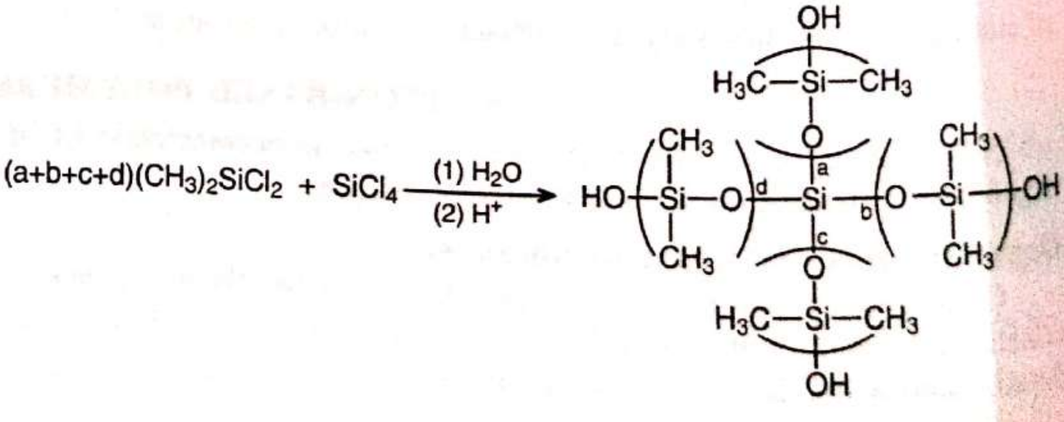

Benitoite mineral


Hexamethylcyclotrisiloxane

The physical properties and the usefulness of organopolysiloxanes (silicones) are determined by the kind and the number of organic groups present on each silicon atom as well as by the manner in which the silane units are hooked together. For example, whereas CH_3 groups on silicon promote fluidity, low viscosity, low melting point and high liquid compressibility, the phenyl groups on silicon induce the contrasting properties in the silicones. The number of organic groups on silicon establishes the functionality of individual siloxane building units and thereby controls the linearity or complexity of polysiloxanes.

Preparation of Silicones. The preparation of organosilicones by the condensation of silanols has already been described in Chapter 16. The condensation of dihydroxy silanes (which are obtained by the hydrolysis of dichlorosilanes) yields linear polymers. Chain branching in silicones is introduced by condensation of tri and/or tetrafunctional silanols with other silanols in the catalytic presence of H^+ ions, as shown.





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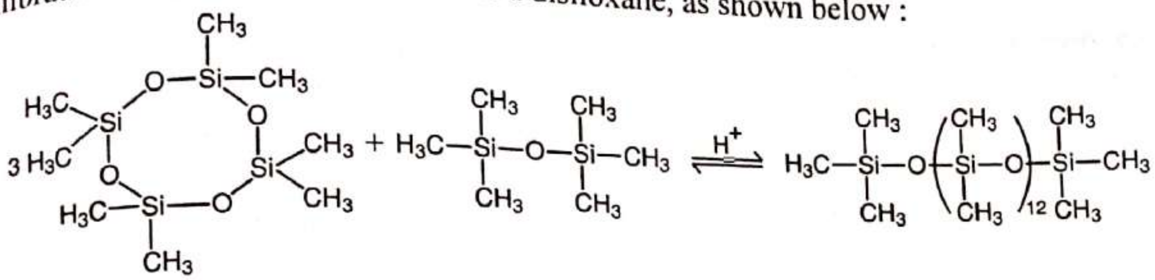
A general method for preparing straight chain silicones involves the opening up of appropriate cyclic polysiloxanes by heating them alone or with di or trisilanes in the catalytic presence of an acid or a base. The process ends in a thermodynamic equilibrium between the reactants and the products which consist of simple or mixed siloxanes depending upon the nature of the reactants. This process is known as equilibration of cyclopolysiloxanes.

A brief description of various types of silicones is given below.

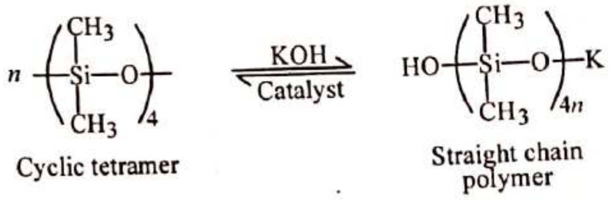
1. Fluid or Liquid Polysiloxanes. These are low molar mass straight chain polymers which are obtained by the equilibration of cyclopolysiloxanes with a disiloxane, as shown below :



These polysiloxanes can also be prepared by the hydrolysis of dichlorosilanes, as already discussed in Chapter 16.

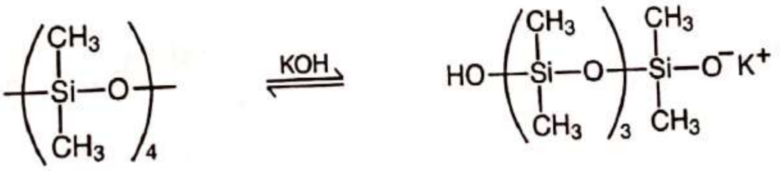
Uses. Liquid polysiloxanes are used as insulators in electrical appliances. They are also used as lubricants since they do not become viscous even at very low temperatures. Because of their adequate stability and high boiling points, they are used in vacuum pumps and high temperature oil baths.

2. High Polymer Organosiloxanes or Polysiloxane Gums. Polysiloxane gums which are high molar mass organosiloxanes can be prepared by equilibration of cyclic siloxanes in the absence of monofunctional groups. The resulting straight chain polymers are end-blocked by the catalyst, as shown.

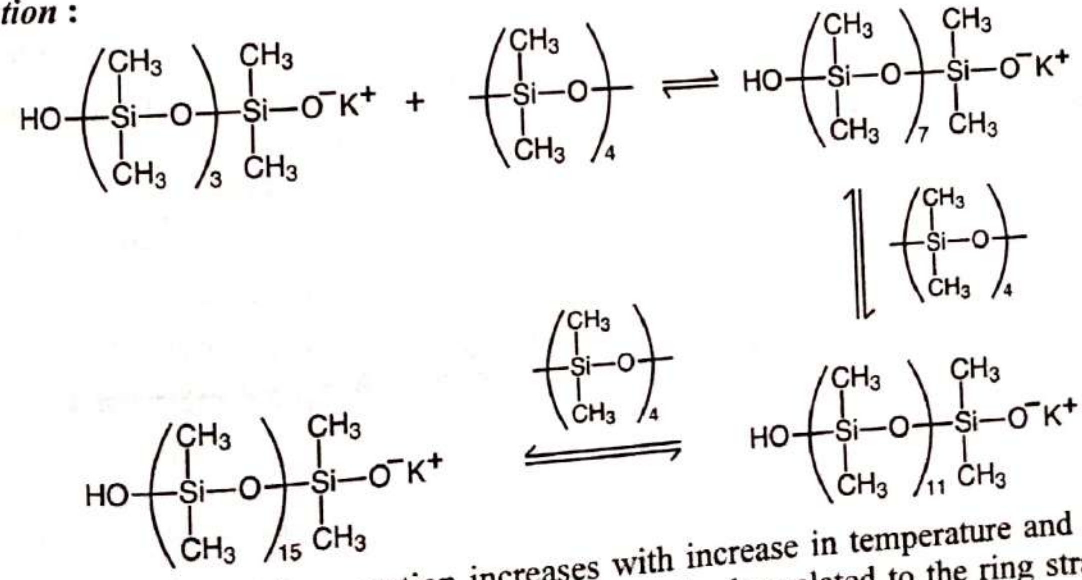


The above reaction is supposed to take place through the following steps :

Initial step **:**



Condensation **:**



The rate of the polymerisation reaction increases with increase in temperature and is related to the square root of the concentration of the cyclic tetramer. It is also related to the ring strain in the cyclic polymer taken for equilibration. Thus, cyclic hexamer is more easily equilibrated than cyclic tetramer.

The average molar mass of the polymer obtained is independent of temperature and varies inversely with the concentration of the catalyst. The molar mass of hydroxy end-blocked gums can be increased further by azeotropic removal of water with toluene or by heating the polymer under vacuum. Catalysts such as amine salts or some metal salts also increase the average molar mass.

Polysiloxane gums are used as lubricants and as antifoams. They are also used in textile finishing.

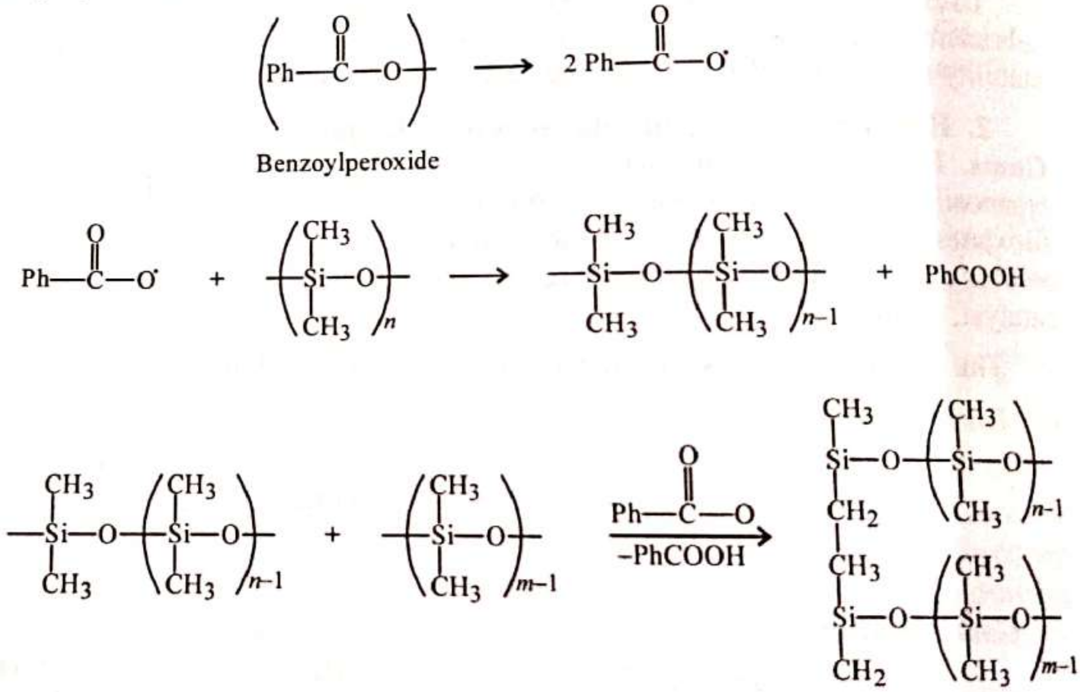
3. Silicone Rubber or Elastomers. Preparation of silicon rubbers involves two steps, *viz.*, *compounding* and *cross linking*.

Compounding. It consists of milling (or mixing under high pressure) of polysiloxane gum, a filler and a cross-linking agent together with certain additives to obtain desired physical properties. A typical formulation comprises of 100 parts of benzene-soluble polysiloxane gum, 20–50 parts of SiO_2 as filler, 6 parts of benzoyl peroxide as vulcanising agent and suitable amounts of additives.

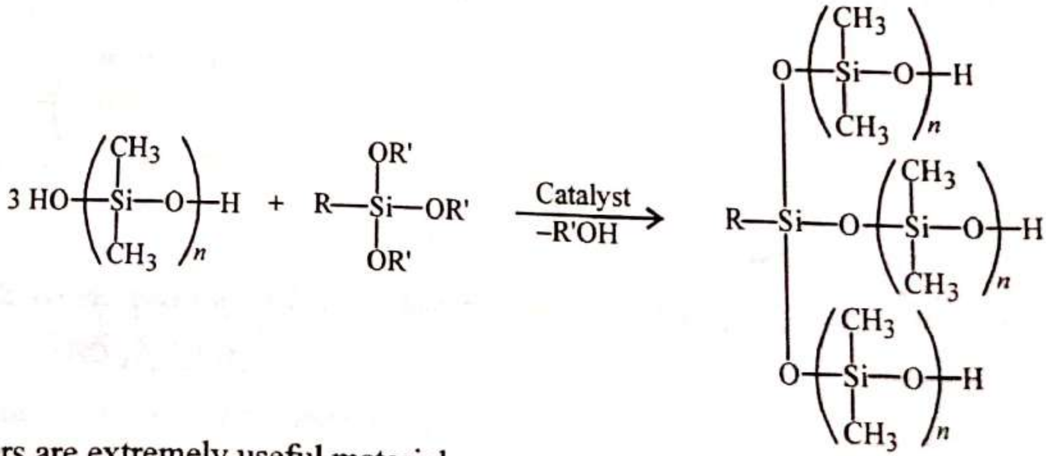
Cross Linking. This step involves the cross-linking and curing processes which connect polymer molecules with one another so that it becomes an elastomer of desired properties.

The polysiloxane gum required for making silicone rubber should be a linear polymer of high molar mass since the tensile strength of the elastomer increases with increase in the size of the gum polymer. Fillers are added to reinforce the polysiloxane gum which, in itself, is soft and weak. Silica, which is used as a filler, is in a very fine state of subdivision. It is prepared by the action of HCl on Na_2SiO_3 or by the hydrolysis of $SiCl_4$.

Cross linking is achieved by the addition of several reagents, the most common of which are benzoyl peroxide, 2,4-dichlorobenzoylperoxide or tertiary butyl perbenzoate. The vulcanising temperature ranges between 120° and 130° C when the cross-linking agent is benzoyl peroxide. The mechanism of cross linking step is as shown.


Benzoylperoxide

Cross linking or vulcanisation can be affected even at room temperature if the process is carried out in the presence of catalysts such as organotin or organ o lead compounds, as shown below :



Silicone rubbers are extremely useful materials on account of their high thermal stability, low temperatu performance, reluctance towards oxidation, chemical stability, water repelling power and flexibility.

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4. Silicon Resins. Silicone resins contain ring structures and have a much higher cross link density than is found in silicone elastomers. In a stretched elastomer, the molecular chains uncoil through rotation about the –Si–O– bonds. In a resin, such rotation is highly restricted and the response to stress occurs largely through bending and stretching of bonds. The properties of resins are a function of R/Si ratio where R is alkyl group. As the R/Si ratio is lowered from 2·0 to 1·0, the polymers become progressively less fluid, less soluble and less fusible. Most of the resins have R/Si ratio between 1·00 and 1·6 and their properties are intermediate between those of fluid silicones and those expected of a highly cross-linked structure with R/Si ratio equal to 1·00.

For the preparation of silicone resins, a mixture of chlorosilanes such as CH_3SiCl_3, $(CH_3)_2SiCl_2$, $C_6H_5SiCl_3$, $(C_6H_5)_2SiCl_2$, $C_6H_5(CH_3)SiCl_2$ are first hydrolysed. During hydrolytic reaction, about 90 per cent of silanol groups (*i.e.*, Si–OH groups) condense to form siloxane linkages. In this process of random condensation, some ring closure invariably occurs because of extreme flexibility of Si–O–Si chains. The remaining 10 per cent of silanol groups condense more slowly and with increasing difficulty because fewer fruitful molecular collisions can now occur since the increasing viscosity renders molecular motion slow. Also, with the growing size of the polymer, the remaining hydroxy groups get fixed in the network too far apart to get condensed with one another.

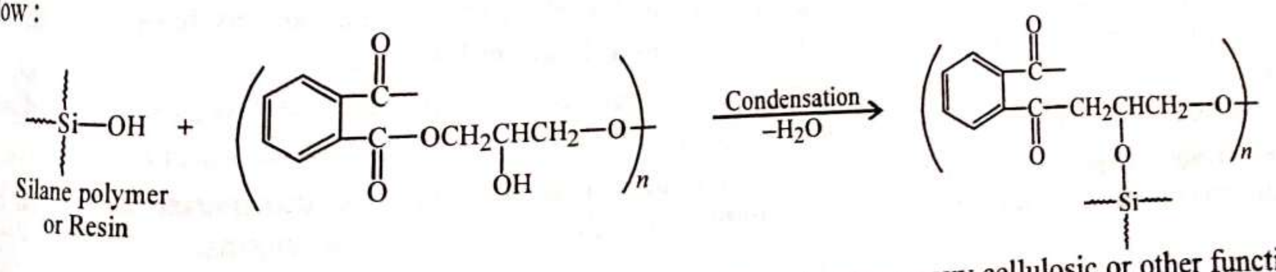
After hydrolysis the product is shaken with an organic solvent and the organic layer is separated. This organic layer is then washed thoroughly to remove the Cl^- ions in order to check the reversibility of the hydrolytic reaction.

The silanol groups (*i.e.,* Si–OH) left uncondensed in the finished resin impart typical properties to the resin. These groups contribute towards viscosity of the product which is an important property that determines the usefulness of a resin. For instance, the viscosity of resin used for laminating purposes should be relatively low so that it may impregnate the glass fibres better. The silanol groups also determine the shelf life of the resin. The resins, on storage, constantly go on condensing and cross-linking depending upon temperature. This type of condensation is extremely slow in solid resins, slow in concentrated solutions and fast in dilute solutions.

Final curing of the resin involves further reaction of the residual silanol groups. The ultimate condensation of these silanol groups occurs after the resin is applied. This process can be hastened by heating the resin in the presence of a suitable catalyst. The most common catalysts are metal salts of organic acids such as naphthalates of cobalt, zinc, lead and tin.

The nature of the substituents on Si alters the characteristics of the resin. For example, while CH_3 groups give flexibility, C_2H_5, C_3H_7, etc., groups make the resin softer, increase its solubility in organic solvents and increase its water-repellence. The phenyl groups increase resistance towards heat and so on.

Copolymeric resins of desired properties can be obtained by condensing two polymers, as shown below :



The silicon resins can be copolymerised with phenolic polyester, epoxy cellulosic or other functional resins. The properties of these copolymeric resins depend upon the nature of the condensing polymers and the degree of condensation.

Uses. Silicon resins are used as electrical insulators. They are also used for coatings on metals, for lamination purposes and for coating cooking pans, etc.

Properties of Silicones. Some characteristic properties of silicones are discussed below.

1. Thermal stability. The Si–O–Si bond in siloxanes is shorter than the expected Si–O–Si bond as calculated from their radii. This indicates that there is some ionic character and/or partial double bond

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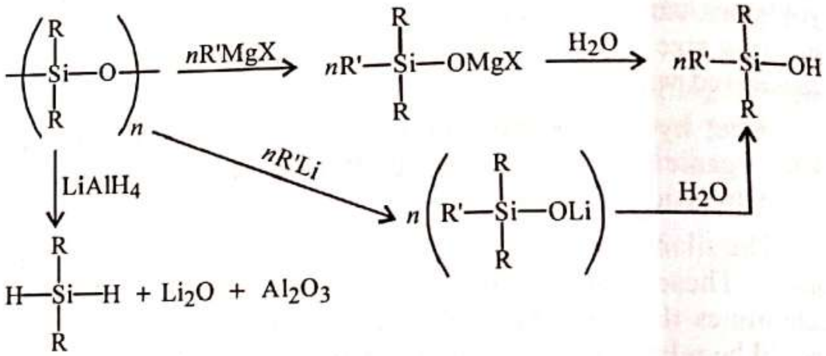
character in Si–O bond due to which it becomes quite stable. This is the reason why polysiloxanes are thermally stable and do not decompose even upto 350–400° C.

2. Chemical stability. Highly polar character of Si–O bond and the ability of Si to expand its valency shell by utilising its *d* orbitals renders polysiloxanes susceptible to attack by several reagents. Strong bases and concentrated acids may cause depolymerisation. Similarly, some electron-deficient salts may cause the cleavage of Si–O as well as the Si–C bonds. Dry chlorine attacks silicones resulting in chlorination of alkyl groups. Except for the above reactions, polysiloxanes are chemically inert. Common chemical reagents such as dilute acids and bases, metal salts, water at room temperature, H_2O_2, NH_4OH, etc., have little effect on polysiloxanes. Polysiloxanes are quite resistant to attack by oxygen. However, minor oxidation does occur above 200° C. At higher temperatures, oxidation becomes considerable when fluid polysiloxanes get cross linked through oxygen atoms to yield a rubber-like gel in a few hours. Silicon resins, being already cross linked, show much less change in viscosity with change in temperature. The presence of aromatic groups on Si atom increases the oxidative stability of the polysiloxanes.

3. Chemical reactivity. Siloxane bond can be cleaved by Grignard reagents, alkyl lithium as also by lithium aluminium hydride, as shown.



The siloxanes may undergo hydrolysis and alcoholysis at elevated temperatures in the presence of strong acids and bases to give silanols and alkoxysilanes. In general, the greater the extent of substitution on Si atom, the greater is the ease of hydrolysis in the presence of acids and the greater is the difficulty of hydrolysis in the presence of bases.

4. Properties dependent on molecular structure. Many of the observed physical properties of polysiloxanes such as compressibility, small temperature coefficient of viscosity and surface properties have been attributed largely to almost regularly coiled structure (helical structure) of polysiloxanes and weak intermolecular forces. The molecules have pronounced kinked and coiled structures at low temperatures. With increase in temperature, the kinked structure opens out which results in a greater interaction and entanglement of polymer molecules. This results in an increase in viscosity which partly compensates the normal decrease in viscosity caused by greater thermal motion of molecules due to increase in temperature. The net result of these two opposite factors is that the viscosity of polysiloxanes does not change appreciably with change in temperature.

The ability of polysiloxanes to coil, in contrast to analogous linear organic polymers or other types of polymers possessing relatively rigid structures, may be attributed to larger size of silicon atom compared to that of carbon atom. The coiling may also be facilitated by flexibility in the magnitude of Si–O–Si bond angle which can have values varying from 104° to 180° in different polysiloxanes.

Polysiloxanes are water-repellent. When glass is coated with polysiloxanes, the oxygen atoms of polysiloxanes adhere to the glass surface while the R groups on Si are directed outwards, *i.e.*, towards the air.

5. Other properties. Polysiloxanes are electrical insulators. They are transparent to visible light but absorb considerable amount of ultraviolet light, especially of shorter wave lengths.

V. COORDINATION POLYMERS

The development of coordination polymers as useful materials is still at a very primitive stage. The characterisation of these polymers is quite troublesome because of solubility problems which also hinder determination of the degree of polymerisation.

Any macromolecular species which contains coordinate covalent bonds between the metal and the ligands is termed as a **coordination polymer**. The coordination polymers are considered as inorganic polymers although a large number of ligands employed are of organic origin. If the metal to ligand distances are less than the sum of the radii of metal cation and ligand anions, it is taken as a proof of the presence of a coordinate covalent bond in the polymer.

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CHAPTER

10

METALS AND METALLURGY

Elements have been broadly divided into *metals* and *non-metals* on the basis of their physical and chemical properties. Metals have generally low ionisation energies because of which they have high electrical and thermal conductivities. They are malleable and ductile and display bright metallic lustre particularly when freshly cut. They have high tensile strength. Of the 110 elements known at present, about 70 are metals. In the present chapter, we shall study the occurrence and general methods used for the extraction of metals from their ores.

Occurrence of Metals

Metals occur in nature sometimes free but mostly in the combined state. The earth's crust is the biggest source of metals. Some soluble salts of metals are also found in sea water.

Noble metals which have little or no affinity for oxygen and which resist the attack of water and other chemical reagents, occur in the free, *i.e.,* the **native state.** Thus, metals such as silver, gold and platinum occur in nature in native state along with alluvial impurities such as clay and sand. Sometimes lumps of pure metals are also found. These are called **nuggets.**

The standard electrode potentials (*i.e.*, reduction potentials) of *noble metals* are always *positive* which means that the ions of such metals have a tendency to accept electrons and get reduced to the corresponding metals. That is why these metals occur in metallic, *i.e.*, native state.

The standard electrode potentials of *active metals*, on the other hand, are *negative* which means that these metals have a tendency to get oxidised to their ions. In other words, the ions of such metals are reluctant to get reduced to the metallic state. That is why the active metals occur in nature in the form of their compounds, *i.e.*, in the **combined state**. These compounds are known as **minerals.**

The minerals from which metals can be conveniently and economically extracted are referred to as **ores**.

Active metals occur in the form of the following categories of ores :

Sulphide ores. Metals such as iron, mercury, copper, etc., occur as their sulphides, *e.g.*, *iron pyrites* (FeS), *galena* (PbS), *cinnabar* (HgS), *copper pyrites* ($CuFeS_2$), *zinc blende* (ZnS), etc.

Oxide ores. Metals such as iron, aluminium, manganese, tin, zinc, etc., occur as their oxides, *e.g.* *haematite* (Fe_2O_3), *bauxite* ($Al_2O_3.2H_2O$), *pyrolusite* (MnO_2), *cassiterite* (SnO_2), *zincite* (ZnO), etc.

Carbonate ores. The important carbonate ores are of magnesium, iron, copper, zinc and lead, *e.g.* *magnesite* ($MgCO_3$), *dolomite* ($CaCO_3,MgCO_3$), *siderite* ($FeCO_3$), *malachite* [$Cu(OH)_2.CuCO_3$], cerussite ($PbCO_3$), calamine ($ZnCO_3$), etc.

Halide ores. Chloride ores are the most common among the halide ores. The chlorides of sodium, potassium and magnesium are found in salt beds on the surface of the earth and in sea water. *Carnallite* ($KCl.MgCl_2.6H_2O$), *rock salt* (NaCl) and *horn silver* (AgCl) are common examples of chloride ores.

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Bromides and iodides of potassium and magnesium are present in small amounts in sea water. The fluoride ores include *fluorspar* (CaF_2) and *cryolite* ($AlF_3.3NaF$).

Sulphate ores. Many sulphide ores get converted into sulphates by atmospheric oxidation. The common sulphate ores are *barytes* ($BaSO_4$), *anglesite* ($PbSO_4$), *epsomite* ($MgSO_4.7H_2O$), *anhydrite* ($CaSO_4$), etc.

Metallurgy

The process of extracting metals from their ores is called **metallurgy.** The metallurgical process would necessarily depend upon the nature of the ore which is to be worked out for the extraction of the metal. It is not possible to chalk out a universal scheme for the extraction of all metals since the extraction of each metal involves individual procedures depending upon its nature and properties. However, heavy metals such as copper, iron, zinc, lead, tin, etc., are extracted from their ores by the conventional 'Roasting and Smelting' processes. The active metals such as alkali metals, magnesium, calcium, aluminium, etc., are obtained by the electrolysis of their chlorides, oxides or hydroxides in fused state and the noble metals such as gold and silver are obtained by the amalgamation or the cyanide process.

Various Steps Involved in Metallurgical Processes. The various steps essentially involved in the extraction of pure metals from their respective ores are as follows.

1. Concentration of the Ore

Metallic ores are often found mixed with rocky material, *e.g.,* quartz, felspar, mica and other silicates. These impurities are known as **gangue**. Before the ore is subjected to metallurgical process, it is necessary to remove these unwanted impurities mechanically. This operation is known as concentration of the ore. The common methods of concentration are as follows :

a. Hand picking. Quite often, the ore is separated from the main stock in a sufficient degree of purity by simply picking it by hand and then eliminating the adhering rocky material by breaking with hammer.

b. Gravity separation. The ore can be concentrated by taking advantage of the differences in the specific gravities of metallic ore and the earthy impurities. The ore, after grinding, is washed with a running stream of water. The heavy ore settles down rapidly while the lighter earthy material (gangue) is washed away. The two common techniques of gravity separation are described below.

Hydraulic Classifier. Finely powdered ore is dropped into a conical reservoir, called *hydraulic classifier,* from the top. A powerful stream of water is introduced from the bottom of the reservoir. The gangue, being lighter, is carried away by water and the heavier ore particles accumulate at the apex of the cone. The conical shape of the reservoir helps in reducing the velocity of water and thus prevents the ore particles from being carried away along with the stream of water.

Wilfley Table. Wilfley table is a wooden table having a slanting floor on which long wooden strips called cleats or riffles are fixed. The powdered ore is suspended in a stream of water and delivered at the upper end of the table which is then given a bumping motion. The heavier ore particles are obstructed by the cleats while the lighter impurities pass over and are carried away by the stream of water. The ore particles which collect behind in the cleats move to one side as a result of the motion of the table and are collected.

c. Magnetic separation. Ferromagnetic ores, as of iron, that are affected by a magnet, are separated from the non-magnetic impurities by means of magnetic separators. A magnetic separator consists of a leather belt moving over two rollers, one of which is magnetic. The powdered ore is dropped on the belt at one end. At the other end, the magnetic portion of the ore is attracted by the magnetic roller and falls nearer to the roller while the non-magnetic impurities fall farther off.

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d. Electrostatic separation. This method is based on the fact that the particles which are good conductors of electricity become electrically charged as soon as they are brought into an electrostatic field and are consequently repelled by the electrode carrying the like charge. Lead sulphide and zinc sulphide ores which occur together in nature are separated by this technique. The mixed ore, after grinding, is fed upon a roller in a thin layer and subjected to the influence of an electrostatic field. Lead sulphide ore, being a good conductor, gets charged immediately and is thrown away from the roller due to electrical repulsion. The zinc sulphide ore which is a poor conductor is not charged and hence drops vertically from the roller.

e. Froth flotation. This process is based on the principle of *preferential wetting of solids by liquids*. Metallic sulphides, for instance, are wetted by certain oils, like pine oil, but not by water.

The finely divided ore is put in water to which a small quantity of oil (*e.g.*, pine oil) has been added. The water is agitated violently with air (Fig. 1) when froth is formed at the air–water interface. The ore which is preferentially wetted by the oil rises to the surface along with the foam while the stony matter (gangue) which is preferentially wetted by water remains in the water below the foam, as shown on the right of the figure. The foam separates out and, in due course, settles down as shown on the left of the figure. This process is known as **froth flotation process.**

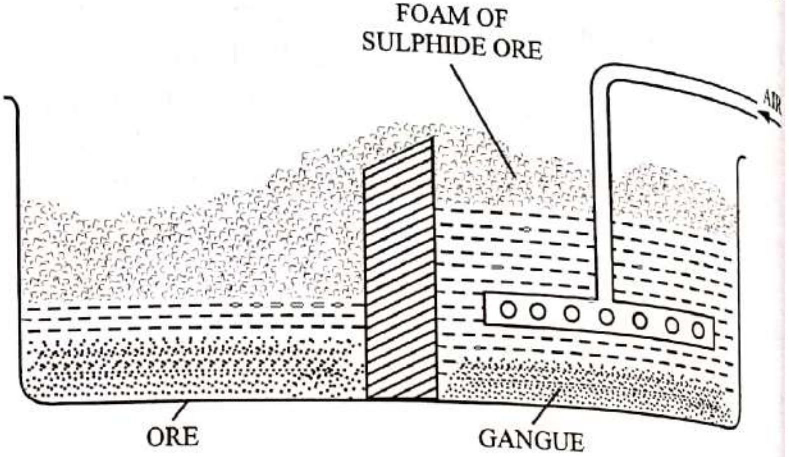

Fig. 1. Froth flotation process.

f. Leaching. This is a chemical method for the concentration of ores. In this method, the powdered ore is treated with some suitable reagent which may dissolve the ore but not the impurities. The impurities are filtered off and the ore is recovered from the solution by suitable chemical methods. For example, during the extraction of aluminium from bauxite ($Al_2O_3.2H_2O$) ore, the finely divided ore is treated with hot sodium hydroxide solution. Alumina present in the ore dissolves forming soluble sodium metaaluminate but impurities are left behind as such and are filtered off.

2. Calcination

Calcination is a process in which the ore is heated in a limited supply of air at a temperature insufficient to melt it. During calcination, organic matter, volatile impurities and moisture present in the ore are expelled and the remaining mass becomes porous. Calcination is also done to remove water from hydrated oxide ores or carbon dioxide from a carbonate ore. For example, when limestone is heated, carbon dioxide is given off and limestone is said to be calcined. When bauxite is calcined, water is removed and anhydrous alumina is left behind. Similarly, iron ores on calcination give anhydrous iron oxide. The various chemical changes are represented below :

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$Al_2O_3.2H_2O \longrightarrow Al_2O_3 + 2H_2O$$

$$2Fe_2O_3.3H_2O \longrightarrow 2Fe_2O_3 + 3H_2O$$

Calcination is generally done in a reverberatory furnace (Fig. 2). It renders the ore porous and easily workable in subsequent stages.

3. Roasting

Roasting is a wider term used to denote the process in which the ores (usually sulphide ores) either

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alone or with the addition of other materials, are subjected to the action of heat in the presence of air, at temperatures well below their melting points, in order to bring about their oxidation.

$$2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$$

$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$

Sometimes, during roasting, oxidation of sulphides takes place only upto sulphates. For example,

$$ZnS + 2O_2 \longrightarrow ZnSO_4$$

$$PbS + 2O_2 \longrightarrow PbSO_4$$

During roasting , the non-volatile impurities like sulphur, arsenic, phosphorus, etc., are removed in the form of their volatile oxides which escape as gases through the chimney.

$$S + O_2 \longrightarrow SO_2 \uparrow$$

$$4As + 3O_2 \longrightarrow 2As_2O_3 \uparrow$$

$$P_4 + 5O_2 \longrightarrow 2P_2O_5 \uparrow$$

Roasting is carried out either in a reverberatory furnace or in a blast furnace. In a reverberatory furnace (Fig. 2), the charge is placed on the hearth and heated by the flames deflected from its roof. The reverberatory furnace is used in roasting the ores of copper, tin, lead, etc.

Blast furnace is a long vertical furnace (Fig. 3), made of steel plates, lined inside with fire–clay bricks. It is provided with an arrangement for blowing in air near the base, as shown in the figure. It is also provided with a hole for removing the slag and a tapping hole for taking out the metal.

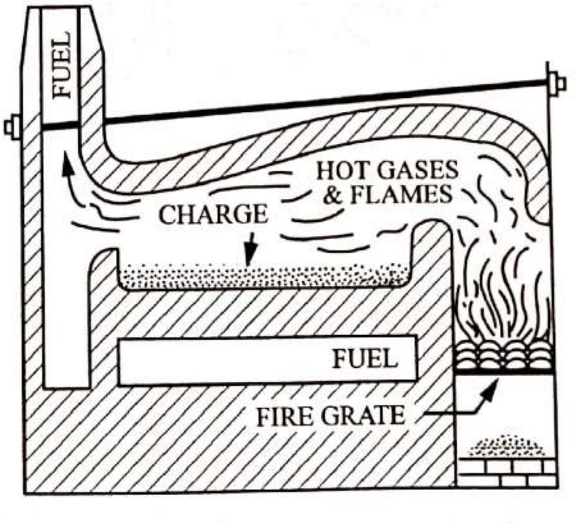

Fig. 2. A reverberatory furnace.

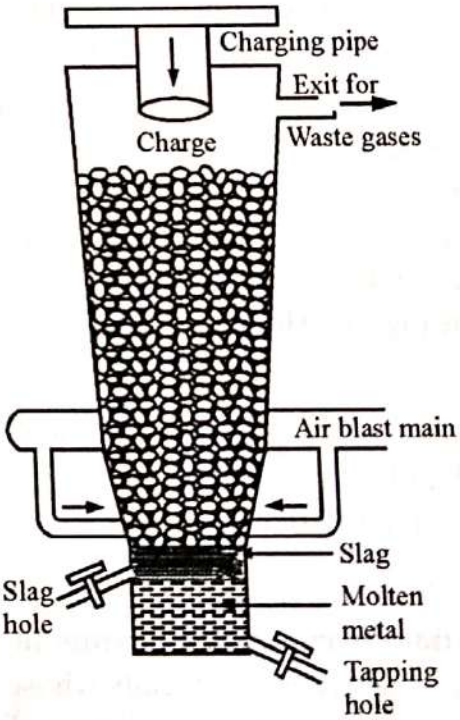

Fig. 3. A blast furnace.

4. Smelting. Reduction of Metal Oxides by Carbon

A large number of metal oxides obtained during roasting can be reduced to metals by heating with carbon at elevated temperatures (> 1000°C). This process is called **smelting.**

The roasted ore is mixed with a suitable quantity of carbon (coal or coke) and heated to a high temperature above the melting point of the metal. Carbon and carbon monoxide (produced by the

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incomplete combustion of carbon) reduce the oxide to the free metal. For example,

$$Fe_2O_3 + 3C \longrightarrow 2Fe + 3CO$$
$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$
$$PbO + C \longrightarrow Pb + CO$$
$$PbO + CO \longrightarrow Pb + CO_2$$

During reduction, an additional substance, called the *flux*, is added to the ore. It combines with impurities to form easily fusible product known as **slag**.

$$\underset{\text{(Present in the ore)}}{\text{Impurities}} + \text{flux} \longrightarrow \underset{\text{Slag}}{\text{fusible product}}$$

Slag is not soluble in molten metal. Being lighter, it can be easily skimmed off from the surface of the molten metal.

The choice of flux depends upon the impurities present in the ore. For example, if the ore contains acidic impurities such as SiO_2, P_2O_5, then basic fluxes like lime (CaO), magnesite ($MgCO_3$), haematite (Fe_2O_3), etc., are used.

$$\underset{\text{Acidic impurity}}{SiO_2} + \underset{\text{Basic flux}}{CaO} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

On the other hand, if the ore contains basic impurities such as CaO, FeO, $MgCO_3$, then acidic fluxes like sand and borax are used.

$$\underset{\text{Basic impurity}}{FeO} + \underset{\text{Acidic flux}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{FeSiO_3}$$

Smelting is generally carried out in a **reverberatory furnace** (Fig. 2) or a **blast furnace** (Fig. 3) in a controlled supply of air.

In the case of metals which are volatile in nature (for example, zinc), smelting cannot be done in an open furnace. In such cases, reduction of the oxide ore is carried out in fire-clay retorts. The vertical retort, which is now in common use, is shown in Fig. 4. Heating is done by producer gas.

It is to be noted that reduction with carbon is practical only if the required temperature is achieved conveniently which may not be so always.

Reduction by controlled heating in air. In the case of less active heavy metals whose oxides are unstable towards heat, only roasting in air is enough for the separation of the metal. For example, roasting of the sulphide ore of mercury (*cinnabar*) gives the metal rather than its oxide.

$$HgS + O_2 \longrightarrow Hg + SO_2$$

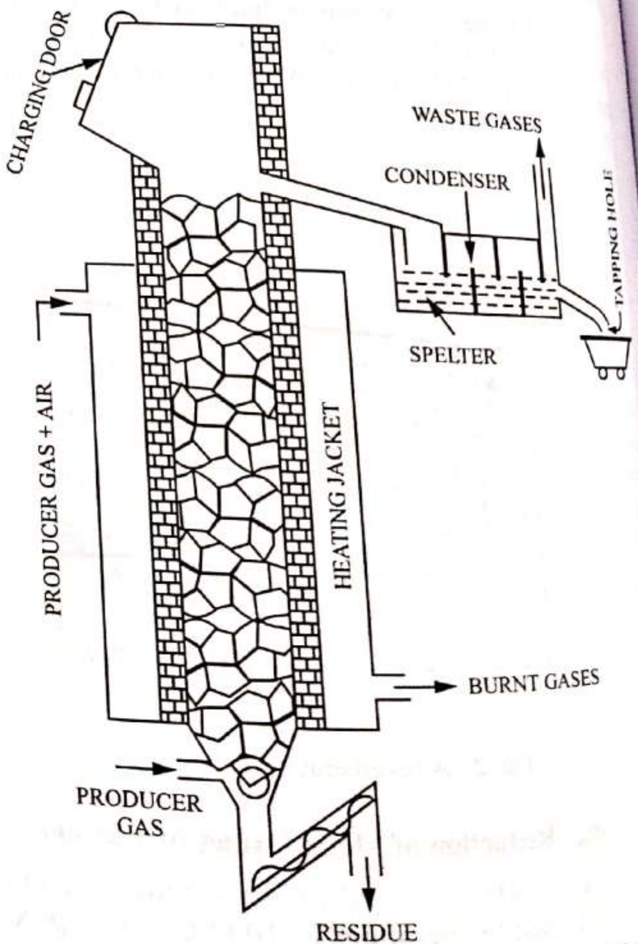

Fig. 4. A vertical retort furnace for the smelting of zinc ore.

Mercury vapours are condensed to the liquid state in the condensing chambers. This process is known as **air reduction** process. The Idrian furnace commonly used for the process is shown in Fig. 5.

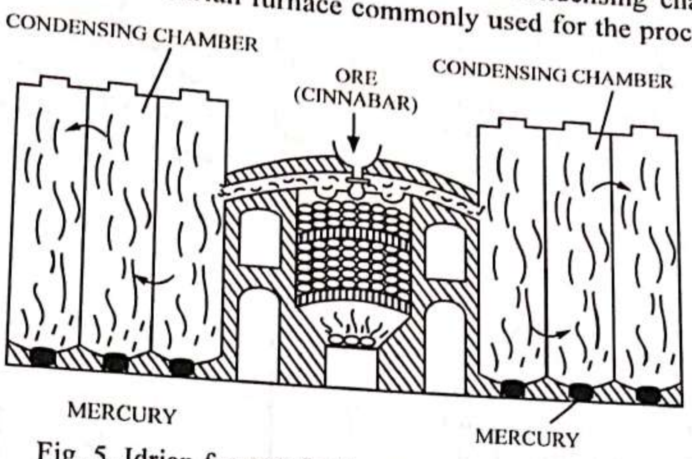

Fig. 5. Idrian furnace for the extraction of mercury.

Sulphide ores of several metals such as Pb, Cu, Sb, may be first roasted in a limited supply of air to partially convert them to oxides. These are further roasted in the absence of air when the sulphides and the oxides formed react to give the metals. For instance,

$$Cu_2S \xrightarrow[\text{in limited supply of air}]{\text{Roasting}} \underbrace{Cu_2S + Cu_2O} \xrightarrow[\text{absence of air}]{\text{Roasting in}} Cu + SO_2$$

This process is known as **self reduction.**

Electrometallurgy. The carbon reduction methods are not applicable for the chemically active metals such as alkali metals, alkaline earth metals, aluminium, etc. The oxides of these metals are very stable and have to be heated very strongly with carbon in order to reduce them to metals. But at high temperatures, these metals combine with carbon to form carbides. Hence, these metals are extracted by the electrolysis of their oxides, hydroxides or chlorides in fused state. The metal is liberated at the cathode.

Other Methods for Reduction of Oxides of Metals. If the temperature required for the reduction of the oxide by carbon is not easily attainable, then reduction is carried out by another metal such as aluminium. This is called **Goldschmidt thermite process.** Examples are :

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr$$

$$3Mn_3O_4 + 8Al \longrightarrow 4Al_2O_3 + 9Mn$$

In a few cases, as for example, in the case of Ag_2O, reduction is carried out by thermal decomposition alone. Such cases have been dealt with below on the basis of the **Elingham diagram.** The thermodynamics of carbon reduction process and the electrolytic process have also been discussed with the help of this diagram.

Thermodynamics of the Oxidation of Metals to Metal Oxides. The Ellingham Diagram

Consider a general oxidation reaction of a metal M in which $2x/y$ moles of the metal react with one mole of oxygen to form the oxide M_xO_y :

$$\underset{\text{solid}}{(2x/y)\,M} + \underset{\text{gas}}{O_2} \longrightarrow \underset{\text{solid}}{2/y\,M_xO_y}$$

Thermodynamically, the oxidation reaction would be feasible and the oxide formed would be stable if the free energy change ΔG of the oxidation reaction is negative. Free energy change of a

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reaction is given by the well known thermodynamic relation $\Delta G = \Delta H - T\Delta S$ where ΔH is the enthalpy change and ΔS is the entropy change accompanying the reaction. Since oxygen, being a gas, has higher entropy than the metal and the metal oxide, there would be a decrease in entropy in going from the reactants to the product. In other words, ΔS for the oxidation reaction would be negative. Obviously, the term $T\Delta S$ would become more and more negative and thereby ΔG would become less and less negative with increase in temperature. If the temperature is very high, ΔG may become zero and even positive in which case the oxidation reaction would no longer remain feasible. The variation of ΔG with increase in temperature for the oxidation of some common metals to their oxides (using one mole of oxygen in each case) is represented in Fig. 6. This figure is known as the **Ellingham diagram.** Similar diagrams can be drawn for the conversion of metals to metal sulphides or metal halides using one mole of sulphur or the halogen, as the case may be.

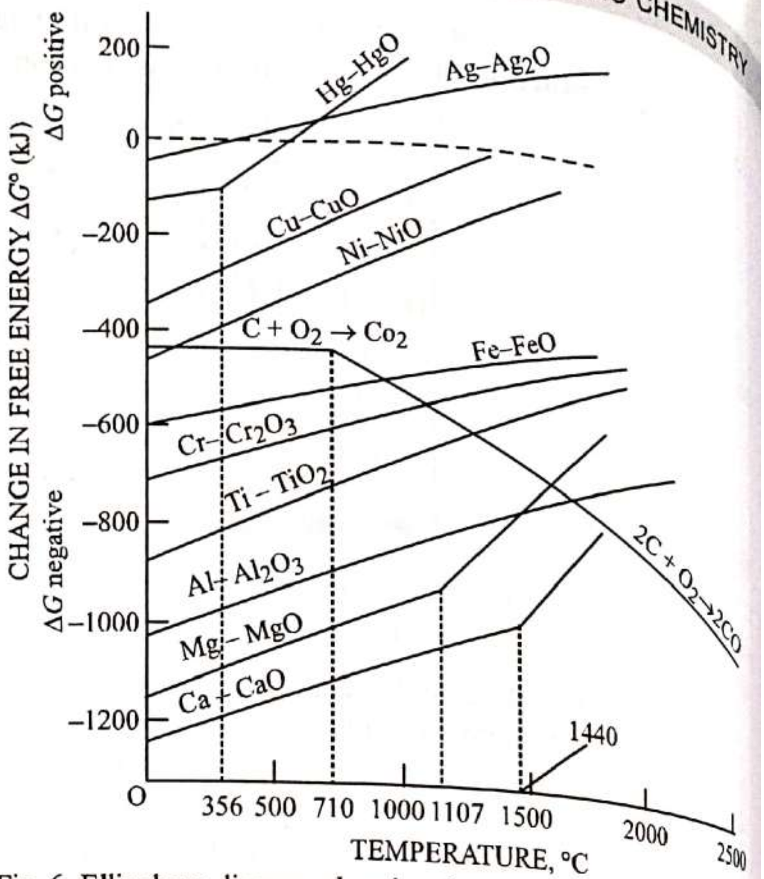

Fig. 6. Ellingham diagram showing the change in free energy ΔG with temperature for metal–metal oxide reactions, based on one mole of oxygen in each case.

Consider the relation,

$$\Delta G = \Delta H - T\Delta S$$

Differentiating with respect to T (assuming that ΔH does not vary with change in temperature), we get

$$d(\Delta G)/dT = -\Delta S$$

Thus, for a reaction with *negative* ΔS, the slope of the line obtained by plotting ΔG vs T will be *positive* while the slope of a similar line for a reaction with *positive* ΔS will be *negative*. Since for the reaction of metals with oxygen to give metal oxides, ΔS is negative, the slope of the lines obtained by plotting ΔG vs T, will be *positive*. Since for a reaction such as $C(s) + O_2(g) \longrightarrow CO_2(g)$, ΔS is zero, the slope of the line will be zero and the plot of ΔG vs T will be parallel to the temperature axis. The slope of the line for the reaction $2C(s) + O_2(g) \longrightarrow 2CO(g)$, for which ΔS is obviously positive, has to be *negative*, as actually observed.

The Ellingham diagram for the oxidation of metals to metal oxides, represented in Fig. 6, has a number of significant features :

1. All the ΔG vs T lines slope upward since ΔG becomes less and less negative with increase in temperature.

2. The ΔG vs T graphs are straight lines upto the temperatures at which the metals remain in solid state. There is a large change in entropy when the metals undergo fusion or vaporisation. This considerably changes the slopes of ΔG vs T lines. Thus, the slopes of Hg – HgO, Mg – MgO and Ca – CaO lines change appreciably at 356°, 1107° and 1440°C which are, respectively, the boiling points of Hg, Mg and Ca.

3. With continuous increase in temperature, a state would be reached when the ΔG vs T graphs cross the $\Delta G = 0$ line. Below these temperatures, ΔG is negative, *i.e.*, the heats of formation of the oxides are negative and hence the oxides formed are stable. Above these temperatures, ΔG would be positive and the oxides formed would, therefore, be unstable and would decompose to give the metals and oxygen.

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According to the Ellingham diagram, all oxides should decompose to give the metal and oxygen provided the temperatures are sufficiently high at which ΔG becomes positive. Such temperatures are, in practice, not easily attainable. The Hg – HgO and Ag – Ag_2O lines, however, cross the $\Delta G = 0$ line at temperatures which are easily attainable. These oxides, therefore, decompose easily to give the metals. This is the reason why Hg and Ag are obtained by thermal decomposition of their oxides.

4. Quite frequently, one metal is used to reduce the oxide of another metal. For example, aluminium is used to reduce Cr_2O_3 to Cr. Any metal would reduce the oxides of other metals which lie above it in the Ellingham diagram. This has been illustrated below.

Consider the following reactions taking place at a particular temperature :

$$4/3\,Cr + O_2 \longrightarrow 2/3\,Cr_2O_3\,; \qquad \Delta G = -x\,kJ \qquad ...(1)$$

$$4/3\,Al + O_2 \longrightarrow 2/3\,Al_2O_3\,; \qquad \Delta G = -y\,kJ \qquad ...(2)$$

We see from the Ellingham diagram that the ΔG vs T line for $Al - Al_2O_3$ system lies below the ΔG vs T line for $Cr - Cr_2O_3$ system so that $|y| > |x|$. Subtracting Eq. 1 from Eq. 2, we get

$$4/3\,Al - 4/3\,Cr \longrightarrow 2/3\,Al_2O_3 - 2/3\,Cr_2O_3\,; \qquad \Delta G = -y-(-x)\,kJ \qquad ...(3)$$

or

$$4/3\,Al + 2/3\,Cr_2O_3 \longrightarrow 4/3\,Cr + 2/3\,Al_2O_3 \quad ; \qquad \Delta G = (x-y)\,kJ \qquad ...(4)$$

Since $|y|>|x$, hence $(x-y)$ is negative, that is, ΔG accompanying reaction (4) is negative. Reaction (4) is, therefore, thermodynamically feasible, *i.e.*, Al would reduce Cr_2O_3 to Cr.

Now subtracting Eq. 2 from Eq. 1, we get

$$4/3\,Cr + 2/3\,Al_2O_3 \longrightarrow 2/3\,Cr_2O_3 + 4/3\,Al\,; \quad \Delta G = (y-x)\,kJ$$

Since $y - x$ and hence ΔG for the above reaction is positive, it would not occur, *i.e.*, Cr would not reduce Al_2O_3 to Al. However, Mg – MgO line lies below the $Al - Al_2O_3$ line in Ellingham diagram. Hence, Mg would reduce Al_2O_3 to Al.

5. As can be seen from the Ellingham diagram, the ΔG vs T graph for the oxidation of carbon is typical in itself. Two reactions are possible for the reaction of carbon with oxygen :

$$C + O_2 \longrightarrow CO_2$$

$$2C + O_2 \longrightarrow 2CO$$

In the first reaction, there is practically no change in entropy because the volume of CO_2 produced is the same as the volume of O_2 used. As a result, the ΔG vs T graph for $C \longrightarrow CO_2$ reaction is practically horizontal, as shown. The second reaction is accompanied by an increase in entropy because one volume of O_2 produces two volumes of CO. Since ΔS is positive, hence ΔG (= $\Delta H - \Delta S$) goes on becoming more and more negative with increase in temperature. As a result, the ΔG vs T graph for the second reaction slopes downward, as shown. The two graphs cross at about 710°C. Below this temperature, carbon reduces metal oxides to metals which lie above the horizontal line in Ellingham diagram, carbon itself being oxidised to CO_2. Above 710°C, reduction of oxides results in the formation of CO. Since the ΔG line for $C \longrightarrow CO$ slopes downwards, it would eventually cross all other metal–metal oxide graphs and would lie below all of them. This implies that, in principle, carbon can be used for reducing any metal oxide to metal provided a sufficiently high temperature is made available for the purpose. But, sometimes it is difficult to attain such high temperatures and, therefore, other techniques are used for the reduction of the metal oxides.

It can thus be concluded from the above discussion that HgO and Ag_2O can be reduced to their respective metals simply by heating since the temperatures at which ΔG for the oxidation reactions $Hg \longrightarrow HgO$ and $Ag \longrightarrow Ag_2O$ becomes positive and hence ΔG for decomposition reactions $HgO \longrightarrow Hg$ and $Ag_2O \longrightarrow 2Ag$ becomes negative are easily attained. The process in which the metal is obtained simply by heating the oxide ore to an easily attainable temperature is called **pyrometallurgical process.**

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The extraction of other metals simply by heating their oxides is difficult since the temperatures at which ΔG for the decomposition reactions of their oxides becomes positive, are not easily attainable. In such cases, the metal oxide is reduced by heating it with coke to temperatures at which C – CO line in the Ellingham diagram lies below the metal–metal oxide line. Thus, iron is obtained from its oxide ore by heating it with C at temperatures around 1000°C at which the C – CO line lies below the Fe – FeO line (Fig. 6).

The reduction of SiO_2 with C is extremely difficult as the temperature at which C can reduce SiO_2 is very high, viz., around 1500°C (the Si – SiO_2 line is not shown in the diagram).

If the temperatures at which the reduction of metal oxides with C can be affected are difficult to achieve, then reduction is carried out electrolytically. In this technique, the process of reduction of the oxide gets coupled with the electrolytic process for which ΔG is sufficiently negative so as to make the overall ΔG for the coupled process decidedly *negative*. The process, therefore, becomes feasible. Thus,

$$\begin{aligned}\Delta G &= \Delta G \text{ (reduction process)} + \Delta G \text{ (from external cell)}\\ &= \Delta G \text{ (reduction process)} - (nFE_{\text{external}})\end{aligned}$$

(E_{external} is the potential difference applied across the two electrodes of the electrolytic cell).

In order that ΔG (overall) is negative so that the reduction process becomes feasible, the factor [ΔG (reduction process) – nFE_{ext}] should be negative, *i.e.*, nFE_{ext} should be greater than ΔG (reduction process). Thus, E_{ext} should be greater than ΔG (reduction process)/nF.

A question may arise in reader's mind : Why do we almost invariably convert metal sulphides into metal oxides before reducing them with carbon ? Why can't we directly reduce metal sulphides with carbon ? The answer is that there is no compound CS analogous to CO for which ΔG vs T graphs slope downwards. Therefore, the sulphide ores are first converted into the oxides and then reduced by carbon.

Hydrogen is of limited use as a reducing agent for extracting metals from their oxides. This is because of two reasons. Firstly, the ΔG vs T line for the oxidation of hydrogen ($2H_2 + O_2 \longrightarrow 2H_2O$) runs parallel to most of the metal–metal oxide lines so that only a very few metals, having metal-metal oxide lines above the hydrogen line, can be reduced by hydrogen. The increase in temperature will not be of any use because at elevated temperatures hydrogen reacts with many metals forming hydrides.

The thermodynamic treatment discussed above has two limitations as well. These are :

1. The treatment is based on the assumption that the reactants and products are in a state of equilibrium which is often not true.

2. The treatment only predicts the feasibility of the reaction. It gives no information about the rate of the reaction.

Specialised Techniques for the Extraction of Metals

Some specialised techniques are also employed for the extraction of metals in specific cases. These techniques include amalgamation, hydrometallurgy, solvent extraction and ion-exchange chromatography.

a. Amalgamation. This process is used for the extraction of gold which occurs native. The finely crushed auriferous quartz is brought into contact with mercury which takes up the metal forming an amalgam. The metal is then recovered by distilling the amalgam.

b. Hydrometallurgy. Hydrometallurgy involves bringing the metal in solution by the action of suitable chemical reagents. This is followed by the recovery of the metal by the use of suitable precipitating agents. For example, native silver or poor ores of silver are suspended in dilute solution of sodium cyanide and air is blown through it. The native silver or silver ore goes into solution as the argentocyanide complex from which the metal is precipitated by adding zinc turnings.

$$4Ag + 8NaCN + O_2\ (\text{air}) + 2H_2O \longrightarrow 4Na[Ag(CN)_2] + 4NaOH$$

or

$$AgCl + 2NaCN \longrightarrow Na[Ag(CN)_2] + NaCl$$

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN)_4] + 2Ag \downarrow$$

c. Solvent Extraction. Solvent extraction is a technique in which the solution of a solute in a solvent is brought into contact with a second solvent which is essentially immiscible with the first solvent in order to bring about the transfer of the solute into the second solvent. It can be shown in a smiple manner that with a given volume of the extracting liquid, the extraction is more complete if it is used in a number of instalments than if the whole of it is used in a single operation. The efficiency of the process largely depends upon the partition coefficient which tells how many times the solute is more soluble in the extracting liquid.

The solvent extraction process is successfully employed in the desilverization of lead by zinc (Parke's process). In this process, argentiferous lead is melted by heating to about 800°C. Molten zinc is then added. Molten lead and molten zinc behave as two immiscible liquids in contact with each other and silver behaves as a solute which is more soluble in zinc than in lead, the partition coefficient being of the order of 300 at 800°C. Silver, therefore, passes readily from the heavier lead layer into the lighter zinc layer which is separated. By repeating the process three or four times, almost the entire amount of silver passes into the zinc layer from which it can be recovered by distilling off zinc.

d. Ion exchange Chromatography. This technique is effectively employed for the separation of lanthanoids. This has been discussed in details in Chapter 25.

5. Refining or Purification

After various metallurgical operations, the metal first obtained is usually impure. The impurities largely consist of

(*i*) other metals produced by the simultaneous reduction of their respective oxides originally present in the ore.

(*ii*) unreduced oxides and sulphides of the metals and

(*iii*) substances such as residual slag, flux, etc.

The impure metal is, therefore, subjected to certain purifying processes which depend upon the metal under treatment and the nature of the impurities to be removed. The usual refining processes are :

a. Liquation process. This process is employed when the impurity is less fusible than the metal itself. The impure metal is placed on the sloping hearth of a furnace and gently heated. The metal melts and drains away leaving behind the infusible material on the hearth.

b. Distillation process. This process is employed for purification of volatile metals like mercury, zinc and cadmium. The impure metal is heated in a retort and its vapours are condensed in a receiver. While the pure metal distils over, the non-volatile impurities are left behind in the retort.

c. Oxidation processes. Oxidation processes are employed for refining when impurities consisting of other metals get oxidized more readily than the metal itself. The impure metal is exposed in a molten state to the oxidizing influence of air in a suitable furnace. The oxides of other metals which are formed are removed from the surface by skimming. Sometimes, the oxide of the metal itself is added which provides the oxygen to the impurities. Thus, copper oxide is added to impure molten copper to provide oxygen required for the oxidation of impurities.

d Thermal decomposition of suitable compounds. In this method, the impure metal is converted nto some volatile compound which decomposes easily to yield the pure metal. Two examples are given elow.

(*i*) Mond Process. Impure nickel is treated with CO at 50°C when $Ni(CO)_4$ gas is produced which hen heated to 250°C in a closed vessel decomposes to give CO and pure nickel. CO is recycled to react ith more of the impure nickel. This process is known as Mond process.

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***(ii)* Van Arkel-de-Boer Process.** This method is used for ultrapurification of Zr and Ti. The impure metal is heated with iodine to give volatile MI_4 (M = Ti, Zr). The iodide is then heated electrically in a closed container when MI_4 decomposes to give the metal which deposits on the tungsten filament of the electric heater. The iodine liberated is recycled to react with further quantity of the impure metal. The tungsten filament is then drilled out leaving behind the hollow bar of pure titanium or zirconium, as the case may be.

e. Electrorefining. A large number of metals are refined electrolytically. The impure metal in the form of blocks is made the anode of an electrolytic cell while the cathode is a thin plate of the pure metal. A solution of a suitable salt of the metal is used as the electrolyte. On passing the electric current, the pure metal dissolves from the anode and is deposited on the cathode. The soluble impurities go into solution while the insoluble matter settles down at the bottom and is called the *anode mud*.

f. Zone refining. This technique is employed for preparing extremely pure metals. This is based on the principle that when the melt of an impure metal is allowed to cool, the pure metal crystallizes out while the impurities remain in the melt. In this technique, the impure metal is converted into a bar which is heated *at one end* with a moving circular heater. The impure metal melts at this end and forms a molten zone. As the heater is moved slowly along the length of the rod, the pure metal cystallizes out of the earlier molten zone while the impurities pass into the adjacent newly created molten zone. This process is carried out throughout the length of the rod. As a result, the impurities are completely driven to one end of the rod which is cut off and discarded. The process is carried out in an inert atmosphere to prevent oxidation of the metal.

QUESTIONS

1. How do metals occur in nature ? Describe the general procedure of extracting a metal from its sulphide ore.
2. What is meant by the term metallurgy ? Describe the various steps involved in getting a pure metal from its ores.
3. Explain the terms : Mineral, Ore, Gangue, Flux and Slag. Give examples.
4. Write short notes on :
   (1) Dressing of the ore
   (2) Electrometallurgy
   (3) Hydrometallurgy
   (4) Electrorefining
   (5) Zone refining
5. What is meant by the term concentration of the ore ? Describe the various methods used for the purpose.
6. Describe the various methods employed for the refining of crude metals.
7. Differentiate between :
   (*i*) mineral and ore
   (*ii*) calcination and roasting
   (*iii*) gangue and flux
8. Discuss briefly the various methods used for the reduction of the roasted ores to the metallic state.
9. Give a brief description of specialised techniques for the extraction of metals.
10. What is an Ellingham diagram. Discuss briefly the applications of this diagram.
11. Explain how with the help of an Ellingham diagram, we can fix the criterion for each
   (*i*) Reduction of a metal oxide by carbon at a given temperature.
   (*ii*) Reduction of an oxide X_2O_3 by a metal Y
   (*iii*) Reductio

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Enamels: or Gloss Finishes.

Pigmented varnishes are usually known as enamels.

[Varnish: Varnishes are transparent viscous liquids and contain no pigments. It is a homogeneous colloidal dispersion of resins in drying oils and volatile solvents].

The purpose of preparing enamels is to get a good gloss, because after drying, the enamels form a very good lustrous and glossy finish. Pigments, vehicles, driers, thinners are the various ingredients used in the preparation of enamel. They make use of pigments having fine texture and easily dispersable capacity. For example, Titanium dioxide (TiO_2), calcium sulphate are used for white enamel while coloured enamels are formed by replacing some or whole of the white pigment.

The vehicle used is either oleoresinous (oil plus resin) or only resin.

Oleoresinous vehicle is prepared by cooking together one or more resins (such as phenolic resins, limed resin etc) with one or more drying oils (such as linseed oil, tung oil, fish oil, soyabean oil, dehydrated castor oil etc) The resin is used as a solution of resin in a solvent and

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drying oil.

Alkyd resins are most commonly used in the manufacture of enamels because these resins are capable of providing many desired properties such as high gloss, permanence, washability, good levelling, good initial colour.

Emulsifying agents:

Emulsifying agents help to form an emulsion. Depending on the type of pigments and vehicles used, different emulsifying agents are chosen. Tetrasodium phosphate, sodium lauryl sulphate, ammonia are the examples of emulsifying agents.

SPECIAL PAINTS:

Heat retardant / Heat resistant paints:

The paints which are capable of resisting heat even upto red heat are called heat resistant paints.

- * These paints generally contain base of metallic powder like tin, zinc, graphite, aluminium etc. Some paints also contain polyphenyl silicones.
- * These paints are generally used in furnaces, oil stills,

Fire retardant paints:

These paints contain such type of materials (called Binders) which breakdown at high temperatures and produce non inflammable gases such as HCl, HBr, CO_2, NH_3, water vapour etc.

- * These gases serve to dilute the inflammable gases, produced by breakdown of the other components of the paint. Chlorinated rubber, PVC, alkyds and epoxides etc. breakdown to produce corresponding non-inflammable hydrogen halides. Carbonate pigment yield carbondioxide, water base paints yield water vapour and used formaldehyde resins yield NH_3.

Paints containing magnesium phosphate, zinc ammonium pyrophosphate, calcium ammonium phosphate or zinc ammonium tungstate etc. form a glass like melt at elevated temperatures. ~~This~~

* This melt prevents combustion by serving a barrier between air and inflammable substance.

Eco-friendly paints:

Eco-friendly paints which are having low or minimal VOC (volatile organic compounds)
In paints VOCs tend to be solvents such as white spirit, which evaporate as paint dries, releasing pollutants into the environment. They also contain heavy metals such as arsenic, lead and chromium.

Once these enter into the air we inhale, they can go into our lungs and create a toxic effect on our bodies. These paints not only harm the human body, but also the environment.

Eco-friendly paints can be classified into three types.

1. Zero-VOC paints: total VOC content less than 5gram per liter of paint.
2. Low-VOC paints: VOC content from 5 to 200gram per liter of paint.
3. Natural paints: Made of natural compounds such as tree resins, water, plant oil, essential oil and natural dyes, do not contain any VOCs

Plastic paints: Plastic emulsion paint is water based wall paint. It is based on acrylic and provide a smooth matt finish to the walls.

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Wax polishing:

Polishing is the process of creating a smooth and shiny surface by rubbing it or using a chemical action leaving a surface with a significant specular-reflecti

Waxes are a diverse class of organic compounds that are lipophilic, malleable solids near ambient temperatures.

They are insoluble in water but soluble in organic, non polar solvents. They include higher alkanes and lipids typically with melting points above 40°C, melting to give low viscosity liquids.

Mainly polyethylene and polypropylene waxes are use in the formulation of coatings.

They are also used in paints as they confer matti effects and wear resistance.

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Classification of surface coatings:

Surface coatings

- Organic
  - Paints
  - Varnishes
  - Lacquers
  - Enamels
  - Wax and polishes.
- Inorganic
  - Metallic
    - Electrolytic
    - Electroless
  - Non-metallic

(A) <u>Metallic coatings</u>: In this method, the metallic article which is to be protected is known as <u>base metal</u>. The metal which is used for coating is known as <u>coat metal</u>. Therefore metallic coatings are applied over the base metal surface is done by two methods.

(i) Electroless (ii) Electroplating.

<u>Electroless plating</u>: It is a process of plating which is done entirely by chemical reaction.

* No external source of electric current is required in this case.

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It involves :

→ Deposition of metal onto the part of the surface occurs in an aqueous solution containing ions of the coat metal.

→ The process uses a reducing agent and work part of the surface. Catalyst reduces metal to ions.

→ Nickel and Nickel alloys are used for this plating. Others are iron, aluminium, Titanium etc.

Autocatalytic immersion of steel in an aqueous solution of coat metal to get an uniform coating.

Hot dipping:

* The base metal/article to be coated is dipped in a bath of molten coat metal or its alloy for sufficient time to get a uniform coating.
* The base metal must be very clean so that it will be wetted by the molten metal and a uniform coating will result.
* This method is used for producing a coating ~~of~~ low melting metals such as zinc, tin or lead on iron, steel and copper which have higher melting points.

The hot dipping involves the galvanisation method.

→ The process of coating a base metal (iron/steel) with a thin coat of zinc to prevent it from rusting.

This method involves,

* Iron/steel cleaned by pickling it in dil. HCl and removing all the impurities and rust from the surface.
* It is washed well, dried & immersed in a bath containing molten zinc and ammonium chloride flux.
* Temperature of bath is maintained at 430°C.
* Coating occcurs and then the coated metal is passed through a pair of rollers to remove the excess of molten metal and to obtain a thin uniform coating.
* It is cooled slowly.

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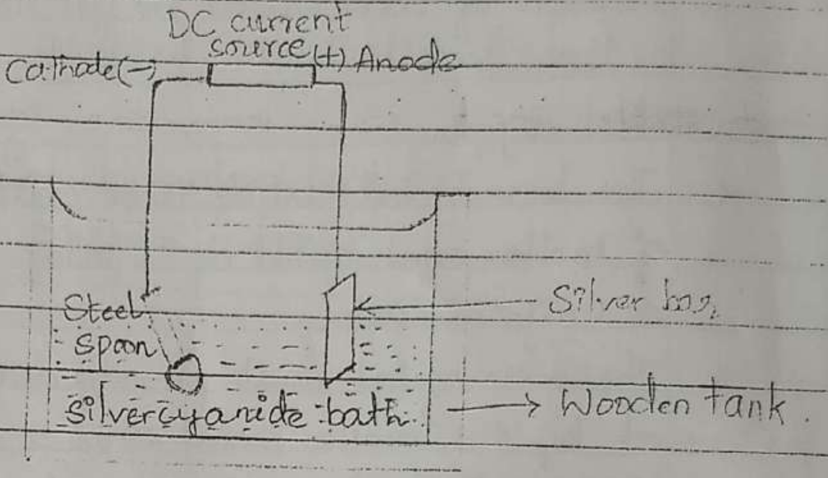
Uses: Protection of iron pipes, roofing sheets. protection of screws and bolts from atmospheric corrosion

Electroplating: It is also known as electrodepositing.

- * It is based on the principle of electrolysis.
- * A process by which, the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing a soluble salt of coat metal.



- * In the actual process, the metal which is to be electroplated (base metal) is taken as cathode and coat metal is taken as anode.
- * A solution of the coat metal salt is used as electrolyte.
- * Now the anode and cathode are dipped in the electrolyte the electrodes are connected to a battery and current is passed.
- * Electrolysis takes place and a thin layer of the coat metal is obtained.

The thickness of electroplating depends on;

→ The current density.
→ Time of deposition.
→ Temperature of electrolytic bath.
→ Concentration of bath electrolyte.

This method is most important & most commonly employed method for producing metallic coatings and it

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gives a fine coating.

→ It is also used in making jewellery and ~~finely~~ fancy articles.

Metal spraying:

* The surface to be coated must be clean and rough so that the coat metal in the molten state is sprayed on to the rough surface of the base metal by means of a spray gun.

* The coating may be applied to a particular area of the article and thickness can be controlled.

Advantages:

* Irregular objects can be easily given a uniform coat.

* Coatings can be applied on a non metallic base made of glass, wood or plastic.

(B) Non-Metallic coatings:

* Here non-metals are used as coating material.

* Common types of such coatings plastic or rubber coating.

* It involves application of layer of the given polymer on to a substrate material.

Different coatings of such type are known:

(i) **Wire and cable coating:** In this case, whole length of conducting wire or electrical cable is coated with plastic or polymer to provide thermal or electrical insulation.

(ii) **Planar coating:** It involves coating of a flat film over a flat surface.

(iii) **Contour coating:** It is applied over a 3-dimensional

ANODIZING:

- * It is a process of deposition of oxide film ~~of~~ on a metal surface with the help of an anode and oxidation phenomenon.
- * The aluminium coated surfaces requires oxidation to convert the metal to its inert oxide.
- * It is carried out by using ~~amalgam~~ aluminium coated article as the anode in a bath of 10-15% H_2SO_4 and electrolysing.
- * Any inert material can be cathode.
- * When current is passed, chromic acid oxidises aluminium to its oxide which is porous.
- * After electrolysis, the article is kept in a boiling water bath which results in the formation of $Al_2O_3 \cdot H_2O$.
- * The formation of oxide leads to the expansion of the film thus reducing the porosity.
- * Coloured coats can be obtained by adding dyes to the electrolytic bath.

Application:

Aircrafts parts, pistons and machine parts are anodised using this method.

The anodised coatings provides.

→ High electrical insulation and

→ Resistance to abrassion and corrosion.

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Tumakuru

Notes on -“Nucleic acid”

NA by BLM

By

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Nucleic acid

Introduction

A most remarkable property of living cells is their ability to produce exact replicas of themselves. This is due to the cells containing fact that all the instructions needed for making the complete organism of which they are a part. Nucleic acids are the molecules within a cell that are responsible for these amazing capabilities. The first isolation of nucleic acid we now refer to as DNA was accomplished by Swiss physiologist Johann Friedrich Miescher circa 1870 while studying the nuclei of white blood cells. In the 1920's nucleic acids were found to be major components of chromosomes, small gene-carrying bodies in the nuclei of complex cells. Elemental analysis of nucleic acids showed the presence of phosphorus, in addition to the usual C, H, N & O. We now know that nucleic acids are found throughout a cell, not just in the nucleus, the name nucleic acid is still used for such materials.

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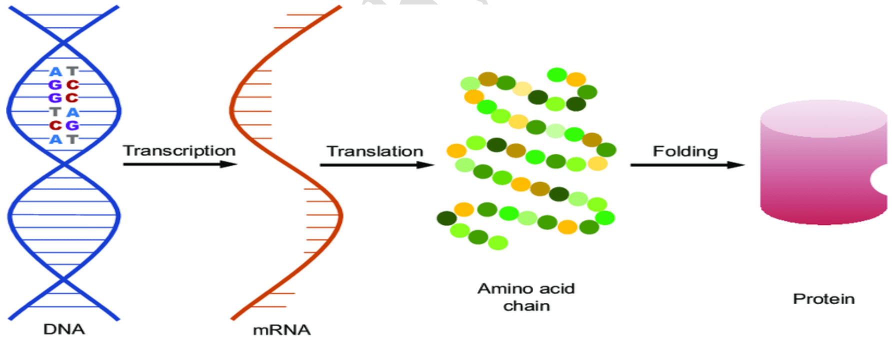
Central dogma: The central dogma of molecular biology. Defined as “The genetic information encoded in the DNA is first transcribed into the mRNA, which is then translated into the protein”.

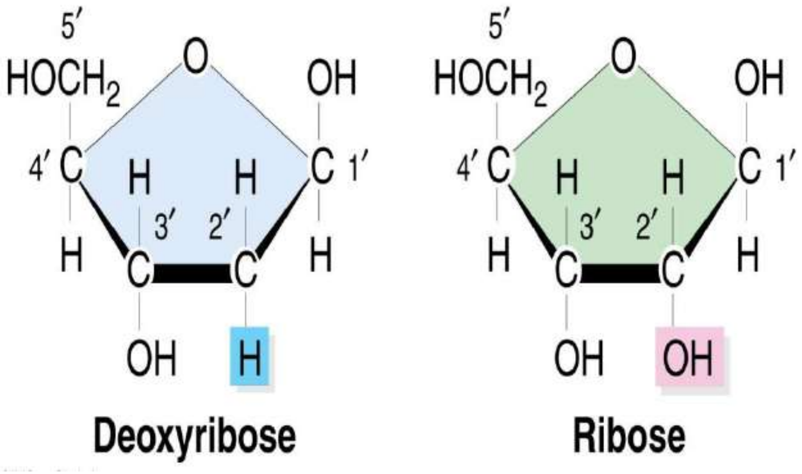


A nucleic acid (NA)is a polymer in which the monomer units are nucleotides. There are two Types of Nucleic Acids: DNA: Deoxyribonucleic Acid: Found within cell nucleus for storing and transfering of genetic information that are passed from one cell to other during cell division RNA: Ribonucleic Acid: Occurs in all parts of cell serving the primary function is to synthesize the proteins needed for cell functions.

Components Of nucleic acids

Nitrogenous bases: PURINES and PYRIMIDINES

Sugars used are:



Base present

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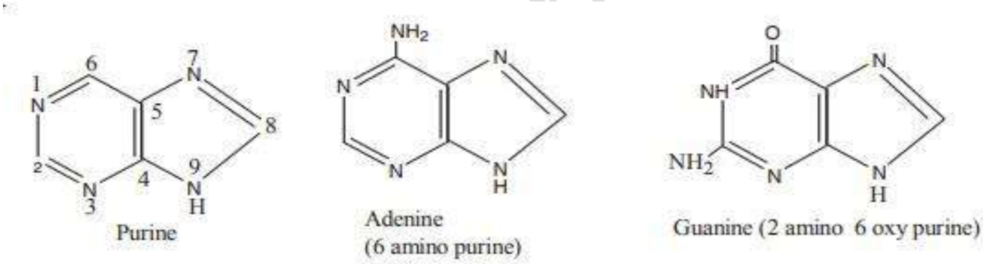
Purines: Fused 6 & 5 membered hetero CN-ring system, usually unsaturated. Two common purines in biological systems are adenine and guanine, both used in DNA and RNA, as well as in energy carriers (ATP & GTP).

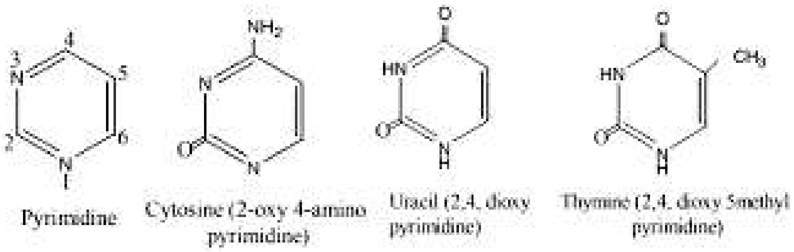

Purine

Adenine (6 amino purine)

Guanine (2 amino 6 oxy purine)

Structure of purine bases

Pyrimidines: 6 membered CN-ring, usually unsaturated. Three common Pyrimidines found in biological systems are cytosine(C) , uracil (U)and thymine(T): two (C & T) present in DNA, and two (C & U) used in RNA.


Pyrimidine

Cytosine (2-oxy 4-amino pyrimidine)

Uracil (2,4, dioxy pyrimidine)

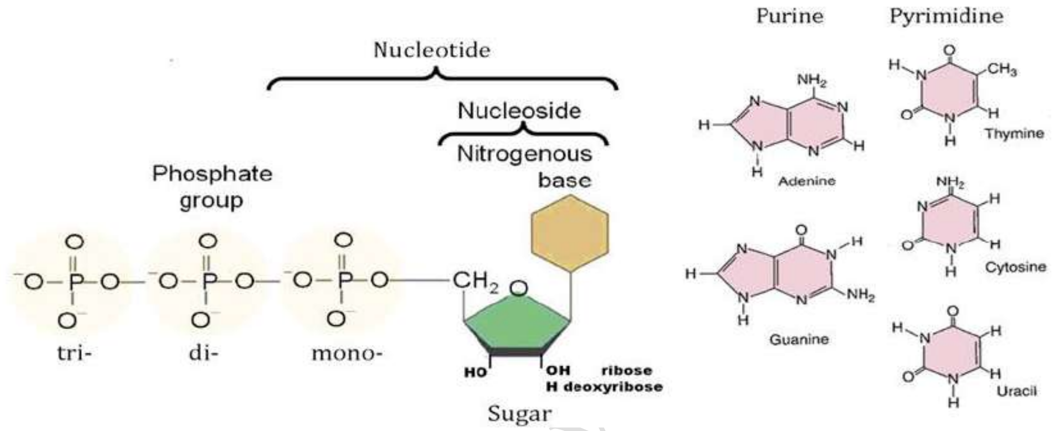
Thymine (2,4, dioxy 5methyl pyrimidine)

Structure of pyrimidine bases

Nucleoside and nucleotide structure

Nucleosides : are structure consisting of a Nitrogenous base plus sugar is termed a nucleoside.

Nucleotides: are structure consisting of a Nitrogenous base plus sugar plus phosphate is termed a Nucleotides.



NA by

The nucleic acids are made up of polymers of four different nucleotide residues each.

RNA uses AMP, CMP, GMP, and UMP

DNA use the deoxy forms: dAMP, dCMP, dGMP, and dTMP

The two nucleic polymers differ by both the 2‘functional group (-OH or -H) and the use of either uridine or thymine as the fourth base.

Though only four different nucleotide bases can occur in a nucleic acid, each nucleic acid contains millions of bases bonded to it. The order in which these nucleotide bases appear in the nucleic acid is the coding for the information carried in the molecule. In other words, the nucleotide bases serve as a sort of genetic alphabet on which the structure of each protein in our bodies is encoded.

Primary Nucleic Acid Structure Polynucleotide

In polynucleotide, nucleotides are joined to one another by covalent bonds between the phosphate of one and the sugar of another. These linkages are called phosphodiester linkages. This nucleic acids found in the cell have primary structures that arise from the end-to-end polymerization of single nucleotide units. The links between each nucleotide are formed by esterification reactions between the sugar's C3′ hydroxyl group and the - phosphate of an incoming nucleoside triphosphate (NTP) to form a phosphoester linkage.

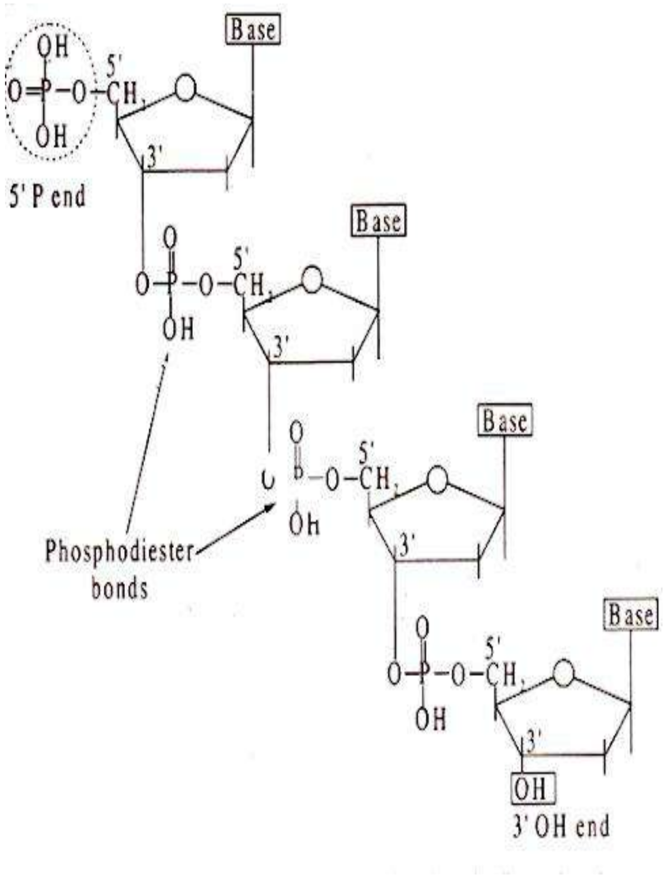


Figure: Polynucleotide chain bound by phosphodiester bond

Deoxyribonucleic acid

Deoxyribonucleic acid (DNA) is a nucleic acid containing the genetic instructions used in the development and functioning of all known living organisms. DNA is made and resides in the nucleus of living cells. DNA gets its name from the sugar molecule contained in its backbone(deoxyribose); however, it gets its significance from its unique structure. Four different nucleotide bases occur in DNA: adenine (A), cytosine (C), guanine (G), and thymine (T).DNA consists of two long polymers of simple units called nucleotides, with backbones made of sugars and phosphate groups joined by ester bonds. These two strands run in opposite directions to each other and are, therefore, anti-parallel. Attached to each sugar is one of four types of molecules called nucleobases (informally, bases).

DNA structure

The DNA Double Helix : The 1962 Nobel Prize in Physiology or Medicine was awarded to Crick, Watson and Wilkins for the discovery of the molecular structure of DNA – the double helix.

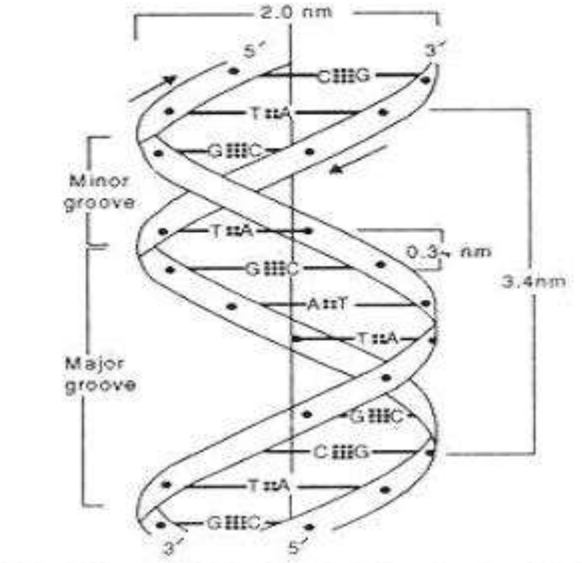


Figure: The structure of Watson and crick model of double helical structure of the Right handed or B-form of DNA

The important features of Watson – Crick Model or double helix model of DNA are as follows:

1. The DNA molecule consists of two polynucleotide chains or strands that spirally twisted around each other and coiled around a common axis to form a right-handed double-helix.

2. The two strands are antiparallel i.e. they ran in opposite directions so that the 3′ end of one chain facing the 5′ end of the other.

3. The sugar-phosphate backbones remain on the outside, while the core of the helix contains the purine and pyrimidine bases.

4. The two strands are held together by hydrogen bonds between the purine and pyrimidine bases of the opposite strands.

5. Adenine (A) always pairs with thymine (T) by two hydrogen bonds and guanine (G) always pairs with cytosine (C) by three hydrogen bonds. This complimentarily is known as the base pairing rule. Thus, the two stands are complementary to one another.

6. The base sequence along a polynucleotide chain is variable and a specific sequence of bases carries the genetic information.

7. The base compositions of DNA obey Chargaff s rules (E.E. Chargaff, 1950) according to which A=T and G=C; as a corollary ∑ purines (A+G) = 2 pyrimidines (C+T); also (A+C) = (G+T). It also states that ratio of (A+T) and (G+C) is constant for a species (range 0.4 to 1.9)

8. The diameter of DNA is 20nm or 20 A. Adjacent bases are separated 0.34 nm or by 3.4 A along the axis. The length of a complete turn of helix is 3.4 nm or 34 A i.e. there are 10bp per turn. (B- DNA-Watson rick DNA)

9. The DNA helix has a shallow groove called minor groove (-1,2nm) and a deep groove called major groove (- 2.2nm) across.

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Some other characteristics of DNA:

1. The amount of DNA per nucleus is constant in all the somatic cells of a given species.

2. The total amount of DNA in a haploid genome is a characteristic of each organism and is known as C-value.

3. Only a small fraction of DNA is functional in eukaryotes.

4. DNA is the chemical basis of heredity and is organized into genes or cistrons.

5. DNA replicates to form DNAs and transcribes to form RNAs.

6. DNA replication occurs in the S-phase of cell cycle.

7. DNA replication is semi conservative in which two daughter DNA molecules formed; each receives one of parental strand and one new strand.

8. One strand of DNA directs the synthesis called template strand, or antisense or non-coding strand. The other strand is called coding or non template of sense strand which has the same sequence as the RNA transcript except for T in place of U.

9. DNA has many repeated base sequences, some of which ire mobile.

10. DNA can easily undergo denaturation (melting) and renaturation with any change in pH, temperature and salt concentration. DNA with a high G+ G content are more resistant to thermal melting than A + T rich molecules.

11. DNA can be synthesized in vitro (in the laboratory).

12. DNA can be measured by the unit picogram (lpg= 10 g)

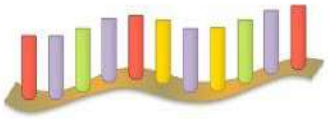
Ribonucleic acid

Ribonucleic acid (RNA) functions in converting genetic information from genes into the amino acid sequences of proteins. Like DNA, RNA is a long polymer consisting of nucleotides.

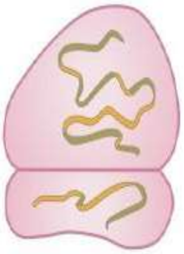
RNA is a single-stranded helix.

1. The strand has a 5′end (with a phosphate group) and a 3′end (with a hydroxyl group).
2. It is composed of ribonucleotides.
3. The ribonucleotides are linked together by 3′ –> 5′ phosphodiester bonds.
4. The nitrogenous bases that compose the ribonucleotides include adenine, cytosine, uracil, and guanine.

The three universal types of RNA include transfer RNA (tRNA), messenger RNA (mRNA), and ribosomal RNA (rRNA). Messenger RNA acts to carry genetic sequence information between DNA and ribosomes, directing protein synthesis. Ribosomal RNA is a major component of the ribosome, and catalyzes peptide bond formation. Transfer RNA serves as the carrier molecule for amino acids to be used in protein synthesis, and is responsible for decoding the mRNA. In addition, many other classes of RNA are now known. RNA functions to transfer genetic instructions from the nucleus to the cytoplasm, where the information is decoded



Messenger RNA (mRNA)



Ribosomal RNA (rRNA)

Transfer RNA (tRNA)

There are three types of RNA which cooperate to complete the central dogma

Messenger RNA (mRNA)

a transcript copy of a gene which encodes a specific polypeptide.

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- Accounts for about 5% of the total RNA in the cell.
- Most heterogeneous of the 3 types of RNA in terms of both base sequence and size.
- It carries the genetic code copied from the DNA during transcription in the form of triplets of nucleotides called codons.
- As part of post-transcriptional processing in eukaryotes, the 5’ end of mRNA is capped with a guanosine triphosphate nucleotide, which helps in mRNA recognition during translation or protein synthesis.
- Similarly, the 3’ end of an mRNA has a poly A tail or multiple adenylate residues added to it, which prevent enzymatic degradation of mRNA. Both 5’ and 3’ end of an mRNA imparts stability to the mRNA.
- **Function**

  mRNA transcribes the genetic code from DNA into a form that can be read and used to make proteins. mRNA carries genetic information from the nucleus to the cytoplasm of a cell.

Transfer RNA (tRNA)

carries the polypeptide subunits (amino acids) to the organelle responsible for synthesis (ribosome)

- tRNA is the smallest of the 3 types of RNA having about 75-95 nucleotides.

- tRNAs are an essential component of translation, where their main function is the transfer of amino acids during protein synthesis. Therefore they are called transfer RNAs.
- Each of the 20 amino acids has a specific tRNA that binds with it and transfers it to the growing polypeptide chain. tRNAs also act as adapters in the translation of the genetic sequence of mRNA into proteins. Therefore they are also called adapter molecules.

Structure of tRNA

tRNAs have a clover leaf structure which is stabilized by strong hydrogen bonds between the nucleotides. Apart from the usual 4 bases, they normally contain some unusual bases mostly formed by methylation of the usual bases, for example, methyl guanine and methylcytosine.

- Three structural loops are formed via hydrogen bonding.
- The 3′ end serves as the amino acid attachment site.
- The center loop encompasses the anticodon.
- The anticodon is a three-base nucleotide sequence that binds to the mRNA codon.
- This interaction between codon and anticodon specifies the next amino acid to be added during protein synthesis.

Function

Transfer RNA brings or transfers amino acids to the ribosome that correspond to each three-nucleotide codon of rRNA. The amino acids then can be joined together and processed to make polypeptides and proteins.

Ribosomal RNA (rRNA)

a primary component of the ribosome and is responsible for its catalytic activity

- Found in the ribosomes and account for 80% of the total RNA present in the cell.
- Ribosomes consist of two major components: the small ribosomal subunits, which read the RNA, and the large subunits, which join amino acids to form a polypeptide chain. Each subunit comprises one or more ribosomal RNA (rRNA) molecules and a variety of ribosomal proteins (r-protein or rProtein).
- Different rRNAs present in the ribosomes include small rRNAs and large rRNAs, which denote their presence in the small and large subunits of the ribosome.

- rRNAs combine with proteins in the cytoplasm to form ribosomes, which act as the site of protein synthesis and has the enzymes needed for the process.
- These complex structures travel along the mRNA molecule during translation and facilitate the assembly of amino acids to form a polypeptide chain. They bind to tRNAs and other molecules that are crucial for protein synthesis.

Function

- rRNA directs the translation of mRNA into proteins.

NA by BLM

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Notes on -" Vitamins"

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Vitamins by BLM

Vitamins

Introduction

Vitamins are organic compounds that are needed in small quantities to sustain life. Most vitamins need to come from food. A vitamin is one of a group of organic substances that is present in minute amounts in natural foodstuffs. Vitamins are essential to normal metabolism. If we do not take enough of any kind of vitamin, certain medical conditions can result.

A vitamin is both:

- an organic compound, which means it contains carbon
- an essential nutrient that body cannot produce enough of and which it needs to get from food

Each organism has different vitamin requirements. For example, humans need to consume vitamin C, or ascorbic acid, but dogs do not. Dogs can produce, or synthesize, enough vitamin C for their own needs, but humans cannot.

There are currently 13 recognized vitamins.

Different vitamins have different roles, and they are needed in different quantities.

- Vitamins are either water-soluble or fat-soluble.
- Fat-soluble vitamins are easier for the body to store than water-soluble.
- Vitamins always contain carbon, so they are described as “organic.”
- Food is the best source of vitamins, but some people may be advised by a physician to use supplements.

Types of vitamin base on solubility

- **Fat-soluble vitamins**
- **water-soluble Vitamins.**

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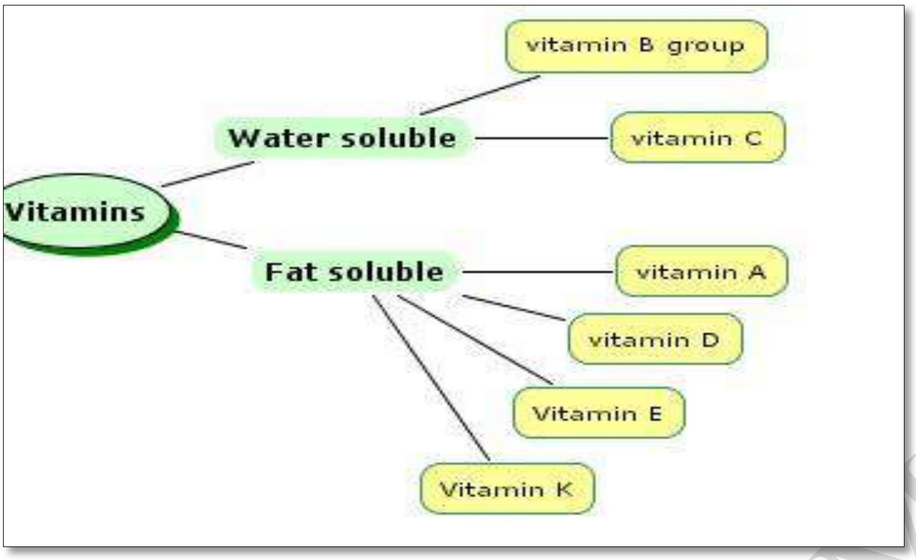


Vitamins by BLM

Fat-soluble vitamins

Fat-soluble vitamins are stored in the fatty tissues of the body and the liver. Vitamins A, D, E, and K are fat-soluble. These are easier to store than water-soluble vitamins, and they can stay in the body as reserves for days, and sometimes months. Fat-soluble vitamins are absorbed through the intestinal tract with the help of fats, or lipids.

Vitamin A

Chemical names: Retinol, retinal, and four carotenoids, including beta carotene.It is fat soluble.

Deficiency may cause night-blindness and keratomalacia, an eye disorder that results in a dry cornea.

Good sources include: Liver, cod liver oil, carrots, broccoli, sweet potato, butter, kale, spinach, pumpkin, collard greens, some cheeses, egg, apricot, cantaloupe melon, and milk

Vitamin D

Chemical names: Ergocalciferol, cholecalciferol.It is fat soluble.

Deficiency may cause rickets and osteomalacia, or softening of the bones.

Good sources: Exposure to ultraviolet B (UVB) through sunlight or other sources causes vitamin D to be produced in the skin. Also found in fatty fish, eggs, beef liver, and mushrooms.

Vitamin E

Chemical names: Tocopherols, tocotrienols

Deficiency is uncommon, but it may cause hemolytic anemia in newborns. This is a condition where blood cells are destroyed and removed from the blood too early.

Good sources include: Kiwi fruit, almonds, avocado, eggs, milk, nuts, leafy green vegetables, unheated vegetable oils, wheat germ, and whole-grains.

Vitamin K

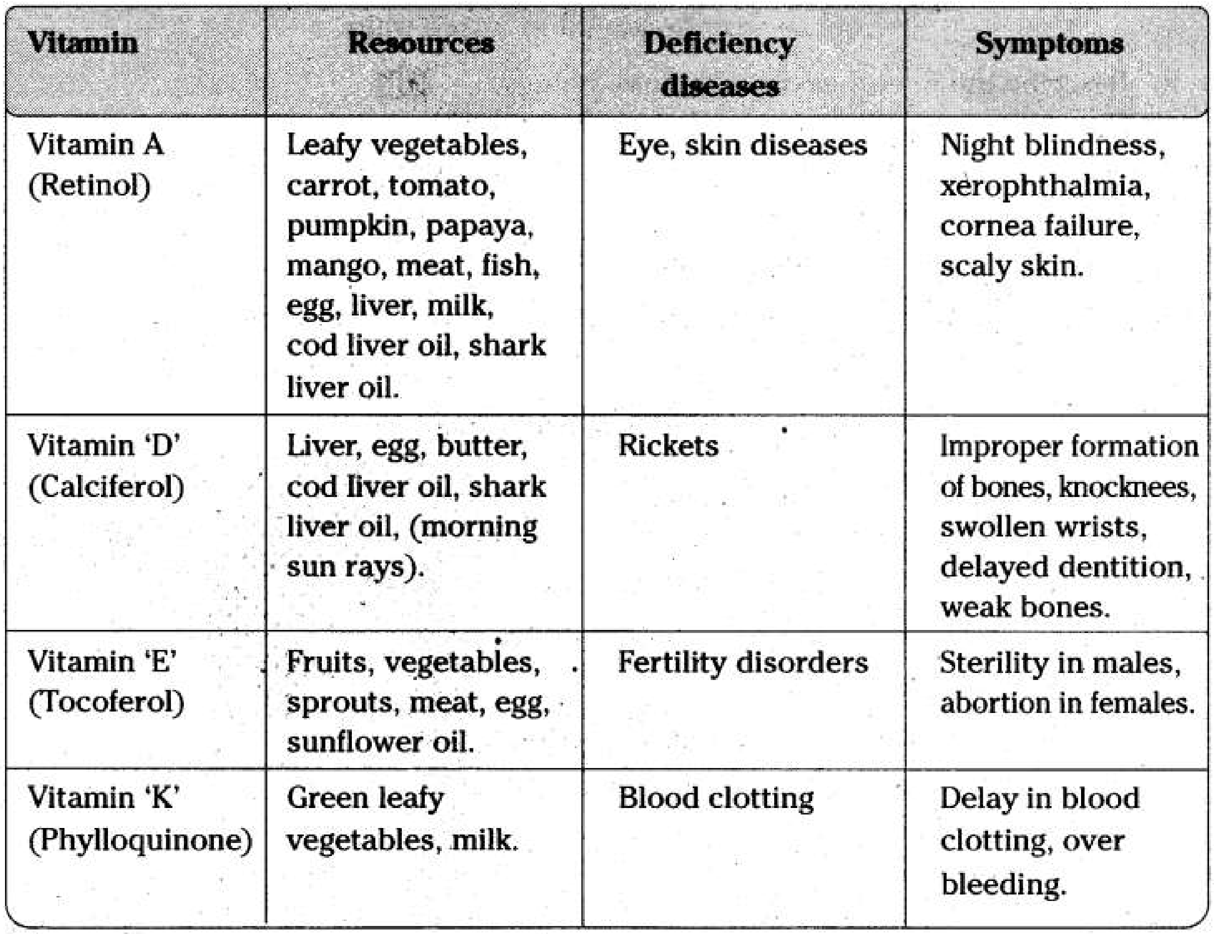
Chemical names: Phylloquinone, menaquinones

Deficiency may cause bleeding diathesis, an unusual susceptibility to bleeding.

Good sources include: leafy green vegetables, avocado, kiwi fruit. Parsley contains a lot of vitamin K.

Vitamins by BLM

Table : Fat soluble vitamins resources and deficiency diseases



Vitamin	Resources	Deficiency diseases	Symptoms
Vitamin A (Retinol)	Leafy vegetables, carrot, tomato, pumpkin, papaya, mango, meat, fish, egg, liver, milk, cod liver oil, shark liver oil.	Eye, skin diseases	Night blindness, xerophthalmia, cornea failure, scaly skin.
Vitamin 'D' (Calciferol)	Liver, egg, butter, cod liver oil, shark liver oil, (morning sun rays).	Rickets	Improper formation of bones, knocknees, swollen wrists, delayed dentition, weak bones.
Vitamin 'E' (Tocoferol)	Fruits, vegetables, sprouts, meat, egg, sunflower oil.	Fertility disorders	Sterility in males, abortion in females.
Vitamin 'K' (Phylloquinone)	Green leafy vegetables, milk.	Blood clotting	Delay in blood clotting, over bleeding.

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Water-soluble vitamins

Water-soluble vitamins do not stay in the body for long. The body cannot store them, and they are soon excreted in urine. Because of this, water-soluble vitamins need to be replaced more often than fat-soluble ones. Vitamin C and all the B vitamins are water soluble

Types

1. Vitamin A, or Retinol
2. Vitamin B1, or Thiamin
3. Vitamin B2, or Riboflavin
4. Vitamin B3, or Niacin

5. Vitamin B5, or Pantothenic Acid
6. Vitamin B6, or Pyridoxine
7. Vitamin B7, or Biotin
8. Vitamin B9, or Folic Acid (Folate)
9. Vitamin B12, or Cobalamin
10. Vitamin C or ascorbic acid

Vitamin B$_1$

Chemical name: thiamine.

Deficiency may cause beriberi and Wernicke-Korsakoff syndrome.

Good sources include: yeast, pork, cereal grains, sunflower seeds, brown rice, whole-grain rye, asparagus, kale, cauliflower, potatoes, oranges, liver, and eggs.

Vitamin B2

Chemical name: Riboflavin

Deficiency may cause ariboflavinosis

Good sources include: asparagus, bananas, persimmons, okra, chard, cottage cheese, milk, yogurt, meat, eggs, fish, and green beans

Vitamin B3

Chemical names: Niacin, niacinamide

Deficiency may cause pellagra, with symptoms of diarrhea, dermatitis, and mental disturbance.

Good sources include: liver, heart, kidney, chicken, beef, fish (tuna, salmon), milk, eggs, avocados, dates, tomatoes, leafy vegetables, broccoli, carrots, sweet potatoes, asparagus, nuts, whole-grains, legumes, mushrooms, and brewer’s yeast.

Vitamins by BLM

Vitamin B5

Chemical name: Pantothenic acid

Deficiency may cause paresthesia, or “pins and needles.”

Good sources include: meats, whole-grains (milling may remove it), broccoli, avocados, royal jelly, and fish ovaries.

Vitamin B6

Chemical names: Pyridoxine, pyridoxamine, pyridoxal

Deficiency may cause anemia, peripheral neuropathy, or damage to parts of the nervous system other than the brain and spinal cord.

Good sources include: meats, bananas, whole-grains, vegetables, and nuts. When milk is dried, it loses about half of its B6. Freezing and canning can also reduce content.

Vitamin B7

Chemical name: Biotin

Deficiency may cause dermatitis or enteritis, or inflammation of the intestine.

Good sources include: egg yolk, liver, some vegetables.

Vitamin B9

Chemical names: Folic acid, folinic acid

Deficiency during pregnancy is linked to birth defects. Pregnant women are encouraged to supplement folic acid for the entire year before becoming pregnant.

Good sources include: leafy vegetables, legumes, liver, baker’s yeast, some fortified grain products, and sunflower seeds. Several fruits have moderate amounts, as does beer.

Vitamin B12

Chemical names: Cyanocobalamin, hydroxocobalamin, methylcobalamin

Deficiency may cause megaloblastic anemia, a condition where bone marrow produces unusually large, abnormal, immature red blood cells.

Vitamins by BLM

Good sources include: fish, shellfish, meat, poultry, eggs, milk and dairy products, some fortified cereals and soy products, as well as fortified nutritional yeast.

Vitamin C

Chemical name: Ascorbic acid

Deficiency may cause megaloblastic anemia.

Good sources include: fruit and vegetables. The Kakadu plum and the camu camu fruit have the highest vitamin C contents of all foods. Liver also has high levels. Cooking destroys vitamin C.

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Table: Water soluble vitamins: coenzyme form, function and deficiency diseases

Vitamin	Coenzyme form	Function	Diseases/disorders
Vitamin B_1 (Thiamine)	Thiamine pyrophosphate (TPP)	Aldehyde group transfer	Beriberi, Wernicke-Korsakoff's syndrome
Vitamin B_2 (Riboflavin)	FMN and FAD	Hydrogen group transfer	Seborrheic dermatitis, glossitis and cheilitis/cheilosis
Vitamin B_6 (Pyridoxine)	Pyridoxal phosphate (PLP)	Amino group transfer	Epileptiform convulsions in infants, glossitis and indirect pellagra
Vitamin B_3 (Niacin)	NAD^+/$NADP^+$	Hydrogen group transfer	Pellagra: Dermatitis, dementia and diarrhoea
Vitamin B_9 (Folic acid)	Tetrahydrofolic acid (THF)	Transfer of one carbon fragment	Megaloblastic anaemia and neural tube defects
Vitamin B_7 (Biotin)	Biotin bound to carboxylases	Transfer of carboxyl group	Not well established
Vitamin B_{12} (Cobalamin)	Methylcobalamin and 5'-deoxyadenosylcobalamin	Methyl group and H-atom transfer	Pernicious anaemia: megaloblastic anaemia with neurological disorders
Vitamin B_5 (Pantothenic acid)	Coenzyme A	Acyl group transfer	Not well established
Vitamin C (Ascorbic acid) (L-ascorbic acid)	Acts as coenzyme in hydroxylation of proline and lysine residues of collagen.	Maturation of collagen (collagen synthesis)	Scurvy Required for synthesis of osteocalcin, a Ca-binding protein in bones and teeth.

Dietary sources

The *2015-2020 U.S. Dietary Guidelines* focus on the overall diet as the best way to get enough nutrients for good health. Vitamins should come firstly from a balanced and varied diet with plenty of fruit and vegetables. However, in some cases, fortified foods and supplements may be appropriate.A health professional may recommend vitamin supplements for people with certain conditions, during pregnancy, or for those on a restricted diet.Those taking supplements should take care not to exceed the stated maximum dose, as health problems can result. Some medications can interact with vitamin supplements, too, so it is important to talk to a healthcare provider before using supplements.

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